# Element variability in the coralline alga *Lithophyllum yemenense* as archive of past climate in the Gulf of Aden (NW Indian Ocean)

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## Abstract

This study presents the first algal thallus (skeleton) archive of Asian Monsoon strength and Red Sea influence in the Gulf of Aden. Mg/Ca, Li/Ca, Ba/Ca were measured on *Lithophyllum yemenense* from Balhaf (Gulf of Aden) using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), and  Mg/Ca ratio oscillation has been used to reconstruct the chronology (34 years). Oscillations of element rates corresponding to the algal growth between 1974 and 2008 were compared with recorded climate and oceanographic variability. During this period the sea surface temperatures (SST) in Balhaf recorded a warming trend of 0.55°C corresponding to an increase in Mg and Li contents in the algal thallus of 2.1 mol % and 1.87 µmol % respectively. *L. yemenense* recorded decadal SST variability by Li/Ca, and the influence of the Pacific El-Niño Southern Oscillation (ENSO) on the NW Indian Ocean climate system by Ba/Ca. Additionally, algal Mg/Ca, Li/Ca and Ba/Ca show strong and significant correlations to All Indian Rainfall in the decadal range indicating that these proxies track the variability of the Indian Monsoon System. This might be explained by changes of the surface wind system, with deep water upwelling in summer, and a distinct seasonality.

## 1. Introduction

Coralline algae (Corallinophycidae, Rhodophyta) are a major calcifying component of marine benthos from tropical to polar oceans at all depths within the photic zone and in almost every habitat type (Bjork et al. 1995, Fabricius and De’ath 2001, Kuffner et al. 2007, Basso 2012, McCoy and Kamenos 2015). Over the past decade, they have increasingly been used as climate proxy archive due to their wide occurrence and longevity (Halfar et al. 2007). They are excellent records of paleotemperatures (Mg/Ca) (Ries 2006, Kamenos et al. 2008, Caragnano et al. 2014, Williamson et al. 2014, McCoy and Kamenos 2015), although it is not clear to what extent the algal metabolism exerts a control on Mg-carbonate chemistry (Halfar et al. 2000, Frantz et al. 2000).

The Mg/Ca incorporation in marine calcite depends on the temperature and Mg/Ca ratio of the seawater (Berner 1975, Chave and Wheeler 1965, Ries 2006). Moreover, the Mg/Ca in the skeleton/thallus of calcifying organisms may vary with factors that affect growth, such as light availability (Andersson et al. 2008), seawater carbonate saturation state (Andersson et al. 2008, Ries 2011, Egilsdottir et al. 2013) and salinity (Kamenos et al. 2012).

While Mg/Ca ratios have been widely used as a temperature proxy, the application of Li/Ca ratio as paleoceanographic proxy in calcifying organisms is restricted and discussed controversially. An inverse correlation between Li/Ca and temperature is reported in studies on inorganic calcite, and in calcite of brachiopod shells and aragonite skeletons of corals (Delaney et al. 1989, Marriott et al. 2004a, b, Case et al. 2010, Hathorne et al. 2013). On the contrary, other studies on corals and planktonic foraminiferal tests found no significant correlation between Li/Ca and temperature (Delaney et al. 1985, Hall and Chan 2004, Rollion-Bard et al. 2009). However, lithium (as Li/Ca) has been proven to be a good seawater temperature proxy for coralline algae (Caragnano et al. 2014) and the Li/Mg ratios observed in corals from diverse tropical, temperate, and deep-water environments showed a high correlation with temperature (Montagna et al. 2014).

Barium content of foraminiferal tests and coral aragonite were used to reconstruct oceanic Ba distribution as nutrient/organic matter proxy (Lea et al. 1989, Lea and Martin 1996, Tudhope et al.

1996) or as alkalinity proxy (Henderson 2002, Rubin et al. 2003). Barium has been widely studied in coral skeletons, while it is poorly investigated in coralline algae (Hetzinger et al. 2011, Chan et al. 2011, Hetzinger et al. 2013, Caragnano et al. 2014). The Ba/Ca ratio has been used as indicators of coastal freshwater runoff (Chan et al. 2011, Hetzinger et al. 2013), and as indicator of local sedimentation rates (Caragnano et al. 2014).

Although an increasing number of studies are devoted to the biogeochemistry of the coralline red algae thallus and its relationship with climate and oceanographic condition of ambient seawater, much more needs to be done to understand the mechanisms of element incorporation in the algal thallus. Some studies revealed a phylogenetic control on micro and nano-scale biomineral variations within the Corallinales (Fragoso et al. 2010), as well as an offset between the incorporation of Mg in coralline algae and in inorganic calcite (Lea et al. 1999), with a species-specific vital effect (Caragnano et al. 2014). Therefore, the investigation of the biogeochemistry of a greater number of species belonging to different genera and from a suite of different environments and geographic areas is fundamental to test the extent and the nature of the biological control on thallus calcification.

The climate and hydrography in the Gulf of Aden (area of sample collection) is strongly affected by the Indian monsoon system (Al Saafani and Shenoi 2004), that induces upwelling events. The surface water in the Gulf is a mixture of local water, western Arabian Sea water, Red Sea surface water, as well as deep water enriching the surface during upwelling events (Al Saafani and Shenoi, 2007). Few studies investigated the geochemical signals of the Asian monsoon recorded in the carbonate skeletons of corals from the Indian Ocean, disregarding the Gulf of Aden (Tudhope et al. 1996, Charles et al. 1997, Cole et al. 2000, Pfeiffer and Dullo 2006, Storz and Gischler 2011a-b).

The potential of the genus *Lithophyllum* (one of the most abundant genera on the tropical reefs) as paleoclimatic archive over a short time period has been previously demonstrated (Caragnano et al. 2014). The present contribution presents high-resolution geochemical analyses of Mg/Ca, Li/Ca and Ba/Ca ratios along a multi-decadal interval measured on the same sample of the non-geniculate encrusting species *Lithophyllum yemenense* Basso, Caragnano, Le Gall & Rodondi (2015), previously identified as *Lithophyllum kotschyanum* f. *affine* (Caragnano et al. 2014). The analysis of a longer record enabled to put in the right context the problem of the interspecific and interannual variability of the geochemical proxies, and to explore their relationship with the Indian monsoon system, and the climate and oceanographic connection with the surrounding oceanic area (Red Sea, Arabian Sea and Indian Ocean).

## 2. Materials and Methods

### *2.1. Regional Setting*

A detailed description of the geographic area, including environmental and oceanographic features is already available (Caragnano et al. 2014), and briefly summarized here.

The Gulf of Aden is a long and narrow part of the north-west Indian Ocean, about 1800 m deep, connecting the Red Sea with the Arabian Sea (Al Saafani and Shenoi 2004, Caragnano et al. 2014). Its hydrography and climate is strongly affected by the Indian monsoon system (Al Saafani and Shenoi 2004, Al Saafani 2008). The Red Sea water, one of the most saline water mass in the world oceans, constitutes about 37 vol % of the total water mass of the Gulf (Bethoux 1988, Al Saafani 2008). *In situ* regular records of the oceanographic parameters from Balhaf are not available. Hence, gridded instrumental climate records have been used. Sources and references of all climate datasets used in this paper are given in Table 1. Monthly sea level pressure (SLP) from International Comprehensive Ocean-Atmosphere Data Set (ICOADIS) gridded over 46-48°E, 12-14°N was used in this study as an indicator of monsoon current strength, as well as the zonal surface current (SSC) from Simple Ocean Data Assimilation reanalysis (SODA, Table 1). The SST shows distinct seasonal variability in the study area (Fig. 1), with highest values in May-June (31-32 °C), lowest in October-January (24-25 °C) in response to winter monsoonal north-easterly winds (Al Saafani 2008). Moreover,  during the summer monsoon in July-August there is a cooling (29-30 °C), depending on the strength of westerly monsoon winds, followed by a heating (up to 30 °C). The westerly winds during the summer monsoon season cause upwelling of cooler, nutrient-rich water along the northern part of the gulf (Sheppard et al. 1992, Al Saafani 2008).

The Sea Surface Salinity (SSS, SODA) of the study area reveals distinct seasonal variability following the SST (Fig. 1). Thus, the SSS is higher during the months of pre- and post- summer monsoon, and lowest during winter.

### *2.2. Coralline algae collection*

The fruticose *Lithophyllum yemenense* was collected during a coral monitoring project in Balhaf, Yemen (13°58.5N, 48°10.5E, Caragnano et al. 2014) by SCUBA diving in November 2008 between 6 and 8 m of water depth (Fig. 2). Preliminary results of the analyses conducted on the crustose thallus (on hard coral substrate, DB659) were presented in a previous work (Caragnano et al. 2014). The results of further analysis from a different portion of the same specimen (DB659bis) were reported here, with the aim to analyze a longer term relationship between the coralline thallus chemistry and the oceanographic data.

### *2.3. Sample preparation*

The air-dried coralline specimen was sectioned parallel to the direction of growth using a low speed saw with diamond blades (Fig. 2B). The sectioned part was prepared for analysis following Caragnano et al. (2014), and organic matter was removed by immersion in a solution of diluted hydrogen peroxide (Mertz-Kraus et al. 2008).

### *2.4. Element Analysis*

Li, Mg, Ca and Ba concentrations were determined using an Agilent 7500ce Quadrupole ICP-MS coupled to a New Wave research NWR 193 laser ablation system (193 nm wavelength, Nd:YAG Laser) at the Department of Geosciences, Johannes Gutenberg-Universität, Mainz, Germany.

Measurements were carried out with laser energy densities of 2.7 J $cm^{-2}$ and helium as carrier gas. Typical instrument parameters and detection limits can be found in Jacob (2006). Transects of 50 μm width, parallel to the direction of growth were analyzed with a scan speed of 10 μm $s^{-1}$, and 10 Hz pulse rate. Pre-ablation was carried out before data acquisition at the same laser energy density and transect widths, but with scan speeds of 100 μm $s^{-1}$. In the present study, because the characteristic change of the growth direction of the fruticose algae, and in order to avoid endolithic organisms and the reproductive cavities (conceptacles) that might alter the chemical of the algal thallus, it was decided to split the transect of measurement. Therefore, four consecutive transects following the variations in growth direction, and attempting to follow the main axis of growth, were analyzed, and were combined to get a single transect of 12.2 mm length from the surface (the youngest) to the base (the oldest) of the algal protuberance (Fig. 2B). Redundant data from overlapping portions of consecutive transects (Fig. 2B) were removed from further analysis. $^{43}Ca$ was used as internal standard, and silicate glass reference material NIST (US National Institute of Standard and Technology Standard Reference Material) SRM 610 was the external standard. Data reduction was carried out with the commercial software GLITTER 4.4.2 (Macquarie University, Sydney) to obtain time-averaged concentration values, and Excel spreadsheet routines were used for time-resolved data reduction. Values for NIST SRM 610 reported in the GeoReM database were used as the “true” concentrations in this reference glasses (Jochum et al. 2006). Detection limits (99% confidence) for the spot measurements of the NIST glasses were: $^{7}Li$=0.04 ppm, $^{25}Mg$=0.02 ppm and $^{137}Ba$=0.03 ppm. NIST SRM 612 glass was measured as an unknown (n = 12) before and after each transect in order to check for accuracy and reproducibility. Values obtained in the course of this study are reproducible within 2% for Ba and Sr and 10% for Li and Mg, respectively of the GeoReM recommended values.

### *2.5. Elements and temperature time-series development*

The element ratios reported in the text are ppm (=µg/g) ratios. The equation used for converting the element ratios in mmol/mol is:

mmol/mol=(element ratio in ppm/Cf) * 1000

Where Cf is the conversion factor for the element, as follows:

Cf=standard-atomic weight of the element/standard-atomic weight of Ca

The age models were established based on the pronounced seasonal cycles in algal Mg/Ca (Hetzinger et al. 2009) and by observation under optical microscope of banding growth and zonal formation of conceptacles, that occur every year in this species (Caragnano et al. 2014). Monthly and annual time series were calculated by averaging the values within each chronological series.

### *2.6. Statistical analysis*

The time series of the element transects were compared to the gridded climate and oceanographic datasets (Table 1). Least square regressions were calculated with the statistical software Past 2.12 (Hammer et al. 2001) with the aim to explore correlations among the proxy time series along the same transect, and between these proxy records and gridded climate and oceanography datasets. Spectral analyses were applied to investigate correlations between alga and instrumental climate records on spectral range. This method is the most widely used method for data analysis in geophysics, oceanography, and several other fields. Spectral analysis may reveal hidden periodicities in the studied data, that may be associated with cyclic processes. It allows to compare two different time series in the spectral range, when ordinary least square correlations are not significant. For these analyses, the software Analyseries 2.0.4.2 (Paillard et al. 1996) was used. Prior to spectral analyses, the individual time-series were detrended by removing the linear trend and normalizing to unit variance. The Blackman Tukey method was applied (Blackman and Tukey 1958), since it is robust against spurious spectral features. The algorithm computes first the autocovariance of the data, then applies a window (Barlett), and finally Fourier-transforms the covariance functions to compute a power spectrum (Paillard et al. 1996). The chosen window should not considerably affect the results for typical short and noisy time series.

Additionally, field correlations between our proxy record and instrumental climate datasets were analyzed with climate explorer (http://climexp.knmi.nl, Van Oldenborgh and Burgers 2001).

## 3. Results

### 3.1. Element/Ca analysis

Scanning electron microscopy (SEM) images did not show any evidence of diagenetic alteration of the sample thallus, such as recrystallization and/or alteration in the carbonate structure of the thallus.

The area investigated in our sample corresponds to a continuous thallus growth in the time interval 1974-2008 (annual extension rate= 337.75±124.08 µm). The specimen contained an average of 20.3 mol % $MgCO_3$ (4.6 SD), 8.8 µmol % $LiCO_3$ (2.8 SD) and 0.5 µmol % $BaCO_3$ (0.2 SD).

All time series show fluctuations of the element ratios from surface (the youngest algal cells) to older parts of the thallus (Fig. 2B), and both Mg/Ca and Li/Ca time series displayed a similar trend (Fig. 1).

The Mg/Ca and Li/Ca monthly means showed a positive and significant correlation ($r = 0.69$, $p < 0.0001$). Monthly Mg/Ca and Li/Ca time series reveal a temporal coherence except in the time interval from 1978 to 1980 (Fig. 1). Furthermore, the Mg/Ca mean ratio coincides with seasonal variations in SST (Fig. 1) and the linear regressions between element ratios and SST are positive (Fig. 3 and Table 2). The relationship between Mg/Ca and Li/Ca with SST is weak, but significant ($r = 0.34$-$0.37$, $p < 0.0001$).

The annual Mg/Ca mirrors the annual oscillations in SST except from 1976 to 1980, where the two time series appear to follow an opposite trend (Fig. 4). Annual Mg/Ca and Li/Ca time series revealed a temporal coherence except in 1979 and 1992 (Fig. 4). Linear regressions between element ratios and reconstructed SST were calculated using annual values, and a positive weak relationship was observed for Li/Ca (r = 0.42, p = 0.01), as well as for Mg/Ca, although not statistically significant (r = 0.31, p = 0.07).

The regressions between monthly Mg/Ca (measured as ppm) with SSTs revealed a Mg/Ca to SST relationship of 0.0038 ratio °C$^{-1}$ (standard deviation (SD) of slope=0.0005, SD of intercept=0.0148, unexplained variation (error)=0.177), thus 0.62 mol % of $MgCO_3$ °C$^{-1}$ (Fig. 3A). The regression of Li/Ca ratio (measured as ppm) with SSTs revealed an algal Li/Ca-SST relationship of $8*10^{-7}$ ratio °C$^{-1}$ (SD of slope=$9.7*10^{-8}$, SD of intercept=$2.8*10^{-6}$, unexplained variation=$6*10^{-9}$), thus 0.46 µmol % of $LiCO_3$ °C$^{-1}$ (Fig. 3B).

From 1974 to 2007 the annual Mg/Ca and Li/Ca ratio (measured as ppm) respectively showed an increase of 0.013 (=2.1 mol % of $MgCO_3$) and 3.3E-06 (=1.87 µmol % of $LiCO_3$), as well as the SST that recorded an increase of 0.55 °C in the same period (Fig. 4). The error on the element increment is 2.88 mol % for Mg and 1.61 µmol % for Li (based on 10% reproducibility).

The increase and decrease of Mg/Ca in the monthly averaged time series mirrors the Ba/Ca trend, except in 1992 and from 1974 to 1982 (Fig. 1). However, no significant correlation was found between the two ratios (r = 0.08 , p = 0.1). Correlation between monthly Ba/Ca and gridded SST was not significant (r = 0.03, p = 0.58). On the contrary, a significant and positive correlation was found between annual Li/Ca and Ba/Ca ratio (r = 0.49, p = 0.003). Indeed the annual Ba/Ca oscillation follows those of Li/Ca better than Mg/Ca (Fig. 4). Moreover, although Mg and Li showed a positive linear trend from 1974 to 2007, following the SST, the annual Ba/Ca revealed an opposite linear trend (Fig. 4), showing a decrease of -1.93E-05 µmol % of $BaCO_3$.

## *3.2. Elemental variability in algal thallus as proxies of climate and oceanographic oscillations*

### *3.2.1. Elemental variability as proxies of climate oscillations*

The Mg/Ca cross-spectral analysis revealed several peaks from decadal to inter-annual range centered at ~17-18 yrs, ~8 and ~5 yrs, but cross-spectral density between annual Mg/Ca record and gridded SST did not show coherence for these periods (Fig. 5A).

The Li/Ca cross-spectral analysis revealed a decadal peak for period centered at ~17-18 yrs (Fig. 5B). This period shared 83% of the Li/Ca variance in the algal thallus (Fig. 5B).

Although a significant and negative correlation was found between annual Mg/Ca and Niño 3.4 index ($r = -0.49$, $p < 0.01$), the cross-spectral analysis between the Mg/Ca record and Niño 3.4 index did not show a significant coherence.

On the contrary, the cross-spectral analysis between the Ba/Ca record and Niño 3.4 index revealed coherence within a period of 9-13 yrs (Fig. 6) at 3-4 yrs. Cross-phase analysis showed that Ba/Ca record lags Niño 3.4 index by 2 yrs (Fig. 6).

### *3.2.2. Elemental variability as proxies of Asian monsoon system*

Negative correlations between low pass-filtered records of annual Mg/Ca, Li/Ca and Ba/Ca of DB659bis elements ratios and the All India Rainfall (AIR) index were strong and significant (respectively $r = -0.63$, $-0.72$ and $-0.59$; $p < 0.01$ and $0.001$ for Li/Ca). Additionally, significant and negative correlations were found between annual Mg/Ca, Li/Ca and the Core-Monsoon India Rainfall (CORIN; respectively $r = -0.73$ and $-0.75$, $p < 0.001$). Field correlations of low-pass filtered records of annual elements and rainfall (Jan-December CRU TS3.22, Harris et al. 2014) revealed fields of significant positive correlations over Eastern Africa and significant negative over the Indian subcontinent, respectively (Fig. 7).

The cross-spectral analysis between the Mg/Ca record and Sea Surface Current (SSC) in Balhaf revealed coherence for period of about 17 yrs and 5 yrs (Fig. 8).

## 4. Discussion

This study reveals a high variability in the Mg and Li incorporation in the *Lithophyllum* thallus. Although SST variability on a decadal scale is the main control on the incorporation of these elements, our study demonstrates that there are other still unexplored factors affecting the coralline uptake of these elements. On the contrary, Ba is not influenced primarily by SST, and the controls on its incorporation in *Lithophyllum* remain poorly resolved. Nevertheless, Ba/Ca, Li/Ca and Mg/Ca (measured as ppm) show a multi-decadal pattern of cyclicity controlled by the main climate system in the Gulf of Aden,

### *4.1. Mg and Mg/Ca in coralline algae*

Mg concentration in coralline algae is variable, depending not only on environmental factors, but also on the genus (Smith et al. 2012). Mg contents in free-living coralline algae (rhodoliths), for example, vary between 7.7 and 28.8 mol % $MgCO_3$ (Chave 1954). A variable Mg content between 7.7 and 18 mol% for *Lithothamnion* spp. in subarctic species and between 13.2 to 22.4 mol % in subtropical species is reported in literature (Halfar et al. 2000). It has been shown that their Mg content vary as a function of SST (Chave and Wheeler 1965, Halfar et al. 2000, Kamenos et al. 2008, Hetzinger et al. 2009, Caragnano et al. 2014) and therefore it is suggested that within a given genus, those species sampled in warmer regions should contain higher $MgCO_3$. In agreement with Caragnano et al. (2014) the Mg content measured in *L. yemenense* was 20 mol % $MgCO_3$, thus significantly higher than 11.6-16.4 mol % $MgCO_3$ found in *Lithophyllum* spp. of the temperate New Zealand environment (Smith et al. 2012).

The relationship between Mg and SST in *L. yemenense* ranges between 0.62 and 2.06 (from Caragnano et al. 2014 for DB659a) mol % $MgCO_3$ $°C^{-1}$, which confirms the high intra-specific variability (Caragnano et al. 2014). This is twice the amount observed in the subarctic species: *L. glaciale* (Henrich et al. 1996, Halfar et al. 2000, Kamenos et al. 2008, Ragazzola et al. 2013), *P. calcareum* (Kamenos et al. 2008), *C. compactum* (Moberly 1968). Considering exclusively the lowest value presented here (0.62 mol % $MgCO_3$ $°C^{-1}$), the relationship is similar to that found in *C. compactum* (Chave and Wheeler 1965) and *Corallina* spp. (Williamson et al. 2014).

Beside the intra- and inter- specific variability, other reasons for the variable Mg-SST relationship are: wide geographic provenance of the samples (subarctic *vs*. tropic), application of different sampling techniques (i.e. higher sampling resolution of transects than spots, Hetzinger et al. 2011), poor annual resolution in low-growth thallus intervals (Hetzinger et al. 2011), quality of SST datasets used in this study in comparison to more reliable data of *in situ* SST datasets (Kamenos et al. 2008), and use of different technologies (electron microprobe analysis *vs*. LA-ICP-MS). In particular, LA-ICP-MS line transect data highlight more fine-scale heterogeneities and are therefore able to better capture seasonal extremes in comparison to electron microprobe analysis (Hetzinger et al. 2011). Additionally, although since 1954 the prevailing theories considered the calcified thallus of coralline algae formed by high-Mg calcite (Chave 1954), in recent studies the tropical alga *Porolithon onkodes* living on shallow coral reefs was found to contain disordered dolomite (Nash et al. 2011, Nash et al. 2012). Although SEM images of our samples did not show any evidence of diagenetic alteration of the thallus , secondary filling by carbonate precipitation with high peaks in the value of Mg was observed in correspondence of conceptacles in a previous study on *L. yemenense* (Caragnano et al. 2014). Therefore, the possible presence of dolomite or magnesite in the cell walls of our specimen cannot be fully ruled out, although our results are not in the range that would be expected if dolomite or magnesite were present (Nash et al. 2011).

Because the fruticose growth form and high occurrence of endolithic organisms (Fig. 2) led frequent changing of algal growth direction, the growth linear extension rates (=algal growth in thickness) in sample DB659bis were low. The reduced deposition of calcium carbonate implies a reduction of the element variability resolution in the algal thallus, which might affect the Mg-SST relationship, as well as the other elements measured (Carré et al. 2006).

The Mg-SST correlation reported here is lower than that calculated in our previous study of different portions of the same sample, although still significant (Caragnano et al. 2014). Indeed, in the last 34 yrs the SST in Balhaf has increased by 0.55°C as recorded by a positive increment of Mg content in the algal thallus, even though this increment should be not considered significant from a statistical point of view (2.88 mol% error > 2.1 mol% measured increment; Fig. 4). Although it was suggested that the Mg content in calcite of coralline red algae depends on growth rates (Moberly 1968), no significant relationship between yearly mean Mg/Ca and algal extension rate was observed in *L. yemenense* (as *L. kotschyanum* f. *affine*, Caragnano et al. 2014). However, a low extension rate could negatively affect the resolution of the analyses, preventing the detection of the extreme Mg values and smoothing the variability (Carré et al. 2006, Halfar et al. 2011). Thus the observed difference in the resolution of Mg-SST relationship as presented here, compared with a different portion of the same specimen analyzed by Caragnano et al. (2014) should be primarily attributed to the differing growth rate in these parts, since the two studies analyzed a different transect length.

### *4.2. Lithium in coralline algae*

In agreement with our previous study on *L. yemenense* from Yemeni coast (Caragnano et al. 2014), Li/Ca time series mirror the Mg/Ca curve with strong and significant correlation. Since SST was considered the main factor controlling the incorporation of Mg in coralline algal thallus, and since significant correlation was found between monthly average Li/Ca and SST, we confirm that SST is also a dominant factor controlling Li-carbonate chemistry in *L. yemenense* in agreement with the literature (Delaney et al. 1989, Marriott et al. 2004a, Case et al. 2010, Caragnano et al. 2014, Montagna et al. 2014). Indeed, the annual Li/Ca ratio showed a positive increment during the 34 yrs of algal growth, following the local SST increase, and on the contrary of Mg this increment is significant, because the calculated error is lower than the increment (respectively 1.61 µmol% and 1.87 µmol%; Fig. 4). On the contrary to what is observed in inorganic calcite, foraminifers, brachiopods and scleractinian corals (Delaney et al. 1989, Marriott et al. 2004a, Case et al. 2010, Montagna et al. 2014), the relationship between Li/Ca and SST in *L. yemenense* was found to be positive (Table 2), even after normalization of Li/Ca over Mg/Ca (Li/Mg) (Caragnano et al. 2014). Although in scleractinian corals the Li/Mg ratio resulted in a more robust proxy for ambient SST than Mg/Ca and Li/Ca time series (Montagna et al. 2014), the monthly Li/Mg ratio in *L. yemenense* did not improve the element ratio-SST relationship (Li/Mg-SST: $r = 0.2$, $p < 0.0001$; Li/Ca-SST: $r = 0.37$, $p < 0.0001$).

The relationship between Li/Ca and water salinity in the inorganic calcite is significant and positive, as shown by benthic foraminifers, although with some vital effects (Marriott et al. 2004b). Conversely, in the skeletons of deep-sea scleractinian corals, the Li/Ca ratio has no correlation with salinity (Case et al. 2010). Although SODA SSS (sea surface salinity) is a reanalysis dataset, that should be interpreted with caution, it is continuously corrected (every 10 days) by contemporaneous observations, especially in the surface fields (Carton and Giese 2008). The Li/Ca-SSS relationship was weak ($r = 0.2$, $p < 0.0001$) in the present study, likely due to the lower extension rates, despite a significant positive relationship between Li/Ca and SSS was already recorded (Caragnano et al. 2014),. No significant correlation between annual Li/Ca variability and coralline algae extension rate was observed here, although the growth rate of the organism could affect the Li/Ca ratio in the biogenic carbonate, as observed in the mollusks *A. islandica* and *Pecten maximus* (Thébault et al. 2009, Thébault and Chauvaud 2013).

Despite the limitations of the use of gridded dataset for SST it is suggested that in *L. yemenense* mainly SST controls the Li carbonate chemistry. On the other hand, when dealing with a large number of observations of natural phenomena, outliers or non-fitting data are very common, as well as lower resolution in lower growth rates. These were probably the main reasons of the weak Li-SSS and Mg-SST correlations found over the 34 yrs record, compared with the higher correlations found in the 3-year record in Caragnano et al. (2014).

### *4.3. Barium in coralline algae*

The Ba/Ca ratio is used as nutrient and temperature proxy in scleractinian corals tracking upwelling of cold, nutrient-rich waters to the surface (Lea et al. 1989), although some exceptions have been recently reported (Hart and Cohen 1996, Tudhope et al. 1996, Sinclair 2005). In coralline red algae the Ba/Ca ratio was found to be a robust proxy for freshening of the Alaska coastal current (Chan et al. 2011), for 20th century northwestern North Atlantic surface ocean freshwater variability

(Hetzinger et al. 2013), and for the increase of local sedimentation along the Yemeni coast of Gulf of Aden (Caragnano et al. 2014). Low and negative correlations between Ba/Ca and Mg/Ca, and weakly negative or no significant relationship between Ba/Ca and gridded SST were observed in the coralline algae *Clathromorphum* spp. (Hetzinger et al. 2011).

Conversely, the Ba/Ca-SST relationship in *L. yemenense* has been always found weakly positive or not significant (Table 2), suggesting that SST plays only a minor role in the incorporation of Ba into the algal high-Mg calcite lattice. Indeed, annual Ba/Ca ratio revealed a negative trend during the 34 years of algal growth, opposite to the ambient SST trend (Fig. 4).

The annual Core-Monsoon India Rainfall, and the surface zonal current in Balhaf (indices of the monsoon intensity) revealed a negative trend between 1974 and 2008, which is mirrored by the annual Ba/Ca ratio (Fig. 9). Contrariy to previous observations in the Northwest Atlantic (Hetzinger et al. 2013), no significant correlation was observed between Ba/Ca ratio and the SSS variability in the study area, although both show a negative trend in the considered period. Since the Ba/Ca ratio increases during the spring-summer monsoon (May to September) in this area, it is likely that its seasonality, might be linked to the monsoon-induced nutrient entrainment of deep water into the surface environment (Caragnano et al. 2014).

Moreover, barium revealed a strong relationship with annual Li/Ca ratio, although annual Ba/Ca was not correlated with Mg/Ca. Because the incorporation of Mg and Li in the coralline thallus seems mainly due to SST, it is suggested that Ba and Li might have a common factor that affected their incorporation in the algal thallus, such as the availability of elements by upwelling.

### *4.4. Elemental variability in algal thallus as proxies of climate and oceanographic oscillations*

Although an increasing number of studies are devoted to the biogeochemistry of the coralline red algae thallus and its relationship with climate and oceanographic condition of ambient seawater, the use of coralline algae as archive of climate and oceanographic oscillations is still uncommon. The $^{14}C$ variability in the sub-tropical *Lithothamnion crassiusculum* was associated to the El Niño-

Southern Oscillation (ENSO) (Frantz et al. 2000). Measurement of $\delta^{18}O$ and Mg/Ca ratio in the subarctic *C. nereostratum* thallus were well correlated with the Pacific Decadal Oscillation (PDO), ENSO, and the SST variability in the North-Pacific-Bearing Sea (Halfar et al. 2007, Hetzinger et al. 2009, Gamboa et al. 2010). The cross-spectral analysis between Li/Ca of *L. yemenense* and gridded SST revealed a decadal coherence for a period of about 17-18 yrs, (Fig. 5B), and this period shared 83% of algal thallus Li/Ca variance (Fig. 5B). Although a periodicity of 17-18 yrs in a time series of only 34 yrs might be statistically controversial, cyclicality in a similar range of 18-19 yrs has been found in annual extension rates of Maldivian coral, in zonal current and in South India Rainfall variability (Storz and Gischler 2011a-b). Periodicities in this range were not found in the annual mean $\delta^{18}O$ record in the coral from Maldives (Storz and Gischler 2011a, b), neither in the annual mean coral $\delta^{18}O$ records of the NW Indian Ocean reported by Charles et al. (1997), Cole et al. (2000), and Pfeiffer and Dullo (2006). Storz and Gischler (2011b) suggested that this is likely due to the fact that variations in monsoon strength are not accompanied by measurable SST and salinity changes. Hence, although a weak relationship was found between monthly and annual coralline Mg/Ca, Li/Ca record and gridded SST, and the limitation in the use of reconstructed database for SST, the weak coherence observed between coralline record and SST for a period of 17-18 yrs may be due to the fact that Climate and Oceanography in the Gulf of Aden are coupled with both, the monsoon system and the Red Sea Climate and Oceanography (Bethoux 1988, Al Saafani and Shenoi 2007). Thus variations in monsoon strength are not accompanied in Balhaf by measurable variation in monsoon SST, likely because the Balhaf area is not strongly affected by monsoon (Al Saafani and Shenoi 2007), rather by variation in nutrient content in sea water.

Since the Asian monsoon is characterized by seasonal reversal of the winds, forcing the reversal of Sea Surface Current (SSC), the latter is another index used for Asian monsoon strength, as well as Southern Indian Rainfall (SIR). Although decadal variability in the Mg/Ca record was not linked to SST oscillation, cross-spectral analysis between the element record and SSC in Balhaf revealed coherence for periods of about 17 yrs and 5 yrs (Fig. 8). Cyclicality in similar ranges has been observed in annual extension rates of coral from Maldives, in zonal current variability (Storz and Gischler 2011a). As previously discussed, the amount of Mg incorporated in the coralline algae varies as a function of SST, but it might be affected by other factors such as lower growth rates, and consequent lower resolution (Moberly 1968) and other algal "vital effects".

Periods of stronger Indian monsoons generate stronger monsoon rainfall over India, and enhanced SW monsoon current velocities in the NW Indian Ocean; elevated hydrodynamic energy leading stronger deep water upwelling in the Gulf of Aden would explain reduced elements contents in the algal thallus during such periods. Although cross-spectral analysis between elements record and SIR did not showed any coherence, the field correlations of low-pass filtered records of annual Mg/Ca, Li/Ca and Ba/Ca of *L. yemenense* from Balhaf and AIR revealed a significant and negative correlations between the elements and AIR anomalies (Fig. 7). This negative relationships suggests that the strongest Asian monsoon fosters the upwelling of deeper and saltier water mass (Bethoux 1988, Al Saafani and Shenoi 2007). The resulting increase in SSS affects the "partitioning coefficient" by reducing the element incorporation in the algal carbonate (Curti 1999).

The dipole relationship identified between equatorial Africa and India showed in the field correlations (Fig. 7) is consistent with temporal variations in the strength of the Intertropical Convergence Zone (ITCZ). Phases of higher monsoon strength over the Indian subcontinent are accompanied by drier conditions over equatorial Africa (Janicot 2009). A statistical link was found between a combined coral $\delta^{18}$O index (Seychelles, Kenya and Mayotte), land temperatures and rainfall over India, equatorial East Africa, and southeast Africa (Zinke et al. 2009).

Cross spectral analysis between the Ba/Ca record and Niño 3.4 index revealed coherence within a period of 9-13 yrs (Fig. 6), even though Mg/Ca and Li/Ca records did not revealed ENSO influence on the Gulf of Aden's SST. Gulf of Aden connects the Red Sea with the NW Indian Ocean. Studies on coral proxies from Seychelles (Charles et al. 1997), Kenya (Cole et al. 2000), La Réunion (Pfeiffer et al. 2004b), the Chagos Archipelago (Pfeiffer et al. 2004a), and Maldives (Storz et al. 2013) have demonstrated ENSO-driven inter-annual and decadal climate variability. The Indian

Ocean SSTs are externally forced by ENSO, centered in the central Pacific (Webster et al. 1998). El Niño events in the Pacific lead to a turnaround in the large-scale Walker circulation (Webster et al. 1998). Strong El Niño years cause higher SSTs in the western equatorial Indian Ocean (Webster et al. 1999) and the area of Balhaf revealed a significant but weak relationship with ENSO (Fig. 10). Cole et al. (2000) and Storz et al. (2013) suggested that decadal variability in the coral records is primarily a response to Pacific influences. Therefore, Ba/Ca variability in *L. yemenense* appears as a signal of ENSO intensity in the Indian Ocean with 9-13 yrs periodicity.

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## Figure captions

**Figure 1.** Monthly elements ratio of specimen (DB659bis). Comparison between SSS(SODA, dashed-dotted line), Sea Level Pressure (SLP, ICOADS; thin black line), reconstructed SST (HadISST1, dashed line), Mg/Ca cycle (thick black line), Li/Ca cycle (gray line) and Ba/Ca (darker gray line). Shaded areas indicate years with no coherence between time series of elements. All element ratios based on ppm values.

**Figure 2.** *Lithophyllum yemenense* sample: A) attached specimen (DB659); B) longitudinal section of thallus with drawing of transect analysis by LA-ICP-MS (DB659bis), black arrow shows a conceptacle (reproductive cavity).

**Figure 3.** Regression between: A) mean monthly Mg/Ca ratio and SST (HadISST1); B) mean monthly Li/Ca ratio and SST. All element ratios based on ppm values. The dashed lines reflect the 95% confidence interval.

**Figure 4.** Annual mean with linear trend of: gridded SST (HadISST1, dashed line); Mg/Ca ratio (black line); Li/Ca ratio (gray line); Ba/Ca ratio (dotted line). All element ratios based on ppm values.

**Figure 5.** Cross-spectral analysis of SST (HadISST1) for 1974-2008 *versus* DB659bis A) Mg/Ca ratio; B) Li/Ca ratio. Note multi-decadal coherence between Li/Ca record and SST for period of about 17-18 yrs with a lag of about 4 months of Li/Ca record on SST. For each cross-spectral density the top panel shows the variance spectra for both records, and the bottom panel shows the coherence (the correlation coefficient as the function of frequency between the records). Thin line on the bottom panel indicates the one sided lower error at 90%. Coherence values > 0.8 indicate that over 64% ($0.8^2$) of the variance at these periods is linearly correlated. Number are given in years. The bandwidth (BW) is 0.06 (number of lags: 24). The criteria for this are that the variance peaks are aligned (in the top panel) and that the corresponding coherence exceeds the 80% confidence level (CL). D) Periodograms of autocorrelation functions applied for the annual algal growth record for 1974-2008 and SSS in South Red Sea (SODA), Black lines = spectrum of the time series, dashed lines = significance level ($p < 0.05$). Prior analysis, the time series were detrended. A 5-year filter was applied in order to emphasize the variability in the decadal band.

**Figure 6.** Cross-spectral analysis of DB659bis Ba/Ca ratio *versus* Niño 3.4 index (from HadISST1) for 1974-2008. Note coherence between the two records for period of about 9-13 yrs with a lag of 2 yrs of Ba/Ca record on Niño 3.4 index. For legend see Fig. 5.

**Figure 7.** R-values of field correlations between the observed anomalies in the 12-monthly elemental ratio recorded in *Lithophyllum yemenense* and regional precipitation. A) 12-monthly algal Mg/Ca anomalies; B) 12-monthly algal Li/Ca anomalies; C) 12-monthly algal Ba/Ca anomalies. Jan-December CRU TS3.22 precipitation (Harris et al. 2014) on land for 30-90°E and 30°N-10°S during 1974-2008. A low-pass filter (6-year mean) removed interannual variability (analysis run with the KNMI climate explorer web application, van Oldenborgh and Burgers 2001). Correlations stronger than $r = +0.4$ or $r = -0.4$ are significant at 99% (two-sided Student t-test, r-values with $p>0.10$ are masked out). Blue strong negative correlation, red strong positive correlation. The black circle indicates Balhaf and square Western Ghats region.

**Figure 8.** Cross-spectral analysis of DB659bis Mg/Ca ratio *versus* Zonal Surface Current (from SODA) for 1974-2008. Note coherence between the two records for period of about 17-18 yrs and 5 yrs with respectively no lag and 1.3 yrs of Mg/Ca record on current in Balhaf. For legend see Fig. 5.

**Figure 9.** Annual mean with linear trend of Core-Monsoon India Rainfall (CORIN, gray line); surface zonal current in Balhaf (dashed line); sea surface salinity in Balhaf (SSS, black line).

**Figure 10.** A) Monthly and annual record of the ENSO index Niño 3.4 (based on HadISST1). B) R-values of running correlations between the 12-months averaged high-pass filtered (year-on-year difference) record of Niño 3.4, and SST fields (based on HadISST1) in the Indo-Pacific, based on a grid of 1°x1° for period 1974-2008. Black circles indicates the site sampling Balhaf. A high-pass filter (year-on-year difference) was used in order to highlight the interannual variability by

removing trends or slow variations. Correlations stronger than r = +0.4 or r = -0.4 are significant at 99%, based on a two-sided student t-test. P-values < 0.2 have been masked out. Analysis was run with the KNMI climate explorer web application (Van Oldenborgh and Burges 2001, http://climexp.knmi.nl). C) Blackman-Tukey cross-spectrum between annual mean Niño 3.4 index and gridded SST (HadISST1) from Balhaf for the period 1974 -2008. For legend see Fig. 5.