



Stable Sr-isotope, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios in the scleractinian cold-water coral *Lophelia pertusa*

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ABSTRACT

The aragonitic skeletons of scleractinian cold-water corals can serve as valuable archives in paleoceanographic studies. The potential of $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios of the cold-water coral *Lophelia pertusa* to record intermediate water mass properties has been investigated. Here we used samples from several locations along the European continental margin spanning a large temperature range from 6 to 14 °C. Stable strontium isotope measurements were carried out with the recently developed double spike TIMS technique and our results differ from those obtained with less precise methods. In contrast to the strong positive relationship with temperature of previous studies, our results suggest that $\delta^{88/86}\text{Sr}$ measured in scleractinian cold-water corals is not controlled by seawater temperature, but reflects the Sr isotopic composition of seawater with an offset of $\Delta^{88/86}\text{Sr} = -0.196\%$.

As found in previous studies, the elemental ratios Sr/Ca, Li/Ca and Mg/Li measured in corals are significantly related to water temperature and do not correlate with salinity. Moreover, Sr/Ca ratios in *L. pertusa* display the expected inverse correlation with temperature. However, the variance in the Sr/Ca data severely limits the accuracy of paleotemperature estimates. The Li/Ca and Mg/Ca ratios reveal other influences besides temperature such as pH and/or growth or calcification rate. However, corresponding Mg/Li ratios in *L. pertusa* are more tightly related to temperature as they remove these secondary effects. In particular, the Mg/Li ratio in *L. pertusa* may serve as a new promising paleotemperature proxy for intermediate water masses. Our dataset represents the most extensive geochemical examination of *L. pertusa* to date, revealing a temperature sensitivity of 0.015 mol/mmol/°C for Mg/Li. However, using this temperature dependence and the precision of 5.3% (2SD) only temperature variations larger than ~1.5 °C can be resolved with 95% confidence.

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1. Introduction

Cold-water corals are abundant in the world's ocean and can build-up unique reef and mound like structures especially along the European continental margin (Freiwald et al., 2004; Roberts et al., 2006). Several studies have tried to use their skeletons as archives for intermediate water mass reconstruction (e.g. Smith et al., 2000, 2002; Lutringer et al., 2005). Compared to traditional sedimentary archives, scleractinian corals have some advantages like the incorporation of high concentrations of Uranium in their aragonitic skeleton,

which facilitates accurate dating with the U/Th method (e.g. Cheng et al., 2000). Several geochemical tracers like Sr/Ca, Mg/Li, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, stable strontium isotopes ($\delta^{88/86}\text{Sr}$), etc. can potentially provide vital information about the intermediate oceans of the past (e.g. Cohen et al., 2002; Adkins et al., 2003; Rüggeberg et al., 2008; Case et al., 2010). Significant efforts have been made to identify proxies for temperature reconstructions. Elemental ratios suggested to be related to water temperature are Ba/Ca (Sinclair et al., 2006), Mg/Ca (Mitsuguchi et al., 1996), U/Ca (e.g. Shen and Dunbar, 1995; Min et al., 1995) and Sr/Ca (e.g. Smith et al., 1979; Beck et al., 1992). The Sr/Ca ratio of tropical corals is a widely used and robust temperature proxy (e.g. Beck et al., 1992; Gagan et al., 1998). The combination of Li/Ca and Mg/Ca ratios to obtain Mg/Li ratios has been introduced as a potential paleotemperature proxy in benthic foraminifers (Bryan and Marchitto, 2008), tropical (Hathorne et al., 2013) and cold-water corals (Case et al., 2010). The latter study showed that Mg/Li

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ratios in various scleractinian cold-water corals are primarily controlled by temperature.

Additionally, non-traditional stable isotope systems have been introduced as potential paleotemperature proxies in both cold- and warm-water corals. While the applicability of sea-surface temperature reconstructions in tropical corals with $\delta^{44/40}\text{Ca}$ is very limited (Böhm et al., 2006), the use of $\delta^{88/86}\text{Sr}$ appears instead to be very promising (Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008). The stable strontium isotope system has been introduced by Fietzke and Eisenhauer (2006) as a potential paleothermometer measured in the scleractinian warm-water coral *Pavona clavus*. Subsequently, Rüggeberg et al. (2008) analysed $\delta^{88/86}\text{Sr}$ in the cold-water coral *Lophelia pertusa* to develop a potential new proxy for the reconstruction of intermediate ocean water temperatures. Both studies have shown a similar slope of $\delta^{88/86}\text{Sr}$ with temperature in tropical and cold-water corals, highlighting the potential of $\delta^{88/86}\text{Sr}$ for seawater-temperature reconstructions.

However, besides environmental factors, the element incorporation and stable isotope fractionation ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) is also affected by biological factors known collectively as “vital effects” (e.g. McConnaughey, 1989; Smith et al., 2000, 2002; Adkins et al., 2003; Cohen et al., 2006; Blamart et al., 2007; Gagnon et al., 2007; López Correa et al., 2010; Gaetani et al., 2011). These vital effects have an impact on the compositional variability of geochemical tracers, which can be distinctly different between species. In general, the coral microstructure is characterized by the Centres Of Calcification (COC) and the surrounding theca wall, which is composed of aragonitic needles (Gladfelter, 1982). Several studies have tried to explain the mechanisms controlling the distribution of elemental ratios and isotopes in and between these different coral skeleton features (e.g., Adkins et al., 2003; Cohen et al., 2006; Rollion-Bard et al., 2010; Gaetani et al., 2011). Most of these studies presume that coral calcification occurs within an Extracytoplasmic Calcifying Fluid (ECF, e.g. Adkins et al., 2003). Biomineralization models have invoked various mechanisms, which comprise e.g. (1) a pH-driven control of the solution chemistry on the skeletal composition (e.g. Adkins et al., 2003), (2) carbonate precipitation from a semi-enclosed system (Rayleigh fractionation, e.g. Cohen et al., 2006; Gaetani et al., 2011), and (3) the formation of amorphous aragonite precursor phases of calcium carbonate (ACC, Rollion-Bard et al., 2010). Recent studies highlight that skeletal cations (calcium, strontium and barium) arrive at the site of calcification by direct seawater transport (Erez and Braun, 2007; Tambutte et al., 2011; Gagnon et al., 2012). The observed variability of elemental ratios can be explained by the balance between seawater transport and precipitation (Gagnon et al., 2012).

This study is based on samples collected from the skeleton of the scleractinian cold-water coral *L. pertusa* which is widely distributed in the world's oceans. Along the European continental margin *L. pertusa* occur in Norwegian fjords, on the Irish Margin, the Bay of Biscay, the Gulf of Cadiz and a few occurrences are reported from the Mediterranean Sea (Fig. 1, Freiwald et al., 2004; Taviani et al., 2005). *L. pertusa* occurs at water depths from 40 m (Trondheimsfjord, Norway) to >3000 m on the New England seamount chain (Freiwald et al., 2004) and lives in water with temperatures of 4–14 °C and in salinities from 32.0 in Scandinavian fjords to 38.8 in the Mediterranean Sea (Strømgren, 1971; Taviani et al., 2005). Several studies have shown that *L. pertusa* can extend up to 26 mm/year (Mortensen and Rapp, 1998; Orejas et al., 2008; Gass and Roberts, 2010) and that each polyp can live several years. The distribution, origin, growth and demise of *L. pertusa* and its reefs and mounds on the European continental margin is controlled by oceanographic conditions such as temperature, current strength, nutrient availability and the density of seawater (e.g. Freiwald et al., 2004; Roberts et al., 2006; Rüggeberg et al., 2007; Dullo et al., 2008; Raddatz et al., 2011).

The development of new proxies for reconstructing past intermediate water mass temperatures is important for the study of past climates and ocean circulation. To this end we focus on the temperature

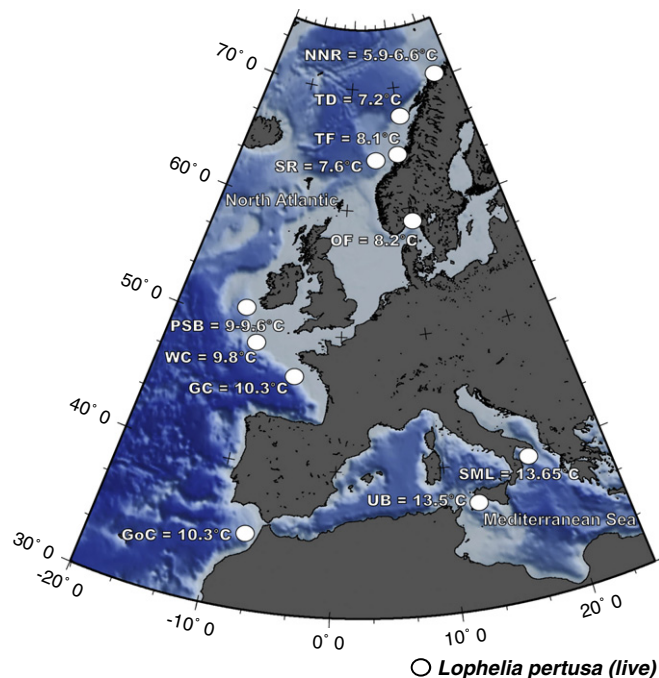


Fig. 1. Locations where live *in situ* *L. pertusa* samples were collected from the European continental margin and the corresponding water temperatures (Table 1). NNR = Northern Norwegian reefs (Stjernsund, Loppahavet, Sotbakken = temperature range), TD = Trøndadjupet, TF = Trondheimsfjord, SR = Sula Reef, OF = Oslo Fjord, PSB = Porcupine Seabight (Galway Mound, Little Galway Mound, Propeller Mound = average water temperature), WC = Whittard Canyon, GC = Guilvinec Canyon, GoC = Gulf of Cadiz, UB = Urania Bank, SML = Santa Maria di Leuca.

and salinity sensitivity of $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios in the scleractinian coral-water coral *L. pertusa* to build a new framework to understand proxies extracted from cold-water coral skeletons. To estimate the dependency of proxies to environmental parameters in *L. pertusa*, geochemical signals measured in the coral skeleton in the theca wall apart from the COC will be calibrated to the instrumental data. Moreover, we also investigated the compositional variability of each geochemical signal within the coral skeleton to estimate the biological control on element incorporation and stable isotope fractionation.

2. Materials and methods

Living cold-water coral samples of *L. pertusa* were collected from different locations along the European continental margin (Fig. 1, Table 1). Initial $\delta^{88/86}\text{Sr}$ data of these samples (Galway Mound, Little Galway Mound, Stjernsund, Trondheimsfjord, Trøndadjupet, Oslo Fjord; Table 1) were previously published (Rüggeberg et al., 2008). In order to extend this study, additional samples were taken from the Norwegian margin (Loppahavet, Sotbakken, Sula Reef, Oslo Fjord), from two different sites in the Mediterranean Sea (Urania Bank and Santa Maria di Leuca), from the Bay of Biscay (Whittard Canyon, Guilvinec Canyon), as well as from the Gulf of Cadiz (Table 1, Fig. 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. All samples were immediately dried at 50 °C and then stored away. Water temperatures and salinity were measured via several CTD downcasts (Conductivity–Temperature–Depth) at the time of sample collection. In general, the CTD downcasts show a reproducibility (SD) of <0.1(°C). For some sites CTD measurements are taken from literature (Table 1). CTD downcasts taken for this study are only snapshots, however they are in good accordance to the annual mean temperatures of the World Ocean Atlas 2009

Table 1
Meta data, environmental data, stable strontium isotopes and element ratios of *Lophelia pertusa* coral samples.

Cruise	Source	Location	Province	Latitude	Longitude	T [°C]	Ref.	Salinity	Depth [m]	$\delta^{88/86}\text{Sr}$ [‰]	Sr/Ca [mmol/mol]	Mg/Ca [mmol/mol]	Li/Ca [μmol/mol]	Mg/Li [mol/mmol]
POS325-433	1	Stjernesund	NNR	70°16.04'N	22°27.37'E	5.9	1	34.97	295	0.226	9.732	4.312	15.664	0.275
POS325-433	1	Stjernesund	NNR	70°16.04'N	22°27.37'E	5.9	1	34.97	295	0.191				
PS70/40-4	2	Sotbakken	NNR	70°45.35'N	18°40.04'E	6.6	2	35.2	265	0.195	9.792	4.720	16.296	0.29
PS70/40-4	2	Sotbakken	NNR	70°45.35'N	18°40.04'E	6.6	2	35.2	265	0.210				
POS391-552-1	2	Lopphavet	NNR	70°26.80'N	21°10.38'E	6.5	2	35	230	0.194	10.051	3.809	14.276	0.267
POS391-552-1	2	Lopphavet	NNR	70°26.80'N	21°10.38'E	6.5	2	35	230	0.209	9.967	4.445	16.316	0.272
POS391-552-1	2	Lopphavet	NNR	70°26.80'N	21°10.38'E	6.5	2	35	230	0.189				
POS391-552-1	2	Lopphavet	NNR	70°26.80'N	21°10.38'E	6.5	2	35	230	0.179				
POS325-356/1	1	Trænadjupet	TD	66°58.40'N	11°06.53'E	7.2	3	35.2	300	0.210	9.732	4.312	15.664	0.275
POS325-356/1	1	Trænadjupet	TD	66°58.40'N	11°06.53'E	7.2	3	35.2	300	0.224				
POS391-561-1	2	Sula-Reef	SR	64°05.98'N	08°05.86'E	7.6	2	35.3	290	0.191	9.968	3.850	13.771	0.28
POS391-561-1	2	Sula-Reef	SR	64°05.98'N	08°05.86'E	7.6	2	35.3	290	0.195				
Røberg #3	1	Trondheimsfjord	TF	63°28.61'N	09°59.72'E	8.1	3	31.2	240	0.172	9.533	4.357	14.365	0.303
POS391-574-1	2	Oslo Fjord	OF	59°04.01'N	10°44.31'E	8.2	2	35.2	115	0.179	9.966	3.870	13.743	0.282
POS391-574-1	2	Oslo Fjord	OF	59°04.01'N	10°44.31'E	8.2	2	35.2	115	0.191				
M61/1-218	1	Little Galway Mound	PSB	51°26.51'N	11°45.43'W	8.96	3	35.53	881	0.189	9.785	3.941	11.489	0.343
M61/3-551	1	Galway Mound	PSB	51°26.94'N	11°45.16'W	9.54	3	35.53	837	0.166				
M61/3-551	1	Galway Mound	PSB	51°26.94'N	11°45.16'W	9.54	3	35.53	837	0.174	9.603	3.242	11.143	0.291
POS265-499 (*)	2	Propeller Mound	PSB	52°08.89'N	12°46.31'W	9.6	3	35.5	729	0.188	9.445	4.243	10.838	0.325
B10-17b Dive 4	2	Whittard Canyon	WC	48°46.79'N	10°34.20'W	9.79	2	35.5	835	0.143	9.677	2.963	9.712	0.305
B10-17a Dive 1	2	Guilvinec Canyon	GC	46°56.20'N	05°21.60'W	10.29	2	35.6	800	0.198	10.054	3.104	10.058	0.309
GeoB12738-1	2	Gulf of Cadiz	GoC	34.59.98'N	07°04.51'W	10.28	4	35.7	738	0.179	9.732	2.986	8.857	0.337
M70/1-677	2	Urania Bank	UB	36°50.34'N	13°09.31'E	13.5	5	38.8	651	0.171	9.393	3.618	9.343	0.387
M70/1-677	2	Urania Bank	UB	36°50.34'N	13°09.31'E	13.5	5	38.8	651	0.196				
COR2-111	2	Santa Maria di Leuca	SML	39°34.89'N	18°23.00'E	13.65	6	38.69	496	0.203	9.267	4.263	11.262	0.378

Province: NNR = Northern Norwegian reefs (Stjernesund, Lopphavet, Sotbakken), TD = Trænadjupet, TF = Trondheimsfjord, SR = Sula Reef, OF = Oslo Fjord, PSB = Porcupine Seabight (Galway Mound, Little Galway Mound, Propeller Mound), WC = Whittard Canyon, GC = Guilvinec Canyon, GoC = Gulf of Cadiz, UB = Urania Bank, SML = Santa Maria di Leuca, source 1 = Rüggeberg et al. (2008), source 2 = this study, (*) = sample represents the mean of four different determinations in one single polyp. References used for oceanographic properties at coral sites: 1 = Rüggeberg et al. (2011), 2 = this study, 3 = Dullo et al. (2008), 4 = Pfannkuche and Shipboard Scientific Party (2007), 5 = López Correa et al. (2010), 6 = Freiwald et al. (2009).

Table 2

Intra-individual heterogeneity test of $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios in a *Lophelia pertusa* specimen from Little Galway Mound (M61/1-218, Porcupine Seabight; Temperature = 8.96 °C, Salinity = 35.53, Depth = 881 m). The position corresponds to the cross section along the coral skeleton from 1 (Theca wall) to 7 (COC), see Fig. 4.

Position	$\delta^{88/86}\text{Sr}$ [‰]	Sr/Ca [mmol/mol]	Li/Ca [$\mu\text{mol/mol}$]	Mg/Ca [mmol/mol]	Mg/Li [mol/mmol]
1	0.190	9.98	9.023	2.938	0.326
2	0.188	9.73	9.084	2.678	0.295
3	0.196	9.92	10.868	3.266	0.300
4	0.202	10.03	12.571	3.508	0.279
5	0.179	10.17	13.213	3.677	0.278
6	0.181	10.25	15.222	3.997	0.263
7	0.208	9.85	14.675	3.884	0.265

(Antonov et al., 2010; Locarnini et al., 2010). Furthermore, for carbonate mounds in the NE Atlantic Mienis et al. (2007) showed, that the annual bathyal temperature variation is <2.5 °C.

2.1. Sample preparation and $\delta^{88/86}\text{Sr}$ measurements

For geochemical analyses the final polyp corresponding to the most recent accretion was taken. About 1 mg of carbonate was sampled with a dremel tool from each polyp according to Rüggeberg et al. (2008) averaging several growth bands by focusing on the theca wall and avoiding the Centres Of Calcification (COC). However, we cannot exclude that our theca wall samples are biased by COC-like structures within the theca wall (e.g. Rollion-Bard et al., 2009). However, we consider the amount of this COC-like material to be neglectable to change the measured signal significantly. Nevertheless, to quantify the range of intra skeleton variations of $\delta^{88/86}\text{Sr}$ and elemental ratios (Sr/Ca, Mg/Ca, Li/Ca, Mg/Li) of *L. pertusa* one longitudinal mid-plan section (Little Galway Mound, M61/1-218, Table 2, Fig. 4) was chosen. Using a micromill we were able to drill seven sub-samples across the skeleton. Coral powder was weighed in Teflon beakers together with 2 ml H₂O (18.2 M Ω Milli-Q water). Then samples were dissolved in 2% HNO₃ and heated for at least 5 h in closed beaker and then dried at 90 °C. Organic matter was removed by adding 200 μl H₂O₂ (30%) and 200 μl 2 N HNO₃ and heated for at least 6 h in closed beaker and evaporated to dryness afterwards. The sample was dissolved again in 2 ml 8 N HNO₃ and separated into two fractions (isotope composition (ic) and isotope dilution (id)) for Sr isotope analysis, where each fraction contained 1000–1500 ng Sr. To the id sample we added the ⁸⁷Sr/⁸⁴Sr double spike (DS) solution (Krabbenhöft et al., 2009). Chromatographic column separation was performed with 650 μm BIO-RAD columns filled to one-third with

Triskem Sr-SPS resin (grain size 50–100 μm). The Sr isotope measurements were carried out at GEOMAR using a Thermo-Ionization-Mass-Spectrometer (TIMS, TRITON ThermoFisher). Here we measured two ic-analyses and two id-analyses for each sample. The ratio of stable Sr is given as $\delta^{88/86}\text{Sr}$ in relation to the SrCO₃ standard SRM987 distributed by the National Institute of Standards and Technology (NIST) (Fietzke and Eisenhauer, 2006). $\delta^{88/86}\text{Sr} = [\frac{^{88}\text{Sr}}{^{86}\text{Sr}}_{\text{sample}} / \frac{^{88}\text{Sr}}{^{86}\text{Sr}}_{\text{SRM987}} - 1] \times 1000$. For the SRM987 standard we used the generally accepted $^{88}\text{Sr}/^{86}\text{Sr}$ value of 8.375209 ($^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$; Nier, 1938) for normalization. The results of Sr isotope measurements are shown in Table 1. The long-term external reproducibility of the $\delta^{88/86}\text{Sr}$ ratios as measured on the JcP-1 *Porites* coral reference material (Okai et al., 2002) measured during the course of this study (n = 10) is $0.197 \pm 0.020\%$ (2SD) and corresponds to the error given in this study.

2.2. Elemental/Ca measurements

The solutions used for stable strontium isotope measurements were also analysed for elemental ratios using an Agilent 7500cs Quadrupole-ICP-MS at GEOMAR. In a first step the Ca concentration was measured and samples were diluted to have 10 ppm Ca and calibrated using standards made from single element solutions. Elemental/Ca ratios were calculated from the raw counts using the method of Rosenthal et al. (1999). Six aliquots of *Porites* sp. coral powder reference material JcP-1 (Okai et al., 2002) were treated like the *Lophelia* samples and the average values obtained during the course of this study (n = 10) were Li/Ca 6.17 ± 0.33 $\mu\text{mol/mol}$, Mg/Ca 4.15 ± 0.15 mmol/mol, Sr/Ca 8.76 ± 0.13 mmol/mol and Mg/Li ratio 0.673 ± 0.048 mol/mmol (all errors are 2 standard deviations (SD)). The corresponding 2 relative standard deviations (RSD) of the analyses are ~5.4% for Li/Ca, ~1.3 for Mg/Ca, ~1.5% for Sr/Ca and ~5.3% for the Mg/Li ratio. The corresponding absolute concentrations measured are within the uncertainties of the recommended JcP-1 values (Okai et al., 2002).

3. Results

The habitats of *L. pertusa* analysed in this study cover a large temperature range from 5.9 °C to 13.8 °C (Fig. 1). In total 25 bulk coral theca samples were analysed for stable strontium isotopes. The $\delta^{88/86}\text{Sr}$ composition of the entire sample set ranges from $0.143 \pm 0.02\%$ to $0.226 \pm 0.02\%$ (Table 1), and does not show a significant correlation with temperature (Fig. 2). Moreover, the $\delta^{88/86}\text{Sr}$ values are significantly

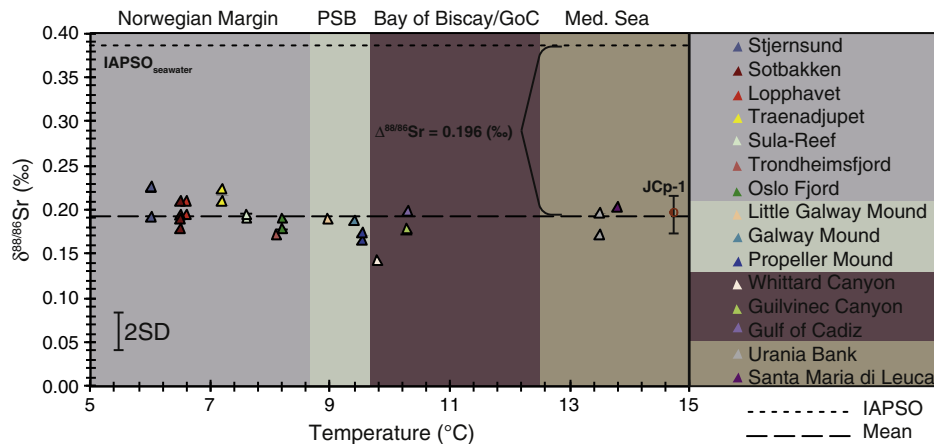


Fig. 2. Stable strontium isotopes in *Lophelia pertusa* samples collected at locations with water temperatures ranging between 6 and 14 °C from various locations along the European continental margin show no correlation to temperature. Results (mean = big dotted line) are the same within the uncertainty of the coral reference material JcP-1 ($0.197 \pm 0.02\%$, red circle). The *L. pertusa* $\delta^{88/86}\text{Sr}$ values display an offset of -0.196% to the IAPSO $\delta^{88/86}\text{Sr}$ seawater (small dotted line) value of 0.386% (Liebetrau et al., 2009; Krabbenhöft et al., 2010).

correlated to any of the measured elemental ratios (Sr/Ca, Mg/Ca, Li/Ca and Mg/Li). The mean of all samples is $0.19 \pm 0.03\%$ (excluding one possible outlier from the Whittard Canyon ($0.143 \pm 0.02\%$)). Note that this value is within the uncertainty the same as for the JcP-1 coral standard with $0.197 \pm 0.02\%$. Samples from the Stjernsund reef grew under the lowest temperatures ($5.9\text{ }^{\circ}\text{C}$) and have an average $\delta^{88/86}\text{Sr}$ value of $0.217 \pm 0.02\%$. Samples from the Mediterranean Sea grew at 13.65 to $13.8\text{ }^{\circ}\text{C}$, the highest water temperatures in our sample set, and the $\delta^{88/86}\text{Sr}$ of these samples is $0.183 \pm 0.02\%$ and $0.203 \pm 0.02\%$. The three samples from the Porcupine Seabight originate from carbonate mounds (Propeller Mound, Galway Mound and Little Galway Mound) and grew at $\sim 9.5\text{ }^{\circ}\text{C}$ showing a mean $\delta^{88/86}\text{Sr}$ value of $0.190 \pm 0.02\%$. The *L. pertusa* sample from Whittard Canyon at $9.79\text{ }^{\circ}\text{C}$ has the lowest $\delta^{88/86}\text{Sr}$ value of $0.143 \pm 0.02\%$.

Sr/Ca ratios vary from 9.27 mmol/mol at $13.8\text{ }^{\circ}\text{C}$ in the Mediterranean Sea to 10.05 mmol/mol at $6.5\text{ }^{\circ}\text{C}$ in the northern reefs (Lopphavet). The Sr/Ca ratios show a significant inverse correlation with temperature by excluding one possible outlier from the Guilvinec Canyon ($r^2 = 0.65$, $p = <0.001$; Fig. 3)

$$\text{Sr/Ca}(\text{mmol/mol}) = -0.083 \pm 0.017 T(^{\circ}\text{C}) + 10.451 \pm 0.16. \quad (1)$$

The Mg/Ca ratios vary from 2.99 to 4.72 (mmol/mol) and do not show a significant relationship with temperature (Fig. 3).

The Li/Ca ratios vary from 8.86 to 16.32 ($\mu\text{mol/mol}$) and exhibit a significant correlation ($r^2 = 0.61$, $p = 0.005$) with temperature. The best fit to the Li/Ca ratios is an exponential equation and can be described as followed:

$$\text{Li/Ca}(\mu\text{mol/mol}) = 23.691e^{-0.073(T^{\circ}\text{C})}. \quad (2)$$

The Mg/Li ratios vary from 0.27 mol/mmol at low temperatures ($5.9\text{ }^{\circ}\text{C}$) to 0.39 mol/mmol at the highest temperature at Santa Maria di Leuca ($13.65\text{ }^{\circ}\text{C}$). The Mg/Li results display a positive linear correlation with temperature ($r^2 = 0.82$, $p = <0.001$; Fig. 3) that can be described by the following equation:

$$\text{Mg/Li}(\text{mol/mmol}) = 0.015 \pm 0.002 T(^{\circ}\text{C}) + 0.174 \pm 0.018. \quad (3)$$

The $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li ratios do not show any significant correlation with salinity (Fig. 3), across the large range from 31.2 in the Trondheimsfjord up to 38.8 in the Mediterranean Sea. A relationship between salinity and the Mg/Li ratios by discarding the Mediterranean samples appears to be a covariance due to the high seawater temperature of $\sim 14\text{ }^{\circ}\text{C}$.

The intra skeleton $\delta^{88/86}\text{Sr}$ values vary from $0.179 \pm 0.030\%$ to $0.208 \pm 0.008\%$ (Fig. 4). All values in this *L. pertusa* sample have a mean of $\delta^{88/86}\text{Sr} = 0.191 \pm 0.020\%$, which coincides with the JcP-1 *Porites* coral reference material ($0.197 \pm 0.019\%$). Similarly, the Sr/Ca values of this coral show no systematic behaviour within the microstructure, but show a variability of 0.53 mmol/mol, which is significant when compared to the external reproducibility (± 0.07) from 9.73 ± 0.07 to 10.25 ± 0.07 mmol/mol.

Both, Li/Ca and Mg/Ca ratios vary strongly across the skeleton between the theca and the COC. The Li/Ca ratios range from ~ 9 to $\sim 15\ \mu\text{mol/mol}$ and Mg/Ca ratios range from ~ 2.7 to ~ 4.0 mmol/mol with the highest ratios in the inner part of the corals close to the COC. The corresponding Mg/Li ratios show related variability of 0.063 mol/mmol change, from 0.325 mol/mmol to 0.263 mol/mmol, decreasing from the outer to the inner part (Fig. 4). These changes in the Mg/Ca and Li/Ca ratios are associated with the COC maxima. However, across the skeletal section and throughout the entire sample set the Mg/Ca and Li/Ca ratios exhibit a strong positive relationship of $r^2 = 0.96$ and 0.61 , respectively (Fig. 5).

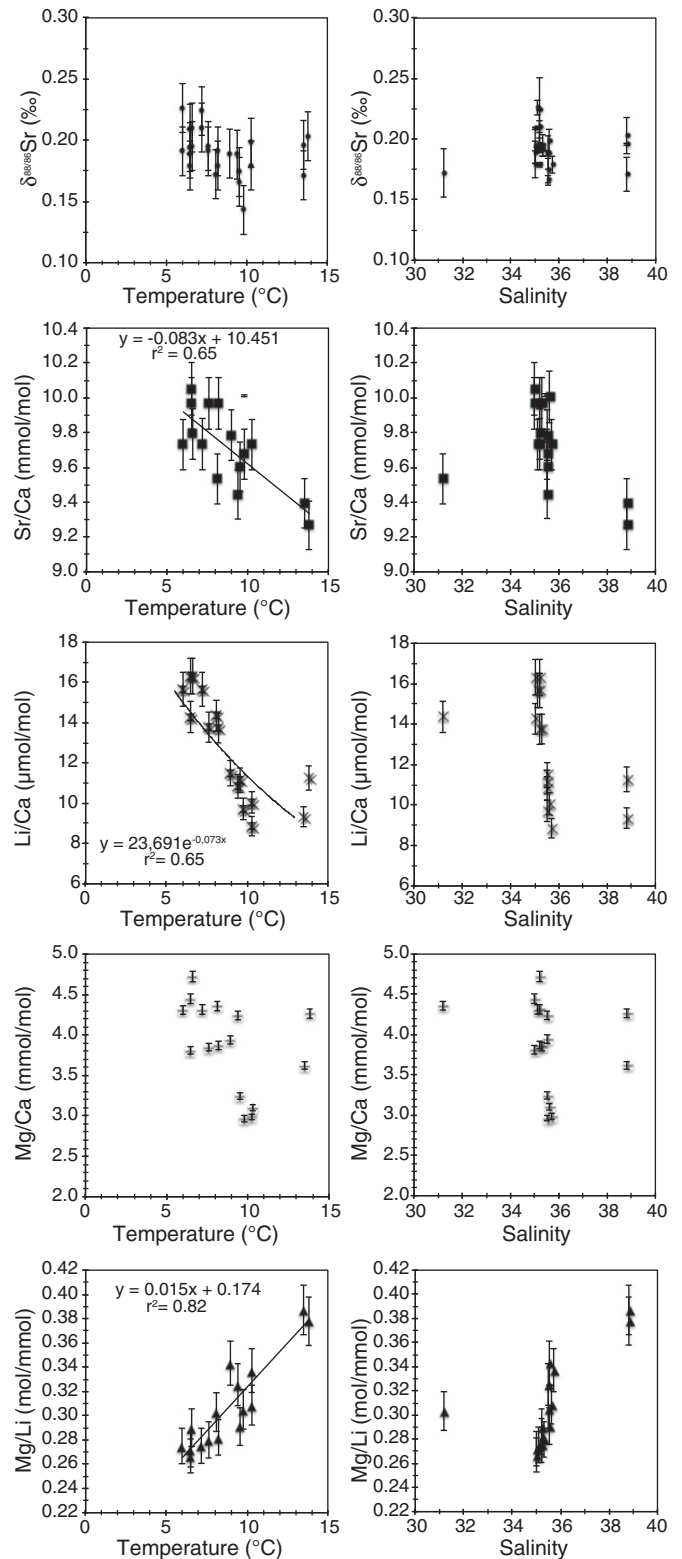


Fig. 3. Temperature and salinity dependence of $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li in *L. pertusa*. Results show that only Sr/Ca, Li/Ca and Mg/Li exhibit significant correlations to temperature ($r^2 = 0.65$ for Sr/Ca, $r^2 = 0.65$ for Li/Ca and $r^2 = 0.85$ for Mg/Li).

4. Discussion

4.1. Stable strontium isotopes in *L. pertusa*

Different methods have been used to determine natural strontium isotope fractionation (Fietzke and Eisenhauer, 2006; Ohno et al.,

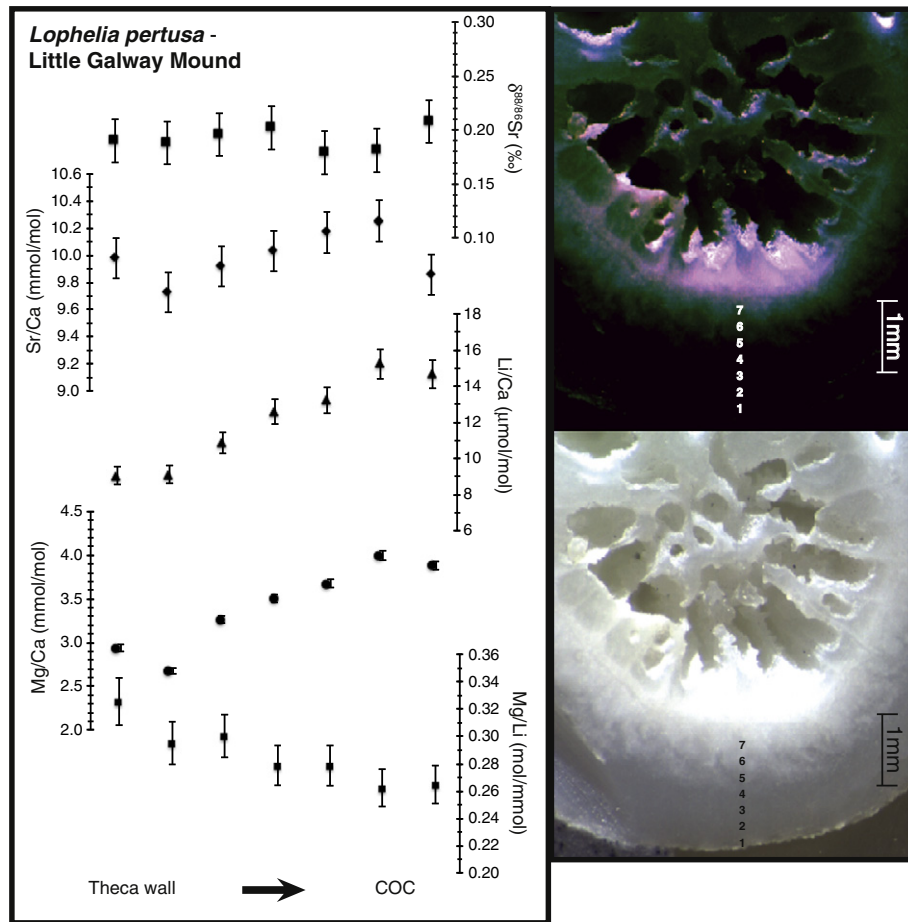


Fig. 4. Intra-individual heterogeneity test of $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li compositions in a *L. pertusa* specimen from Little Galway Mound (M61/1–218). The $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Li ratios are equal within measurement uncertainty, whereas Mg/Ca and Li/Ca show almost a twofold increase within the coral skeleton. All error bars correspond to 2SD. Coral pictures show the sampling profile drilled with the micromill (1–7) from the theca wall into the COC. The displayed coral is a longitudinal section of the Little Galway Mound specimen showing the internal architecture of the skeleton. For the Mg/Ca ratios the error bars are smaller than the dots.

2008; Krabbenhöft et al., 2009). The DS-TIMS method developed by Krabbenhöft et al. (2009) shows a 2–3 times better reproducibility compared to the standard-bracketing MC-ICP-MS method (Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008). In particular, the double spike technique can account for any fractionation during the ion chromatographic Sr separation and the chemical preparation (Krabbenhöft et al., 2009). Therefore, the use of the DS-TIMS overcomes any matrix related mass bias fluctuations, which probably accounts for most of

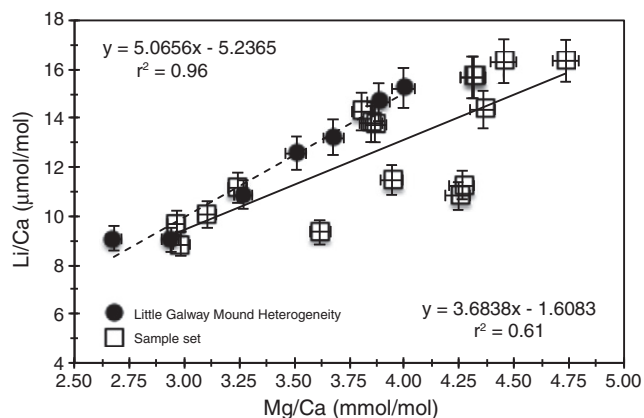


Fig. 5. Intra-individual samples (Little Galway Mound M61/1–218) and the entire sample set exhibit a strong correlation of Mg/Ca and Li/Ca ratios of *L. pertusa*.

the variability seen in the $\delta^{88/86}\text{Sr}$ record of Rüggeberg et al. (2008). These data show a considerable degree of scatter and indeed some of the lowest temperature samples possess $\delta^{88/86}\text{Sr}$ values that are indistinguishable to those that grew at the highest temperature, on average the earlier data do possess a lighter $\delta^{88/86}\text{Sr}$ composition of about 60–80 ppm, indicating that there might have been some problems with Sr loss during chemical preparation. Therefore, the observed discrepancy between our results using DS-TIMS technique with those from previous studies are best explained by different sample preparation and measurement methods (Fig. 6).

Only a few studies have focused on stable strontium isotopes in the marine realm and hence little is known about fractionation processes in marine calcifiers (Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008; Krabbenhöft et al., 2009, 2010; Böhm et al., 2012). In line with our findings the study of Böhm et al. (2012) showed that temperature is not a controlling parameter for stable strontium isotope fractionation in calcitic planktonic foraminifera. In particular, our results display a constant negative strontium fractionation offset of $\sim 0.2\%$ to the isotopic composition of seawater. Strontium is very conservative in seawater and has a residence time of $\sim 2.5 \times 10^6$ years (Hodell et al., 1990). This is very long compared to the mixing time of the oceans (~ 1000 years) and hence the oceans are well mixed with respect to Sr isotopes (Veizer, 1989; McArthur, 1994). These findings are supported by first results of Liebetrau et al. (2009) showing that the $\delta^{88/86}\text{Sr}$ of seawater is homogeneous with $0.386 \pm 0.007\%$ in the North Atlantic, the Gulf of Cadiz and the Mediterranean Sea. However, some of the scatter in our coral $\delta^{88/86}\text{Sr}$ data might be caused by local changes in the seawater

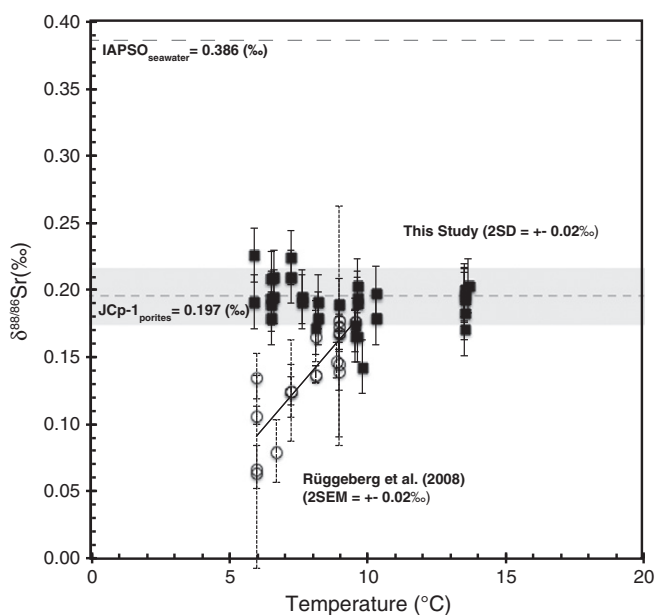


Fig. 6. All $\delta^{88/86}\text{Sr}$ values determined with the DS-TIMS technique compared to $\delta^{88/86}\text{Sr}$ measured with the bracketing standard method in the scleractinian cold-water coral *L. pertusa* (Rüggeberg et al., 2008). IAPSO $\delta^{88/86}\text{Sr}$ seawater value corresponds to 0.386‰ (Krabbenhöft et al., 2009; Liebetrau et al., 2009). The reproducibility of $\delta^{88/86}\text{Sr}$ for the JcP-1 measured in the course of this study is $\pm 0.020\%$ (2SD) ($n = 10$) and is indicated with the grey bar, which covers almost the entire range of $\delta^{88/86}\text{Sr}$ values.

stable Sr isotopic composition especially in fjord settings (river input) (Krabbenhöft et al., 2010). Nevertheless, our results show that coral aragonite records the $\delta^{88/86}\text{Sr}$ of seawater with a constant offset of $\Delta^{88/86}\text{Sr} = -0.196\%$ independently from environmental influences (Fig. 2). Moreover, the coral standard (JcP-1 *Porites*) has a similar offset of $\Delta^{88/86}\text{Sr} = -0.189\%$ to the IAPSO seawater standard $\delta^{88/86}\text{Sr}$ value. This 200 ppm difference between coral aragonite and seawater indicate a simple mass dependent Sr-isotope fractionation during coral calcification (Fietzke and Eisenhauer, 2006). It remains to be tested if other scleractinian corals also show the same constant $\delta^{88/86}\text{Sr}$ fractionation offset. If this is the case, scleractinian offer a promising archive to reconstruct the Sr isotopic composition of past water masses and hence provide new insights into the carbonate burial flux and the strontium budget of the ocean (Krabbenhöft et al., 2010), which extends back to the Triassic period, where the first scleractinian corals in Earth history have been recorded (237 Ma, Stanley and Fautin, 2001).

4.2. Sr/Ca ratios in *L. pertusa*

Our results show that Sr/Ca ratios measured in the theca wall of *L. pertusa* exhibits a relationship with temperature of 0.08 mmol/mol/°C and no significant relationship to salinity (Figs. 3 and 7). Unlike other elemental ratios Sr/Ca display less but still significant compositional variability within the entire coral skeleton (Fig. 4). As discussed by Gagnon et al. (2007) the compositional variability of Sr/Ca might be different between different cold-water corals species (see Cohen et al., 2002; Cohen et al., 2006). Our study supports these findings showing that the Sr/Ca variability throughout the skeleton and the COC is rather ubiquitous.

Strontium to calcium ratios measured in the different genera of cold-water corals (e.g. *Caryophyllia*, *Flabellum*, *Stephanocyathus*) suggests that Sr/Ca ratios are related to seawater temperature (Shirai et al., 2005). Moreover, Sr/Ca ratios measured in the theca wall of the deep-sea coral *Desmophyllum dianthus* agree with the expected Sr/Ca of inorganic aragonite precipitated at the temperature of coral growth (Kinsman and Holland, 1969; Gagnon et al., 2007). Cohen et al. (2006) found a temperature relationship of 0.18 mmol/mol/°C within one growth band of a *L. pertusa* polyp. However, the observed temperature

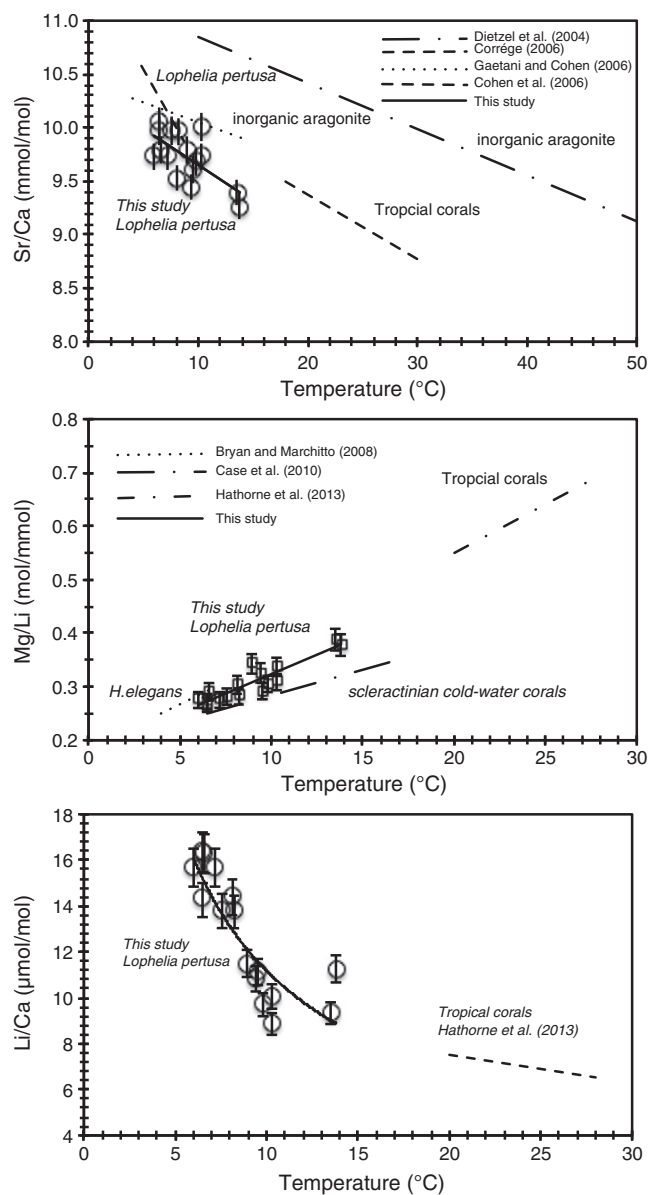


Fig. 7. Sr/Ca, Mg/Li and Li/Ca ratios measured in the scleractinian cold-water coral *L. pertusa* from different locations with seawater temperatures between 6 and 14 °C. Sr/Ca-temperature dependence of this study is compared to the Sr/Ca vs. SST calibration of various scleractinian warm water corals (mean: $\text{Sr/Ca} = -0.0596 T (^{\circ}\text{C}) + 10.596$; Corrège, 2006) and abiogenic aragonite ($\text{Sr/Ca} = -0.043 T (^{\circ}\text{C}) + 11.72$; Dietzel et al., 2004) and *L. pertusa* ($\text{Sr/Ca} = -0.18 T (^{\circ}\text{C}) + 11.44$; Cohen et al., 2006) as well as another abiogenic aragonite ($\text{Sr/Ca} = -0.038 T + 10.43$; Gaetani and Cohen, 2006) Mg/Li ratios of *L. pertusa* lie between the slopes of the aragonitic foraminifera *Hoeglundina elegans* ($0.0143 T (^{\circ}\text{C}) + 0.20$; Bryan and Marchitto, 2008) and those of scleractinian cold-water corals ($0.009 T (^{\circ}\text{C}) + 0.19$; Case et al., 2010) and of warm-water corals ($0.018 T (^{\circ}\text{C}) + 0.19$; Hathorne et al., 2013). The Li/Ca ratios of *L. pertusa* are plotted together with Li/Ca ratios of the scleractinian warm water coral *Porites* ($-0.123 T (^{\circ}\text{C}) + 9.974$; Hathorne et al., 2013).

dependency is too large to be solely explained by the temperature control on Sr/Ca in inorganic aragonite (Cohen et al., 2006). Other studies suggested Sr/Ca ratios in scleractinian cold-water corals are also influenced by vital effects (Montagna et al., 2005; Shirai et al., 2005).

Even though our applied sampling technique does not provide such high-resolution records as the SIMS (Cohen et al., 2006) our study reveals similar findings as the more detailed and higher resolved study of Allison and Finch (2004) on warm-water corals. They showed that the large small-scale Sr/Ca heterogeneity can potentially be calibrated

to seawater temperature when the sampling resolution is decreased. This is supported by our Sr/Ca–T dependency analysed in the theca wall of *L. pertusa* (Fig. 7, Eq. (1)) and is similar compared to that of zooxanthellate tropical corals showing that the Sr/Ca ratio decreases with increasing water temperature (Fig. 7; e.g., Smith et al., 1979; Beck et al., 1992; Gaetani and Cohen, 2006). According to our results both azooxanthellate and zooxanthellate corals are controlled by the same biomineralization processes responsible for the incorporation of Sr/Ca. However, although the Sr/Ca ratios measured here with traditional sampling techniques in *L. pertusa* avoiding the COC are T dependent, the relatively large Sr/Ca scatter in the overall T calibration severely limits the use for paleo-reconstructions. Hence more work is needed to clarify the environmental influence on Sr/Ca ratios in scleractinian cold-water corals and its compositional variability within the coral skeleton.

4.3. Compositional variability of Mg/Ca, Li/Ca and Mg/Li ratios in *L. pertusa*

Unlike, $\delta^{88/86}\text{Sr}$ and Sr/Ca ratios, the Mg/Ca and Li/Ca ratios do show large variations within the coral microstructure. In particular, we were able to detect the COC by measuring Mg/Ca and Li/Ca ratios both showing extremely elevated values, as previously shown by (Case et al., 2010). While some of this variability can be caused by temperature variability the overall variation appears to be too large to be explained by temperature alone. However, such elevated Mg/Ca ratios in COCs of warm and cold-water corals were also reported by several other studies (e.g. Meibom et al., 2004; Cohen et al., 2006; Gagnon et al., 2007; Meibom et al., 2008). Our study reveals that both ratios are significantly correlated within the coral skeleton and throughout the sample set avoiding the corals COC (Fig. 5). If we assume that skeletogenesis occurs within the ECF, our observation can be explained by the Rayleigh fractionation. Both elements have an apparent partition coefficient of <1 and hence a Rayleigh fractionation model would predict a positive correlation between Mg/Ca and Li/Ca. However, Gagnon et al. (2007) and Case et al. (2010) have shown that other processes than Rayleigh fractionation control trace element incorporation into the skeleton of the solitary cold-water coral *D. dianthus*. They found a break in the slope between Li/Ca and Mg/Ca ratios and explained it with either the build up of precursor Amorphous Calcium Carbonate (ACC) or Mg-hosting organics within the COC. But we suggest that the internal pH up-regulation (Adkins et al., 2003; McCulloch et al., 2012) influences the compositional variability and the incorporation of Mg and Li in *L. pertusa*, besides temperature.

The incorporation of Mg and Li into the coral aragonite lattice are still poorly understood. While some studies highlight that Mg is directly substituted for Ca^{2+} (Politi et al., 2010) others have shown that Mg is hosted in organic bindings or ACC (Finch and Allison, 2008). The incorporation of Li^+ into biogenic aragonite is not well constrained, but a recent study on modern aragonitic bivalves showed that it is influenced by calcification rate (Thébault et al., 2009) In warm-water corals the Li/Ca ratio is mainly controlled by seawater temperature (Hathorne et al., 2013). The compositional variability of Mg/Ca and Li/Ca ratios in *L. pertusa* corresponds to the coral microstructure with elevated values within the COC and drastically decreasing values throughout towards the outer theca wall (Fig. 4). Models of coral calcification show that coral aragonite is precipitated from modified seawater within the COC. In this COC the carbonate ion concentration 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; McCulloch et al., 2012). These models are also consistent with our profile throughout the coral skeleton revealing, that in the COC both ratios are higher compared to the rest of skeleton (Fig. 4). In general, a higher seawater pH and/or carbonate ion concentrations facilitate higher calcification rates (Marubini et al., 2008; Form and Riebesell, 2012). The study of Sinclair et al. (2006) demonstrated that Mg/Ca and U/Ca ratios show an inverse relationship in scleractinian

cold-water corals. According to that, recent studies have shown that U/Ca ratios in scleractinian cold-water and warm water corals (Anagnostou et al., 2011; Inoue et al., 2011) are related to changes in carbonate ion concentrations as the amount of uranyl complexes in seawater increase with decreasing seawater pH. Hence, low U/Ca ratios in the COC may be the result of internal pH-up regulation (e.g., McCulloch et al., 2012). If Mg/Ca and U/Ca ratios are controlled by similar mechanisms, the Mg/Ca and Li/Ca ratios may therefore be controlled by pH and/or growth rate. However, as we do not have *in situ* calcification or growth rates we cannot directly compare growth/calcification rates to Mg/Ca and Li/Ca ratios.

4.4. Temperature control on Mg/Ca, Li/Ca and Mg/Li ratios in *L. pertusa*

We show that the Mg/Li ratio in *L. pertusa* is mainly dependent on seawater temperature. In scleractinian corals the Mg/Ca ratio was shown to be dependent on seawater temperature (e.g. Mitsuguchi et al., 1996). However, there is evidence from recent studies that temperature is not the dominant control on Mg/Ca ratios in scleractinian corals (Cohen et al., 2006; Gagnon et al., 2007; Hathorne et al. accepted). Our Mg/Ca data does not show any significant relationship to temperature as expected. This suggests that temperature is not the dominant control on Mg/Ca ratios in cold-water corals. As mentioned above we suggest that this is caused by difference in growth rate and the ability of an internal pH-up regulation of cold-water corals. However, Marriott et al. (2004) and Hathorne et al. (2013) found Li incorporation in the warm-water coral *Porites* to be mainly controlled by temperature (Fig. 7). Lithium is more readily incorporated into carbonates at low temperatures (Marriott et al., 2004) and its incorporation is exothermic and less favoured at higher temperatures. This is in line with our results revealing that Li incorporation is more effective at lower temperatures (Eq. (2), Fig. 7). Similar to our results Case et al. (2010) showed that neither salinity nor carbonate ion concentration or pH control the Mg/Li ratios. By combining the Mg/Ca and Li/Ca ratio any vital effect gets normalized and thus the corresponding Mg/Li ratio is more tightly correlated to seawater temperature (Case et al., 2010, Fig. 7). Using traditional sampling techniques these Mg/Li ratios correlate with temperature in various scleractinian corals from different ocean basins with $r^2 = 0.62$ for all investigated species and with $r^2 = 0.82$ for the family Caryophylliidae (Case et al., 2010). Our results confirm the potential of Mg/Li ratios as a paleothermometer in cold-water corals (Eq. (3)). Our dataset represents the most extensive geochemical examination of *L. pertusa* to date, revealing a temperature sensitivity of $0.015 \text{ mol/mmol}/^\circ\text{C}$ for Mg/Li (Eq. (3)) similar to the Caryophylliidae slope of Case et al. (2010, $0.009 \text{ mol/mmol}/^\circ\text{C}$). The scatter in the Mg/Li record of *L. pertusa* is smaller compared to the scatter in Sr/Ca ratios, but may still restrict temperature reconstructions. Using the temperature dependence of $0.015 \pm 0.004 \text{ mol/mmol}/^\circ\text{C}$ and the precision of 5.3% (2SD) temperature variations larger than 1.5°C can be reconstructed with 95% confidence.

5. Conclusions

This study investigated the potential of the scleractinian cold-water coral *L. pertusa* to serve as an archive for intermediate water temperatures using the geochemical proxies $\delta^{88/86}\text{Sr}$, Sr/Ca, Mg/Ca, Li/Ca and Mg/Li. With the higher precision of the Double-Spike-TIMS technique compared to the bracketing standard MC-ICP-MS technique, it was not possible to reproduce the findings of Rüggeberg et al. (2008) by measuring $\delta^{88/86}\text{Sr}$ of some of the same samples. Our results show that $\delta^{88/86}\text{Sr}$ is not controlled by temperature in *L. pertusa* skeletons. Instead the $\delta^{88/86}\text{Sr}$ values display a constant offset of $\Delta^{88/86}\text{Sr} = -0.196\%$ from seawater and may thus become useful as an archive to record the Sr isotopic composition of the paleocean.

Our measurements of the elemental ratios Sr/Ca, Li/Ca and Mg/Li support earlier studies in showing significant temperature relationships

that may form the basis for paleotemperature proxies. The sensitivity of Sr/Ca in the *L. pertusa* to temperature, however, severely limits the use as a paleotemperature proxy and further studies are needed to analyse Sr/Ca ratios at micrometre-scale in multiple specimens. Although Mg/Ca and Li/Ca ratios appear to be affected by other parameters than temperature the strong dependency of Li/Ca at lower temperature highlights this as a paleothermometer for seawater temperature reconstruction of the intermediate ocean. The scatter of the Li/Ca and Mg/Li record in *L. pertusa* is small showing the promise of those ratios as a reliable paleotemperature proxy for new perspectives to reconstruct past intermediate water dynamics. However, future studies need to investigate the potential of *L. pertusa* as a high-resolution archive for paleoceanographic reconstruction.

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