Trace element and isotopic composition of coral skeletons as proxies for paleoclimate reconstructions and the role of coral physiology in controlling the geochemical composition during the skeletogenesis

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Abstract

The geochemical composition of the aragonite exoskeleton of corals is increasingly recognized as a valuable tool for paleoceanographic studies and the deep-water specimens are considered among the most promising archives for sub-decadal scale resolution of intermediate and bathyal oceanic variability. However, the chemical heterogeneities observed at micron and nanometer size scales suggest that coral physiology imprints a "vital effect" upon different structural regions, which potentially complicates and distorts their interpretations and hence the paleoceanographic reconstructions. A number of geochemical models have been proposed, based on detailed geochemical investigations of stable isotopes (oxygen and carbon) and trace elements in coral skeletons. The large oxygen and carbon isotope variability has been related to the so-called "kinetic" and "carbonate" models, with the former linked to the kinetic fractionation of the two isotopes during calcification *(McConnaughey 1989)* and the latter considering the internal pH as the key parameter *(Adkins et al., 2003)*. The "carbonate" model has been questioned by recent boron isotopic results that predict the presence of amorphous calcium carbonate (ACC) as a transient precursor phase during the biomineralization process. Trace element heterogeneity has been explained by growth-rate related mechanisms, Rayleigh fractionation and differences in cellular function within the calicoblastic cell layer. The physiological component needs to be quantified or removed in order to obtain reliable paleoclimate reconstructions and new promising approaches have been recently tested. These involve the use of geochemically similar elements *(i.e. lithium and magnesium)* and the application of non-traditional and radiogenic isotopes, which are independent of biological fractionation.

Key-words: *Coral Biomineralization, Vital Effect, Trace Elements, Stable Isotopes*

1. Introduction

Annually banded coral skeletons are well-proven archives of the ocean dynamics, recording the physical and chemical parameters of the seawater masses. These marine properties are encoded as specific geochemical signals within the calcareous skeleton, potentially providing century long records at sub-decadal resolution *(Gagan et al., 2000; Corrège, 2006)*. Trace ele-

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ment systematics and stable isotopic data have been successfully applied to scleractinian shallow- and deep-water corals to reconstruct important marine parameters, such as seawater temperature, salinity, nutrient content, pH evolution and water mass circulation *(Mitsuguchi et al., 1996; McCulloch et al., 1999; Gagan et al., 2000; Pelejero et al., 2005; Montagna et al., 2006, 2007)*. The finding that one skeletal high-density/low-density band pair in tropical and temperate corals represents one year of growth enabled the construction of accurate age models for centuries long coral records by counting annual cycles. In addition, the aragonite skeleton of scleractinian corals can be precisely dated by means of AMS radiocarbon and mass spectrometric uranium-series to provide robust chronologies and generate snapshots of paleoclimate *(Mangini et al., 1998; Cheng et al., 2000)*. These coral-based snapshots represent floating chronologies but with an accurate internal age model and are therefore well suited to study past changes in seasonality and interannual to decadal climate variability rarely available from other natural archives.

The chemical heterogeneities observed at micron and nanometer size scales in the coral skeleton suggest that coral physiology imprints a "vital effect" upon different structural regions. Coral biomineralization is a process that occurs in a "biologically-controlled medium" *(Allemand et al., 2004)* and it has the potential to complicate and distort the paleoceanographic reconstructions. Recent data have shown that most of the geochemical signals in corals are biologically mediated and various models have been proposed to explain the role of the coral physiology in controlling the isotopic and elemental uptake. These geochemical models are mainly built on trace elements and stable isotope data obtained from deep-water corals *(Adkins et al., 2003; Rollion-Bard et al., 2003; Blamart et al., 2007; Montagna et al., 2005; Gagnon et al., 2007)*. Because the physico-chemical conditions in the deep sea environment are fairly uniform and the deep-water corals are free from the complications of photosynthetic symbionts, these species bear the potential for better constraining the role of coral physiology during the calcification processes compared to tropical corals. Unfortunately, our understanding of the exact mechanisms driving coral biomineralization remains incomplete and a detailed study of coral geochemistry has yet to be fully explored.

Spatially-resolved geochemical measurements of trace elements and stable isotopes can help in investigating the skeletogenesis and the role of the physiology in modulating the climate signals.

The detailed study of the distribution of geochemically similar elements appears to be one of the most promising approach to overcome the effect of coral biomineralization and retrieve reliable paleoclimate information *(Montagna et al., 2009)*. This requires the use of precise and accurate state of the art analytical techniques which allow the analysis of elemental and isotopic ratios at fine-scale resolution, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), secondary ionization mass spectrometry (SIMS) and NanoSIMS.

On the other hand, coral biomineralization does not seem to have an effect on specific radiogenic isotopic systems that have only recently begun to be exploited in corals, such as neodymium isotopes *(van de Fliert et al., 2006; Montagna et al., 2010)*. The $^{143}Nd/^{144}Nd$ ratio in corals is independent of fractionation induced by biological processes and faithfully record the neodymium isotopic composition of the seawater, which is in turn a tracer of the water mass circulation *(van de Fliert et al., 2006)*.

This paper presents a summary of the state of the current research concerning coral calcification with a particular emphasis on the role of trace elements and stable isotopes in helping to better understand the biomineralization mechanism. This review mainly focuses on the geochemical composition of deep-water corals *(Fig. 1)*, being the most promising candidates to assess the role of coral biomineralization in modifying the climate signals.

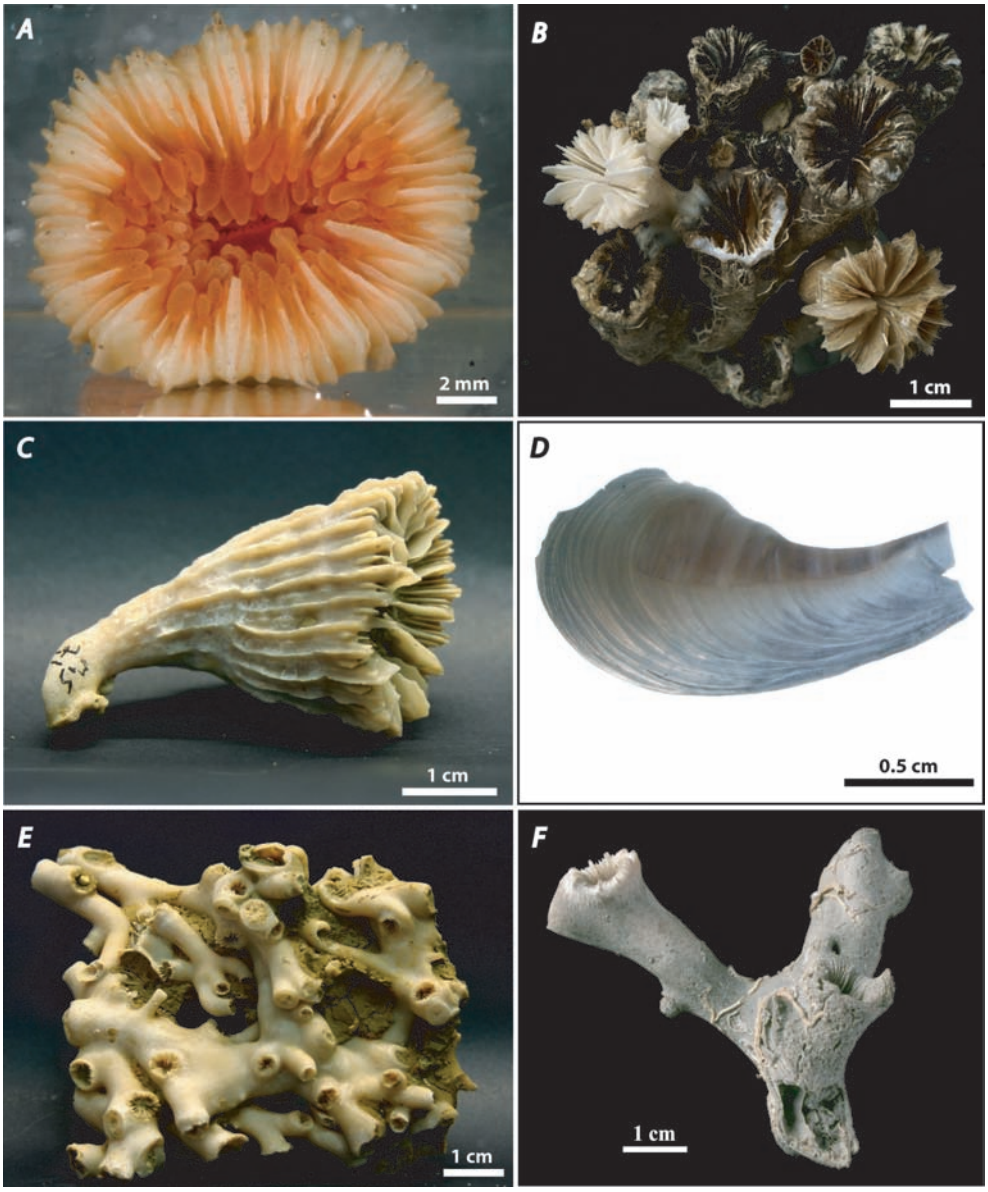

fig. 1. 'Deep-water corals collected in the Mediterranean Sea. A. Distal view of the calyx of a live Desmophyllum dianthus showing the orange tentacles and the septa. B. Fossil D. dianthus colonized by sub-recent and live specimens of the same species. C. Distal-lateral view of a 37kyrs old D. dianthus. D. Transmitted light image of the main septum (S1) of a D. dianthus. White and dark microbands form the density banding characteristic of this species. E. 48kyrs old Lophelia pertusa colony retrieved in the Strait of Sicily. F. 16kyrs old Lophelia pertusa branch collected in the Ionian Sea.

2. Coral calcification

Corals secrete aragonite ($CaCO_3$) to produce supportive skeletons *(Barnes, 1970)* and the mechanisms behind this process are not purely controlled by the rigorous and constant laws of inorganic chemistry but physiology seems to play a significant role. The biomineralization process takes place in the aboral ectoderm layer, know as the calicoblastic epi-

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thelium. The wall of each polyp is composed of two cell layers separated by a gelatinous mesoglea. The outer cell layer, facing the seawater, hosts the calicoblastic cells, which are responsible for the calcification process. This process likely involves a carrier-mediated transport mechanism, by which Ca^{2+} is transfer from the seawater to a nanometer size layer existing between the aboral ectoderm and the skeleton, also known as the "extracellular calcifying space" (ECF) *(Cohen & McConnaughey, 2003)*, although the presence of such a space is difficult to document histologically *(Tambutté et al. 2007)*. Through a cellular alkalinity pump (Ca^{2+} - ATPase) the polyp can exchange two protons for each ion transported, increasing the pH within the calcifying space and thus creating a supersaturated solution, which promotes the carbonate precipitation. In particular, an increase in pH shifts the equilibrium of the carbonate species in solution towards the carbonate ion (CO_3^{2-}), which combines with Ca^{2+} to form $CaCO_3$. The calcification reaction is chemically represented in the following equation:

(1) $Ca^{2+} + CO_2 + H_2O = CaCO_3 + 2H^+$

The dissolved inorganic carbon (DIC) entering the ECF derives from both ambient seawater and metabolically respired carbon dioxide in different proportions depending on the coral species *(Furla et al., 2000; Adkins et al., 2003)*. The CO_2 is then transformed into HCO_3^- through the enzyme carbonic anydrase likely located in the calicoblastic epithelium, as suggested by studies carried out on tropical corals *(Isa & Yamazato, 1984)*. The precipitation of calcium carbonate is believed to occur from the solution present in the ECF directly on the underlying skeleton or on an organic matrix, which seems to play a significant role in the biomineralization process as a framework for skeletogenesis *(Allemand et al., 1998)*.

The information regarding the physiological mechanisms for coral calcification was mostly derived from experiments, using for example microcolony *(Al-Moghrabi et al., 1993; Tambutté et al., 1995)* or micro-electrodes to measure Ca^{2+} and H^+ ion activities at various coral position *(Al-Horani et al., 2003)*. *Al-Horani et al. (2003)*, studying the symbiotic tropical coral *Galaxea fascicularis*, noted that the enzyme Ca^{2+}-ATPase increases the concentration at the calcifying site contemporaneously favouring the transport of protons away and increasing pH, thus increasing the Ca^{2+} concentration at the calcification site. They measured a pH of 9.3 under the calicoblastic layer, a value significantly higher than in the polyp's surface. The above-described mechanism of coral calcification process is a synthesis of a complex topic which has been exhaustively treated by *Cohen & McConnaughey (2003)* and *Allemand et al. (2004)*.

3. The role of biomineralization in controlling elemental and isotopic ratios in coral skeletons

The understanding of coral biomineralization is crucial for paleoclimate reconstructions and it becomes increasingly important to quantify the effects of both physiology and environmental parameters on coral chemical records. These instances are still poorly understood and relationships between mineral phases and organic materials during biomineralization processes are still relatively unknown. Two different possible mechanisms divide researchers on the way corals form their skeletons. The first process assumes that crystals form inorganically inside the membrane in enclosed pockets of fluids, the second one implies that aragonite is precipitated from an organic matrix. These two skeletogenesis mechanisms determine two different chemical pathways for the formation of coral aragonite, being the "inorganic" process mainly controlled by thermodynamic and kinetic laws while the "organic" one by biological factors, such as physiological transport. *Bryan & Hill (1941)* applied a purely mineralogical concept to skeletogenesis concluding that each aragonite fibre is a single orthorhombic crystal formed without biological control. This interpretation is mainly the result of the remarkable resemblance of aragonite fibres to spherulitic crystal morphologies common to all inorganic crystalline systems and is the basis of a physicochemical model of coral calcification. On the other hand, the organic matrix model involves the presence

of an organic matrix controlling crystal mineralogy, orientation and growth. *Goreau (1959)* identified this material as an amorphous mucopolysaccharide gel working as a template for recrystallization, while *Wainright (1963)* observed a spongework of organic chitin fibrils at the surface of the skeleton in a *Pocillipora damicornis*. Biochemical composition of organic matrix in corals is poorly known, although there is evidence for the presence of proteins, polysaccharides, glycosaminoglycanes *(Constanz & Weiner, 1988),* lipids *(Young et al., 1971)* and chitin *(Wainwright, 1963).* Recently, *Cuif et al. (2003)* reported high concentrations of sulphated organic compounds within the calcification centres (COCs), considered to be the first component of the skeleton formed, and lower concentrations in the fibrous aragonite (FA), which represents the bulk of the skeleton, where these compounds form banded patterns. These patterns were interpreted by *Cuif et al. (2003)* as a polycyclic model of crystal growth, involving step-by-step growth of aragonite fibres.

The centres of calcification are composed of tiny crystals surrounded by fibrous aragonitic bundles, and both coral microstructures show characteristic elemental and isotopic patterns, clearly controlled by biological factors, such as, for example, the growth rate. If aragonite is allowed to precipitate slowly from a solution, its oxygen (^{16}O, ^{18}O) and carbon (^{12}C, ^{13}C) isotope composition would be close to the isotopic thermodynamic equilibrium for the aragonite-water system. However, this is not the case for corals that precipitate their skeleton far out of isotopic equilibrium with seawater *(Weber & Woodhead, 1970)*, showing distinctive offsets due to the biological imprint. Deep-water corals are characterized by a strong isotopic disequilibrium with oxygen and carbon isotopes being linearly correlated and significantly depleted compared to equilibrium values (e.g. 5‰ for $\delta^{18}O$ and 15‰ for $\delta^{13}C$; *Sherwood & Risk, 2007).* These "anomalous" isotopic signatures, and the large range of values, cannot be explained by the nearly constant bottom water temperature and salinity fluctuations but must be related to vital or kinetic effects.

McConnaughey (1989) studied the isotopic disequilibrium in corals and he concluded that the reasons for oxygen and carbon isotope disequilibrium in biological carbonates are both kinetic and metabolic. The kinetic effect causes the depletion of skeletal ^{18}O and ^{13}C with respect to isotopic equilibrium due to the kinetic isotope fractionations during CO_2 hydration and hydroxylation, whereas the metabolic effect involves changes of the $\delta^{13}C$ in the internal dissolved inorganic carbon reservoir, due to photosynthesis and respiration processes. Moreover, he observed that faster growing parts of coral skeleton, or faster growing coral colonies, tend to be more strongly depleted in ^{18}O, compared to slower growing parts. The conclusions of *McConnaughey (1989)* were partially overcome by *Leder et al. (1996)*, experimentally studying corals of *Montastraea annularis* in Florida. They suggested that the variations in ^{18}O may be "the result of the reduced sampling rate in slower growing sections of the coral and not solely a result of variable kinetic effects".

Analysing the same experimental corals of *M. annularis, Swart et al. (1996)* did not find significant relationships between growth rate or calcification and skeletal $\delta^{13}C$ as observed by *McConnaughey (1989)*: corals characterized by a different growth rate had similar $\delta^{13}C$ values considering the same coral portions. In a comprehensive study of the effect of light on skeletal $\delta^{13}C$ and $\delta^{18}O$, and interaction with photosynthesis, respiration and calcification, Reynaud-Vaganay et al. (2001) investigated some zooxanthellate corals *(Acropora sp. and Stylophora pistillata)* under controlled conditions in the laboratory. They could observe a significant enrichment in ^{13}C and ^{18}O relative to the calcification increase. The conclusion is in disagreement with the results of *McConnaughey (1989)* who found a depletion in ^{13}C and ^{18}O in coral skeleton when calcification increases. In addition, *Reynaud-Vaganay et al. (2001)* did not find any other correlation between $\delta^{13}C$ and net and gross photosynthesis (Pn and Pg), respiration (R), and the Pg/R ratio. *Juillet-Leclerc et al. (1997)* studied the scleractinian coral *Acropora formosa* and did not find any evidence of relationship between $\delta^{18}O$ ratio and pro-

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ductivity; even if the authors found a positive, statistically significant relationship between $\delta^{13}C$ and productivity, they concluded that this relationship should be explained by the control of external factors other than SST. *Adkins et al. (2003)* developed an alternative model for coral isotope fractionation, analysing six modern deep-water corals *(Desmophyllum dianthus)* for $\delta^{18}O$ and $\delta^{13}C$ at high-resolution using a micro-mill to sample across centres of calcification and fibrous aragonite. They found variations in $\delta^{13}C$ as large as 10‰ and in $\delta^{18}O$ of up to 5‰ within single specimens, with the heaviest $\delta^{13}C$ and $\delta^{18}O$ only slightly depleted relative to equilibrium isotopic compositions predicted from seawater, which can be explained by small amounts of respired CO_2 incorporated in the skeleton. They concluded that the biologically-induced pH gradient produced between the impermeable cell wall and the calcifying fluid is the "master variable" to explain the isotopic fractionation. The "carbonate" model proposed by *Adkins et al. (2003)* attempts to explain the different behaviour between $\delta^{18}O$ and $\delta^{13}C$ at the centres of calcification, with the former being more depleted compared to $\delta^{13}C$, due to the different mechanisms in corals controlling the two isotopic systems. As summarized by *McConnaughey (2003)*, there are different factors which might cause the apparent "kink" in Adkins' equilibration line, such as the changing ratios of CO_2 hydration and hydroxylation, combined with changing contributions of CO_2 to the skeleton and varying degrees of equilibration. *Rollion-Bard et al. (2003)* concluded that "vital effect" in corals is mainly controlled by pH variations at the sites of calcification through the relative fraction of dissolved carbonate species and the kinetics of their isotopic equilibration with seawater before carbonate precipitation.

The "carbonate" model has been recently questioned by *Blamart et al. (2007)* and *Rollion-Bard et al. (2010)*, based on boron isotopic values of the deep-water coral *Lophelia pertusa*. It has been suggested that boron isotopes ($^{11}B/^{10}B$) in calcifying organisms can provide accurate seawater pH reconstructions *(Honisch et al., 2004; Sanyal et al., 2001)*. The theory behind the B-isotopes as pH proxy is quite well established and is based on relatively simple equations. In aqueous solutions boron exists as two species, boric acid and borate ion, with the proportion of the two species being pH dependent. The two species show large isotopic fractionation (~20‰) due to different B-O vibrational energy and molecular geometry *(Kakihana et al., 1977)*. Since only the borate ion is postulated to be incorporated into marine carbonate *(Vengosh et al., 1991)*, and given that the proportions of the aqueous species change according to pH, the boron isotopic composition in marine carbonate should also be a function of the ambient seawater pH during calcification *(Hemming & Hanson, 1992). Blamart et al. (2007)* and *Rollion-Bard et al. (2010)* used an ion microprobe to investigate $\delta^{11}B$ in centres of calcification and surrounding fibrous aragonite of *Lophelia pertusa*. Contrarily to what expected from the "carbonate" model, the $\delta^{11}B$ in the centres of calcification were consistently lower than the surrounding fibres, suggesting a lower pH. Based on these new findings, *Rollion-Bard et al. (2010)* proposed a new geochemical model of coral biomineralization, involving the amorphous calcium carbonate (ACC) as a transient precursor phase to the formation of the centres of calcification. This model predict that ACC crystallization occurs within a layer of organic hydrogel of species specific composition rather than in a seawater-like fluid.

The role of biomineralization in controlling the geochemistry of coral skeletons is evident not only in the stable isotopes but also in the trace and minor element composition. An increasing number of publications shows that COCs and FA have a distinctly different elemental composition in both zooxanthellate and azooxanthellate corals *(Montagna et al., 2005; Shirai et al., 2005; Sinclair et al., 2006; Meibon et al., 2006; Cohen et al., 2006; Robinson et al., 2006; Gagnon et al., 2007)*, confirming that vital effect is active at micron-scale length, affecting the partitioning of most of the elements. The most striking feature is the negative correlation between Mg/Ca and U/Ca ratios in all the scleractinian coral species studied so far. The COCs are enriched in Mg/Ca and depleted in U/Ca

compared to the FA, whereas other elements such as Sr/Ca and B/Ca do not display a clear signature. *Sinclair et al. (2006)* explained this characteristic pattern with the combined effect of growth rate, via an occlusion mechanism of Mg into lattice defects, and a negative rate-dependence of uranium concentration caused by differential transport of Ca^{2+} to the site of calcification relative to uranium. *Gagnon et al. (2007)* studied Sr/Ca and Mg/Ca in the azooxanthellate coral *Desmophyllum dianthus* and found opposing variability patterns for these two element ratios in the central and outer calcification bands. Whereas Sr/Ca shows the least variability in the central band and is overall relatively uniform, Mg/Ca shows large variations throughout the coral skeleton but most significantly in the central band. The overall small variability observed in Sr/Ca led *Gagnon et al. (2007)* to suggest that Sr/Ca, similar to shallow water corals, may provide a deep-sea temperature proxy in scleractinians. For the calcification process in this coral they suggested trace element incorporation is characterized by Rayleigh fractionation from a discrete calcification fluid. The two-fold increase of Mg/Ca ratios in the COCs compared to FA has been explained by *Gagnon et al. (2007)* as a result of the surface entrapment model *(Watson, 2004)* and assuming rapid precipitation in this specific coral microstructure and/or the presence of organic material. *Stolarski (2003)* reported a much higher content of organic-enriched components in COCs with respect to the thickening deposit region (i.e. FA); this difference might be responsible for enriched Mg/Ca. Similarly to *Gagnon et al. (2007), Cohen et al. (2006)* studied Sr/Ca and Mg/Ca ratios at high-resolution in *Lophelia pertusa* using a SIMS and observed seasonal variations larger than those observed in zooxanthellate tropical corals, despite the uniform physicochemical environment that they live in. *Cohen et al. (2006)* concluded that temperature-dependent variations in Sr/Ca partitioning account for ~25% of the Sr/Ca variability, with three-quarters of the signal being driven by the seasonal variation in the saturation state of the coral's calcifying fluid, which drives the skeletal "precipitation efficiency". *Meibom et al. (2006)* investigated the distribution of trace elements (Sr, B, S and Ba) and stable isotopes (O and C) in the zooxanthellate coral *Colpophyllia sp.* using a SHRIMP-RG and a Cameca 1270 ion microprobes. Their data show that COCs have higher trace element concentrations and lighter isotopic compositions than in the FA, concluding that different mechanisms are responsible for the precipitation of the two microstructures. In particular, they suggested that coral precipitation does not occur from a single reservoir and the different geochemical compositions observed in COCs and FA might be the result of differences in cellular function within the calicoblastic cell layer.

4. Methods to overcome the "vital effect" and isotopic systems not affected by coral physiology

From the previously mentioned studies it is clear that coral physiology is actively controlling the chemical composition of different portions of the skeleton, and the temperature reconstructions are often complicated and biased by the overprint of this "vital effect", likely related to the differential skeletal growth rate.

Very recently, a detailed and systematic geochemical study was carried out on the skeletal aragonite of shallow and deep-water corals, retrieved in the field and cultured in aquaria *(Montagna et al., 2009)*. By focusing a laser ablation system on different skeletal portions of living samples of *Cladocora caespitosa* and *Lophelia pertusa (Fig. 2)*, we found that the distribution of most of the elements analysed, including Li, B, Mg, Sr and U is microstructure-related and largely depends on the different calcification mechanisms between the COCs and the FA *(Montagna et al., 2009)*. If these fine-scale variations translate into temperature, they provide a temperature range between 10 and 18°C, depending on the proxy and the calibration applied. Clearly, the chemical composition of the coral skeletons is not primarily controlled by the small temperature fluctuations in deep ocean sites, which are on the order of ± 2°C at most. In addition, we found that this micron-size scale heterogeneity is ubiquitous among different coral species, both zooxanthellate and azooxanthellate, implying similar physio-

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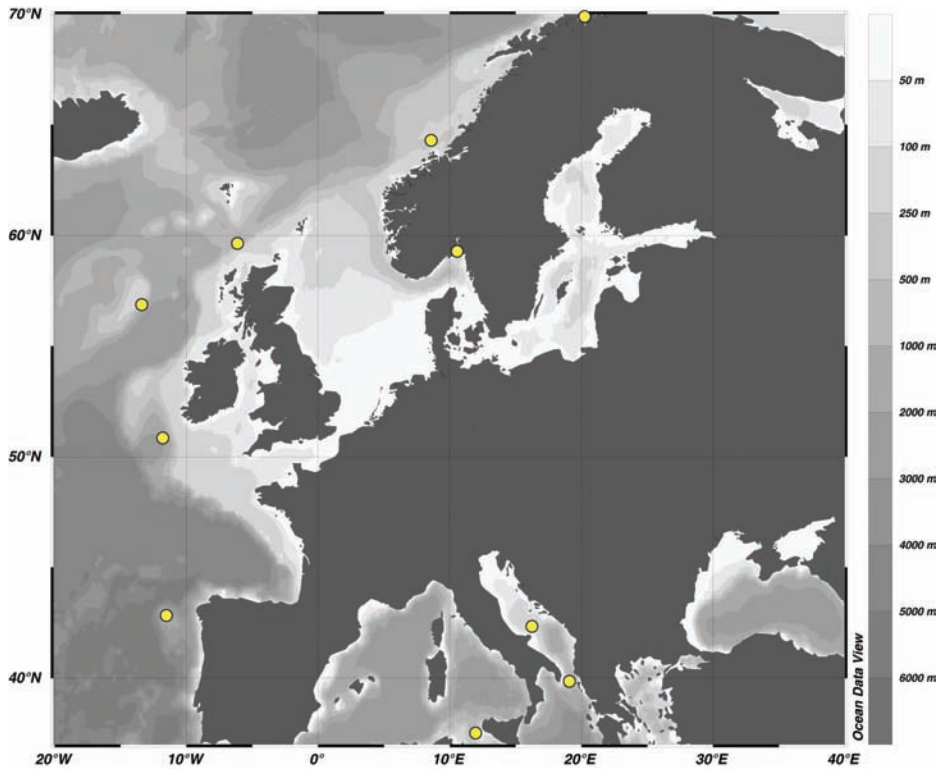

fig. 2. Sampling locations of the live Lophelia pertusa specimens used for Li/Mg measurements.

logical processes during the skeletogenesis.

For the first time we investigated the possibility of deconvolving environmental from physiological effects by analysing Li, Mg and Ca. Lithium and Mg are highly correlated in shallow and deep-water corals and both seem to be similarly affected by the coral physiology. In order to correct for this "vital effect" Li/Ca ratios have been normalized for Mg/Ca ratios, providing a positive and highly significant correlation with the *in-situ* water temperature and suggesting a pure temperature control on Li/Mg ratio.

Regardless of the exact mechanism that controls the uptake of Li and Mg, it seems clear that we can significantly improve the seawater temperature reconstructions with a precision of ± 0.8°C and with a particular sensitivity at low temperature such as those found in the deep ocean.

There have been other attempts to overcome the "vital effect" imprint and reliably use the geochemical proxies in corals for paleoclimate reconstructions. For example, *Rüggeberg et al. (2008)* investigated the use of stable strontium isotopes in *Lophelia pertusa*, reporting a precision for temperature reconstructions of about ± 1°C and the apparent lack of physiological factors on the fractionation of $\delta^{88/86}Sr$. Very recently, a temperature proxy based on "clumped isotope" analyses, the so-called "carbonate clumped isotope thermometry" *(Eiler, 2007)*, has been empirically calibrated for shallow- and deep-water corals *(Thiagarajan et al., 2009)*. This method seems to be independent of the "vital effect", giving a precision in the range of 1-2°C but it is a challenging and time consuming analytical method, still facing technical limitations *(Eiler, 2007)*.

Other isotopic ratios (e.g. $^{143}Nd/^{144}Nd$) have

been shown to be unaffected by biological fractionation and there has been an increasing interest in employing those isotopes in corals for paleoclimate reconstructions *(van de Flierdt et al., 2006; Robinson & van de Flierdt, 2009; Montagna et al., 2010)*. $^{143}Nd/^{144}Nd$ ratios vary in the Earth as a result of α decay of ^{147}Sm, and in the ocean the values reflect the age of the continental sources of dissolved Nd, acting as a fingerprint of the dissolved Nd source regions. Since the residence time of Nd in the ocean is in the order of 500-1000 years *(Tachikawa et al., 2004)*, it can be effectively used as a tool to reconstruct the movement of water masses. Neodymium isotopic values in corals show a close relationship with the composition of the ambient seawater, opening new possibilities to obtain water mass signals and quantify mixing of water masses via pared neodymium isotopes and radiocarbon analyses of absolutely dated (U/Th) fossil corals.

From a paleoclimate perspective, it is essential to address the issues posed by the biomineralization process and how coral physiology can modify the geochemical signals encoded in the carbonate skeletons. Confidence in paleo-climate reconstructions consequently requires an in depth understanding of the absolute magnitude and pattern of "vital effect" upon different architectural elements, their spatial heterogeneities and the use of proper analytical methods with increasing fine-scale resolution.

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