Isotopic and elemental records in a non-tropical coral (Cladocora caespitosa): Discovery of a new high-resolution climate archive for the Mediterranean Sea

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Abstract

A 95-year annual record of skeletal Sr/Ca, Mg/Ca, δ18O and δ13C is reported for a non-tropical, slow-growing coral (Cladocora caespitosa) collected in the north-western Mediterranean Sea. Significant correlations were found for Sr/Ca vs. Mg/Ca, Sr/Ca vs. δ18O and for δ18O vs. δ13C, indicating the possibility of using this non-tropical species as a climatic and paleoclimatic biomarker. The Sr/Ca and Mg/Ca ratios as well as the δ18O composition in corals were compared against the Sea Surface Temperature (SST) data of IGOSS (Integrated Global Ocean Service System Products) for the north-western Mediterranean region. The Sr/Ca ratios show a significant correlation with the SST, according to the following equation: Sr/Ca (mmol/mol) = 11.25(±0.38) – 0.079(±0.026) SST (°C). The δ18O data do not appear to fit with the SST interval used, since the regression obtained is non-significant. This implies that other factors apart from temperature, such as the δ18O seawater, are affecting the coral δ18O. The relationship between Mg/Ca ratio and SST is not statistically significant. This is probably due to the heterogeneities in magnesium content found among the coral microstructures (calcification centres, surrounding fibres and disseminations), along with other factors, such as the presence of microborings and/or organic matter.

The annual record indicates a history of SST variation that is consistent with the instrumental measurements, and strongly suggests the feasibility of using this non-tropical coral as a new proxy for the Mediterranean Sea.

Keywords: Paleoclimate proxy; High-resolution records; Cladocora caespitosa; Mediterranean Sea

1. Introduction

The Mediterranean Sea (MS) is a highly vulnerable semi-enclosed basin where profound and complex
changes are commonly observed (Bethoux et al., 1999).

The understanding of decennial and longer term climate variability in the MS requires reliable measurements of relevant parameters, such as the Sea Surface Temperature (SST).

This requires the availability of a consistent series of climatic parameters with a continuous and detailed temporal and spatial resolution. Over the last century, high-resolution (annual to seasonal) SST records have generally not been available in the temperate area of the MS. Hence, the only possibility to extend our climate database far beyond the instrumental record is by studying well-dated natural archives of climate variability, such as the corals found in tropical and subtropical seas.

The great potential of reef-building corals has been investigated mainly in the tropical regions, where corals are abundant and are characterized by a fast linear extension rate (>10 mm/year).

In the Mediterranean Sea, coral-based paleoclimatic studies are quite rare and mostly make use of sclerochronological data to infer information about SST (Peirano et al., 2004).

However, it has been shown in the Great Barrier Reef (Lough and Barnes, 1990; Alibert and McCulloch, 1997) and in Japan (Mitsuguchi et al., 2003) that Porites sp. corals exhibit an intra-regional inconsistency in the formation of density bands. This implies that density-band formation varies with metabolic or physiological conditions of individual colonies (Mitsuguchi et al., 2003).

On the other hand, the skeletal aragonite of reef-building corals provides chemical and isotopic records that allow us to obtain indications of water temperature, salinity, and isotopic composition as well as oceanic upwelling and anthropogenic inputs. Indeed, the $\delta^{18}O$, $\delta^{13}C$, Sr/Ca and Mg/Ca records derived from coral aragonite are widely used as proxies for paleoclimatic and paleoenvironmental reconstructions.

In particular, $\delta^{18}O$ has been commonly applied in coral skeletons to obtain information on paleo-SST in regions close to the MS such as the Red Sea (e.g., Klein et al., 1992; Felis et al., 1998, 2000, 2003; Al-Rousan et al., 2003; Rimbu et al., 2003) as well as in other tropical and sub-tropical seas (e.g., Fairbanks and Dodge, 1979; Cole and Fairbanks, 1990; Dunbar et al., 1994; Leder et al., 1996; Cardinal et al., 2001; Watanabe et al., 2001). However, coral skeletal $\delta^{18}O$ is not just sensitive to SST alone, since the local precipitation–evaporation balance controls not only the SST but also the marine $\delta^{18}O$ (Craig and Gordon, 1965).

Other studies (Weber and Woodhead, 1970; Erez, 1978; Swart, 1983; Swart et al., 1996; McConnaughey, 1989a,b; Reynaud-Vagany et al., 2001; Adkins et al., 2003; McConnaughey, 2003) have tried to explain the origin of $\delta^{13}C$ variations in the coral skeleton, taking into account both environmental and biological parameters. However, further research is required to understand the carbon isotope fractionation in corals.

The usefulness of coralline Sr/Ca as a proxy for SST was first demonstrated by Beck et al. (1992). Many authors have since derived climatic information using this geochemical proxy (de Villiers et al., 1994; McCulloch et al., 1994; McCulloch et al., 1996; Beck et al., 1997; Alibert and McCulloch, 1997; Gagan et al., 1998; Linsley et al., 2000; Cardinal et al., 2001). The fact that Mg/Ca is sensitive to SST was clearly established by Mitsuguchi et al. (1996). Mitsuguchi and colleagues analysed some skeletons of the coral Porites lutea from the Ryukyu Islands (Japan Sea) and observed a relationship between Mg/Ca ratios and instrumental SST measured at 30 km south of the sampling site.

In this study, we apply all these isotopic and geochemical proxies, normally used in tropical corals, to the non-tropical coral Cladocora caespitosa to identify a new climate archive that could be used to reconstruct patterns of decennial climatic variability in the MS.

In contrast to the calibration approach used for tropical corals, which implies the use of the seasonal SST cycle, we determine the proxy vs. SST calibrations based on the annual SST cycle.

2. Site of study

To provide correlations between geochemical records and environmental parameters, we sampled a colony of C. caespitosa growing along the continental shelf of the Ligurian Sea. The sampling site (Fig. 1), far from fluvial discharge, is located at 28 m water
depth, in the area between Bonassola and Levanto
(44°10′N, 09°34′E), where large colonies of this spe-
cies were identified by Peirano et al. (1999).

This area of the MS is very close to Central Europe
and it is under the direct influence of the Tyrrhenian
Sea cyclonic circulation, which is connected to the
Western Mediterranean geostrophic currents (Elliot,
1979; references in Astraldi et al., 1993 and in
Leoni et al., 1995).

Different processes have been found to affect the
climatic patterns of the two east–west basins forming
the Mediterranean Sea, with the western Mediterra-
enean being mainly subject to perturbations from the
Atlantic Ocean. The Northern part of the Western
Basin (NWB; Gulf of Lions and the Ligurian–Proven-
çal Basin) is known for being one of the few areas
outside the polar regions where Deep Water Forma-
tion occurs. Two currents are responsible for the
circulation pattern of this area, the western Ligur-
ian–Provencal Current (LC in Fig. 1) in the west
and the warmer Tyrrhenian Current (TC in Fig. 1) in
the east, which is always directed to the north (e.g.,
Pinardi and Masetti, 2000).

These hydrodynamic conditions support a cyclonic
circulation throughout the year, this pattern being a
result of the lower mean SST in the Ligurian Sea
compared with Tyrrhenian Sea (Astraldi et al.,
1995). Thus, the geostrophic LC is affected by a
clear seasonal cycle predominantly induced by the
variability of the TC (Bethoux et al., 1982). In the
sample site sector, the littoral drifts are directed
towards the northwest.

The MS shows average temperature profiles typi-
cal of mid-latitude regions, with winter mixing and a
summer thermocline showing variable depth and
steepness (Fig. 2). The monthly SST data derived from the Integrated Global Ocean Service System Products (IGOSS) for the period 1982–2000 (the period of calibration with coral proxies, see below) show a clear annual seasonal variation ranging from ~24.8 ± 0.8 (σ) °C in August to ~12.9 ± 0.4 (σ) °C in February. The year-to-year SST variations correspond to 2.9 and 1.9 °C in August and February, respectively. The SST data come from a 2°–2° box centred on 43°30’N and 09°30’E.

Atmospheric conditions over the NWB are characterized by the presence of relatively warm and wet air masses of Atlantic origin alternating with cold and dry air from polar or arctic regions (Meteorological Office, 1962). Along with the surrounding Alpine zone, the NWB is located at the divergent southern branch of the wintertime polar frontal jet. The area lies between, but not in the middle of, the key centres of action determined by the sub-polar Iceland low and the Azores sub-tropical high.

In addition, the SST of the Ligurian Sea is closely correlated with the air temperature (Bianchi and Morri, 2001).

3. Main aspects of C. caespitosa biology and ecology

C. caespitosa (Scleractinia, Faviidae, Fig. 3a) is the main zooxanthellate colonial coral endemic to the MS (Peirano et al., 2004). It is found in coastal waters from a few metres to 40 m water depth (Metalpa et al., 1999).

The abundance of C. caespitosa is limited to areas where low insolation favours photosynthetic symbionts rather than algae (Cladocora is limited by the dominance of algae, Peirano et al., 1998), which explains why coral banks are only found below the compensation depth of photophilic algae or in coastal turbid environments (Morri et al., 1994; Kühlmann, 1996). The linear growth rate of living C. caespitosa, ranging from 1.30 (Peirano et al., 1999) to 6.2 mm/year (Kružić and Požar-Domac, 2003), is lower than in most major reef-building corals (e.g., P. lutea 3.5 to 30 mm/year; Goniastrea retiformis 4.9 to 8.5 mm/year; Favia pallida 4.1 to 7.1 mm/year in Highsmith, 1979 and in Metalpa et al., 1999). C. caespitosa shows a rectilinear continuous growth of corallites, involving two processes similar to Porites (see reference in Barnes and Lough, 1993), with the lengthen-
ing of the calyx wall and the internal fusion of skeletal elements exhibiting a very regular pattern.

This non-tropical coral deposits two bands per year, a high-density (HD) band forming during periods of low temperature and low light intensity, and a low-density (LD) band corresponding to high temperature and high light intensity. Peirano et al. (1999) observed that more than 50% of the corallites start HD band deposition as a ring at the top of the septa in November, these bands becoming fully developed in March, while the LD bands grow from April to November. Recent sclerochronological analysis on *C. caespitosa* (Peirano et al., 2004) confirmed that the timing of band formation mainly corresponds with seasonal sea temperature and irradiance levels (Peirano et al., 1999).

4. Materials and methods

A living corallite, 18 cm long, 3–4 mm wide (Fig. 3b) and growing continuously since 1906, was collected in 1998 by SCUBA diving from a colony of *C. caespitosa* at 28 m water depth on a rocky bottom. Two HD bands from the same colony were sampled after winter 2000 in order to obtain a comparable and continuous time series over the period from 1906 to 2000.

The longevity of the studied coral is very unusual and the possibility of discovering such ancient colonies of *C. caespitosa* is enhanced by the development of underwater geology and biology by SCUBA diving surveys as well as improvements in diving techniques. X-radiographic images have been used to determine the annual banding of the coral (Buddemeier et al., 1974) (Fig. 3b, c), assuming the deposition of two bands per year (Peirano et al., 1999).

The coralline sample was firstly examined by petrographic observation, X-ray diffractometry and geochemical microanalysis to determine its reliability as a paleo- and actually-living environmental and climate archive (Montagna et al., 2002). We investigated three levels of the corallite (bottom, middle and calyx). Analytical profiles were carried out between the coralline wall and the outer septal portion, as well as between the inner septal portion and the central endothecal palisade of the columella, both in the middle of calcification centres and in the fibrous crystals. In addition, we also analysed the horizontal coralline microstructures (dissepiments). The electron-probe analyses were performed on thin sections over a skeletal distance of ~50 μm.

We obtained 0.5–1 mm wide samples using a diamond micro-blade cutting along the growth axis of the corallite. The cutting was performed on the LD bands, which were completely removed, thus keeping the HD bands intact. The weight of each sample, corresponding to the whole annual HD band, varied from 0.2 to 0.6 mg.

The HD bands were selected in this study for the following reasons:

1. During the spring–summer in the Ligurian Sea, when the LD band is formed, the thermocline is ubiquitous and situated at a depth ranging from −4 to −35 m (Fig. 2). Therefore, the isotopic time series obtained from the sample may not be directly comparable with the SST records actually used (IGOSS SST, see paragraph 6.4), which reflect the SST in the uppermost 10 m of the water column.
2. Based on the above point, this approach gives a representation of the whole water column;
3. Climatic variations can be evaluated during the minimum-temperature period.

Moreover, the HD band can provide information on the period of coral growth when the zooxanthellae activity is weakest. Indeed, the rate of intracellular secretion from the organic matrix is at a minimum compared with extracellular calcification (skeletogenesis) taking place around the template produced in the first step (see model proposed by Highsmith, 1979). In this sense, the isotopic signal due to the coral physiology may be considered negligible.

Stable isotopes were analysed at Harvard University (USA) using an OPTIMA mass spectrometer. During the course of measurements, the precision based on replicates of an internal standard was better than 0.06‰, both for δ18O and δ13C.

Sr/Ca and Mg/Ca ratios were measured on an inductively coupled plasma atomic emission spectrophotometer (ICP-AES) following methods outlined by Schrag (1999). Analytical precision (RSD%), based on analyses of a standard solution, was better than 0.2% for Sr/Ca and 0.4% for Mg/Ca.
5. Coralline Sr/Ca, Mg/Ca, δ¹⁸O and δ¹³C as climate proxies

5.1. Sr/Ca

Strontium is considered one of the most abundant trace elements in coral, with a long resident time of 4–5 million years.

Although the ionic radius of Sr²⁺ (1.31 Å) is a little larger than Ca²⁺ (1.18 Å) (Shannon, 1976), Sr²⁺ fits well into the orthorhombic system of aragonite and it is generally considered to substitute directly for Ca²⁺ in the crystal lattice of inorganic and biogenic aragonite (Kinsman and Holland, 1969; Speer, 1983).

As shown by Weber (1973), the distribution coefficient (Dsr) for Sr in coralline aragonite is negatively related with temperature, while it displays an offset from the inorganic value, indicating that corals do not calcify in equilibrium with seawater. This implies that physiology plays an important role in the uptake of Sr into the lattice of coralline aragonite (Swart, 1981).

Due to the disequilibrium process involved in coral calcification, we need to assume a constant amount of disequilibrium when using Sr/Ca for reconstructing seawater surface temperatures.

The great potential of Sr/Ca as a paleothermometer was established by Beck et al. (1992), using high precision ID-TIMS analyses. This first accurate determination of the Sr/Ca vs. SST relation opened up great possibilities for obtaining palaeo-SST reconstructions, mainly focused in the tropical regions (McCulloch et al., 1994; Shen et al., 1996; Alibert and McCulloch, 1997). Despite the great potential of this method, some studies found a correlation between Sr/Ca and the rate of coral extension (de Villiers et al., 1994, 1995) or calcification (Cohen et al., 2001, 2004), while others (Hart and Cohen, 1996; Allison, 1996a,b; Allison et al., 2001) provided evidence of a significant Sr/Ca heterogeneity over short distances, inconsistent with temperature fluctuations.

Although the mechanisms controlling Sr incorporation into the coral skeleton remain at present poorly understood, some recent experiments (Ferrier-Pagès et al., 2002) tried to explain the role of biological activity during coral calcification. These authors examined the effects of different Ca²⁺ concentration on Sr²⁺ uptake, concluding that Sr²⁺ uses a transcellular transport pathway and that its incorporation into the skeleton depends on both the coral calcification rate and the seawater surface temperature.

5.2. Mg/Ca

Similarly to Sr, the residence time of Mg is long (13 million years), suggesting this element has a long-term stability that is ideal for paleoclimatic reconstructions.

Although the Mg content of skeletal carbonates has been extensively studied (Chave, 1954), the factors controlling Mg incorporation into coral skeleton have not yet been well established. It has been suggested that Mg²⁺ in corals is loosely held in the aragonite crystal lattice, bound to metal sites of organic compounds or adsorbed onto crystal surfaces (Amiel et al., 1973), though the amount of Mg associated with organic matter and adsorbed phases is negligible (Mitsuguchi et al., 1996).

Due to the rhombohedral structure of the CaCO₃–MgCO₃ solid solution, in contrast to the orthorhombic structure of the CaCO₃–SrCO₃ solid solution, the Mg²⁺ might be weakly bound within the lattice (Mitsuguchi et al., 1996). This implies that Mg might be easily affected by diagenesis (Cross and Cross, 1983).

The Mg/Ca vs. SST relation in corals was first investigated by Chave (1954) and Weber (1974), using large sampling volumes and different coral genera, but these authors obtained contradictory results. Subsequently, Oomori et al. (1982) and Hart and Cohen (1996) provided evidence of cyclical variations of Mg/Ca ratios. However, the real potential of Mg as a paleoclimate proxy was demonstrated by Mitsuguchi et al. (1996), who studied a P. lutea coral from the Ryukyu Islands using samples equivalent to about three weeks of growth.

Laser ablation and other micro-beam techniques have revealed a micro-scale heterogeneity that cannot be linked to any SST variations (Allison, 1996a; Sinclair et al., 1998; Fallon et al., 1999), but which is probably related to the presence of Mg not bound in the crystal lattice.

In a recent study, Mitsuguchi et al. (2003) compared Sr/Ca and Mg/Ca ratios from two living colonies of Porites separated by a distance of ~17 km. In spite of the small difference in SST variation between the two sites, they found a significant offset for the Mg/Ca range. They concluded that this “offset is due
to biological/metabolic differences between the two Porites colonies and that coral Mg/Ca ratio may be susceptible to biological/metabolic effects”.

More recently, Meibom et al. (2004) studied the distribution of magnesium in coral skeletons using a NanoSIMS ion microprobe. They reported a banded Mg micro-distribution along the aragonitic fibres, concluding that “temporally and spatially controlled release of Mg to the mineralizing surface plays a key role in the formation of the coral skeleton”.

5.3. $\delta^{18}O$ vs. $\delta^{13}C$

The theoretical basis for the $\delta^{18}O$ thermometer was established by Urey (1947), while subsequent studies by McCrea (1950) and Epstein et al. (1953) confirmed its application to inorganic and biogenic calcite. The coral isotopic composition is depleted compared with slow growing sections of the coral and not solely a result of variable kinetic effects.

McConnaughey (1989a,b) studied the isotopic disequilibrium in corals and concluded that there were two main reasons for oxygen and carbon isotope disequilibrium in biological carbonates: kinetic and metabolic. The kinetic effect causes the depletion of skeletal $^{18}O$ and $^{13}C$ with respect to isotopic equilibrium, due to isotope fractionations during CO$_2$ hydration and hydroxylation. On the other hand, the metabolic effect involves changes of the $\delta^{13}C$ in the internal dissolved inorganic carbon reservoir, due to photosynthesis and respiration processes.

Moreover, this author observed that the faster growing parts of coral skeletons, or faster growing coral colonies, tend to be more strongly depleted in $^{18}O$ compared with slower growing parts.

The conclusions of McConnaughey have been partly modified by Leder et al. (1996), studying experimental corals of Montastraea annularis in Florida. These latter authors 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) failed to find any relationship between skeletal $\delta^{13}C$ and the rate of growth or calcification: corals characterized by different growth rates had similar $\delta^{13}C$ values when considering the same coral sections. This was in contrast with the results of McConnaughey (1989a).

In a comprehensive study of the effect of light on skeletal $\delta^{13}C$ and $\delta^{18}O$, as well as the interaction with photosynthesis, respiration and calcification, Reynaud-Vaganay et al. (2001) investigated some zooxanthellate corals (Acropora sp. and Stylaphora pistillata) under controlled conditions in the laboratory. They observed a significant enrichment of $^{13}C$ and $^{18}O$ in relation to the increase in calcification. The conclusion is in contradiction with the results of McConnaughey (1989a), who found a depletion in $^{13}C$ and $^{18}O$ in coral skeleton with increasing calcification. Moreover, Reynaud-Vaganay et al. (2001) did not report any correlation between $^{13}C$, photosynthesis (net and gross: $P_n$ and $P_g$), respiration ($R$) or $P_g / R$ ratio.

In their studies on the scleractinian coral Acropora formosa Juillet-Leclerc et al. (1997) failed to find any evidence of a relationship between $\delta^{18}O$ ratio and productivity; even if these authors report a statistically-significant positive correlation between $\delta^{13}C$ and productivity, they concluded that this relationship should be explained by the control of external factors.

In an innovative contribution, Adkins et al. (2003) developed an alternative model for coral isotope fractionation, analysing six modern deep-sea corals living without photosynthetic symbionts in a homogeneous growth environment. They concluded that the pH gradient produced between the impermeable cell wall and the calcifying fluid is the key to explaining the isotopic fractionation, which thus depends mainly on conditions at the calcification site.

As summarized by McConnaughey (2003), different factors might lead to the apparent “kink” in Adkins’ equilibration line, such as varying ratios of CO$_2$ hydration and hydroxylation, combined with changing contributions of CO$_2$ and HCO$_3^-$ to the skeleton and varying degrees of equilibration.

In a recent study, Rollion-Bard et al. (2003) conclude that the “vital effect” in corals is mainly controlled by pH variations at the sites of calcification through the relative proportions of dissolved carbonate species and the kinetics of their isotopic equilibration with water before carbonate precipitation”.

Despite our lack of knowledge on the factors controlling oxygen and carbon isotopic disequilibrium, the general applicability of stable isotopes in corals...
is uncontested and the relation between coral $\delta^{18}$O and SST forms the basis of recent paleoclimatic reconstructions in tropical regions.

6. Results and discussion

6.1. Petrographic, mineralogical and geochemical observations

SEM, optical microscopy and diffractometric observations reveal a pristine aragonitic coralline texture and few microborings (3–4 μm in diameter) associated with endolithic algae (Fig. 4).

SEM images show the typical morphology of *C. caespitosa*, with well defined septa fusing together in the central part of the coral to form the columella (Fig. 4, a).

An important feature of corals is the dissepiment, which is a basal structure built by the coral polyp at almost constant intervals along its growth direction. This structure in *C. caespitosa* is “endothecal”, developing horizontally inside the theca. Since the dissepiments in *C. caespitosa* occur at different horizontal levels within the theca, they do not form a continuous basal platform.

The undersurface of these basal structures is characterized by growth increments, showing distinct bundles of crystallites (Fig. 4, b).

As pointed out by Sorauf (1972), the crystallites develop into discrete parallel fibres during periods of slower growth (night), whereas, during rapid growth (day), there is a great number of nucleation centres and the fibres resemble bundles of straw.

Calcification centres are distributed in the form of isolated brownish spots, surrounded by fibrous aragonite bundles (Fig. 4, c), as described by James (1974) and Constantz (1986).

The calcification centres appear as hollows (about 10–15 μm wide) made up of isometric crystals of submicron size (Fig. 4, d). This particular pattern might be due to the presence in these areas of a carbonate texture that is more susceptible to acid etching. Alternatively, it could result from less carbonate material at calcification centres than in the surrounding fibres, as suggested by Allison (1996a).

Another explanation is that the material at the calcification centres might be softer, and therefore it could have been partly removed during sample preparation for the SEM study.

Aragonite crystals in the fibrous bundles show typical orthorhombic prisms (about $2 \times 1 \times 35 \ \mu m$). The fibres radiating from adjacent calcification centres merge at different angles, depending on their positions (Fig. 4, d).

In the lower and middle part of the corallite, we can observe microborings that are generally attributed to the activity of endolithic organisms such as algae and some bacteria (May et al., 1982) (Fig. 4, e and f). These microboring are between 3 and 4 μm in diameter and they cut across the original structure of the corallite.

Montagna et al. (2002) reported significant statistical differences in Mg concentrations between centres-fibres and dissepiments ($p$-value <0.001), whereas no significant differences in Sr concentration were observed in our study (Fig. 5).

Amiel et al. (1973) suggested two phases for Mg in coral skeletons: 1) an aragonite phase in which Mg is loosely bound, and 2) a mineral phase that is more soluble than aragonite.

Cuif and Dauphin (1998), studying a sample of *C. caespitosa* collected in the Mediterranean Sea, found significantly higher (at 5% $\alpha$-level) Mg and S contents in the calcification centres compared to the surrounding fibres. They concluded that these differences are due to the presence of two different sets of organic compounds in the calcification centres and fibrous bundles. In addition, using *Porites* skeletons, Allison (1996a,b) observed that the calcification centres were enriched in both Mg and Sr compared to the surrounding fibrous aragonite. In particular, the Mg and Sr contents in the calcification centres were enriched by 40% and 6%, respectively. These anomalies were related to the presence of adsorbed ions, inorganic precipitation or organic material, with major implications for the palaeoenvironmental analysis of coral skeletons. Other authors observed geochemical heterogeneities in shallow and deep-water coral skeletons at high spatial resolution, suggesting that other factors independent of temperature may play an important role in controlling variations of trace elements and stable isotopes. These factors could include symbiont activity (Cohen et al., 2001, 2002), different calcification processes over different periods (Allison et al., 2001), different organic com-
pounds (Cuif et al., 2003) or the different activity of Ca-ATPase between calcification centres and acicular crystals (Cohen and McConnaughey, 2004; Rollion-Bard et al., 2003).

Since the fine-scale heterogeneity of Sr in *C. caespitosa* has proved to be of minor importance (Montagna, 2004), its effect on paleoclimatic analysis may not be crucial.
Fig. 5. Sr (a) and Mg (b) concentrations for calcification centres, surrounding fibres and dissepiments.
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<th>Year AD</th>
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6.2. Geochemical records (Sr/Ca and Mg/Ca, δ¹⁸O and δ¹³C)

The Sr/Ca and Mg/Ca ratios obtained in this study are shown in Table 1 and plotted in Fig. 6. The range of variation of Sr/Ca ratios between 1906 and 2000 is
0.39, with a minimum value of 9.86, a maximum of 10.25 and a mean value of 10.08. The Mg/Ca ratios vary between a minimum of 3.19 and a maximum of 5.20, with a mean value of 3.62 and a range of 2.01. Both Sr/Ca and Mg/Ca ratios are given in mmol/mol. Clearly, the short-term Mg/Ca variability shown in Fig. 6 cannot be attributed to SST variations and must be related to other causes (see below).

The $\delta^{18}$O and $\delta^{13}$C results are reported in Table 1 and plotted in Fig. 7. The $\delta^{18}$O record varies between $-2.16$ in 1959, and $-0.81$ in 1926, with a mean value of $-1.44$. 

Fig. 6. Comparison between Sr/Ca and Mg/Ca ratios during the period 1906–2000, using data obtained from HD (high-density) bands.

Fig. 7. Comparison between $\delta^{18}$O and $\delta^{13}$C data during the period 1906–2000, using data obtained from HD (high-density) bands.
Finally, δ¹³C data range between a minimum of −5.64 to a maximum of −3.39, with a mean value of −4.29. Both isotopic measurements are given in conventional delta notation in permil units relative to the Vienna Peedee Belemnite.

6.3. Correlation between geochemical records

6.3.1. Sr/Ca vs. δ¹⁸O

The correlation between coral skeletal δ¹⁸O and Sr/Ca ratios is shown in Fig. 8, providing the following linear regression:

\[
\text{Sr/Ca (mmol/mol)} = 10.35(\pm 0.02) + 0.18(\pm 0.01)\delta^{18}O(\text{permil PDB}).
\] (1)

Errors on the regressions are calculated with respect to the dispersion on the y-axis (Lyons, 1991), and are given at 1σ. The correlation is significant \((r=0.76; p\text{-value of } F\text{-test significant at } 1\%\) x-value), and the slope (0.18) is closely similar to that found by Cardinal et al. (2001) on a massive coral (Diploria labyrinthiformis) from north-east Breakers (Bermuda — 32°30’N, 64°40’W), but is lower compared to previous data (Beck et al., 1992; McCulloch et al., 1994) derived from other tropical corals.

Cardinal et al. (2001) found a steeper slope and a more significant linear regression for a D. labyrinthiformis colony from a different site at Bermuda (North Rocks) compared to the colony collected in north-east Breakers. These authors explained the reduced amplitude for north-east Breakers colony by the seasonal variation of linear growth rate associated with the kinetic effect and coupled to sampling.

Similarly to Cardinal et al. (2001), the geochemical and isotopic data for C. caespitosa show a small variation, thus increasing the noise to signal ratio.

According to Craig and Gordon (1965), a difference of more than 1% in salinity roughly corresponds to a difference of about 0.5% in δ¹⁸O of the seawater. The mean annual salinity in the MS ranges between 35% to 38% according to the different areas. In particular, in the Ligurian Sea, the mean annual salinity is higher (38.05%, Pierre, 1999) than the value measured in Northern Australia (35.1%), New Caledonia (35.5%) and Bermuda (36.5%).

6.3.2. Mg/Ca vs. Sr/Ca

The Mg/Ca vs. Sr/Ca correlation is characterized by a low but still significant regression coefficient \((r=-0.51; p\text{-value of } F\text{-test significant at } 1\%\)
\( \alpha \)-value). The correlation shown in Fig. 9 provides the following linear regression:

\[
\frac{\text{Mg}}{\text{Ca}}(\text{mmol/mol}) = 27.44(\pm 4.10) - 2.36(\pm 0.40)\frac{\text{Sr}}{\text{Ca}}(\text{mmol/mol}).
\]

(2)

As mentioned above, Mg distribution in the coral skeleton of \( C. caespitosa \) varies according to the different skeletal microstructures (Montagna et al., 2002). In particular, these authors noted that the Mg concentration is significantly higher in the fibrous bundles than in the calcification centres along the columella region, whereas, in the wall area, the Mg distribution follows an opposite trend (Fig. 5b).

In addition, analysis of the dissepiments revealed a significantly lower Mg concentration compared with the calcification centres and fibrous dissepiments. These geochemical differences, ranging between 1100 ppm (fibrous bundles and calcification centres) and 200 ppm (dissepiments), correspond to an important shift of 3.7 mmol/mol in the Mg/Ca ratio over a skeletal distance of 50 \( \mu \text{m} \).

These fine-scale compositional heterogeneities observed in the coral skeleton were probably averaged during the sampling prior to ICP MS analysis. In fact, the coral powder from the HD band represents a geochemical average between the concentrations of the fibrous bundles, calcification centres and dissepiments, thus affecting the conventional bulk analysis of the paleotemperature proxy.

6.3.3. \( \delta ^{18}O \) vs. \( \delta ^{13}C \)

We found the following linear regression for the relationship between the oxygen and carbon isotopic values:

\[
\delta ^{18}O(\% \text{PDB}) = -0.03(\pm 0.23) + 0.32(\pm 0.05)\delta ^{13}C(\% \text{PDB}).
\]

(3)

Although the correlation is not robust, it is significant \((r=0.52; \ p\text{-value of } F\text{-test significant at }1\%)\).

The skeletal \( \delta ^{18}O \) and \( \delta ^{13}C \) data are plotted in Fig. 10. Even though the correlation is not strong, the proportionality suggests that both fractionations factors are correlated.

To calculate the isotopic value for a biological aragonite precipitated in quasi-equilibrium with ambient seawater in the MS, we used equations 1 and 4 from Grossman and Ku (1986) and assumed a mean winter temperature of 15 \( ^\circ \text{C} \). For the \( \delta ^{18}O_{\text{seawater}} \) and \( \delta ^{13}C_{\text{seawater}} \) values we referred to the paper of Reynaud-Vaganay et al. (2001). We obtained a value of +2.5(\% PDB) for \( \delta ^{18}O \) and +1.5(\% PDB) for \( \delta ^{13}C \).
Like many tropical corals, both the skeletal $\delta^{18}O$ and $\delta^{13}C$ values in *C. caespitosa* are depleted in comparison to the estimated isotopic equilibrium of ambient seawater. As previously reported, the isotopic depletion arises from the fact that corals do not precipitate their carbonate material in isotopic equilibrium with ambient seawater (Land et al., 1975; Erez, 1978; McConnaughey, 1989a,b; Swart et al., 1996).

Regardless of the exact controls on the isotopic disequilibrium, the depletion in both the $\delta^{18}O$ and $\delta^{13}C$ values for the studied specimen suggests that this species fractionates stable isotopes in a similar way to that occurring in tropical corals.

### 6.4. Correlation with environmental parameters

Before the second half of the last century, it was not possible to carry out optimum interpolation (OI) analysis for studying high-quality SST anomalies for a number of reasons, including the lack of satellite data. In 1996, Smith et al. developed a new interpolation method to improve the analysis of SST anomalies by using more accurate OI analyses applied to in situ and bias-corrected satellite data (Reynolds and Smith, 1994) from 1982 onwards. For this reason, we calculate the geochemical record vs. SST relationship here using data derived from Integrated Global Ocean Service System Products (IGOSS), based on the work of Reynolds and Smith (1994) and Smith et al. (1996) for the period 1982–2000. IGOSS data were chosen because of their useful application in previous studies on calibrating monthly geochemical parameters vs. SST in corals (e.g., Linsley et al., 2000).

Specifically, the SST data used here are derived from a $2^\circ \times 2^\circ$ box centred on 43°30’N and 09°30’E.

Note that other SST data sets are available for the MS, such as the one compiled by the Hadley Centre in England (HadlSST, Rayner et al., 2003), which is valid over the last full century with a monthly resolution, or the most recent one from the National Climatic Data Center in North Carolina, USA (ERSST; Smith and Reynolds, 2004). However, a mismatch between the different data sets is reflected by the low correlation coefficients obtained when comparing IGOSS data against the HadlSST data ($r=0.39$) and ERSST data ($r=0.22$) for the period Nov–Jan 1982–2000 (the period used for the calibration with geochemical proxies, see below).

Sr/Ca data for HD bands were compared to IGOSS SST data corresponding to the mean values of November, December and January, with a total of 18 points (1982–2000). This approach, which con-
sists of comparing a particular season over 18 years, differs from that commonly used for tropical corals. This is due to the sampling method applied and the need to obtain sufficient material (0.2–0.6 mg) for the analysis of trace elements and stable isotopes. It is important to note that this approach involves both advantages and disadvantages. The main disadvantage is that the SST dynamic range is rather small (only 1.9 °C at the sampling site), with a resulting increase in the noise-to-signal ratio. On the other hand, the main advantage is that some specific biases are inherent in using the seasonal cycle as a proxy for longer term changes. In particular, seasonal variations in the rates of skeletal extension and thickening, combined with other physiological effects, may lead to smoothing and distortion of the environmental signals by undersampling of the seasonal cycle.

To obtain the most significant calibration equation and statistically validate the sampling approach, we performed four different correlations between Sr/Ca ratios and the SST mean values for four periods in the year, actually using the SST mean values for the periods Nov–Jan, Feb–Apr, May–Jul, and Aug–Oct.

As expected from the sampling method, only the correlation between Sr/Ca ratios and SST data for Nov–Dec–Jan was statistically significant (r = 0.60; p-value of F-test significant at 1% x-value). Similar correlations were not found with the other SST calibrations using other three-month periods (Table 2).

In addition, we investigated the calibration between Sr/Ca ratios and the Nov–Mar SST data. The time span of five months from November to March represents the period of HD band growth and should provide the most significant correlation with Sr/Ca ratios. However, Pearson’s coefficient is very low (r = 0.1), probably because part of the HD bands (February and March) may have been cut during HD band sampling or due to a preferential development of the HD band during Nov–Jan.

However, the correspondence of the HD band with the November–January period is only an approximation, and may not be constant throughout the whole time-series. This could influence the correlation coefficient, although the regression obtained remains significant (see equation below).

In addition, statistical analysis of the Nov–Dec–Jan SST data in the grid centred at 43°30’N 09°30’E—yields a low correlation coefficient with both HadISST (Sr/Ca vs. SST: yrs 1982–2000 r = 0.02) and ERSST (Sr/Ca vs. SST from ERSST: years 1982–2000 r = 0.06) data sets.

The Sr/Ca vs. SST regression is shown in Fig. 11, providing the following equation:

\[
\text{Sr/Ca (mmol/mol)} = 11.25(\pm 0.38) - 0.079(\pm 0.026)\text{SST(°C)}. \quad (4)
\]

Although we obtained this linear regression by calibrating only the HD bands, the correlation is nevertheless significant. In particular, due to the small SST variation (the maximum variation is 1.9 °C, with a maximum of 15.6 °C and a minimum of 13.7 °C) during this period, it is likely that errors on the regression are important due to the high noise-to-signal ratio.

We should remember that the IGOSS SST data represent surface values for a 2°–2° grid and were derived from a single-time measurement, while the C. caespitosa corallite represents a point at 28 m water depth associated with problems in the determination of the monthly growth rate. Bearing these considerations in mind, the correlation obtained clearly supports the potential of Sr/Ca as a proxy for SST in the Mediterranean Sea.

Using Eq. (4), we obtained a continuous SST record starting in 1906 (Fig. 12). This Sr/Ca-derived SST time series represents the mean values of November, December and January for each year from 1906 to 2000, and shows a slight cooling trend since 1916 to 1944, (SST varying between

---

**Table 2**

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<th>Regression coefficient and p-value of F-test from the linear regressions between Sr/Ca, Mg/Ca and δ18O vs. SST IGOSS data</th>
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16.1 and 12.6 °C. The pattern changed to a warming trend (SST varying between 14.1 and 17.5 °C) during the period from 1945 to 1970, followed by another cooling trend from 1971 to 1993 (SST varying between 14.8 to 12.9 °C). After 1993, it seems that a new warming trend started.

Fig. 11. Relationship between the skeletal Sr/Ca ratios and the IGOSS SST for the period 1982–2000. The regression line was calculated using the Sr/Ca ratios obtained for the high-density bands and the IGOSS SST mean values for the period November, December and January.

Fig. 12. Sr/Ca-derived SST record for the period 1906–2000 (black line). Grey line indicates the IGOSS SST data for the period 1982–2000 (i.e., the calibration database).
An analogous correlation was calculated between the Mg/Ca ratios and SST (Fig. 13), providing the following equation:

\[
\text{Mg}/\text{Ca}(\text{mmol/mol}) = -4.41(\pm 3.10) + 0.55(\pm 0.21)\text{SST}(^\circ\text{C}) \quad (5)
\]

\((r=0.54; p\text{-value of } F\text{-test significant at } 5\% \sigma\text{-value})\). Eq. (5) is the most significant equation out of the four calibrations performed for Mg/Ca ratios (Table 2).

As mentioned for the Sr/Ca ratios, the high noise-to-signal ratio, together with chronological uncertainties, might be responsible for the low regression coefficient. In addition, the magnesium heterogeneities found in \textit{C. caespitosa} (Montagna et al., 2002), as well as the presence of organic matter and/or microborings, could influence the Mg/Ca–SST relationship. The organic component has a substantial metal binding capacity (Mitterer, 1978) and it is enriched in Mg and other trace elements compared to the coral skeleton. Even with rigorous cleaning procedures, some inclusions of organic compounds may not be removed since they are finely disseminated throughout the carbonate. Fig. 6 clearly shows a Mg enrichment close to the calyx, probably related to remains of Mg-rich tissue. Organic matter may also occur as a contaminant phase in the microborings, as already reported by Allison (1996a). The presence of microborings along the corallite of \textit{C. caespitosa} noted during the petrographic analysis, might account for the positive shift in Mg concentration in the middle and basal part of the corallite.

Finally, oxygen isotopic data were compared to SSTs (mean values of Nov–Jan) for the period 1982–2000. Despite the very poor and non-significant \((r=-0.36 \text{ and } p\text{-value of } F\text{-test}=0.13)\) correlation, it is nevertheless much better than the other correlations of SST data related to the other three-month periods (Table 2).

The \(\delta^{18}\text{O}\) vs. SST regression is shown in Fig. 14, which provides the following calibration:

\[
\delta^{18}\text{O}(\%_{\text{PDB}}) = 0.91(\pm 1.42) - 0.15(\pm 0.09)\text{SST}(^\circ\text{C}) \quad (6)
\]

The correlation is weak and much of the inaccuracy of \(\delta^{18}\text{O}\) in recording the SST in this region can be explained by variations in \(\delta^{18}\text{O}_{\text{seawater}}\). As pre-

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**Fig. 13.** Relationship between the skeletal Mg/Ca ratio and the IGOSS SST for the period 1982–2000. The regression line was calculated using the Mg/Ca ratios obtained for the high-density bands and the IGOSS SST mean values for the period November, December and January.
viously noted, coral skeletal $\delta^{18}$O is not only sensitive to SST, since it is a combination of SST and the marine $\delta^{18}$O that is controlled by the local precipitation–evaporation balance (Craig and Gordon, 1965). In particular, the evaporation process extracts preferentially the light water molecules with the consequence that the ocean becomes richer in $^{18}$O; unlike evaporation, inflow of $^{18}$O-depleted fresh water, by precipitation or river discharge, causes a decrease of $^{18}$O values of the oceanic water. There is thus a direct relationship between salinity and $^{18}$O values.

Salinity data for winter (November, December and January) collected at Punta Mesco (5 km from the sampling site) since November 2001 were downloaded from the web site of the Italian Ministry of Environment (www.minambiente.it). Unfortunately, data are only available after 2001, so they are not directly comparable with the coral $\delta^{18}$O record. However, the difference in winter salinity observed since 2001 is 1.25 psu, suggesting significant salinity variations at the interannual timescale. This implies that $\delta^{18}$O$_{\text{seawater}}$ variations on this time scale probably have a proportionally larger influence on the coral $\delta^{18}$O signal than SST changes. Such a result has also been found by Felis et al. (2000) studying a Porites coral in the Northern Red Sea. To quantify the $\delta^{18}$O$_{\text{seawater}}$ changes for the same period, we determined the $\delta^{18}$O$_{\text{seawater}}$-salinity regression equation, using only the data collected from the Western Mediterranean Sea by Pierre (1999). The calculated $\delta^{18}$O$_{\text{seawater}}$/salinity slope of +0.34 indicates a $\delta^{18}$O$_{\text{seawater}}$ variation of 0.42‰ for a range of 1.25 psu. This value implies that many of the discrepancies observed between SST and coral $\delta^{18}$O on the two time series could be explained by variations in $\delta^{18}$O$_{\text{seawater}}$.

6.5. Comparison with previous studies

To compare the SST vs. trace element and isotope calibrations for C. caespitosa (Table 3) with previous investigations, we present a list of equations obtained

![Fig. 14. Relationship between the skeletal $\delta^{18}$O and the IGOSS SST for the period 1982–2000. The regression line was calculated using the $\delta^{18}$O values obtained for the high-density bands and the IGOSS SST mean values for the period November, December and January.](image)
from workers studying different coral species mainly collected at low latitudes (Tables 4–6).

The slope of the Sr/Ca vs. SST equation for *C. caespitosa* ($-0.079$) is closely comparable with the main equations available in the literature (Table 15). However, since *C. caespitosa* is a non-tropical coral living at middle latitudes, we might expect the Sr/Ca uptake mechanisms to be different from those of tropical corals (e.g., *Porites*).

As for almost all the Sr/Ca vs. SST equations, the calibration slope for *C. caespitosa* is also significantly different from the slope found by Kinsman and Holland (1969) for inorganic aragonite, and this is not surprising considering that the biological activity of the coral has an effect on the temperature dependence.

Houck et al. (1977) and Smith et al. (1979) related the Sr/Ca disequilibrium to the different distribution coefficients ($\text{Sr/Ca}_{\text{aragonite}}/\text{Sr/Ca}_{\text{seawater}}$) between inorganically precipitated aragonite and coralline aragonite, and attributed it to some form of biological control. Moreover, these authors found that the distribution coefficients varied between coral genera.

The biological control of Sr/Ca uptake into the coral aragonite lattice was subsequently investigated by de Villiers et al. (1995), who studied three *P. lobata* corals from Hawaii.

The calculated Sr/Ca vs. SST equations for three corals belonging to the same species were distinctly different, suggesting a non-linear relationship between Sr/Ca and SST. Nevertheless, some authors (Shen et al., 1996; Alibert and McCulloch, 1997; Marshall and McCulloch, 2002) consider the results of de Villiers et al. (1995) were strongly affected by an erroneous sampling procedure (i.e., not along the maximum growth axis) rather than being due to the presence of different biological controls.

Thus, assuming a correct sampling method (i.e., along the major growth axis) and a constant disequilibrium in the same coral species due to a physiological

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**Table 4**

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<td>Gagan et al. (1998)</td>
<td>Great Barrier Reef</td>
<td><em>P. lutea</em></td>
<td>10.73</td>
<td>-0.063</td>
</tr>
<tr>
<td>Sinclair et al. (1998)</td>
<td>Great Barrier Reef</td>
<td><em>P. mayeri</em></td>
<td>10.8</td>
<td>-0.070</td>
</tr>
<tr>
<td>Schrag (1999)</td>
<td>Galapagos</td>
<td><em>P. lutea</em></td>
<td>10.55</td>
<td>-0.051</td>
</tr>
<tr>
<td>Fallon et al. (1999)</td>
<td>Japan Sea</td>
<td><em>P. lutea</em></td>
<td>10.76</td>
<td>-0.063</td>
</tr>
<tr>
<td>Cardinal et al. (2001)</td>
<td>Bermuda (N.Rocks)</td>
<td><em>D.labyrinthiformis</em></td>
<td>10.03</td>
<td>-0.045</td>
</tr>
<tr>
<td>Yu et al. (2005)</td>
<td>South China Sea</td>
<td><em>P. lutea</em></td>
<td>9.83</td>
<td>-0.042</td>
</tr>
<tr>
<td>Sun et al. (2005)*</td>
<td>South China Sea</td>
<td><em>Porites sp.</em></td>
<td>10.32</td>
<td>-0.053</td>
</tr>
<tr>
<td>This study</td>
<td>Ligurian Sea</td>
<td><em>C. caespitosa</em></td>
<td>11.25</td>
<td>-0.079</td>
</tr>
</tbody>
</table>

(*) $a$ and $b$ were calculated by reversing the equations derived for SST=$a'd'+b' $Sr/Ca.

---

**Table 5**

<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>Species</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mitsuguchi et al. (1996)</td>
<td>Japan Sea</td>
<td><em>P. lutea</em></td>
<td>1.15</td>
<td>0.12</td>
</tr>
<tr>
<td>Sinclair et al. (1998)</td>
<td>Great Barrier Reef</td>
<td><em>P. mayeri</em></td>
<td>0</td>
<td>0.16</td>
</tr>
<tr>
<td>Fallon et al. (1999)</td>
<td>Japan Sea</td>
<td><em>Plobata</em></td>
<td>1.38</td>
<td>0.08</td>
</tr>
<tr>
<td>Wei et al. (2000)*</td>
<td>South China Sea</td>
<td><em>Porites sp.</em></td>
<td>1.63</td>
<td>0.11</td>
</tr>
<tr>
<td>Yu et al. (2005)</td>
<td>South China Sea</td>
<td><em>P. lutea</em></td>
<td>1.32</td>
<td>0.11</td>
</tr>
<tr>
<td>This study</td>
<td>Ligurian Sea</td>
<td><em>C. caespitosa</em></td>
<td>-4.41</td>
<td>0.55</td>
</tr>
</tbody>
</table>

(*) $a$ and $b$ were calculated by reversing the equations derived for SST=$a'd'+b' Mg/Ca.
control during the uptake of Sr in coral aragonite, it seems reasonable to conclude that temperature is the main factor controlling Sr/Ca ratio in the case of *C. caespitosa*.

To test the reliability of the proposed Sr/Ca vs. SST calibration, calibration slope and intercept were plotted in the diagram of Fig. 16, as suggested by Marshall and McCulloch (2002). Our data clearly fit the linear regression obtained from data collected from different corals (Table 7). This suggests that the calibration equation calculated from *C. caespitosa* is suitable for obtaining SST data, as is the

![Table 6](https://example.com/table6.png)

<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>Species</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tarutani et al. (1969)*</td>
<td>–</td>
<td>Inorganic aragonite</td>
<td>3.83</td>
<td>-0.23</td>
</tr>
<tr>
<td>Weil et al. (1981)*</td>
<td>In vitro</td>
<td><em>M. verrucosa</em></td>
<td>0.77</td>
<td>-0.21</td>
</tr>
<tr>
<td>Weil et al. (1981)*</td>
<td>In vitro</td>
<td><em>P. damicornis</em></td>
<td>0.87</td>
<td>-0.23</td>
</tr>
<tr>
<td>McConnaughey (1989a)</td>
<td>Galapagos</td>
<td><em>Porites</em></td>
<td>0.59</td>
<td>-0.20</td>
</tr>
<tr>
<td>McConnaughey (1989a)</td>
<td>Galapagos</td>
<td>Pavona</td>
<td>0.66</td>
<td>-0.20</td>
</tr>
<tr>
<td>McConnaughey (1989a)</td>
<td>Galapagos</td>
<td>Pavona</td>
<td>-0.41</td>
<td>-0.01</td>
</tr>
<tr>
<td>Chakraborty and Ramesh (1993)*</td>
<td>Arabian Sea</td>
<td><em>Porites</em></td>
<td>0.64</td>
<td>-0.21</td>
</tr>
<tr>
<td>Leder et al. (1996)*</td>
<td>Florida</td>
<td><em>M. annularis</em></td>
<td>1.17</td>
<td>-0.22</td>
</tr>
<tr>
<td>Felis et al. (2000)*</td>
<td>Red Sea</td>
<td><em>Porites</em> sp.</td>
<td>0.53</td>
<td>-0.16</td>
</tr>
<tr>
<td>Cardinal et al. (2001)*</td>
<td>Bermuda (N.Rocks)</td>
<td><em>D. labyrinthiformis</em></td>
<td>-1.22</td>
<td>-0.14</td>
</tr>
<tr>
<td>Al-Rousan et al. (2003)*</td>
<td>Red Sea</td>
<td><em>P. cf. lutea</em></td>
<td>-0.17</td>
<td>-0.18</td>
</tr>
<tr>
<td>Al-Rousan et al. (2003)*</td>
<td>Red Sea</td>
<td><em>P. cf. australiensis</em></td>
<td>-1.02</td>
<td>-0.15</td>
</tr>
<tr>
<td>This study</td>
<td>Ligurian Sea</td>
<td><em>C. caespitosa</em></td>
<td>0.91</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

(*) $a$ and $b$ were calculated by reversing the equations derived for SST=$a' + b' \delta^{18}O$. 

![Fig. 15](https://example.com/fig15.png)

Fig. 15. Comparison of some coral Sr/Ca thermometers. 1, present study; 2, *Porites lutea*, Galapagos (Schrag, 1999); 3, *P. lobata*, Shirigai Bay, Japan, 32° N (Fallon et al., 1999); 4, *P. lutea*, Great Barrier Reef (Gagan et al., 1998); 5, *P. lobata*, Hawaii (de Villiers et al., 1994); 6, *P. lutea*, Myr-2, Great Barrier Reef (Marshall and McCulloch, 2002); 7, *P. lobata*, Great Barrier Reef (Alibert and McCulloch, 1997); 8, *P. lobata*, New Caledonia (Beck et al., 1992); 9, *Diploria. labyrinthiformis*, Bermuda, N.Rocks, 32° N (Cardinal et al., 2001). Triangle indicates the slope of the inorganic aragonite (Kinsman and Holland, 1969).
case for many tropical corals, implying that the growth environment of the coral is a factor controlling the coral’s physiology (Marshall and McCulloch, 2002).

By considering the Mg/Ca vs. SST equation and comparing it with other Mg/Ca thermometers (Fig. 17), it is evident that our calibration differs from the others. The factors mentioned above, apart from temperature, could account for the significant lack of agreement.

Finally, Table 6 shows some δ¹⁸O vs. SST equations reported in the literature. Although the slope of

Table 7
Sr/Ca vs. SST linear regression obtained from various coral data and from C. caespitosa, plotted in Fig. 16.

<table>
<thead>
<tr>
<th></th>
<th>A (intercept)</th>
<th>B (calibration slope)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.940</td>
<td>-0.07</td>
<td>Smith et al. (1979)</td>
</tr>
<tr>
<td>2</td>
<td>10.479</td>
<td>-0.06245</td>
<td>Beck et al. (1992)</td>
</tr>
<tr>
<td>3</td>
<td>10.956</td>
<td>-0.07952</td>
<td>de Villiers et al. (1994)</td>
</tr>
<tr>
<td>4</td>
<td>10.286</td>
<td>-0.0514</td>
<td>Shen et al. (1996)</td>
</tr>
<tr>
<td>5</td>
<td>10.577</td>
<td>-0.061</td>
<td>Heiss et al. (1997)</td>
</tr>
<tr>
<td>6</td>
<td>10.480</td>
<td>-0.0615</td>
<td>Alibert and McCulloch (1997)</td>
</tr>
<tr>
<td>7</td>
<td>10.731</td>
<td>-0.0638</td>
<td>Gagan et al. (1998)</td>
</tr>
<tr>
<td>8</td>
<td>10.300</td>
<td>-0.0542</td>
<td>Alibert et al. (1999)</td>
</tr>
<tr>
<td>9</td>
<td>10.375</td>
<td>-0.0593</td>
<td>Marshall and McCulloch (2001)</td>
</tr>
<tr>
<td>10</td>
<td>10.400</td>
<td>-0.0575</td>
<td>Marshall and McCulloch (2002)</td>
</tr>
<tr>
<td>11</td>
<td>10.400</td>
<td>-0.0587</td>
<td>Marshall and McCulloch (2002)</td>
</tr>
<tr>
<td>12</td>
<td>10.383</td>
<td>-0.0587</td>
<td>Crowley et al. (1999)</td>
</tr>
<tr>
<td>13</td>
<td>10.760</td>
<td>-0.063</td>
<td>Fallon et al. (1999)</td>
</tr>
<tr>
<td>14</td>
<td>10.550</td>
<td>-0.0514</td>
<td>Schrag (1999)</td>
</tr>
<tr>
<td>15</td>
<td>10.730</td>
<td>-0.06567</td>
<td>Corrège et al. (2000)</td>
</tr>
<tr>
<td>16</td>
<td>11.250</td>
<td>-0.079</td>
<td>This study</td>
</tr>
<tr>
<td>17</td>
<td>11.650</td>
<td>-0.0895</td>
<td>Seawater value</td>
</tr>
</tbody>
</table>
the equation for *C. caespitosa* is very similar for tropical corals, the comparison with other $\delta^{18}$O vs. SST equations is problematic due to the unacceptably low value of the regression coefficient.

7. Conclusions

All the main isotopic and geochemical proxies typically used in tropical corals (Sr/Ca, Mg/Ca and $\delta^{18}$O) are applied to *C. caespitosa*, providing evidence that this non-tropical coral can be used for paleoclimatic reconstructions in the MS. In this study, we determined the following equations between proxies and SST:

\[
\text{Sr/Ca (mmol/mol)} = 11.25(\pm 0.38) - 0.079(\pm 0.026)\text{SST}({}^\circ\text{C})
\]  
(4)

\[
\text{Mg/Ca (mmol/mol)} = -4.41(\pm 3.10) + 0.55(\pm 0.21)\text{SST}({}^\circ\text{C})
\]  
(5)

\[
\delta^{18}\text{O}(%_{\text{oo}} \text{PDB}) = 0.91(\pm 1.42) - 0.15(\pm 0.09)\text{SST}({}^\circ\text{C})
\]  
(6)

In particular, the Sr/Ca vs. SST equation is the most significant, displaying a slope closely comparable with the majority of other equations available from the literature. This implies that SST is the main factor controlling the Sr/Ca ratio. On the other hand, Mg/Ca seems to be more affected by geochemical heterogeneities and/or the presence of organic matter, either finely distributed as intergranular particles or as fillings of microborings. Finally, a very weak and non-significant correlation was obtained for $\delta^{18}$O vs. SST, indicating that large salinity variations may play a key role in the isotopic composition of coralline aragonite.

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References


Recent scleractinian corals. Palaontologische Zeitschrift 72, 257–270.


Kinsman, D.J.J., Holland, H.D., 1969. The coprecipitation of cations with CaCO\textsubscript{3}. IV. The coprecipitation of Sr\textsuperscript{2+} with aragonite between 16 and 96 °C. Geochimica et Cosmochimica Acta 33, 1–17.


