## Chapter 16 Corals in Estuarine Environments: Their Response to Environmental Changes and Application in Reconstructing Past Environmental Variability

#### Francisca Staines-Urías

Abstract Corals represent a vast and detailed archive of past environmental changes in regions where instrumental data are limited and where our knowledge of multidecadal climate variability is incomplete. In estuarine areas, coral skeletal records provide an opportunity to monitor anthropogenic impacts as well as to investigate natural environmental variability through a range of time scales, from seasonal to millennial. This paper analyzes the status of the field of coral sclerochronology (layer analysis) and geochemistry as it relates to the recovery of past records of environmental variability in estuarine settings. Coral biology, density band formation, and factors affecting the uptake of isotopic and elemental signals in the coral skeleton are explored, as they constitute important aspects in understanding corals as environmental proxies. Density bands in coral skeletons, commonly used for first-order dating, are a reliable proxy for long-term seasonal variability and to identify periods of environmental stress. The stable isotopic composition of coral carbonate has been employed to reconstruct sea-surface temperatures and salinities ( $\delta^{18}$ O), insolation changes ( $\delta^{13}$ C), pH variability ( $\delta^{11}$ B), and water quality ( $\delta^{15}$ N), while changes in the elemental composition of corals constitute robust proxies for sea surface temperature (Sr/Ca) and riverine discharge (Ba/Ca). Additionally, changes in the trace concentration of metals, such as Pb, Cd, Al, Mn and Zn, have been used to monitor pollutants entering estuaries from urban areas and to reconstruct past changes in water quality. However, there is still controversy about the degree to which biological parameters such as metabolism and calcification rate influence the final isotopic and elemental composition of the coral lattice. As a result, a multi-proxy approach to coral-based paleoclimatology has emerged, both from the need to better understand the influences controlling coral environmental records and from recent advances in the analytical techniques for measuring the composition of coral skeletons.

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### **1** Introduction

Reef-building corals are organisms that secrete a calcium carbonate (aragonite) skeleton by extracting calcium (Ca<sup>2+</sup>), carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>) ions from seawater. The extracellular coral skeleton is continuously deposited at the base of the coral tissue as substrate for the polyps that live in the outer 0.5–1.0 cm of the structure (Fig. 16.1). As coral colonies develop, the carbonate skeletons of



Fig. 16.1 Coral polyps are multicellular organisms with cells that exhibit functional specialization. The coral calcification process occurs within the calicoblasts, which are located along the lower portion of the polyp within the calicoblastic ectoderm. The skeleton of an individual scleractinian polyp is known as a corallite. Each corallite is composed of a calice that is the structure holding the polyp, the basal plates, and the septa. Individual corallites are interconnected by aragonite lattice (coenosteum), which together with the thecas conform the coral skeleton. Likewise, polyps are interconnected by living tissue (coenosarcs), which lies on top of the skeleton. Sacs that occur along the tentacles and the coenosarcs hold the zooxanthellae symbionts and the nematocysts

several colonies fuse together creating a framework which provides habitat to a broad range of biological communities that together constitute one of the most diverse ecosystems in the world, the coral reef. Coral reefs provide a variety of valuable goods and services to humans, as millions of people rely on these ecosystems for food, recreational opportunities, coastal protection, and building materials (e.g., Steimle and Zetlin 2000; Hughes 2003; Richmond et al. 2007). Additionally, when reef-building corals are either drilled or collected as intact colonies, their carbonate skeletons enable data on surface ocean conditions to be extended back beyond the instrumental record.

Scleractinian corals comprise the majority of modern day reef-building species. These corals form from a symbiotic association between a cnidarian invertebrate and dinoflagellate algae of the genus Symbiodinium, colloquially called zooxanthellae (Fig. 16.1). Single scleractinian colonies consist of a base (attached to the substratum), a skeletal structure and a growing edge zone (living tissue) where new coral polyps are produced (Fig. 16.2). In most species, individual colonies have long life spans from 200 to 800 years (e.g., Chornesky and Peters 1987). The possession of an edge zone allows scleractinian corals to gain permanent attachment to a stable substrate (Roniewicz and Stolarski 1999). As a result, scleractinian corals dominate modern reef frameworks, especially in high-energy settings where there is an abundance of hard substrata for colonization. Because of the dependence of reefbuilding corals on algal symbionts, light availability is critical for reef building. In turn, light availability is regulated by water depth, turbidity and (in geological time) latitude. Accordingly, scleractinian corals distribution is limited to shallow waters (<100 m depth) in regions within 35° north and 30° south of the equator (Kleypas et al. 1999). Factors that alter light availability in the marine environment will have significant effects on coral calcification rates and reef development. However, the significance of each factor varies through space and time. For instance, in estuarine environments high turbidity levels, due to the load of particulate inorganic and organic nutrients and sediments from river runoff, represent an important limiting factor for coral growth, especially during storm seasons (Smith 1983). In comparison, offshore coral reefs are more strongly affected by increased solar radiation (extreme insolation) that causes massive zooxanthellae expulsion and coral mortality (i.e., coral bleaching, Porter et al. 1989).

Temperature limits the latitudinal distribution of reefs and constrains the rate of skeletal accretion. Decreasing water temperature lowers the saturation state of the major skeleton-forming carbonate minerals, thus reef formation is limited to oceans that do not cool below 18 °C for extended periods of time (Kleypas and Langdon 2006). However, most corals can grow where water temperature commonly falls to 14 °C for short periods (Veron and Minchin 1992; Kleypas et al. 1999).

Extensive study of fossil reefs has shown that the preferential disappearance of corals in several major global extinction events coincided with rapid acidification of the ocean (Knoll et al. 2007; Veron 2008). Changes in the alkalinity of the ocean significantly affect the rate at which corals grow. A decrease in pH, caused, for example, by an increase in the uptake of carbon dioxide ( $CO_2$ ) from the atmosphere (i.e., ocean acidification), produces carbonate ion under-saturation in surface waters.

Fig. 16.2 Asexual budding of polyps leads to the formation of coral colonies (a). Budded polyps form by division of existing polyps or development of new polyps from the tissue between existing polyps (Veron 2000). The edge where the budding polyps appear constitutes the growing edge zone of the colony. As the new polyps grow, their corallites fuse and skeletal accretion occurs (b). Changes in accretionary growth in response to seasonal variability create skeletal bands of contrasting density (c and d). Such bands are revealed by X-radiography of coral thin slabs as a succession of dark (high density) and light (low density) banding (e). Ultimately, the type of polyp/corallite budding determines colony morphology (f)



When carbonate becomes under-saturated, aragonite becomes vulnerable to dissolution. Thus, reef building is halted, even if coral calcification rates remain unchanged (Orr et al. 2005).

Corals, like most cnidarians, have few or no mechanisms for osmoregulation (Muthiga and Szmant 1987). Thus, a deviation from ambient salinity will affect their overall metabolism. Nonetheless, there is considerable variation in environmental tolerances among species, which can have a major influence on the community structure within sites (Brown 1997; Moberg et al. 1997). Rapid reduction of ambient salinity affects the metabolic function of the coral photosynthetic symbionts (i.e., photosynthesis declines). Coral survival under such conditions means that the reduction in net input from the photosynthesis symbiont must be compensated by increased ingestion of organic carbon from heterotrophic feeding (Falkowski et al. 1990). Constant hyposalinity stress results in decreased potential for growth, reproduction and survival (Coles and Jokiel 1992). A literature survey suggests that most species of reef corals are killed when ambient salinity decreases by 15% for 24 h or more (Coles and Jokiel 1992). In laboratory experiments conducted on Porites corals, Moberg et al. (1997) observed that significant short-term salinity reductions (up to 20% below normal condition sustained for less than 24 h) lower photosynthetic rates proportionally to the salinity change but without increasing respiration rates, thus decreasing net coral metabolism. They also observed that zooxanthellae symbionts were capable of resuming normal photosynthetic function soon after salinity returned to normal. This finding is significant in understanding the development of coral reefs in estuarine regions, as salinity reductions in these regions often occur very rapidly (e.g., for only a few hours during low tide or extreme rainfall events), but are of a temporary nature.

## 2 Corals in Estuarine Environments

Coral reefs have long been considered stenotolerant to environmental changes and are believed to survive over only very narrow ranges of abiotic conditions. Likewise, reef-building corals have been regarded as highly stenohaline organisms (e.g., Wells 1957) and unable to survive in environments with reduced salinity, high and variable sediment and nutrient loading, and other estuarine characteristics. However, the environmental tolerance of these organisms is now known to be greater than previously suspected. Several on-site and laboratory-based studies suggest that reefbuilding corals are far more adaptable to physical stresses than was previously believed (e.g., Muthiga and Szmant 1987; Harland and Brown 1989; Coles 1992; Coles and Jokiel 1992; Brown 1997; Moberg et al. 1997). Hence, reef-building corals are now recognized as part of the fauna of many coastal systems legitimately classified as estuaries (Guinotte et al. 2004).

Global distribution data show that reef-building corals grow naturally at salinities ranging from 25 to 42% (Coles and Jokiel 1992; Kleypas et al. 1999) and that coral reefs can be found living under nutrient, light and sedimentation conditions that may significantly vary, in both space and time (e.g., Gratwicke and Speight 2005). For instance, estuarine coral reefs in the Indo-West Pacific, which often experience a high degree of environmental variability, appear resilient to the effects of seasonal salinity and temperature changes, as well as to temporal increments in sedimentation and nutrient loading (Richmond et al. 2004). Reef communities also change naturally when influenced by conditions characterized by fluctuating salinity, more variable or higher nutrient load, sediment pollution (siltation) and turbidity. In the Florida Keys (Appendix), high sedimentation and turbidity associated with low water quality, which is generally assumed to kill corals, resulted in reefs with increased coral diversity and higher living-coral cover (Fisher 2004). On the other hand, very few coral species are able to survive extreme disturbance events such as unusually high wave forces associated with hurricanes, frequent bombardment and scouring by waterborne objects, rapid and persistent sea surface cooling (e.g., La Niña events), or large sewage discharges. Reefs that are seldom exposed to such disturbances are likely to become dominated by one or a few species (the stronger competitors), resulting in low-diversity reefs, while frequent exposure to extreme events is more likely to result in massive coral death and reef decay (Jokiel et al. 1993; Fabricius 2005). Environmental disturbances associated with extreme storm events are especially damaging for estuarine coral reefs because of the synergetic effect of several stress factors (Crabbe et al. 2008). For example, a storm flood that occurred on the 31st of December 1987 in Kaneohe Bay, Hawaii (Appendix), reduced the salinity of the surface waters by 15% and resulted in massive coral mortality. However, decreased salinity was not the sole cause of the massive mortality of coral-reef organisms observed after the flood. In the weeks following, a large phytoplankton bloom occurred increasing water turbidity. Phytoplankton growth was stimulated by high concentrations of nutrients derived partially from dissolved material transported by flood runoff and partially by decomposition of marine organisms killed by the flood. The extremely rapid phytoplankton growth led to rapid nutrient depletion, which resulted in the crash of the phytoplankton population; further reducing dissolved oxygen concentrations due to bacterial activity (i.e., oxidation of organic matter). By the time water quality parameters returned to longterm average values (~2-3 months), virtually all coral was killed to depths of 1-2 m in the western and southern portions of the bay (Jokiel et al. 1993). Shallow-water reef communities were particularly vulnerable to freshwater damage because low salinity water is less dense than seawater and formed a persistent surface layer. However, massive coral mortality in deeper zones occurred due to the combination of reduced light penetration, hypoxia, increased sediment load and reduced salinity (Jokiel et al. 1993; Jokiel 2008). In Kaneohe Bay, the elimination of several coral species during this exceptional event resulted in coral-reef communities dominated by the coral Porites compressa, a species that is tolerant to lower salinities and lowoxygen concentrations. Comparison of the 1987 flood event, with a previous major flash-water flood that occurred in 1965 when sewage was discharged into Kaneohe Bay, indicates that coral reefs can recover quickly from natural disturbances, but not under polluted conditions (Jokiel et al. 1993). As catastrophic-flood disturbances play an important role in determination of coral-community structure, past changes in coral-reef diversity can be used to track the frequency and magnitude of episodic climate events such as hurricanes and volcanic eruptions (Hoeke et al. 2011) and may also help to evaluate anthropogenic influences in coastal areas (Jokiel et al. 1993; Rodgers et al. 2012).

## **3** Corals as Environmental Records

Modern corals represent a vast archive of past climate variability in regions where instrumental data are limited and where our knowledge of multi-decadal climate variability is incomplete. In addition, fossil corals offer the possibility to extend data on the variability of surface ocean conditions back beyond historical instrumental records. Coral-carbonate records are considered ideal for paleoenvironmental reconstructions because: (a) coral reefs are widely distributed throughout tropical and subtropical regions; (b) reef-building corals are sensitive to environmental changes; (c) corals have large growth (calcification) rates; (d) individual colonies have long life spans; (e) the coral skeleton presents growth bands that provide annual and sub-annual chronologies; and (f) coral aragonite is suitable for high-precision <sup>230</sup>Th/<sup>234</sup>U (U-series) dating (errors associated with this method are <1% for samples that are up to 200,000 years old, Edwards et al. 1987). Much like tree rings, corals can track climate changes within annual cycles, allowing sea-surface conditions to be reconstructed with reference to specific seasons. Seasonally resolved paleoclimate data are essential for reconstructing climate phenomena such as oscillations of monsoon systems, winddriven upwelling variability and the El Niño-Southern Oscillation (ENSO).

In considering coral skeletal components as paleoenvironmental indicators, it is crucial that the biogenic constituents reflect conditions at the time of carbonate deposition. Accordingly, it has been shown that the physical characteristics of the coral skeleton do vary in response to environmental changes. Furthermore, as trace elements are incorporated by elemental substitution within the aragonite lattice of corals, the elemental composition of skeletal calcium carbonate reflects changes in the marine environmental conditions (e.g., Lough 2004; Carricart-Ganivet and Barnes 2007). However, relating physical and chemical signatures in the coral lattices to water composition, and ultimately to climatic and oceanographic processes, remains a complex task in constant development.

## 3.1 Paleoenvironmental Interpretation of Physical Signatures in Coral Skeleton Records

#### 3.1.1 Sclerochronology

Sclerochronology is the estimation of time intervals from the growth patterns in biogenic carbonate deposits (Buddemeier 1978). The method has been applied to the exoskeletons of corals and molluscs, to encrusting calcareous algae, and to fish

otoliths. Coral sclerochronology refers to the study of density banding formation, historical growth records, and the reconstruction of environmental records based on the physical characteristics of coral skeletons.

Coral skeleton formation encompasses two separate aspects: coral growth and reef building. These aspects are closely linked, both functionally and in evolutionary terms. Coral growth constitutes the establishment, survival and increase in size of individual coral colonies, while reef building represents the development of coral populations and communities. The coral growth rate is the rate at which the coral calcifies (accretes) a skeleton. Growth rates vary enormously according to the type of colony under construction, which is species-specific. Rates of reef growth are dependent on both coral growth and coral erosion rates. Four processes control coral-erosion rates: physical erosion, seawater chemistry, bioerosion and rainwater dissolution (Edinger et al. 2000). Coral calcification is the biological process of calcium carbonate synthesis, meaning the product of both skeleton linear extension and skeleton density. A given rate of calcification is manifest in a coral skeleton as the rate of linear extension (cm year<sup>-1</sup>) of a particular density (g cm<sup>-3</sup>), reported in g cm<sup>-2</sup> year<sup>-1</sup> (Scoffin et al. 1992; Lough and Barnes 2000; De'ath et al. 2009; Cantin et al. 2010). Accretion rates of calcium carbonate by reef-building corals vary greatly (from 0.3 to 2 cm year<sup>-1</sup>, Vermeij 2006; Crabbe 2009) depending on the coral species and a number of environmental factors (e.g., light penetration, nutrient exposure, temperature, alkalinity). In most coral species, accretion of high- and low-density bands within the skeletal matrix occurs in response to environmental variability (Fig. 16.2). A year of growth typically consists of one high-density band and one low-density band (Fig. 16.3). This characteristic provides a built-in chronometer that enables first-order dating as well as identification of particular years and specific seasons. Knutson et al. (1972) confirmed the annual nature of density banding in corals from the Eniwetok Atoll, Marshall Islands (Appendix), which were exposed to nuclear weapons testing, by identifying density banding (by X-radiography) and radioactivity banding (by radioautography) in skeletal slabs. The number of density-band couplets in between the radioactivity bands corresponded with the number of years between nuclear detonations, while the number of density-band couplets after the last radioactivity band corresponded with the number of years between the last nuclear test and coral collection dates, thus providing a straightforward proof of the annual nature of coral-density banding. The annual nature of density banding was later confirmed for different species by radiometric analysis (Dodge and Thomson 1974; Moore and Krishnaswami 1974) and by radiometric analysis in combination with staining and direct measurement (Macintyre and Smith 1974).

In estuarine environments, the vast majority of corals used for paleoreconstructions are massive scleractinian colonies (e.g., *Porites* sp., *Goniopora* sp., *Diploastrea* sp.). Coral samples for paleoenvironmental reconstructions were originally collected as whole colonies. However, the currently preferred method is to collect skeletal cores (5–12 cm in diameter) by pneumatic drilling, as this method minimizes impact on coral reefs provided that core holes are restored with appropriated plugs (Edwards and Gomez 2007). The cores are then sectioned into 0.4–1.0 cm thick Fig. 16.3 Positive print of the X-radiography of a coral core slab (left) showing the skeletal density band pattern. One high-density band (*dark*) and one adjacent lowdensity band (*light*) represent the skeletal accretion of 1 year. In the line diagram (right), lines are drawn at high- to low-density shifts to show annual growth increments. The core top corresponds with the edge (surface) of the colony. Therefore, in living colonies the age of the top density band should correspond with the core collection date (Weber et al. 1975)



slabs oriented along the primary growth axis of the coral. For accurate and comparable density determination, core slabs must be consistent to a very precise thickness. Subsequently, each slice is X-ray radiographed to reveal the density bands that characterize the coral skeleton (Chalker and Barnes 1990; Carricart-Ganivet and Barnes 2007). A dark (high-density) and a light (low-density) band together represents 1 year (Fig. 16.3). The density of each band can be determined by relative optic density based on a gray scale (0–245). In sections where banding is absent or

poorly defined, the seasonal cycling of high resolution oxygen or carbon isotope records can be used to fill gaps (Fairbanks and Dodge 1979; Cole et al. 1993; Gagan et al. 1996; Evans et al. 1998). When working with fossil corals it is necessary to date each core radiometrically, and most commonly the Uranium-Thorium (U-series) method is used, as the precision is not affected by changes in the marine radiocarbon (<sup>14</sup>C) reservoir (Fairbanks et al. 2005). Subsequently, annual and sub-annual chronologies can be established, within the time frame, based on band counting. Application of cross-dating procedures should allow most coral records to achieve true annual chronologic precision.

Coral growth rates, based on annual-density bands, serve as an indicator for environmental change as well as a template for isotopic and elemental analysis of the skeleton. Once the basic premise that coral skeletons possessed annual density bands was established, growth rates were calculated to investigate the relation between growth and environmental conditions (Buddemeier et al. 1974). The investigation of corals from different regions (Pacific, Atlantic and Indian Oceans) revealed a spatial relationship between growth and temperature, where corals of the same species growing in warmer regions exhibited larger extension rates than those in cooler regions (Huston 1985a and references within). The comparison of density bands in coral skeletons with instrumental records revealed that higher extension rates occurred during warmer years, while lower extension rates were observed during cooler years (e.g., Clausen and Roth 1975; Dodge and Lang 1983; Wírum et al. 2007). The analysis of coral-skeleton density on sub-annual time scales further revealed that high-density bands are formed during the season of higher sea-surface temperature (SST), while low-density bands are formed during seasonal periods of lower SSTs (e.g., Highsmith 1979; Huston 1985b; Lough and Barnes 2000; Cantin et al. 2010). Because variations in calcification rates are related to both variations in the extension rate and density, the positive relationship between temperature and skeletal density may not hold true with respect to coral-growth rates and temperature. Studies on the seasonal variability of skeletal growth have indicated that rates are affected by variations in available light, cloud cover, turbidity, salinity and reproductive time rather than by temperature changes (Coles and Jokiel 1978; Guzman and Cortes 1989; Edinger et al. 2000; Wírum et al. 2007). Thus, as coral growth represents a complex phenomenon controlled by endogenous metabolic processes (e.g., reproduction, respiration, photosynthesis) that are modulated by environmental factors (e.g., temperature, light, nutrient load), caution should be used in interpreting coral-growth rates as responses to single factors and in extrapolating findings to other locations.

Growth rates are also useful for testing hypotheses regarding variations in growth attributable to climatic changes, such as rising  $CO_2$  levels (Allemand et al. 2004). Additionally, coral growth can be analyzed for spatial variations, such as depth dependence (Hubbard and Scaturo 1985) and latitudinal effects (Burgess et al. 2009), as well as periodic variations such as El Niño events (Le Bec et al. 2000; Rein 2004). Coral-growth records including extension, density and calcification determinations are mostly short-term (decadal scale) studies to evaluate site-specific growth ecology (e.g., Scoffin et al. 1992; Carricart-Ganivet et al. 2000; Worum

et al. 2007). Long-term coral growth records have generally been limited to extension rate measurements (e.g., Hudson 1981; Dodge and Lang 1983; Hudson et al. 1994). Relatively few studies have measured all three parameters for the long-term. In particular, to test the effect of long-term SST variability on coral growth, Lough and Barnes (1997) and Bessat and Buigues (2001) measured extension, density and calcification on centennial-length records and reported a positive relationship between SST and calcification over the twentieth century. However, recent studies based on multi-century and many decadal-growth records show significant declines in calcification (>10%) since 1990 despite increasing SSTs over the same period (Cooper et al. 2008; De'ath et al. 2009; Tanzil et al. 2009). These recent declines suggest that the positive relation between SST and calcification observed over the twentieth century may not be holding up under current environmental conditions. Such inconsistencies highlight the need for further analyses to investigate the role that changes in surface  $CO_2$  concentration and reduced aragonite saturation may have played on the recent decline in coral growth.

#### 3.1.2 Coral Luminescence

By illuminating a coral slab with ultraviolet light, luminescent lines are revealed. The occurrence and intensity of these bright luminescent lines has been used to improve dating of coral records as well as provide a proxy for fresh-water runoff into coastal areas. For instance, based on the relationships between the luminescent banding pattern in *Solenastrea* corals and flow records of the two major outlets of freshwater from the Florida Everglades in the USA (subtropical western Atlantic), Smith et al. (1989) reconstructed past fresh water flow into the Florida Bay estuary (Appendix). The coral records showed significantly higher luminescence in early sections of the skeleton (before 1932) than later (after 1932). Notably, the onset of decreased luminescence corresponds with the timing of construction of the extensive network of drainage canals to the east and south of Lake Okeechobee, which is the main source of freshwater to Florida Bay. These canals diverted water into the Atlantic Ocean that would normally have flowed into the Everglades. Thus the changes in luminescence indicate decreased freshwater flow from the Everglades into Florida Bay, perhaps by as much as 59%.

Measurements of luminescence in corals have also been used to demonstrate a quantitative relationship with river discharge (Isdale 1984; Smith et al. 1989; Susic and Isdale 1989; Isdale et al. 1998; Nyberg 2002), to infer precipitation changes (Fang and Chou 1992), wind speed variability (Nyberg 2002), monsoonal and upwelling intensity changes (Tudhope et al. 1996), rainfall and river flow (Lough 2007, 2011; Lewis et al. 2011), and hurricane activity (Nyberg et al. 2007). Lough et al. (2002) graded the intensity of luminescent lines in 232 corals from 30 reefs on the Great Barrier Reef in Australia (Appendix) and concluded that coral luminescence is a robust proxy record of mainland influence (i.e., distance from mainland, position respect to river plumes, annual river flow) on reefs along the length of the Great Barrier Reef. This study also revealed that luminescence changes can be induced by drops in salinity of ~1–2‰.

However, the exact cause of luminescent banding is still debated and the nature of the fluorescent bands in the coral skeleton has been brought into question as a possible artefact of skeletal density variations (Barnes et al. 2003; Barnes and Taylor 2005). The incorporation of terrestrial humic acids, carried to the nearshore environment during periods of high terrestrial runoff was first proposed as the likely cause of luminescence, meaning increasing runoff would boost humic acid erosion and therefore the incorporation of the fluorescent compound into the skeleton (Isdale 1984). However, the incorporation of humic acids does not explain certain features of coral luminescence, particularly luminescence in corals that grew far from terrestrial influence (Barnes and Taylor 2005; Grove et al. 2010). Coral skeletal density has also been proposed as the likely cause of luminescence lines, as aragonite itself is fluorescent (Barnes and Taylor 2001, 2005; Grove et al. 2010). Because luminescence is enhanced where there are cavities in the aragonite lattice (i.e., multiple reflections within cavities result in greater luminescence), changes in luminescence have been related with variations in the configuration of the coral skeleton (Barnes and Taylor 2001). Luminescence occurs in lower density regions of the skeleton, as these regions have larger holes and less even and/or pierced surfaces. Accordingly, luminescent bands in corals that grew far from land correspond with low-density regions that occur because of altered growth during periods of lowered salinity (Barnes and Taylor 2001, 2005). Barnes et al. (2003) pointed out that such bands have been confused with the narrower luminescent bands associated with runoff. These authors proposed that the two types of luminescence bands be distinguished, somewhat artificially, by calling those produced by runoff "luminescent bands" and those density related "luminescent lines."

## 3.2 Geochemical Tracers in Corals

Within the density banding of the aragonite lattice of reef-building corals, it is possible to differentiate microlaminations. These microlaminae carry isotopic and chemical indicators that track the temperature, salinity and isotopic composition of surface waters as well as site-specific features including turbidity, runoff and upwelling intensity, thus providing a wealth of information about past environmental conditions (Gagan et al. 2000; Lough 2004). Over the last few decades there has been an effort to identify new climatic tracers in corals and develop better techniques for data extraction and measurement. As a result, a multi-proxy approach to coral-based paleoclimatology is emerging. A high priority in coral research today is to produce quantitative indicators of specific aspects of climate that can be integrated with other high-resolution paleoclimate data derived from tree rings, ice cores and varved sediments.

#### 3.2.1 Stable Isotope Ratios

#### Oxygen Stable Isotopes

Changes in the stable oxygen isotope ratios ( $\delta^{18}$ O; representing  $^{18}$ O/ $^{16}$ O) of coral skeleton microbands have been employed to reconstruct SST and sea-surface salinity (SSS) variability (e.g. Wellington et al. 1996; Asami et al. 2004; Rosenheim et al. 2004). The  $\delta^{18}$ O composition of coral carbonate, which is expressed as parts per thousand with respect to the Vienna Pee Dee Belemnite (VPDB) isotopic standard, depends on both the temperature-dependent fractionation that occurred during precipitation and the isotopic composition of seawater ( $\delta^{18}O_w$ ) in which the skeleton was formed (Cole and Fairbanks 1990; Fairbanks et al. 1997; Kim and O'Neil 1997). Modern surface  $\delta^{18}O_w$  reflects the hydrological balance between changes in evaporation (18O enrichment), precipitation (18O depletion) and meteoric water input from terrestrial runoff (i.e., the surface salinity). Over longer time scales  $\delta^{18}O_w$ is also a function of the extent of continental ice sheets. It has been calculated that the  $\delta^{18}$ O of coral skeletal aragonite varies inversely with SST at a rate of -0.17 to -0.21% for every 1 °C increase in water temperature (Epstein et al. 1953; Weber and Woodhead 1970, 1972). Thus, in regions of low SSS variability, coral skeletal  $\delta^{18}$ O is primarily regarded as a recorder for SST (e.g., Wellington et al. 1996; Rosenheim et al. 2004). However, in regions where the  $\delta^{18}O_w$  is most strongly controlled by precipitation/evaporation/runoff, coral δ<sup>18</sup>O provides a record of changes in the hydrological balance (Pfeiffer et al. 2004). If the coral  $\delta^{18}$ O records of these areas are positively correlated with precipitation, coral  $\delta^{18}$ O can be used to reconstruct past regional rainfall (e.g., Charles et al. 1997; Gagan et al. 2000). However, if SST variability is large and/or the coral  $\delta^{18}$ O signal does not correlate with precipitation, the evaluation of past hydrological changes requires pairing of the coral  $\delta^{18}$ O with another geochemical SST proxy, such as coral Sr/Ca ratios (Zinke et al. 2004; Pfeiffer et al. 2006). This approach assumes that all variations in coral Sr/Ca are due to SST changes, and that variations in coral  $\delta^{18}$ O are due to the combined influences of SST and seawater  $\delta^{18}$ O (Ren et al. 2003). The advances in the analytical techniques for measuring trace elements in carbonates allow these multi-proxy studies to become more common, so there is less reliance on assuming a dominant SST or hydrological driver in interpreting coral  $\delta^{18}$ O records. However, one potential problem of the application of coral  $\delta^{18}$ O records in multi-proxy paleoenvironmental reconstructions, is the existence of kinetic and biologically induced isotopic disequilibrium in coral  $\delta^{18}$ O with respect to ambient seawater (Urey et al. 1951; Epstein et al. 1953; McConnaughey 1989). Kinetic fractionation results from discrimination against heavy isotopes of both carbon and oxygen during the hydration and hydroxylation of CO<sub>2</sub> (McConnaughey 1989). This effect produces a simultaneous depletion of <sup>13</sup>C and <sup>18</sup>O in coral carbonate relative to the composition of ambient seawater (McConnaughey 1986, 1989). Kinetic fractionation (the so-called "vital effect") occurs when precipitation of coralline aragonite takes place at rates faster than the establishment of isotopic equilibrium within the coral's calicoblasts (Gagan et al. 2000). Rates of kinetic fractionation increase during accelerated coral

growth (Suzuki et al. 2005). Accordingly, within the same species, the disequilibrium offset may not always be constant, as growth rates vary between colonies and within each colony (Land et al. 1975; McConnaughey 1989). Notably, growth effects can be minimized by sampling for  $\delta^{18}$ O along major corals growth axes (i.e., avoiding sampling the slow-growing sides of the colony; McConnaughey 1989; Cohen and Hart 1997).

Prior to interpretation,  $\delta^{18}$ O records must be calibrated. Calibrations are needed to evaluate the effect of particular environmental parameters on coral  $\delta^{18}$ O and to assess the significance of biological disequilibrium offsets. At present, the majority of calibrations have been carried out in the field by comparing coral skeletal  $\delta^{18}$ O series with instrumental data (e.g., Al-Rousan et al. 2003; Tsuyoshi Watanabe et al. 2006: Saenger et al. 2012). Few calibrations have been carried out in laboratories under controlled conditions to understand the effect of each environmental parameter (temperature, light, nutrition, CO<sub>2</sub> concentration) on coral stable isotopic composition (e.g., Reynaud-Vaganay et al. 1999; Marubini et al. 2001; Reynaud et al. 2002; Suzuki et al. 2005) or to evaluate changes in the isotopic composition of corals due to biological effects. For instance, Reynaud-Vaganay et al. (1999) confirmed that different colonies of Acropora spp. cultured under identical temperature settings yielded statistically identical  $\delta^{18}$ O measurements. However, when comparable measurements were performed on colonies of Stylophora pistillata, 818O measurements varied greatly (up to 2%); Reynaud et al. 2002). Thus, to obtain meaningful environmental reconstructions based on coral  $\delta^{18}$ O records it is necessary to produce both species- and site-specific calibrations.

#### Carbon Stable Isotopes

During the stable isotope analysis of coral aragonite, carbon stable isotope ratios ( $\delta^{13}$ C; representing  $^{13}$ C/ $^{12}$ C) are measured simultaneously with  $\delta^{18}$ O, hence a large quantity of archived  $\delta^{13}$ C data is available. The interpretation of such records, however, is not straightforward owing to the wide range of factors that modulate coral  $\delta^{13}$ C. Whereas the  $\delta^{18}$ O of the coral skeleton is used for reconstruction of past information on seawater,  $\delta^{13}$ C is considered as a proxy for physiological processes, principally photosynthesis and respiration. However, the fractionation of carbon isotopes in coral skeletons is still unclear.

Various environmental factors play a role as forcing mechanisms on coral skeletal  $\delta^{13}$ C. For instance, the concentration of environmental CO<sub>2</sub> and the degree of CO<sub>2</sub> exchange between seawater and the coral internal carbon pool will affect the degree of expression of metabolic and kinetic carbon fractionation (e.g., McConnaughey et al. 1997). The isotopic composition of the environmental CO<sub>2</sub> further affects coral  $\delta^{13}$ C. Fitly, the anthropogenic addition of isotopically lighter CO<sub>2</sub> into the atmosphere and surface-ocean has been reported as a secular-scale decreasing trend in coral  $\delta^{13}$ C over the twentieth century, commonly referred to as the "Suess Effect" (Keeling et al. 1980; Swart et al. 1996, 2010; Quinn et al. 1998; Linsley et al. 1999; Liu et al. 2009). In addition, dissolved inorganic carbon of fluvial origin (Moyer and Grottoli 2011) and changes in the productivity of the water column (Rau et al. 1992) influence the  $\delta^{13}$ C of seawater, further complicating the interpretation of coral  $\delta^{13}$ C records.

Numerous metabolic processes related to coral autotrophy and heterotrophy produce isotopically altered carbon that might be incorporated into the coral lattice, affecting its  $\delta^{13}$ C signal. These processes include the photosynthetic modulation of the isotopic composition of the coral internal carbon pool (Juillet-Leclerc et al. 1997; Omata et al. 2008), the status of the symbiotic relationship between coral tissue (polyps) and zooxanthellae (Allison et al. 1996) and changes in proportions of heterotrophic to autotrophic feeding (Carriquiry 1994; Swart et al. 1996; Felis et al. 1998; Reynaud et al. 2002). Coral reproductive cycles (Gagan et al. 1994, 1996), colony topography (Cohen and Hart 1997) and kinetic effects associated with the rate of coral calcification (Aharon 1991; De Villiers et al. 1995; Allison et al. 1996; Cohen and Hart 1997; Heikoop 1997; Guzman and Tudhope 1998; Omata et al. 2008) are also important factors. As kinetic effects tend to obscure the  $\delta^{13}$ C metabolic signals related to light availability, photosynthesis and respiration, it is often difficult to distinguish correlations between  $\delta^{13}C$  and environmental variables (Heikoop et al. 2000). If these kinetic effects are resolved, however, information on depth, water clarity, and insolation may be deduced from coral  $\delta^{13}$ C.

Based on experiments showing that coral aragonite lattice, polyps and zooxanthellae become increasingly  $\delta^{13}C$  depleted with increasing depth (Weber and Woodhead 1970; Land et al. 1975; Weber et al. 1976), Goreau (1977) proposed a theoretical model in which polyps and zooxanthellae share a common dissolved inorganic carbon (DIC) pool affected by photosynthesis, respiration and calcification. Later, Swart et al. (1996) documented that coral skeletal  $\delta^{13}$ C reflects changes in the  $\delta^{13}$ C of ambient DIC. However, they observed that skeletal  $\delta^{13}$ C, when corrected for changes in ambient  $\delta^{13}$ C, are not correlated with productivity but are negatively correlated with the ratio of daily primary production to daily respiration (P/R). Although such findings apparently contradicted Goreau's model, Swart et al. (1996) noted that the inverse association between  $\delta^{13}$ C and P/R occurred because of a positive association between  $\delta^{13}$ C and respiration. Carriquiry (1994) explained that the variability of  $\delta^{13}$ C could be due to shifts of the symbiosis from autotrophy to increase heterotrophy modulated by irradiance changes. Thus, the annual periodicity of the  $\delta^{13}$ C signal could indicate a relationship between  $\delta^{13}$ C and seasonal insolation changes (Fairbanks and Dodge 1979). Long-term culture experiments confirmed the effect of zooxanthellae photosynthetic activity in  $\delta^{13}$ C (Omata et al. 2008). To prevent autotrophy to heterotrophy variations, corals were grown without food (in sand-filtered water), thus they subsisted from zooxanthellae photosynthesis only. As daily irradiance increased (imitating seasonal insolation), skeletal growth rates increased and mean oxygen and carbon isotope compositions shifted. At higher irradiation, the  $\delta^{13}$ C became heavier (increased) and the  $\delta^{18}$ O became lighter (decreased). Skeletal  $\delta$  <sup>18</sup>O decrease coincided with increasing skeletal growth, indicating the influence of kinetic effects. However, the observed  $\delta^{13}$ C increase should be subject to both kinetic and metabolic isotope effects, with the latter reflecting skeletal <sup>13</sup>C enrichment due to symbiont photosynthesis. Accordingly, the  $\delta^{13}$ C

fractionation curve related to metabolic effects correlated well with the photosynthesisirradiance curve, indicating the direct contribution of photosynthetic activity to metabolic isotope effects. In contrast,  $\delta^{13}$ C fractionation related to kinetic effects gradually increased as the growth rate increased. Based on these results, Omata et al. (2008) established that the kinetic and metabolic isotope effects in coral  $\delta^{13}$ C can be differentiated by pairing  $\delta^{13}$ C and coral-growth records, and by observing the relationship between  $\delta^{18}$ O and  $\delta^{13}$ C. Considering that the rate at which photosynthesis takes place is dependent upon the amount of incoming solar radiation, by isolat-

sis takes place is dependent upon the amount of incoming solar radiation, by isolating metabolic-related changes in  $\delta^{13}$ C it is possible to reconstruct long-term variability in seasonal cloud cover (Watanabe et al. 2002) and changes in monsoondriven upwelling (Ahmad et al. 2011).

The  $\delta^{13}$ C of coral carbonate has also been used, in combination with <sup>14</sup>C records, to establish changes in terrestrial carbon input to coastal areas. The transfer of carbon from land to the coastal ocean is a significant, but severely unquantified, component of the global carbon cycle. Most studies have focused on temperate coastal areas adjacent to large riverine systems, while tropical rivers, which potentially deliver a significant amount of carbon to the oceans, have seldom been studied. Available literature shows that the stable ( $\delta^{13}$ C) and radioactive ( $\Delta^{14}$ C) carbon isotopic compositions of temperate coastal DIC are influenced by the  $\delta^{13}$ C and  $\Delta^{14}$ C of the DIC transported by the adjacent rivers (Raymond and Bauer 2001; Mayorga et al. 2005; Moyer 2008). Such a pattern should also exist in tropical coastal areas and, hence, in coral carbonate. Therefore, coral carbonate records have the potential to advance our understanding of tropical land–ocean carbon transfers. Furthermore, since very few multi-decadal or longer records of land carbon delivery to the ocean are available for any region of the Earth (but see Macreadie et al. 2012), corals could provide such records in tropical regions.

The major sources of carbon to riverine DIC are dissolution of carbonate minerals, soil CO<sub>2</sub> derived from microbial decomposition of organic matter (mainly of terrestrial origin), and CO<sub>2</sub> from root respiration. Due to its origin, riverine DIC  $\delta^{13}$ C is characteristically lower than seawater DIC (Aucour et al. 1999). Hence, the input of riverine DIC to coastal oceans causes depletion in coastal seawater DIC  $\delta^{13}$ C, which is tracked by the  $\delta^{13}$ C of coral skeletons (Swart et al. 1996).

Radiocarbon (<sup>14</sup>C) enters the ocean through gas exchange of atmospheric CO<sub>2</sub> and thus, surface seawater DIC  $\Delta^{14}$ C values reflect a combination of atmospheric  $\Delta^{14}$ C values and surface ocean processes. Riverine DIC has lower  $\Delta^{14}$ C than seawater DIC because it is largely derived from the respiration and photo-oxidation of aged terrestrial organic matter (e.g., Mayorga et al. 2005). Thus, the input of riverine DIC to coastal waters should decrease  $\Delta^{14}$ C in coastal seawater DIC and coral skeletons. The  $\Delta^{14}$ C values of coral skeletons, measured as the difference between sample radioactivity and the 1950 international standard corrected for age and  $\delta^{13}$ C, have been shown to closely reflect the <sup>14</sup>C composition of the seawater DIC in which they grow, independent of metabolic fractionation effects (Druffel and Linick 1978; Nozaki et al. 1978; Konishi et al. 1981).

In recent studies, the use of paired measurements of DIC  $\delta^{13}$ C and  $\Delta^{14}$ C have been shown to be more effective than using either isotope alone for calculating

fluxes and residence times of carbon in terrestrial and marine aquatic systems (Raymond and Bauer 2001; Mayorga et al. 2005; Moyer 2008). In corals, this dual isotope approach allows for a much clearer distinction between coral  $\delta^{13}$ C variability brought about by changes in the isotopic composition of DIC and those due to metabolic fractionation effects.

Moyer and Grottoli (2011) paired measurements of  $\delta^{13}C$  and  $\Delta^{14}C$  in the Rio Fajardo, Puerto Rico (Appendix), the adjacent coastal ocean, and estuarine corals to investigate the linkages between riverine DIC and coral carbonate. They confirmed that riverine DIC was always more depleted in  $\delta^{13}C$  and  $\Delta^{14}C$  than seawater DIC, and observed a synchronous decrease in both coral  $\delta^{13}C$  and  $\Delta^{14}C$  coherent with the timing of peak river discharge. Additionally, the correlation of  $\delta^{13}C$  and  $\Delta^{14}C$  was found to be the same in the coral skeleton, the DIC of the river, and coastal waters. These results indicate that coral skeletal  $\delta^{13}C$  and  $\Delta^{14}C$  effectively track the delivery of riverine DIC to the coastal ocean. Thus, coral records could be used to develop proxies of historical land–ocean carbon flux for many tropical regions and to improve our understanding of long-term variability in tropical carbon fluxes to the ocean in the context of land-use change and global climate change.

#### Boron Stable Isotopes

Reconstructing the recent trend and natural variability of ocean pH is crucial to understand the possible consequences of ocean acidification on marine ecosystems due to the absorption of anthropogenic CO<sub>2</sub> by seawater. The boron isotope-pH proxy is established on a theoretical model of carbonate  $\delta^{11}$ B variation with pH that assumes that the boron isotopic composition of carbonates reflects the boron isotopic composition of borate in solution ( $\delta^{11}B_{carbonate} = \delta^{11}B_{seawater borate}$ ). This model benefits from understanding the chemical kinetics and thermodynamic basis on the equilibrium fractionation factor between the two dominant boron-bearing species in seawater, dissolved boric acid B(OH)<sub>3</sub> and borate ion B(OH)<sub>4</sub><sup>-</sup>. However, because of our inability to determine this factor experimentally, meaning to measure the degree of boron isotope exchange between boron species, the value has only been known through theoretical estimates (Zeebe 2005).

Culture experiments on *Porites* and *Acropora* corals have confirmed that boron isotopes ( $\delta^{11}B$ ) in coral skeletons faithfully record variations of seawater pH (e.g., Hönisch et al. 2004; Reynaud et al. 2004). Measurements in *Acropora* spp. (branching scleractinian corals) confirmed that the coral boron isotope composition shows a clear pH effect, but no temperature effect, and that corals do not seem to significantly alter ambient seawater for calcification with respect to pH (Reynaud et al. 2004). The calibration of  $\delta^{11}B$  with seawater pH for *Porites* is in good agreement with the theoretical curve for the borate species (Hönisch et al. 2004). Furthermore, no systematic changes in skeletal  $\delta^{11}B$  were observed in response to changes in physiological processes such as photosynthesis and respiration associated with increased light intensity or food availability. However, there is still uncertainty about how biological modulation of boron uptake associated with coral calcification may influence paleo-pH records (Gaillardet and Allègre 1995).

Three multi-century records of seawater pH from corals have been determined for Porites corals from the South Pacific Ocean (Appendix) in the Flinders Reef in the Coral Sea (Pelejero et al. 2005), the central Great Barrier Reef (Liu et al. 2009) and Fiji (Douville et al. 2009). The Flinders coral  $\delta^{11}$ B record, commencing in 1708. shows large variations in pH that covary with the Pacific Decadal Oscillation (PDO). The results indicate that locally significant natural cycles in reef pH can modulate the impact of ocean acidification on coral-reef ecosystems. The Great Barrier Reef coral  $\delta^{11}$ B record, covering the period from 1800 to 2004 AD, shows an overall trend, since 1940, of ocean acidification with a pH decrease of 0.2-0.3 units. The result suggests that increasing levels of atmospheric CO<sub>2</sub> have already caused significant acidification of the ocean surface. In good agreement with the two aforementioned studies, the Fiji  $\delta^{11}$ B record, encompassing from 1750 to 2000 AD, shows a progressive decrease of seawater pH by ~0.1 pH units between 1900 and 2000 AD, and reveals that seawater pH changes in the Fiji area are strongly affected by regional processes linked to the PDO. The spatial and temporal conformity of these three pH reconstructions highlight the potential of the  $\delta^{11}$ B-pH technique for studying past changes of ocean dynamics.

#### Phosphorous and Nitrogen Isotopes

Coastal and estuarine coral reefs are subject to environmental degradation due to human activity. As human populations along coastal areas expand, environmental pressure on coral reefs has increased. In particular, increasing sedimentation rates due to human activities on land (e.g., agriculture, construction, deforestation) and the use of synthetic fertilizers has resulted in noticeably higher nutrient loads to estuarine areas. Nutrient enrichment creates an imbalance in the exchange of nutrients between the zooxanthellae and the host coral. Eutrophication also reduces light penetration to the reef due to nutrient-stimulated phytoplankton blooms and may produce the propagation of seaweeds. However, nutrient enrichment does not occur alone, as sewage discharges also enrich coastal waters with organic matter, which stimulates proliferation of oxygen-consuming microbes. These organisms may kill corals, either directly by anoxia or by related hydrogen sulphide production. Thus, eutrophication leads to reduction in both larval recruitment and species diversity in coral reefs. The result is the alteration of trophic structures, as corals are being replaced by microalgae in shallow waters and by heterotrophic communities in deeper water (Dubinsky and Stambler 2006).

Phosphorous (P) and nitrogen isotopes ( $\delta^{15}N$ ) in corals have been used to reconstruct the history of sewage and agricultural pollution in nearshore reef settings. Phosphate acts as a crystal poison of calcification (Simkiss 1964). A crystal poison is a compound that settles on the surface of a crystal and interferes with the continued formation of the crystal lattice. Using radioactive phosphorus (<sup>32</sup>P) as a tracer, it is possible to investigate the exchange of phosphate between components of the reef bottom and the water column (Sorokin 1992). It has been shown that coral records from the subtropical Atlantic present variations in P concentrations that are consistent with the local sewage and pollution history (Dodge et al. 1984).

Pristine corals, those unaffected by terrestrial processes or anthropogenic activities, have similar  $\delta^{15}$ N to that of macroalgae collected from the same locations, indicating that corals are isotopically similar to primary producers, and therefore suitable for assessing sources of dissolved inorganic nitrogen (Sherwood et al. 2010). Synthetic nitrogenous fertilizers are depleted in <sup>15</sup>N relative to the inorganic nitrogen dissolved in seawater. In principle, the  $\delta^{15}N$  of residual organic nitrogen in coral skeletons should reflect temporal changes in the balance between natural and synthetic nitrogen sources in coastal reef waters (e.g., Marion et al. 2005). This principle has been used to trace the history of nutrient loading in coastal oceans via  $\delta^{15}$ N analysis of organic nitrogen preserved in corals (Cooper et al. 2009 and references within). Marion et al. (2005) measured  $\delta^{15}N$  in *Porites* corals to show that western-style agricultural practices have contributed to the degradation of coastal reefs in Bali, Indonesia (Appendix). They found that coral cores from areas exposed to untreated sewage (terrestrial discharges) were enriched in  $\delta^{15}$ N, while offshore corals reflected background oceanic signals characterized by lower  $\delta^{15}N$  values. Additionally, they observed that skeletal  $\delta^{15}N$  values were negatively correlated with rainfall, suggesting that in coastal waters  $\delta^{15}N$  lowers during flood-borne influxes of synthetic fertilizers. Thus, coral  $\delta^{15}$ N records track changes in sewage contamination in coral-reef environments and can be used to reconstruct historic changes in agricultural activities or land usage. However, short-term variability in nitrogen cycling and isotopic fractionation may obscure long-term trends (Sherwood et al. 2010).

#### 3.2.2 Elemental Geochemical Tracers

#### Paleothermometers

Among the elements in the beryllium group (alkaline earth metals), magnesium (Mg<sup>2+</sup>) and strontium (Sr<sup>2+</sup>) form the most important solid solutions with carbonate species (aragonite and calcite). However, due to the difference in the ionic radius of each element (large in Sr<sup>2+</sup>, small in Mg<sup>2+</sup>) SrCO<sub>3</sub> crystals (orthorhombic) are isostructural with the aragonite lattice, whereas the MgCO<sub>3</sub> crystal cell (rhombohedral) is isostructural with calcite. Magnesium, strontium, and calcium (Ca) have relatively long oceanic residence times (i.e., Mg  $\approx$  13 Ma, Sr  $\approx$  5 Ma and Ca  $\approx$  1 Ma). Hence, on timescales  $<1 \times 10^6$  years, Mg/Ca and Sr/Ca ratios in seawater are nearly constant. On this basis, the variability of Sr/Ca in coral skeletons has been applied as a tracer for environmental changes. Many studies have indicated that the Sr/Ca in coral aragonite lattices is primarily regulated by water temperature (Beck et al. 1992; Alibert and McCulloch 1997; Gagan et al. 1998). A negative relationship exists between SST and the amount of Sr incorporated into the aragonite lattice. Given the long oceanic residence time of Sr, variations in skeletal Sr/Ca are assumed to mainly reflect SST variability (e.g., Sun et al. 2005). However, recent studies suggest that secondary non-temperature effects, such as disequilibrium offsets and extension rate variability, also play an important role in determining skeletal Sr/Ca

ratios (Cohen and Gaetani 2010; Gaetani et al. 2011). The examination of Sr/Ca-SST relationships in Porites corals (Marshall and McCulloch 2002) revealed that the slope of the Sr/Ca-SST relationships, derived at different sites from different individual corals, is generally consistent. However, among nearby sites, the intercepts of the linear relationship are significantly different. These differences can be attributed, in part, to disequilibrium between skeletal Sr/Ca and seawater Sr/Ca. Thus, the different intercepts for coral Sr/Ca-SST relationships reflect the fact that the disequilibrium offset can vary between corals, even those of the same species. Relatively little is known about the degree to which biological parameters such as metabolism and calcification rate influence the final Sr/Ca in coral skeleton. However, evidence indicates that Sr incorporation into the skeleton may be inversely related to the calcification rate (Ferrier-Pages et al. 2003). Some of the skeletal Sr/ Ca heterogeneity is apparently due to differences between skeletal elements deposited at night time versus day time calcification (Cohen et al. 2001). During night time, small crystals are deposited at the axial spines of the corallites (centres of calcification), while larger crystals are formed during the day on all surfaces of the precipitating skeleton. Microprobe analyses of Sr/Ca showed that the night time and day time crystals have significantly different Sr/Ca (e.g. Cohen et al. 2001; Shirai et al. 2012). Developing a replicated coral Sr/Ca series from a specific site or in a specific region could potentially help to separate climate-related Sr/Ca variability from variability induced by biologic or diagenetic processes, improving the accuracy of the coral Sr/Ca thermometer in modern corals and further facilitating the interpretation of Sr/Ca data from fossil corals. Nevertheless, as long as adequate sites are selected and coral-specific temperature calibrations are carried out, Sr/Ca can be used to accurately reconstruct water paleotemperatures.

Other coralline geochemical proxies for temperature have been explored (e.g., Hart and Cohen 1996; Fallon et al. 2003; Mitsuguchi et al. 2003), including uraniumcalcium ratios (Min et al. 1995) and magnesium-calcium ratios (Inoue et al. 2007), which are most commonly used in biogenic calcite from foraminifera. Nonetheless, Sr/Ca ratios remain as the most robust coral-derived paleothermometer.

Similar to all other paleoclimate proxy records, corals are biased by factors unrelated to climate. For example, the upward growth of a coral can lead to the exposure of its surface to shallower water depths, and in turn slightly different temperature, salinity and light intensity levels. This has potential ramifications for the isotopic and geochemical records obtained (Gagan et al. 2000; Felis et al. 2003; Suzuki et al. 2005; Inoue et al. 2007; Reynaud et al. 2007; Omata et al. 2008). One way to identify and adequately consider such effects is to cross match coral records and/or create composite records (Cahyarini et al. 2008; Pfeiffer et al. 2009). Some studies have attempted to quantify the reliability of climate proxies contained within coral records through local, regional and global cross matching, as well as comparing single and composite coral records with instrumental data (Guilderson and Schrag 1999; Evans et al. 2002; Hendy et al. 2003; Cahyarini et al. 2008; Pfeiffer et al. 2009). However, many studies continue to rely on the implicit assumption that variations identified in a single coral record are attributable to one or more climatic variables (Lough 2004). Although caution needs to be applied in utilizing coral records, if the various potential influences on proxies contained within corals are well understood, and the coral records obtained are well calibrated and validated, they provide an extremely powerful tool for understanding climate change and environmental variability at seasonal, decadal, centennial and millennial time scales.

#### Geochemical Tracers of Sediment Runoff

In estuarine environments, barium (Ba) is release from terrigenous particles when fresh- and saltwater mix together (Alibert et al. 2003; McCulloch et al. 2003; Fleitmann et al. 2007). Ba is then mixed into the water column and later incorporated into coral skeletal carbonate (Coffey et al. 1997). Thus, elevated Ba/Ca ratios in skeletal carbonate are indicative of increased sediment runoff.

In the absence of historical records of sediment pollution, ratios of coral Ba/Ca can be used to track sedimentation changes over time. Based on the observation that growing rates of Molokai coral reefs, Hawaii (Appendix), have decreased significantly over the past decade, Prouty et al. (2010) measured Ba/Ca ratios to investigate changes in sedimentation rates as the possible cause for coral-reef decay. Results show that skeletal Ba/Ca ratios co-vary with the abundance of terrigenous sediment delivered to the coast. Furthermore, a statistically significant upward trend was displayed by the Ba/Ca series, indicating a persistent increment in fluvial sediment input into Molokai catchment basins, which buried the coral reef and accelerated coral decay, thus explaining the observed reduction in reef growth. Similarly, the effect of European settlement on water quality in the Great Barrier Reef of Australia has been inferred based on variations in skeletal Ba/Ca ratios. Fluvial sediment transport to this area of the Australian coastline has increased substantially since European settlement (e.g., Perry et al. 2008), but the magnitude and ecological effects of this increment remains uncertain. McCulloch et al. (2003) measured Ba/Ca ratios in Porites coral to establish a record of sediment fluxes from 1750 to 1998 AD. The observed changes in skeletal Ba/Ca indicate a 500-1000 % increase in sediment input after the beginning of European settlement with the highest fluxes occurring during drought-breaking floods. They concluded that changes in land-use practices (e.g., clearing and overstocking) associated with European settlement led to major degradation of the semi-arid river catchments, resulting in substantially increased sediment loads entering the Great Barrier Reef.

# Coral Records in Monitoring Water Quality and Pollutant Delivery to Coastal Regions

Eutrophication is considered to be nutrient pollution when the concentration of limiting nutrients (nitrogen, phosphorous, organic matter) is significantly higher than naturally observed. In coastal areas around the world, the release from nutrient limitation has contributed to the decay of many coastal reefs. Eutrophication produces environmental changes that directly affect reef development and coral growth. Higher nutrient availability results in reduced light penetration, as turbidity increases in response to higher pigment concentrations. Changes in sediment properties, due to the binding of silt particles with organic matter, can create flow-on effects that alter deposition rates and sediment distribution within and around reefs. Excess suspended organic matter also affects light penetration, but most significantly, higher levels of suspended organic waste result in anomalously high microbe populations, which consume oxygen during oxidative processes, leading to anoxic conditions. The vulnerability of specific reefs to damage by eutrophication increases in shallow regions or when reefs are located in deficiently flushed areas, such as semienclosed bays or coastal lagoons (D'elia and Wiebe 1990 and references within). Historic studies and ecological studies on dynamics of coral reefs in polluted estuaries around Hong Kong (Appendix) revealed that most reefs in this region present signs of increasing pollution stress (Morton 1989; Scott 1990), as coral growth rates, species number, abundance and diversity, show marked declines during periods of decreasing water quality (Scott 1990; Fabricius and McCorry 2006). Scott (1990) further determined that the periodicity of ecological changes observed in the Hong Kong reefs is coherent with changes in trace-metal content of coral skeletons, demonstrating that changes in water quality are recorded by changes in coral carbonate trace-metal concentrations. However, the transport of trace metals (e.g., Al, Cd, Ce, Cu, Co, Cr, Fe, La, Li, Mg, Mn, Ni, Pb, V, Y, Zn) to coastal areas and resulting metal uptake by corals is not a straightforward process. In estuaries, the mixing of river water and seawater results in flocculation which precipitates a large amount of the dissolved metals supplied by the river (Gerringa et al. 2001). Thus, concentration of some trace metals, such as Al, Cd and Mn, is greatly reduced by estuarine flocculation (Sholkovitz 1978). Accordingly, while trace metal concentration in corals reflects changes in riverine-metal contribution to coastal areas, the riverine metals' concentration may be underrepresented in the coral carbonate record (Scott 1990; Ramos et al. 2004). Nonetheless, changes in metal-to-calcium (Me/Ca) ratios in coral skeletons have been used to monitor pollutants from urban areas to estuaries and to reconstruct past changes in water quality. For example, Me/Ca ratios in Porites corals from the Hija River estuary in Okinawa (north western Pacific) were evaluated by Ramos et al. (2004) in order to estimate the trace metal anthropogenic contribution by riverine input to Okinawa coastal waters. They determined that Pb/ Ca in the estuarine corals were two and three times higher than baseline levels, indicating Pb enrichment in the river mouth. However, Pb is only moderately high in the Hija River water compared to surface seawater, thus Pb may have accumulated in the estuarine water and sediments, resulting in an elevated concentration of Pb available for coral uptake.

Coral skeletal trace metal concentrations have also been used to monitor changes in water quality related to mining activities. Inland basement rock exploited by the mining industry has distinctive local or regional trace element patterns (e.g., high abundances of Mn, Zn and Pb) and the sediments transported by rivers from the mining areas into the near-shore environment have considerably higher than normal trace metal concentrations. Therefore, the onset of mining activities results in the metal enrichment of the corresponding estuarine and coastal waters. Accordingly, Fallon and McCulloch (2002) measured Y, La, Ce, Mn, Zn and Pb concentrations in *Porites* corals from Misima Island in Papua New Guinea (southwestern Pacific, Appendix). Fallon and McCulloch (2002) determined that trace metal levels in surrounding coastal waters were lower prior to the commencement of mining activities on the island in 1988. However, each trace metal showed distinctive temporal variability patterns. Coral concentrations of Y, La, and Ce showed dramatic increases associated with increased sedimentation (runoff) at the onset of the mining activities as well as rapid decreases following the closure of the mine. On the other hand, Zn and Pb do not show increasing concentrations until after ore processing began in 1989. Furthermore, levels of Zn and Pb in corals did not decrease after the cessation of mining, indicating ongoing transport into the reef of these metals via sulphaterich waters (Barnes and Lough 1999; Fallon and McCulloch 2002).

Changes in coral metal content are also a good recorder of changes in the atmospheric transport of pollutants. It has been shown that Pb/Ca ratios in coral skeletons mirror local and global inputs of industrial heavy metal pollution to the oceans (e.g., Shen and Boyle 1987, 1988; Shen et al. 1987). Using coral cores collected from eight locations around the western subtropical Pacific, Inoue et al. (2006) determined changes in coral Pb/Ca ratios to investigate changes in atmospheric transport of anthropogenic Pb. Their results showed a clear pattern of atmospheric Pb transport from the Asian continent to the open ocean since the late nineteenth century. Similarly, Shen and Boyle (1987) analyzed coral skeletal records from the Bermuda area to investigate atmospheric fluxes of industrial pollution from the continental USA. They determined that anthropogenic Pb emissions in this area have been dominated by the industrialization of North America, particularly by the introduction of leaded gasoline circa 1920 and its phase-out in the mid-1970s. Peak Pb/Ca ratios correlated with the use of tetraethyl lead in automobile gasoline, while low Pb/Ca ratios occur prior to the introduction of leaded gasoline and a little after its total phase-out in the 1990s.

Research has shown that coral reefs exhibit a response to environmental change that is more complicated than previously expected. Estuarine corals, which survive in areas where temperature, salinity, sedimentation and nutrient load variability is high, constitute remarkable examples of adaptation or acclimatization to environmental change. Therefore, estuarine corals represent case studies to identify species and ecosystems responses to future environmental change.

## 4 Conclusions

Coral skeletons are valuable natural archives of paleoenvironmental conditions in tropical and subtropical regions. Living colonies can provide centuries of annual, and sub-annual scale environmental tracking and fossil corals can be used to reconstruct conditions over millennial time scales. Changes in the density banding of coral skeletons constitute a proxy for long-term seasonality changes, while luminescent bands are a robust indicator of changes in river outflow and sediment load.

Variability in the isotopic composition of coral carbonate has been used to reconstruct changes in SST and SSS ( $\delta^{18}$ O), light availability (e.g., cloud cover, seasonal irradiance) and plankton intake ( $\delta^{13}$ C), pH variability ( $\delta^{11}$ B), water eutrophication  $(\delta^{15}N)$ , and land-to-ocean carbon delivery ( $\Delta^{14}C$ ). Corals can be used to monitor land-based increasing stress over estuarine and coastal regions. The variability in skeletal concentration of trace element, measured against calcium concentration, records changes in water temperature (Sr/Ca ratios), riverine discharges (Ba/Ca) and gasoline usage (Pb/Ca). Likewise, changes in water quality are tracked by the trace concentration of metals in coral carbonate (e.g., Zn/Ca, Al/Ca, Mn/Ca). However, despite the success in the use of corals as paleoenvironmental proxies, several concerns regarding their applicability remain. There is a current need to fully understand the underlying physiological processes that control isotopic and elemental variations in coral skeletons, as well as the specific climate mechanisms that are responsible for producing the geochemical signals in corals. Furthermore, the optimal application of coral records in paleoenvironmental research requires the replication of long-term isotopic and elemental records to determine the precision of the environmental signal based on differences between records. Additionally, to evaluate natural variability in estuarine environments it is necessary to expand the multi-proxy approach to integrate compatible data sets. Such an approach, for instance, would integrate coral data with land-based paleoclimate records from tree rings, varved sediments and speleothems.

## 5 Appendix

Geographical location of coral reefs discussed in the text.



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