Stable strontium isotopes ($\delta^{88/86}$ Sr) in cold-water corals – a new proxy for reconstruction of intermediate ocean water temperatures

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Abstract

Zooxanthellate scleractinian corals are known as archives for temporal variations of climate variables, such as sea surface temperature, salinity or productivity. The use of azooxanthellate cold-water corals as potential archives for intermediate water mass properties and climate variability was tested recently. However, the correlation of established proxies such as δ^{18} O and δ^{13} C with temperature is difficult since there is no direct temperature equation applicable as in shallow-water corals. Other temperature proxies such as Sr/Ca, Mg/Ca and U/Ca are influenced by the complex microstructure of the aragonite skeleton, the rate of calcification, and other vital effects observed for coral species.

For the first time we show that the stable strontium isotope ratio $\delta^{88/86}$ Sr incorporated in the skeletons of the cold-water coral species *Lophelia pertusa* portrays the ambient seawater temperature. The temperature sensitivity from live samples collected along the European continental margin covering a temperature range from 6° to 10 °C is 0.026±0.003‰/°C (2 σ standard error) which is a sensitivity similar to the tropical shallow water coral record *Pavona clavus*. This indicates a similar fractionation process of strontium for both, zooxanthellate and azooxanthellate corals. For coral aragonite the $\delta^{88/86}$ Sr ratio may serve as a new paleotemperature proxy and introduces new perspectives in paleoceanography with respect to intermediate water dynamics.

Keywords

Stable strontium isotopes, cold-water coral, *Lophelia pertusa*, temperature reconstruction, temperature proxy, intermediate waters, MC-ICP-MS

1 Introduction

Cold-water corals are known to be abundant in the world's oceans forming unique reef structures mainly built up by colonial azooxanthellate scleractinians *Lophelia pertusa* and *Madrepora oculata*. Focusing on the European continental margin, these cold-water coral reefs occur on moraine ridges off Norway to small coral topped mounds and huge coral banks in the Rockall Trough, the Porcupine Seabight, the Gulf of Cadiz, but only have a patchy occurrence in the Mediterranean Sea (Freiwald et al., 1999; De Mol et al., 2002; Kenyon et al. 2003; Álvarez-Pérez et al., 2005; Taviani et al., 2005). Their distribution and development is supposed to be related to climatic changes governing the local oceanographic regime where strong

bottom currents control the sedimentation and food supply (Freiwald et al., 2004; Roberts et al., 2006; Rüggeberg et al., 2007; White, 2007).

Lophelia pertusa occurs in water depths as shallow as 40 m in some Norwegian fjords down to over 3000 m on the New England seamount chain (Freiwald et al., 2004). This species tolerates temperatures between 4° and 14 °C (Freiwald, 2002) and salinity values from as low as 32 psu in Scandinavian fjords to at least 38.8 psu in the Mediterranean (Strømgren, 1971; Taviani et al., 2005). The growth rate of L. pertusa varies between 5 and 25 mm/yr (Mikkelsen et al., 1982; Freiwald et al., 1997; Mortensen and Rapp, 1998; Spiro et al., 2000), which indicates that a branch of several coral polyps can represent an archive of several years to few decades. Previous studies intend to use cold-water corals as a potential archive of intermediate water temperatures and salinity (Smith et al., 2000, 2002; Blamart et al., 2005; Lutringer et al., 2005; Shirai et al., 2005; Cohen et al., 2006). Smith et al. (2000) and later Lutringer et al. (2005) presented δ^{18} O-temperature relationships, corrected to seawater δ^{18} O, between the linear regression of δ^{18} O and δ^{13} C of aragonite and the δ^{13} C seawater DIC. These calculated temperatures have a precision of ±1.5 °C (Smith et al., 2000) and ±0.7 °C in higher resolution sampling (Lutringer et al., 2005). Nevertheless, the problem of this acquisition is the enormous sampling procedure and stable isotope analysis (N¹⁵ measurements) for one determined temperature value. However, it was found that stable isotopes ($\delta^{18}O$, δ^{13} C) as well as elemental ratio analyses (Sr/Ca, Mg/Ca, U/Ca) exhibit strong vital effects (Smith et al., 2000, 2002; Shirai et al., 2005; Cohen et al., 2006) and that the aragonite skeleton of *L. pertusa* has not been precipitated in isotopic equilibrium with the ambient seawater. Latter observations challenge the application of these proxies for ambient seawater reconstructions in cold-water corals. In this study we further evaluate cold-water corals as an archive for intermediate seawater variability. In particular, we follow recent findings of Fietzke and Eisenhauer (2006) who found that the stable strontium isotope ratios in tropical corals are temperature dependent and may serve as a reliable temperature proxy for cold-water corals. Furthermore, we used the stable strontium isotope method on the same coral species from different environmental and therefore temperature settings to determine the variability of this isotope ratio and to establish the method as tool for paleoceanographic questions.

2 Material and Method

Sampling locations of living specimens of *L. pertusa* are the Norwegian shelf, the Skagerrak, the Rockall Bank, and the Porcupine Seabight (Fig. 1, Table 1). The corals were collected from water depths between 100 m and 1 000 m using box corers, the remotely operating vehicle ROV QUEST of MARUM (University of Bremen), and the manned submersible JAGO of IFM-GEOMAR (Kiel). All samples were immediately dried at 50 °C and then stored away. Water temperatures and salinities were collected from CTD measurements of same sample position during same cruises.

2.1 Sample Preparation

For bulk analyses of δ 88/86Sr in cold-water coral *L. pertusa*, the final polyp corresponding to the youngest one was embedded in epoxy resin and cut perpendicularly to the growth direction using a diamond saw. A minimum of 0.5 mg of skeleton powder was drilled from the cut surface using a dental drill (Fig. 2). Attention was paid to avoid centers lines of calcification during sampling, since these show a different fractionation behavior at least for oxygen and carbon isotopes

(Smith et al., 2000; Blamart et al., 2005) and some element ratios (Shirai et al., 2005; Cohen et al., 2006).

Drilled skeleton powder was weighted in a Teflon beaker and dissolved using 4 N HNO_3 . After careful dissolution, samples were evaporated to dryness, redissolved in 1 ml 4 N HNO_3 and finally loaded onto a column with 300 µl Eichrom SrSpec resin (Fietzke and Eisenhauer, 2006). The sample matrix was separated by washing the column with 4 ml 4 N HNO_3 . Strontium was eluted with 3 ml ultrapure water (18.2 M Ω). Solutions (50 ppb Sr) were prepared using nitric acid (5 %) for MC-ICP-MS measurements. In order to prevent isotope fractionation due to a chromatographic effect on the corals the columns have been tested for a complete strontium recovery.

2.2 Measurement systematic

For the determination of stable strontium isotopes we applied the bracketing standard approach using strontium standard SRM NBS987 as previously presented by Fietzke and Eisenhauer (2006). This standard shows an internal reproducibility of 24 ppm (1 σ RSD) during a non-stop 16 h data acquisition indicating the stability of the measurement conditions (Fietzke and Eisenhauer, 2006). The $\delta^{88/86}$ Sr values of different dilutions (25 ppb, 40 ppb, 50 ppb) of the same coral sample agree within 4 ppm (RSD) showing the robustness of this bracketing standard method (Fietzke and Eisenhauer, 2006). Data acquisition was carried out in alternating 15-minute runs for bracketing sample and standards. Each run corresponds to 300 scans with an integration time of 3 s per scan. Wash out times are short because the signal dropped below 1 ‰ of its in run intensity within less than a minute.

3 Results

First stable strontium isotopes on *L. pertusa* were analysed against the strontium standard SRM NBS987 in different sessions between September 2005 and September 2007. This standard is certified for radiogenic strontium but not for stable strontium isotopes as no such standard yet exists. Therefore, we additionally used samples 636-05 and 811-05 as internal lab standard to normalize the δ 88/86Sr values of *L. pertusa* between sessions. The resulting stable strontium isotope values are illustrated in Fig. 3 and listed in Table 2.

The $\delta^{88/86}$ Sr composition of *L. pertusa* samples originating from the inner skeletal part (Fig. 2) ranges from 0.04‰ to 0.2‰ (Table 2). Norwegian corals sampled at 6 °C water temperature (Stjernsund, STS) show lowest $\delta^{88/86}$ Sr values of around 0.08‰. With increasing water temperature, coral $\delta^{88/86}$ Sr values increase to 0.12‰ at Trænadjupet (TD = 7.2 °C), 0.14‰ at Trondheimsfjord (TF = 8.1 °C), and around 0.15‰ at West Rockall Bank/Porcupine Seabight (WRB/PSB = 8.8–9.5 °C; Figs. 1 and 3). Linear regression lines between $\delta^{88/86}$ Sr and temperature for each session display clear positive correlations (0.31 < R < 1) with slopes of regression lines between 0.0205±0.007‰/°C and 0.0319±0.006‰/°C (2 σ standard error, Fig. 3). The weighted mean temperature sensitivity of *L. pertusa* is 0.026± 0.003‰/°C (2 σ standard error. Fig. 2). The significant correlation of $\delta^{88/86}$ Sr values of *L. pertusa* is 0.026± 0.003‰/°C (2 σ standard error. Fig. 2).

standard error, Fig. 3). The significant correlation of $\delta^{88/86}$ Sr values of *L. pertusa* to temperature can be expressed by the following equation (R=0.61, n=25):

 $\delta^{88/86} \text{Sr} (\text{\%NBS987}) = (0.026 \pm 0.003) \text{ x T} (^{\circ}\text{C}) - 0.059$ (1)

The temperature sensitivity of 0.026%/°C and the currently possible accuracy of 0.024% for a single δ 88/86Sr measurement (1 σ RSD) allow a precision for temperature reconstructions of about ±1 °C. This uncertainty lies between the

accuracy of Lutringer et al. (±0.7 °C, 2005) and Smith et al. (±1.5 °C, 2000) for calculated temperatures based on high-resolution $\delta^{18}O/\delta^{13}C$ analyses. Correlation to other environmental parameters like salinity, dissolved oxygen or pH available for almost all sites, could not be identified.

4 Discussion

4.1 Temperature reconstruction in cold-water corals

Several studies tested different isotope systems ($\delta^{18}O$, $\delta^{13}C$) and element ratios (Sr/Ca, Mg/Ca, U/Ca) as potential temperature proxies in cold-water corals. Cohen et al. (2002) proposed that Sr/Ca ratios measured in non-symbiotic corals could be considered to be primarily controlled by variations in sea-water temperature, whereas the Sr/Ca ratios recorded in symbiotic species are largely biologically controlled. Reynaud et al. (2004) determined the strong vital effect of symbiotic corals in cultural experiments. They showed that a strong correlation exists between Sr^{2+} uptake and growth rate following the same pattern as Ca^{2+} uptake, both ions being regulated by the calcification biochemistry independently of temperature but of light and nutrient concentrations. Montagna et al. (2005) analysed Sr/Ca element ratios of cold-water coral Desmophyllum dianthus and found no correlation between the variation in element ratio and temperature, but related it to vital or kinetic effects as the driving force for Sr/Ca changes. Shirai et al. (2005) analysed different coldwater corals from the Japan Sea and the Pacific from 70 to 3000 m water depth confirming this observation. In their study δ^{18} O values and Sr/Ca (Mg/Ca) ratios show a weak negative (positive) correlation with temperature of bulk skeleton samples. The authors relate the element incorporation to the calcification rate being an important factor for the chemical composition in cold-water corals and one of the most significant mechanisms related to the vital effect. From the observation that temperature-dependent variations in elemental partitioning accounts for <25% of the Sr/Ca variability. Cohen et al. (2006) concluded that temperature information may be recorded in cold-water coral skeletons to some extent. However, observed variations are too large due to vital effects to use these ratios as temperature proxies in coldwater corals.

So far, the classical method applying stable oxygen isotopes to reconstruct temperatures seems to be the most reliable one. The existing data of stable oxygen and carbon isotopes derived from cold-water corals exhibit a wide range (δ^{18} O: -4.2‰ to +4‰, δ^{13} C: -15‰ to -0.7‰). Therefore, Smith et al. (2000, 2002) introduced the linear correlation of both isotopes as a possible tool to reconstruct the temperature of the ambient seawater. Nevertheless, the $\delta^{13}C_{DIC}$ value of the ambient seawater is a prerequisite for this method, indicating the disadvantage for reconstructing paleo-temperatures, as the coral's $\delta^{13}C$ is offset from seawater.

Our results on the $\delta^{88/86}$ Sr-temperature relationship exhibit a statistical uncertainty of about ±1 °C. Latter result is comparable to the value obtained by the Lutringer et al. (2005) approach (0.7 °C) and better than the Smith et al. (2000, 2002) approach (±1.5 °C). However, this method has the potential for more precise temperature reconstructions of ±0.5 °C, which represents highest possible precision in combination of normalizing two values of same sample but different sessions. With a certified standard for stable strontium isotopes, normalization would be unnecessary and temperature reconstructions with an error of ±0.25 °C would be possible. Although Sr/Ca partitioning coefficients are different between inorganic and biologically generated aragonite precipitation (Dietzel et al., 2003; Gagnon et al.,

2007), we do not have identified so far any influence of a physiological factor on the fractionation of stable strontium isotopes, but final inference is pending.

Seasonal variation of water temperature is small ranging within about 1 °C for the southern coral provinces (WRB, PSB in Fig. 1), while it increases to about 2.5 °C with increasing latitude (OF, TF, TD, STS in Fig. 1). In Fig. 3 the $\delta^{88/86}$ Sr data of *Lophelia* are plotted against in-situ temperatures of sampling dates, which may explain the little wider scatter of data from Stjernsund where seasonal temperature variation is largest. The general pattern of Sr isotopes, however, portray perfectly the water temperatures of the water masses bathing the living corals, irrespectively if they are deeper surface water masses as in the north or intermediate water masses along the Celtic margin.

4.2 Temperature reconstruction in Lophelia pertusa applying $\delta^{88/86}$ Sr ratios

The overall temperature sensitivity of L. pertusa $\delta^{88/86}$ Sr record is similar to the one of the tropical coral of Pavona clavus (0.033 ± 0.005‰/°C; Fig. 4) although there is a considerable offset in their $\delta^{88/86}$ Sr ratios. The larger scatter of stable strontium isotope values of L. pertusa compared to P. clavus (Fig. 4) may reflect sample inhomogeneity. However, coral polyps of different coral stocks from same locales and both, white and pink colour-morphs of L. pertusa were investigated to determine intraspecific variability, which seem to be low. But lower growth rates of L. pertusa compared to P. clavus result in a lower time resolution per sampled interval averaging seasonal variations especially for samples of the northern provinces. However, the similar temperature sensitivity between the cold- and warm-water corals (Fig. 4) indicates that similar biochemical processes for Sr²⁺ uptake operate in symbiotic and non-symbiotic scleractinian corals during their calcification process. This is in line with earlier statements of Sinclair et al. (2006) who investigated tropical and deep-sea coral Mg/Ca and U/Ca ratios showing both the same relationship, which let the authors conclude that all scleractinian corals are controlled by similar biochemical processes.

Although the $\delta^{88/86}$ Sr-temperature gradients of the tropical and the cold-water coral show identical slopes they are offset to each other (Fig. 4) by about 0.5‰ suggesting that the biogeochemical processes fractionating trace elements may differ between coral genera (Sinclair et al., 2006). Latter observation resembles the $\delta^{44/40}$ Catemperature relationship in foraminifera. There, the $\delta^{44/40}$ Catemperature relationship of the cold-water foraminifera *Neogloboquadrina pachyderma* is offset from the $\delta^{44/40}$ Catemperature relationship of *Globigerinoides sacculifer* although both species show about the same $\delta^{44/40}$ Ca temperature gradient (Hippler et al., 2002, 2007). Latter similarity is most likely related to species-specific trace element transport mechanisms and their corresponding biomineralization processes pending further investigations.

 $\delta^{88/86}$ Sr values of individual samples from same location and/or relatively constant water temperatures (West Rockall Bank/Porcupine Seabight) may indicate that intraspecific variability of strontium isotope fractionation in cold-water coral Lophelia pertusa is probably small. Nevertheless, different cold-water coral species and corals from different regions (e.g., Mediterranean Sea, Gulf of Mexico, Brazilian and West African Margin), where the oceanographic setting significantly differ from the NE Atlantic regime, are subject of ongoing research to determine the coral's and bottom water's $\delta^{88/86}$ Sr ratio. Preliminary $\delta^{88/86}$ Sr data of bottom water from same coral locales indicate that the isotope ratio is fairly uniform at least for the NE Atlantic, while samples from marginal seas like the Mediterranean Sea tend to isotopically heavier values (data not shown). Nevertheless, the residence time of Sr in seawater is with \geq 4Ma long in comparison to the mixing rate of the oceans of <103 years (e.g., Veizer, 1989) supporting the restriction of stable strontium isotope variability to marginal seas and shelf areas where freshwater influx is large or weathering processes are strong.

As a result of the observed temperature dependence of 0.026%/°C and the currently possible precision of 0.024% (1 σ RSD) for a single $\delta^{88/86}$ Sr measurement only temperature variations exceeding <2 °C can significantly be recorded by coral $\delta^{88/86}$ Sr. The external reproducibility of ±1 °C may be related to the sampling technique strongly influencing the result of such reconstructions. Lutringer et al. (2005) reported for temperature reconstruction using δ^{18} O and δ^{13} C that a large portion of the isotopic variability inherent to the coral is lost using the macrosampling technique although the dependence of the isotopic signal on environmental controls remains extractable. In contrast, micro-sampling technique probably yields most of the isotope variability giving more precise estimates of the ambient seawater temperature with a better external reproducibility. Due to the large sample volume of <0.5 mg for the determination of $\delta^{88/86}$ Sr values and the complex microstructure of the skeleton of *L. pertusa* (Blamart et al., 2005; Cohen et al., 2006), it is necessary to improve the measurement precision and reduce the sample amount to study small-scale variability of stable strontium isotopes in cold-water coral skeletons.

5 Conclusion

For the first time we show that stable strontium isotopes ($\delta^{88/86}$ Sr) may be a useful new proxy for reconstructing temperatures from coldwater corals. This isotope ratio is temperature dependent with a sensitivity of 0.026 ± 0.003‰/°C (2 σ standard error). The similarity of the $\delta^{88/86}$ Sr-temperature calibration between cold-water and tropical coral implies that similar strontium fractionation processes in symbiotic and non-symbiotic corals occur. Our new proxy data portray temperatures of the ambient water masses around living corals. Hence, the analysis of $\delta^{88/86}$ Sr on fossil biogenic carbonates may be a useful tool to reconstruct paleo-temperatures on different carbonate-secreting organisms. Additionally, studies of the strontium isotope fractionation processes and combined Sr–Ca-isotope studies in cold and tropical corals may provide an excellent tool for a better understanding of biogenic calcification processes.

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Figure 1. Locations of live-sampled cold-water coral *Lophelia pertusa* from the Norwegian shelf, the Skagerrak, the Rockall Trough, and the Porcupine Seabight. Mean water temperature of coral depths is increasing from <6 °C in the north to <10 °C in the south (see also Table 1). STS = Stjernsund, TD = Trænadjupet, TF = Trondheimsfjord, OF = Oslofjord, RB = Rockall Bank, WRB = West Rockall Bank, PSB = Porcupine Seabight.



Figure 2. Schematic illustration of vertical and cross sections of a final polyp of *Lophelia pertusa*. The full and dotted lines indicate main growth bands, centre line of calcification and sampled area between two main septa

Vertical section of final polyp



Figure 3. Stable strontium isotope ratios ($\delta^{88/86}$ Sr) of cold-water coral *Lophelia pertusa* samples of investigated locations vs. temperature. All regression lines (dashed lines) show similar positive slopes around 0.025%/°C indicating temperature dependent strontium isotope fractionation. The weighted mean regression line (thick solid line) expresses the mean $\delta^{88/86}$ Sr-temperature relationship (0.026±0.003‰/°C) of *L. pertusa*. The $\delta^{88/86}$ Sr-error bars correspond to a 2 σ -standard deviation whereas temperature errors bars represent the range of seasonal variations.



Figure 4. The $\delta^{88/86}$ Sr-temperature relationship of cold-water coral *Lophelia pertusa* (diamonds) and tropical coral *Pavona clavus* from Galapagos (squares, from Fietzke and Eisenhauer, 2006) in comparison to IAPSO seawater standard (Fietzke and Eisenhauer, 2006). Both, azooxanthellate and zooxanthellate corals show a comparable temperature sensitivity but a large data offset.

Lab	Sample				Date of	Sampling	
code	code	Lokation	Latitude	Longitude	collection	Depth (m)	Temp. (°C)
812-05	POS325-433	Stjernsund	70°16.04' N	22°27.37' E	27.07.2005	365	5.90
813-05	POS325-433	Stjernsund	70°16.04' N	22°27.37' E	27.07.2005	365	5.90
811-05	POS325-356/1	Traenadjupet	66°58.40' N	11°06.53' E	17.07.2005	300	7.24
634-05	# 3	Trondheimsfjord	63°28.61' N	09°59.72' E	21.10.2004	240	8.10
635-05	# 3	Trondheimsfjord	63°28.61' N	09°59.72' E	21.10.2004	240	8.10
802-06	AL275-422	Oslo Fjord	59°05.65' N	10°47.94' E	27.03.2006	91	6.70
636-05	M61/1-218	PSB	51°26.51' N	11°45.43' W	24.04.2004	881	8.96
637-05	M61/1-218	PSB	51°26.51' N	11°45.43' W	24.04.2004	881	8.96
638-05	M61/3-551	PSB	51°26.94' N	11°45.16' W	05.06.2004	837	9.54
803-06	M61/3-614	SW RB	56°29.80' N	17°18.60' W	12.06.2004	680	8.80
804-06	M61/1-218	PSB	51°26.51' N	11°45.43' W	24.04.2004	881	8.96
805-06	M61/1-218, Q1	PSB	51°26.51' N	11°45.43' W	24.04.2004	881	8.96

Table 1. Coral samples and locations along the European continental margin.

PSB = Porcupine Sea Bight, SW RB = South West Rockall Bank

Table 2. Mean and normalized mean stable strontium isotope ($\delta^{88/86}$ Sr) values relative to standard NBS987 of the investigated coral samples (*samples used for normalization).

Lab code	Sample code	Session	Mean δ ^{88/86} Sr (‰ NBS987)	Error ±2SEM	Norm. mean δ ^{88/86} Sr (‰ NBS987)
635-05	#3	Sep_1 2005	0.137	0.005	0.137
636-05*	M61/1-218	Sep_1 2005	0.168	0.012	0.168
637-05	M61/1-218	Sep_1 2005	0.178	0.008	0.178
638-05	M61/3-551	Sep_1 2005	0.177	0.008	0.177
634-05	# 3	Sep_2 2005	0.579	0.019	0.166
635-05	# 3	Sep_2 2005	0.550	0.009	0.137
636-05*	M61/1-218	Sep_2 2005	0.582	0.012	0.168
636-05*	M61/1-218	Nov 2005	0.259	0.014	0.168
813-05	POS325-433	Nov 2005	0.197	0.021	0.107
636-05*	M61/1-218	Feb 2006	0.134	0.007	0.168
811-05*	POS325-356/1	Feb 2006	0.090	0.011	0.125
811-05*	POS325-356/1	May 2006	0.328	0.038	0.125
475-06	M61/1-218, Q1	May 2006	0.376	0.089	0.173
811-05*	POS325-356/1	Oct 2006	0.232	0.020	0.125
812-05	POS325-433	Oct 2006	0.175	0.016	0.068
813-05	POS325-433	Oct 2006	0.171	0.072	0.064
802-06	AL275-422	Oct 2006	0.187	0.024	0.080
803-06	M61/3-614	Oct 2006	0.254	0.013	0.147
804-06	M61/1-218	Oct 2006	0.252	0.020	0.145
805-06	M61/1-218, Q1	Oct 2006	0.246	0.050	0.140

Errors correspond to the analytical precision and were considered in the weighting of the temperature slopes of each and final session. The external reproducibility of the $\delta^{88/86}$ Sr corresponds to a temperature uncertainty in the order of about ±1 °C (see text).