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# Recent advances in coral biomineralization with implications for paleo-climatology: a brief overview.

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**Abstract.** The tropical oceans drive climatic phenomena such as the El Niño-Southern Oscillation (ENSO) and the Asian-Australian monsoon, which have global scale impacts. In order to understand future climatic developments, it is essential to understand how the tropical climate has developed in the past, on both short and longer time scales. However, good instrumental records are limited to the last few decades. The oxygen isotopic ( $\delta^{18}\text{O}$ ) composition and strontium/calcium (Sr/Ca) ratio of massive corals have been widely used as proxies for past changes in sea surface temperature (SST) of the tropical and subtropical oceans, because the geochemistry of the skeleton is believed to vary as a function of several environmental parameters (such as seawater temperature, salinity, light,...). However, recent micro-analytical studies have revealed large amplitude variations in Sr/Ca and oxygen isotopic composition in coral skeletons; variations that cannot be ascribed to changes in SST or in salinity. Such micro- and nano-meter scale studies of geochemical variations in coral skeletons are still few and somewhat scattered in terms of the species studied and the problems addressed. But collectively they show the great potential for determining chemical variations at length scales of direct relevance to the biomineralization process. For example, it is now possible to measure geochemical variations within the two basic, micrometer-sized building blocks of the coral skeleton: Early Mineralization Zones (EMZ) and aragonite fibres. Such micro- and nano-meter scale observations, in combination with controlled laboratory

culturing of corals, hold the promise of yielding important new insights into the various biomineralization processes that may affect the chemical and isotopic composition of the skeletons. One aim of these efforts is to better understand the elemental and isotopic fractionation mechanisms in order to improve the conversion of the geochemical variability into environmental changes.

**Keywords:** Corals, Oxygen isotope, Strontium/Calcium ratio, Palaeothermometer, Biomineralization

## 1. Introduction.

Accurate estimation of human impacts on climate variability is an important subject, not only for scientists and environmentalists, but also for law-makers, politicians, and for society in general. In order to predict the effects of anthropogenic activities on the future climate it is necessary to document how the climate has fluctuated in the past. Instrumental records can extend up to about 150 years (Kaplan *et al.*, 1998), but have limited geographical distribution. Satellite-based temperature surveys of the oceans cover large regions, but high quality data are limited to the last two decades. On the other hand, the global climate of the last few centuries is known to have been variable and complex, spatially as well as temporally (e.g. Jones and Mann, 2004).

Massive, hermatypic corals are present today in the tropical and sub-tropical oceans and can be found in a significant fraction of the geologic record extending back to the middle Triassic. These corals potentially provide high-resolution records of climate variability in the tropical oceans that, through ocean-atmosphere interactions, greatly affect the Earth's climate system (Dunbar and Cole, 1999). Paleo-environmental records based on modern corals can go back in time as far as 300-400 years (Quinn *et al.*, 1998; Linsley *et al.*, 2004, Cobb *et al.*, 2004) and the annual density banding of coral skeletons provides an accurate chronology (Knutson *et al.*, 1972; Barnes and Lough, 1993). Thus, corals offer many advantages for climate reconstructions, provided that precise proxies for environmental change, including sea surface temperature (SST), can be developed. In this paper, we discuss, briefly, recent advances in the use of corals as proxies for past SST variations with special attention to progress made in understanding the effects of biomineralization processes on the chemical and isotopic composition of the coral skeletons.

## 2. Development and problems associated with coral paleo-temperature proxies

The oxygen isotopic ( $\delta^{18}\text{O}$ ) and strontium/calcium (Sr/Ca) ratios of massive coral skeletons have been widely used as proxies for past changes in SST of the tropical and subtropical oceans because both geochemical parameters are believed to depend on the temperature of the ambient seawater.

The temperature dependency of the oxygen isotopic composition in inorganically precipitated carbonates was established by Urey (1947), but it was realized early on that the  $\delta^{18}\text{O}$  of biogenic carbonates reflects a combination of environmental parameters and biological processes, so-called "vital effects" (Urey *et al.*, 1951, Epstein *et al.*, 1953,

McConnaughey, 1989). In spite of a biologically induced isotopic disequilibrium with respect to seawater, corals in general provide the best  $\delta^{18}\text{O}$  paleo-records of ambient SST variations in waters with near constant  $\delta^{18}\text{O}$ , i.e. waters in hydrologic balance (e.g. Leder *et al.*, 1996; Wellington *et al.*, 1996). (Alternatively corals can provide a record of changes in hydrologic balance in regions where the temperature is nearly constant; e.g. Cole and Fairbank (1990)). However, seasonal variations in  $\delta^{18}\text{O}$  of the seawater on the reef are often relatively large (Leder *et al.*, 1996) and in some cases, the effect of seawater  $\delta^{18}\text{O}$  variations on the  $\delta^{18}\text{O}$  vs. SST calibration can be quantified (McCulloch *et al.*, 1994; Juillet-Leclerc and Schmidt, 2001). Modern approaches to the construction of  $\delta^{18}\text{O}$  paleo-environmental records typically involve coring of living coral heads and calibration to (5-10 year) instrumental temperature records obtained in close vicinity to the coral (Stephans *et al.*, 2004).

Temperature dependence of the Sr/Ca ratio in aragonite was demonstrated by Smith *et al.* (1979). However, initially the analytical errors associated with the analyses of coral Sr/Ca ratios were large ( $\pm 2^\circ\text{C}$ , if converted to temperature) limiting the use of the coral Sr/Ca temperature-proxy to localities where temperature variations are significantly larger. Later, Beck *et al.* (1992) developed isotope dilution and thermal ionization mass spectrometry (TIMS) techniques that allowed the measurement of Sr/Ca ratio with an analytical error corresponding to less than  $\pm 0.5^\circ\text{C}$  for reconstructed SST. In contrast with the isotopic composition of seawater, the Sr/Ca ratio of seawater has been assumed to be essentially constant because of the long residence times of strontium in the ocean ( $5.1 \times 10^6$  years; Broecker and Peng, 1982). However, more recent observations of the ocean Sr/Ca ratio from different depths and localities raise some doubt about the general validity of this assumption (de Villiers *et al.*, 1994, de Villiers, 1999).

McCulloch *et al.* (1994) assessed  $\delta^{18}\text{O}$  fluctuations in seawater by removing the temperature dependency from the  $\delta^{18}\text{O}$  signal using the calibrated Sr/Ca vs. SST relationship. This method was extended to reconstructions of past sea surface salinity (SSS) (Gagan *et al.*, 1998, Ren *et al.*, 2002) assuming a linear relationship between the  $\delta^{18}\text{O}$  of seawater, SSS and SST. With the development of automated methods for rapid sampling and analyses of carbonate powders, different methods for reconstruction of SST have been applied to century-long coral records covering most of the tropics (Fig.1), as well as to climatically important periods in the more distant past, such as the Last glacial maximum (e.g. Guilderson *et al.*, 1994), Little Ice Age (Watanabe *et al.*, 2001), and last Interglacial warm period (Tudhope *et al.*, 2001). At the same time, it has become clear that coral-based paleo-climatic

reconstructions suffer from problems that are not only related to the analytical challenge of obtaining high quality  $\delta^{18}\text{O}$  and Sr/Ca data. Fig. 2. shows the large discrepancy among reported modern calibrations both for coral  $\delta^{18}\text{O}$  (Fig.2.a) and Sr/Ca (Fig.2.b). These discrepancies suggests that simple application of different coral species, localities, and methods can lead to large discrepancies among different reconstructions of past SST (Marshall and McCulloch, 2002, Watanabe *et al.*, 2002).

### 3. Biological sources of discrepancies in modern calibrations

Although biological- or “vital” effects are broadly recognized as a source of uncertainty or discrepancy in coral paleo-climatic records there has been relatively little attention given to the study of how corals form their skeletons and how, in detail, these biologically processes can affect the geochemical composition of the skeletons. For example, the isotopic effect of seawater temperature on skeletal  $\delta^{18}\text{O}$  has been tested in laboratory by using cultures of corals (Reynaud-Vaganay *et al.*, 1999). Whereas all the nubbins were cultured in the same conditions, in the same aquarium, and originated from one parent colony, their isotopic measurements could be scattered over 1‰ for an identical temperature (Fig. 3). Although oxygen isotopic ratios as well as Sr/Ca ratios often are in disequilibrium with respect to their ambient seawater, the observed elemental and isotopic fractionations are usually treated in the context of thermodynamic equilibrium, modified by kinetic effects associated with the precipitation of the skeleton (McConnaughey, 1989, Gagan *et al.*, 1998, Ren *et al.*, 2002, Adkins *et al.*, 2003). Among geochemists, a widespread idea is that the skeleton is largely produced by simple physiochemical precipitation of calcium carbonate concentrated from seawater. However, from recent studies of coral skeletons, conducted at length scales of relevance to the biomineralization processes, it has become clear that this idea is too simplistic to be right. In the following we briefly discuss recent progress in the study of biologically driven isotopic and trace element variations at the mm- to nm- length scales. In general, it seems true that we need to understand the coral biomineralization process at the cellular scale, the fundamental length scale of life, before we can reliably use these structures to draw conclusions about environmental changes on a global scale.

*Geochemical heterogeneity at the millimetre length scale*

It is well known that even within the same locality, where water chemistry is essentially the same, the use of different coral species can lead to different SST calibrations, presumably due to biological differences (e.g., Gagan *et al.*, 2000, Marshall and McCulloch, 2002, Watanabe *et al.*, 2002, 2003). Even among the same coral species from the same location, SST calibrations can differ among colonies (Allison, 1996, Wellington *et al.*, 1996, Linsley *et al.*, 1999, Watanabe *et al.*, 2003). Some of these discrepancies can be explained by different sampling resolution, variations in skeletal growth-rate, and small environmental heterogeneities in the reef environment. However, millimetre-scale observations of geochemical heterogeneity within different skeletal elements of the same corallite in a given colony present an additional complication. The aragonitic skeletons of hermatypic corals are comprised of thousands of individual corallites, each with a more or less well defined theca-wall, columellae, septa, and dissepiments (Fig 4). Theca-wall and columella are growing in the vertical direction; the direction for extension. Septa are growing vertically and horizontally at the same time, and dissepiments define horizontal layers within each corallite, like floors in a tall building (Barnes and Lough, 1993, Barnes *et al.*, 1995). Differences in growth-direction and growth-rate of each skeletal element could affect the reconstructed climate signals. Land *et al.* (1975) and Watanabe *et al.* (2002, 2003) examined the isotopic heterogeneities among different skeletal components using coral species with relatively large corallites and wide inter-corallite spacing. The results suggested that there is a rather large difference in the stable isotope chemistry between vertically and horizontally growing skeletal elements. Vertically growing elements, such as the theca wall, yield a certain stable isotopic signature, but the inclusion of horizontally growing skeletal elements change this signature significantly (Fig. 4). The coral species most commonly used for paleo-climatic reconstructions is *Porites*, which has relatively small corallites (0.5 – 1 mm) for which it is difficult to sample separately each type of skeletal element using conventional sampling techniques (e.g. dentist drill). On the other hand, a smaller corallite size allows better, more representative average compositions to be obtained. Still, it seems essential to understand the cause of the variable stable isotope signatures in different skeletal components at the mm length scale.

Since late 1990's, microanalytical methods such as Laser ICP-MS and Secondary Ion Mass Spectrometry (SIMS) have been applied more or less systematically for measurements of trace element of coral skeletons (Allison, 1996, Hart and Cohen, 1996, Sinclair *et al.*, 1998, Fallon *et al.*, 1999). However, the most striking result of these analyses was the large data

scatter, often with amplitudes that were impossible to interpret as the result of changes in environmental conditions.

Two dramatic examples of  $\mu\text{m}$ -scale geochemical variations are illustrated in Fig. 5, which show conventional ion microprobe analyses of  $\delta^{18}\text{O}$  and Sr/Ca ratios in wall segments and septa of the *Porites* skeleton. Both data sets show oscillating variations with amplitudes that are impossible to explain by fluctuations in SST or changes in any other local environmental parameter (Rollion-Bard *et al.*, 2003; Meibom *et al.*, 2003). Indeed, if converted to temperature, the  $\delta^{18}\text{O}$  and Sr/Ca variations displayed in Fig. 5 would correspond to changes of more than  $15^\circ\text{C}$ , which is three times more than the seasonal SST variations at the sites where these corals lived. Similar, but less distinctly oscillating Sr/Ca variations were reported by recent works (e.g. Allison and Finch, 2004, Cohen and Sohn, 2004). The negative isotopic values can only be explained by supposing that coral skeleton is partially deposited according to a kinetic process. The boron isotopic measurements at micrometer scale in the same spots than oxygen analyses (Rollion-Bard *et al.*, 2003) indicate that a variation of one pH unit is in good agreement with direct micro-electrodes measurements (Al-Horani *et al.*, 2003). In addition, the  $\delta^{18}\text{O}$  and Sr/Ca oscillations, are characterized by an approximately monthly wavelength, which could be caused by biological processes changing in response to the lunar cycle (Meibom *et al.*, 2003). We suggest that the pH controls the  $\delta^{18}\text{O}$  of the growing carbonate skeleton through the relative fractions of dissolved carbonate species and through the kinetics of their isotope equilibration with water via hydration and hydroxylation.

#### *Geochemical heterogeneities at the ultra-structural level*

Figure 4 illustrates the general morphology of the coral skeleton at the scale of one millimeter. However, in all coral skeletons there is an additional level of structure at the micrometer and nanometer length scales, which is directly related to the mechanism of skeletal formation – we refer to this as the coral “ultrastructure”. Figure 6 illustrates the ultrastructure of a *Porites* skeleton, but we emphasize that the ultrastructure of all coral skeletons, although species dependent, share the same components and overall architecture. The coral skeleton consists of early mineralization zones (EMZ), which are small aggregations of nanophase calcium carbonate, embedded in sulfated polysaccharides and other organic molecules. EMZ were previously called as centres of calcification (COC), but ‘EMZ’ has been proposed as better description in context with the overall growth process

(Cuif *et al.*, 2003; Cuif and Dauphin (2005). EMZs are arranged by the coral in a pattern that reflects the overall morphology of the skeleton. Indeed, one could say that it is the organization of the EMZ (which is completely controlled by the coral) that defines the overall morphology of the skeleton. The EMZ are overgrown by subsequent layers of fibrous aragonite that serve to give the skeleton bulk mass and mechanical strength (Fig. 4). Of direct relevance to the utilization of coral skeletons to paleo-climatic reconstructions is the discovery of dramatic geochemical variations at the ultra-structure level.

Using conventional ion microprobe, Cohen *et al.* (2001) analyzed the Sr/Ca ratio in both EMZ and fibres of *Porites* and found that the Sr/Ca vs. SST relationship differed dramatically for EMZ and aragonite fibres. Cohen *et al.* (2001) concluded that the Sr/Ca ratio of the aragonite fibres was strongly influenced by biological activity of symbiotic algae during daytime precipitation. In another study, Cohen *et al.* (2002) compared the Sr/Ca vs. SST relationship between symbiotic and asymbiotic coral colonies of *Astrangia poculata* and found again the Sr/Ca ratio in symbiotic corals to be strongly perturbed from the thermodynamic equilibrium values.

Cuif and Dauphin (1998) observed chemical heterogeneity (strontium, magnesium, and sulphur) between fibres and EMZ in the septa of fifteen different coral species. Using synchrotron based XANES analyses, Cuif *et al.* (2003) further established that sulphur in the coral skeleton is almost exclusively associated with sulphated polysaccharides, which are highly concentrated in the EMZ, but also present in the fibrous aragonite part of the skeleton, where they display a layered distribution corresponding to the layered organization of the fibres (Fig. 6).

These findings were subsequently extended to other trace elements by Meibom *et al.* (2004) who reported a distinct zonation of Mg in the coral *Pavona clavus*, again corresponding closely to the layered structure of aragonite fibres (Fig. 7). Meibom *et al.* (2004) furthermore found the EMZ to be greatly enriched in Mg. Strontium, on the other hand did not show similarly banded distributions and it seems that different trace elements have different (metabolic?) pathways from the seawater to the coral skeleton.

#### **4. Conclusions**

Taken together, the observations described in this brief overview suggest that the distribution of trace elements and stable isotopic composition of hermatypic coral skeletons are strongly affected by, if not completely controlled by, biological processes. From a paleo-climatic point of view, the main challenge for the future is to establish the degree to which the

SST affects these biological processes; i.e. how much of the trace element and stable isotope variation can be ascribed to seasonal and interannual SST oscillations and how much other environmental and biological factors affect the skeletal chemistry (Reynaud-Vaganay *et al.*, 1999, Ferrier-Pages *et al.*, 2002, Reynaud-Vaganay *et al.*, 2001; Reynaud *et al.*, 2002; Reynaud *et al.*, 2004). There are strong indications that the degree of biological control and the sensitivity of the coral to variations in SST is species dependent (Weber and Woodhead, 1972, Weber, 1973). Understanding the coral biomineralization processes in detail has become more important than ever. At the moment, relevant experimental efforts are still somewhat scattered and limited in scope, but the development of new micro-analytical techniques, such as the NanoSIMS, enable to precisely measure the recording process in the stepping growth layers and has opened up the field of biomineralization to a new generation of studies that may hold the key to more precise coral-based records of past environmental parameters.

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## Figure captions

### Fig. 1

Coral records of  $\delta^{18}\text{O}$  and Sr/Ca ratio from modern corals. Thick lines represent 5 years running averages. Data are available at the World Data Center for Paleoclimatology (<http://www.ngdc.noaa.gov/paleo/corals.html>).

### Fig. 2

Diagrams showing the disagreement between different calibrations of SST vs. (a) the oxygen isotopic composition in *Porites lutea* and (b) the Sr/Ca ratio in coral *Porites*. Each calibration has been calculated from samples collected along main growth axis, by comparing the geochemical measurement with the SST variability.

### Fig. 3

Diagram showing discrepancy between calibrations of SST versus skeletal  $\delta^{18}\text{O}$  for 5 nubbins coming from the same parent colony of *Acropora* sp. cultured by the method of Reynaud-Vaganay *et al.* (1999). Note that these five nubbins were growing in aquarium under constant condition, except temperature.

### Fig. 4

(a) Morphology of coral skeletal structures and (b) millimetre scale heterogeneity in isotopic compositions for different skeletal elements in *Diploastrea* and *Montastrea* (Watanabe *et al.*, 2002, 2003).

**Fig. 5**

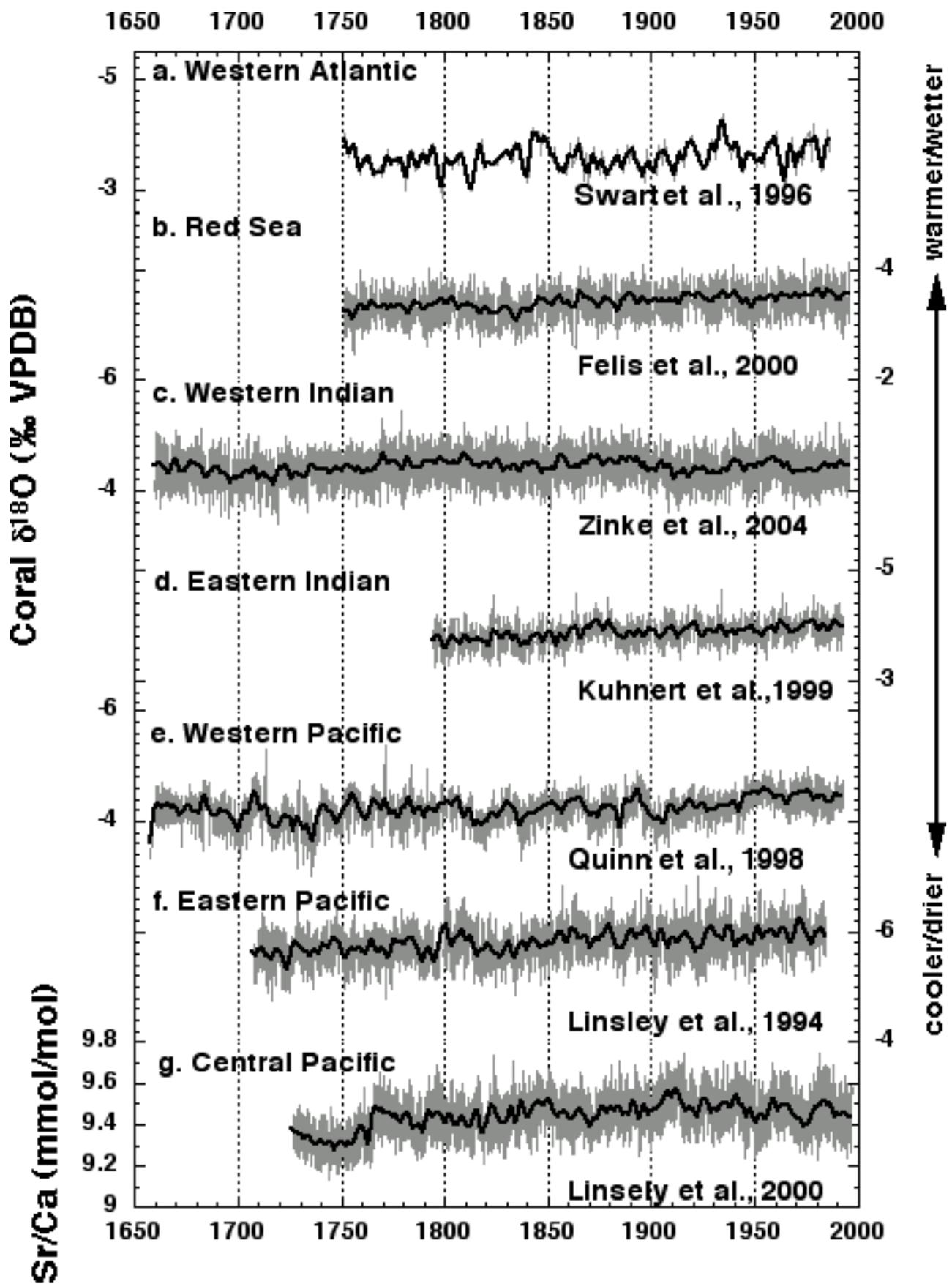
Micro-scale heterogeneity observed in coral *Porites* of  $\delta^{18}\text{O}$  (a; Rollion-Bard *et al.*, 2003) and of Sr/Ca (b; Meibom *et al.*, 2003) measured by ion microprobe.

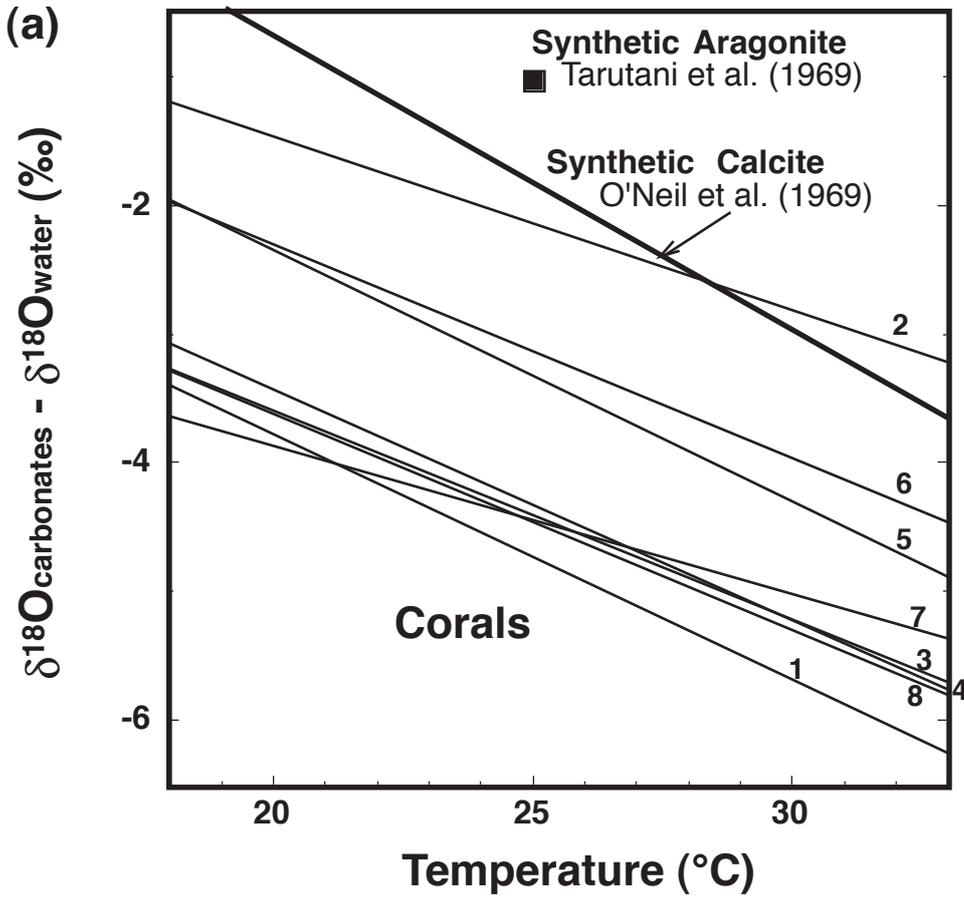
**Fig. 6**

Microstructure of coral skeleton of *Porites* showing different sizes and shapes of the early mineralization zones (EMZ) and fibres. (a) Calice morphology, (b) Radiating fibres, (c) The stepping growth mode of fibres: each biomineralization growth layer is the elemental environment recording unit.

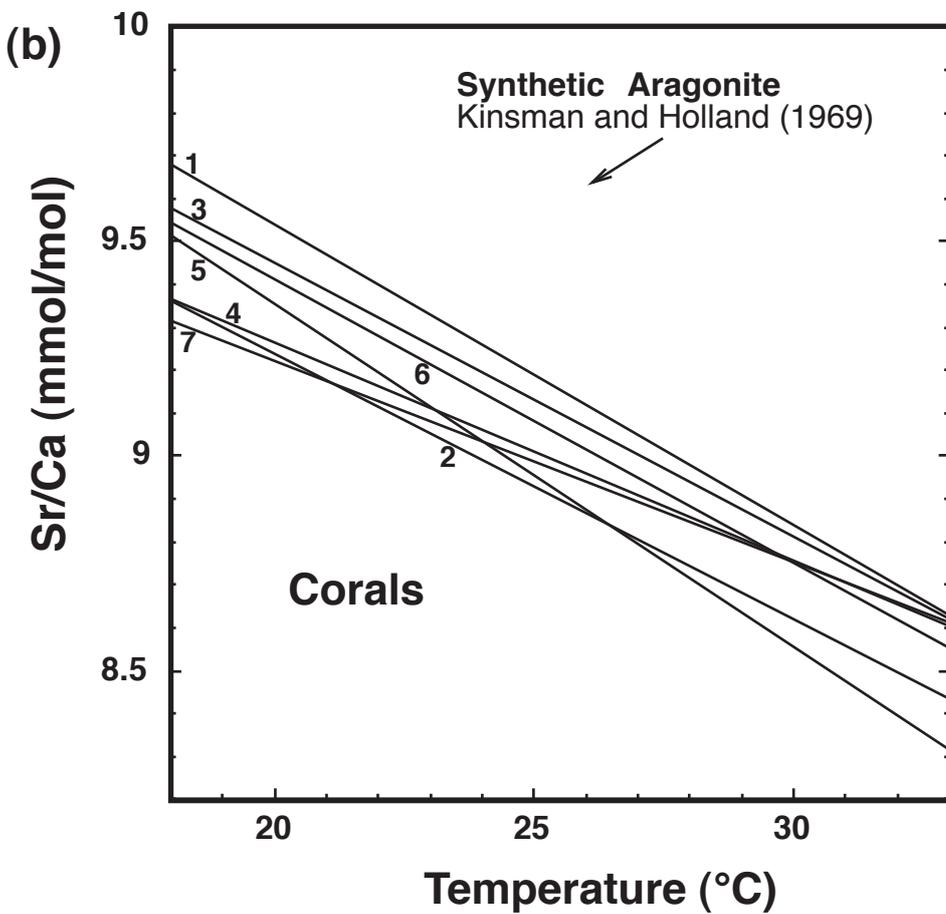
**Fig. 7**

The distribution of Mg in different parts of the *Pavona clavus* skeleton from Meibom *et al.* (2004). Dark blue colors correspond to relatively low Mg concentrations; green, yellow and red colors correspond to increasingly high Mg concentrations. EMZ have the highest concentration of Mg. Arrow indicates direction of growth. Scale bars are 10  $\mu\text{m}$ .





- 1 Quinn et al. (1996)
- 2 Mitsuguchi et al. (1996)
- 3 Gagan et al. (1998)
- 4 Abe et al. (1998)
- 5-6 Heiss et al. (1999)
- 7-8 Castellaro (1999)



- 1 Smith et al. (1979)
- 2 Beck et al. (1992)
- 3 de Villiers et al. (1994)
- 4 Shen et al. (1996)
- 5 Gagan et al. (1998)
- 6 Correge et al. (2000)
- 7 Linsely et al. (2000)

