An assessment of the Sr/Ca ratio in shallow water hermatypic corals as a proxy for sea surface temperature

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Abstract—The high precision measurement of the Sr/Ca ratio in corals has the potential for measuring past sea surface temperatures at very high accuracy. However, the veracity of the technique has been questioned on the basis that there is both a spatial and temporal variation in the Sr/Ca ratio of seawater, and that kinetic effects, such as the calcification rate, can affect the Sr/Ca ratio of corals, and produce inaccuracies of the order of 2–4 °C. In the present study, a number of cores of the massive hermatypic scleractinian coral *Porites*, from the central Great Barrier Reef, have been analyzed for Sr/Ca at weekly to monthly resolution. Results from a 24 year record from Myrmidon Reef show an overall variation from 22.7 °C to 30.4 °C. The record shows a warming/cooling trend with maximum warming centred on the 1986–1987 summer. While some bleaching was reported to have occurred at Myrmidon Reef in 1982, the Sr/Ca record indicates that subsequent summer temperatures were much higher. The 4.5 year record from Stanley Reef shows a maximum SST of 30 °C during the 1997–1998 El Niño event. The calibrations from Myrmidon and Stanley Reefs are in excellent agreement with previously published calibrations from nearby reefs. While corals do not calcify in equilibrium with seawater due to physiological control on the uptake of Sr and Ca into the lattice of coralline aragonite, it can be argued that, provided only a single genus such as *Porites* sp. is used, and that the coral is sampled along a major vertical growth axis, then the Sr/Ca ratio should vary uniformly with temperature. Similarly, objections based on the spatial and temporal variability of the Sr/Ca activity ratio of seawater can be countered on the basis that in most areas where coral reefs grow there is a uniformity in the Sr/Ca activity ratio, and there does not appear to be a change in this ratio over the growth period of the coral. Evidence from several corals in this study suggest that stress can be a major cause of the breakdown in the Sr/Ca–SST relationship. Thermal stress, resulting from either extremely warm or cool temperatures, can produce anomalously low Sr/Ca derived SSTs as a result of the breakdown of the biological control on Sr/Ca fractionation. It is considered that other stresses, such as increased nutrients and changes in light intensity, can also lead to a breakdown in the Sr/Ca–SST relationship. Two of the main issues affecting the reliability of the Sr/Ca method are the calibration of the Sr/Ca ratio with measured SST and the estimation of tropical last glacial maximum (LGM) palaeo-temperatures. Instead of producing a constant calibration, just about every one published so far is different from the others. What is obvious is that for most calibrations while the slope of the calibration equation is similar, the intercepts are not. While the cause for this variation is still unknown, it would appear that corals from different localities around the world are responding to their own particular environment or that certain types of environments exert a control on the corals' physiology. Sr/Ca derived SST estimates for the LGM and deglaciation of 5 °C–6 °C cooler than present are at odds with estimates of 2 °C–3 °C cooling by other climate proxies. The apparent lack of reef growth during the LGM suggests that SSTs were too cold in many parts of the tropics for reefs to develop. This would lend support to the idea that tropical SSTs were much cooler than what the CLIMAP data suggests. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Stoichiometric trace element ratios within the aragonite skeleton of hermatypic corals are known to have temperature dependent seawater/coral partition coefficients that can provide a proxy for sea surface temperature (SST). Elemental ratios that have some temperature dependent correlation are known to include B/Ca (Sinclair et al., 1998; Fallon et al., 1999), Mg/Ca (Mitsuguchi et al., 1996), Sr/Ca (Smith et al., 1979; Beck et al., 1992), and U/Ca (Min et al., 1995; Shen and Dunbar, 1995). One of the most promising SST proxies has been the high precision measurement of the Sr/Ca ratio in coral skeletons using a combination of isotope dilution (ID) and thermal ionization mass spectrometry (TIMS) (Beck et al., 1992), and

more recently inductively coupled plasma—atomic emission spectroscopy (ICP–AES) (Schrag, 1999).

Sea surface temperature is a crucial parameter because of its linkage with climate phenomena such as El Niño. Only in the past two decades has a sufficient volume of instrumental data been acquired to observe the onset and development of El Niño, but even now our understanding of what initiates it and how it propagates is rudimentary because of the variability inherent in this phenomenon (Cane et al., 1995). In order to create better prediction models it is necessary to extend the El Niño record back by several centuries so as to assess the frequency and magnitude of key variables, such as SST. While the instrumental record is very sketchy at this time scale, massive corals, such as *Porites* sp., have the ability to live for up to 300–500 years or more, and, because their growth rate is commonly of the order of 1–2 cm yr^{-1}, it is possible to retrieve high resolution (weekly to monthly) SST records by measuring their

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Sr/Ca ratio. Modern scleractinian corals not only have the capability of providing continuous climate data, but, by means of radiocarbon and U-series dating, their fossil counterparts can provide snapshots of climatic conditions for the last few hundred thousand years or so, and possibly longer.

Hermatypic scleractinian corals contain about 7500 ± 500 ppm Sr, although because of vital effects there can be distinct differences between genera (Weber, 1973). Apart from these vital effects, the ratio of Sr to Ca in the coral is believed to be controlled predominantly by two factors: (i) the Sr/Ca activity ratio of seawater; (ii) the Sr/Ca distribution coefficient between aragonite and seawater (Smith et al., 1979; Beck et al., 1992).

1.1. The Sr/Ca Activity Ratio of Seawater

Because of the long residence times of Sr and Ca in the oceans [5.1×10^6 yr for Sr and 1.1×10^6 yr for Ca (Broecker and Peng, 1982)], it has generally been assumed that the Sr/Ca activity ratio has remained essentially constant over the past 100 000 years or so. This assumption has been brought into question recently as a result of model studies of Sr release from shelf carbonates during low sea level (glacial) events (Stoll and Schrag, 1998), and variations in foraminiferal Sr/Ca during late Quaternary glacial/interglacial cycles (Martin et al., 1999; Stoll et al., 1999). When Sr-rich aragonitic shallow marine sediments, such as corals and the green alga *Halimeda*, are exposed on the shelf during eustatic sea level lowering subaerial diagenesis of aragonite to low-Mg calcite by meteoric water occurs, resulting in the release of strontium. It has been proposed by Stoll and Schrag (1998) that this may raise Sr/Ca$_{seawater}$ by 1 to 2 percent. While this increase is small, it has the ability to produce a shift of 2 °C–3 °C in palaeotemperatures derived from coral Sr/Ca ratios. Measurements of the Sr/Ca ratio in planktonic and benthic foraminifera show variations of up to 12% over glacial/interglacial cycles (Stoll et al., 1999). While this variation is much greater than the model results of Stoll and Schrag (1998), a large part of it can be explained by selective dissolution of foraminiferal tests and other environmental effects such as temperature and *p*H (Martin et al., 1999). However, both Stoll et al. (1999) and Martin et al. (1999) maintain that up to 3–5% can be attributed directly to Sr/Ca$_{seawater}$ variations.

From direct measurements of the Sr/Ca composition of seawater, it had earlier been noted that depletions of both elements of the order of 1–3% can occur in surface waters (e.g., Brass and Turekian, 1974). Much of this has been attributed to removal of Ca and Sr by surface dwelling organisms during skeletogenesis. Traditionally, the Sr/Ca value representative of the marine environment has been reported as 8.6 ± 0.4 mmol mol^{-1} (Kinsman, 1969). Analyses of seawater samples by de Villiers et al. (1994) using ID–TIMS show significant variation in their Sr/Ca ratio (8.5–8.7 mmol mol^{-1}). Additional Sr/Ca analysis of surface waters from the Atlantic and Pacific Oceans by de Villiers (1999) averaged 8.539 ± 0.0045 mmol mol^{-1}, and it was suggested that surface waters are depleted by 2–3% relative to the deep ocean as a result of skeletal formation of celestite (SrSO$_4$) by acantharians (e.g., Bernstein et al., 1987).

1.2. Temperature Dependence of the Sr/Ca Distribution Coefficient

The aragonitic skeletons of corals have a preference for Sr (0.65–1.1% by weight) rather than Mg (0.06–0.43% by weight), whereas skeletons made of Mg calcite (such as coralline algae) typically have much higher Mg contents (3.4–4.8% by weight). In general, aragonite will accommodate more Sr than calcite. The higher uptake of Sr into aragonite rather than calcite is a function of the higher distribution coefficient for the former (Bathurst, 1976). The distribution coefficient, $D_{Sr}^A =$ (Sr/Ca)$_{aragonite}$/(Sr/Ca)$_{seawater}$, for corals is considered to be close to unity (Weber, 1973), whereas for inorganically precipitated aragonite it is about 1.15 (Kinsman and Holland, 1969). While D_{Sr}^A for inorganically precipitated aragonite is strongly temperature dependent (Kinsman and Holland, 1969), earlier experiments regarding temperature dependence in corals were equivocal. Some workers (e.g., Thompson and Livingston, 1970; Thompson and Chow, 1955) found no correlation between temperature and Sr/Ca, whereas others (e.g., Houck et al., 1977; Kinsman, 1969; Smith et al., 1979) found that the Sr/Ca ratio varied as a simple function of temperature. In his comprehensive study of the incorporation of Sr into corals, Weber (1973) found an inverse relationship between temperature and D_{Sr}^A, but considered growth rate and other "species effects" to be more important. Both field and laboratory studies carried out by Houck et al. (1977) and Smith et al. (1979) further strengthened the case for temperature dependence. They maintained that there is a distinct linear relationship between the Sr/Ca ratio and the ambient water temperature at which the precipitation of skeletal aragonite occurs, which is basically independent of growth rate. They were also able to show that D_{Sr}^A for corals is significantly different from inorganically precipitated aragonite, and that D_{Sr}^A varies between different coral genera. This was attributed to some form of biological control, whereby the Sr/Ca ratio in the tissue of the coral is slightly modified from the seawater Sr/Ca ratio.

It was acknowledged by Smith et al. (1979) that Sr/Ca ratios measured by such techniques as atomic absorption spectrophotometry (AAS) were hampered by a lack of precision. The errors associated with this method, when converted to temperature, were of the order of ±2 °C. As pointed out by Beck et al. (1992), this is the same as the typical SST range observed in the tropics. It was not until the introduction of ID–TIMS (Beck et al., 1992) that it was possible to measure SSTs with an accuracy of better than ±0.5 °C.

1.3. Previous Work

In their original experiments Beck et al. (1992) measured the Sr/Ca ratio for the coral species *Porites lobata* from Noumea and Tahiti. The corals were sampled along the growth axis at roughly monthly intervals. Rather than calibrate the Sr/Ca directly against the *in situ* instrumental SST record, Beck et al. (1992) calibrated it against δ ^{18}O-derived SSTs from the same samples. Their relationship between Sr/Ca and SST of

$$\text{Sr/Ca} \times 10^3 = 10.72 - 0.0624 \times \text{SST} \qquad (1)$$

is similar to the Smith et al. (1979) calibration for *Porites*, but with greater precision. However, Beck (1994) later revised

their original calibration [the revised calibration of $Sr/Ca \times 10^3 = 10.479 - 0.06245 \times SST$ is used hereafter for all references to Beck et al. (1992)], with the result that there was now a 4 °C difference between the two. In their paper, Beck et al. (1992) show a good correlation between the instrumental SST records from Noumea and Papeete and the Sr/Ca-derived SSTs, with an average difference of 0.34 °C between the two.

While Beck et al. (1992) were able to show a good correlation between the Sr/Ca ratio and SST, a note of caution was introduced by de Villiers et al. (1994). They suggested that interspecific differences, variable calcification, and extension rates, and variability in the Sr/Ca composition of seawater could introduce significant errors (1–2 °C) in the use of this method. In a subsequent paper (de Villiers et al., 1995), the Sr/Ca-based proxy was further called into question on the basis of biological control of Sr/Ca uptake. They measured three specimens of *Porites lobata* from Hawaii; two of which were only 20 m apart and the $Sr/Ca_{seawater}$ showed no measurable difference. All three grew at the same rate of 12 mm yr^{-1} and SST records from both areas are substantially the same. Their results show three different trends in Sr/Ca, and consequently three distinctly different calibrations, with differences from the same reef as much as 2 °C–3 °C.

Evidence of biological control on the uptake of Sr/Ca has been refuted subsequently by several studies. In southern Taiwan, Sr/Ca measurements on *Porites lobata* and *P. lutea* by Shen et al. (1996) showed that species differences and growth rate variations did not appear to affect the Sr/Ca–SST relationship. Similar conclusions were reached by Alibert and McCulloch (1997) for the central Great Barrier Reef, where they found that the relationship holds true for a large range of annual extension and calcification rates, but provided that sampling was conducted along the major growth axis. They found that sampling off axis introduced errors of 1 °C–2 °C because corallites from different growth periods were being sampled simultaneously, whereas this effect was negated by sampling along the major axis of growth. Such off axis sampling could account for the variable results of de Villiers et al. (1995).

Another problem has been the lack of consistent calibration of the Sr/Ca ratio with SST. Ideally, the comparison between the coral Sr/Ca ratio and an *in situ* instrumental SST record for the same time period from the same reef is the best method, but, with a few exceptions, this has not proved feasible. The main reason is that few reefs in the world have recorded continuous SST measurements for any length of time. In only a few examples have the corals been calibrated against the *in situ* SST record (e.g., Alibert and McCulloch, 1997; Crowley et al., 1999). However, even in this situation the calibrations can be nonuniform. Alibert and McCulloch (1997) derived separate calibrations for five *Porites* sp. from Davies Reef in the central Great Barrier Reef. While three corals (Davies 2, 8, 11) produced calibrations with an accuracy of ±0.5 °C, two others (Davies 3 & A) showed errors of up to ±1.5 °C. This anomaly is further examined in the Discussion (see Sect. 5.5).

A major reason for testing the Sr/Ca thermometer on modern corals is to be able to accurately measure palaeotemperatures in ancient corals. The results of Sr/Ca-based palaeotemperature estimates of corals indicate that tropical SSTs during the LGM were some 5 °C cooler than today (Guilderson et al., 1994), with SSTs rising 5 °C–6 °C during the deglaciation phase

between 8–14 kyr (Beck et al., 1997; Guilderson et al., 1994). However, other proxy records, such as alkenones (Bard et al., 1997) and stable isotope analysis of foraminifera from deep sea sediments (Curry and Oppo, 1997), have produced palaeotemperatures for the LGM more in line with CLIMAP results, with maximum cooling of only 2 °C–3 °C (Crowley, 2000).

While the veracity of the Sr/Ca ratio method has been confirmed from several sites, more work is still required to confirm it as a reliable proxy. In particular, Sr/Ca records from nearby reefs, the same reef, and even from the same coral head need to be examined in detail to demonstrate their reliability and accuracy. In order to produce an accurate SST record, there is a requirement for the coral record to be calibrated against a long term instrumental SST record. To date, very few studies have been able to measure Sr/Ca derived SSTs with *in situ* instrumental SST from the same reef. Many studies must rely on data from SST stations that are remote to the coral site (e.g., de Villiers et al., 1994), and this is considered to be a significant uncertainty in deriving accurate Sr/Ca–SST relationships. The present study is designed to partly address some of the above requirements. A coral from Myrmidon Reef on the shelf edge of the central Great Barrier Reef (Fig. 1) has been analyzed for Sr/Ca in order to compare it to a 9 year instrumental record from the same reef. This is one of the longest instrumental datasets on any reef so far that has also been analyzed for Sr/Ca. In addition, a three year Sr/Ca derived SST record from Stanley Reef, a mid-shelf reef about 130 km southeast of Myrmidon Reef (Fig. 1), has been produced. These two Sr/Ca-derived SST records are compared to others in the area, such as Davies Reef (Alibert and McCulloch, 1997), Pandora Reef (McCulloch et al., 1994), and Orpheus Island (Gagan et al., 1998) so as to determine if the Sr/Ca–SST calibrations from a single region are consistent. Using these results, and studies from elsewhere, we discuss the problems, both real and apparent, that have been raised regarding the reliability of the method.

2. SAMPLES

Myrmidon Reef lies close to the edge of the continental shelf, approximately 150 km from the coast, and it is the outermost reef in this region (Fig. 1). Because of its distance from the coast, it is not affected by mainland runoff, but it is subjected to periodic upwelling (Andrews and Gentian, 1982). The reef has been the focus on ongoing research by the Australian Institute of Marine Science (AIMS), and as part of this monitoring of reef processes an automatic weather station has been installed on the reef flat since late 1987. Sea surface temperature, measured at hourly intervals, has been one of the parameters measured almost continuously at this site. The largest break in recording up until July 1996 had been 31 days in February 1992, and only three breaks had occurred previously that were longer than 10 days.

Two modern corals were cored with an underwater drill at Myrmidon Reef in July 1996. The drill unit uses compressed air from a scuba tank to drive a pneumatic drill attached to a 50 cm long barrel. With the use of extension rods, it is possible to recover a 48 mm diameter core of up to 1.5 m in length. These cores were all taken from large (>1 m) *Porites* sp. heads from a site near the entrance of a prominent gutter at the northeastern
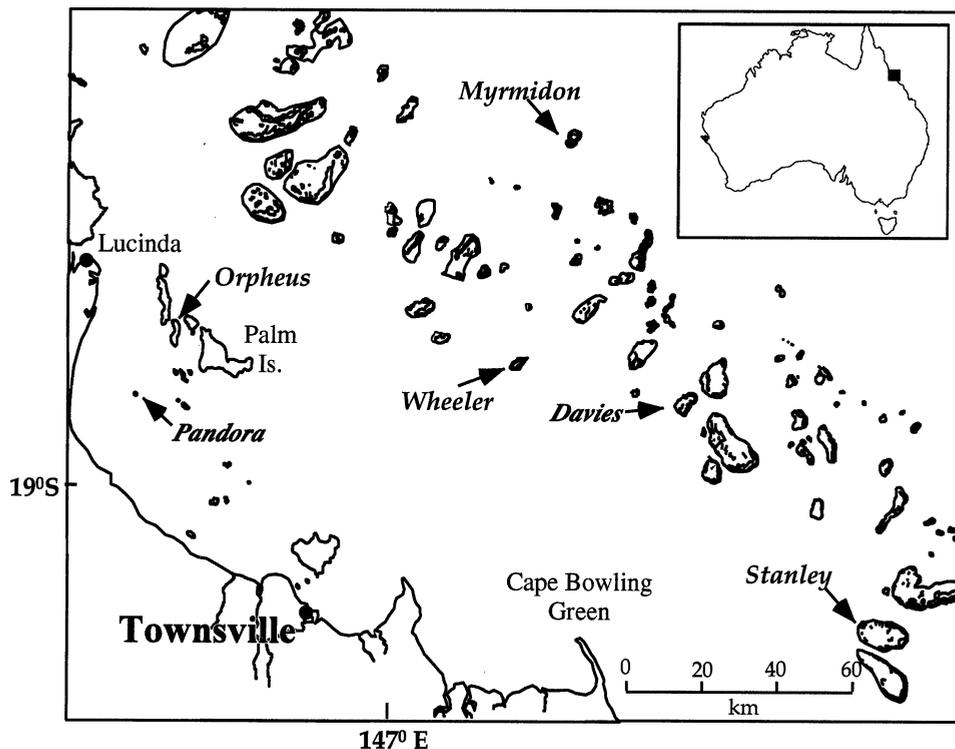
Fig. 1. Map of the central GBR off Townsville showing the location of Myrmidon and Stanley Reefs, plus other reefs in the region where Sr/Ca results have been published.

end of the reef. Core Myr-2 from a *Porites lutea* colony growing at a depth of 8 m was selected for detailed Sr/Ca analysis in this study.

Stanley Reef lies some 150 km south east of Myrmidon Reef and 70 km south east of Davies Reef, on the inner edge of the reef tract (Fig. 1). The reef is one of the larger ones in the region, being some 15 km long and 10 km wide. It has a well developed reef front and windward reef flat, a large lagoon with numerous patch reefs, and a narrow leeward reef flat. Beyond the leeward margin there is a shallow submerged platform, with numerous patch reefs. Two large (>1.5 m), living *Porites* sp. heads from the shallow platform behind Stanley Reef, and another large head at Old Reef, directly to the south of Stanley Reef (Fig. 1), were drilled in January 1999. The top part of core St-1 drilled at a depth of 2.7 m was analyzed for Sr/Ca in this study.

3. EXPERIMENT

3.1. Coral Preparation

Prior to cutting the core in half, the tissue zone at the top of each core is immersed in 50% v/v H_2O_2 for 24–36 hours to oxidize any organic material. The cores are cut either by hand, using a conventional rock saw or bandsaw or, more commonly, a purpose-built cutting device consisting of a diamond blade mounted on a precision lathe. In the latter case, the coral core is mounted onto the bed of the lathe, and the center of the core is aligned with the blade. The lathe-mounted coral is automatically moved at slow speed into the blade to give an even,

smooth cut. Each coral core is cut in half lengthwise, and one or several 8 mm thick slices are cut from one half. After the slice(s) is cut, it is cleaned in 18 MΩ water in an ultrasonic bath for 30 minutes to remove any fine coral powder produced during cutting. The slice is then either air dried or dried in an oven at 25 °C for 24 hours.

Each slice is examined under ultraviolet (UV) light to determine if there is any fluorescence. Either prior to or after UV light examination, the slice is x-rayed to produce an image of the density variation in the coral (Fig. 2). X-radiography was carried out at public hospitals or private imaging clinics in Canberra. The coral slice is simply placed horizontally on a single sided emulsion film and exposed for 0.1 seconds at 40 mA and 42 kV. The positive print of the x-ray is used to count density bands to give some idea of the age and growth rate, and to determine the direction of the major growth axis. The major growth axis is often at an angle to the core, and sometimes several growth axes must be selected, with overlapping growth bands, in order to effectively sample down the core. The core is then cut along this axis (or axes) with a bandsaw.

For sampling, the 8 mm thick coral slice is mounted on a perspex holder attached to the base of a computer-controlled moveable table such that the growth axis edge extends out from the holder by about 1 cm, with a clearance of about 5 mm beneath. Using a 20 mm diameter drill bit, a ledge is cut by thinning the exposed edge from 8 mm to about 2 mm. This is done automatically by moving the table at a speed of 0.5 mm s^{-1} beneath the rotating bit and sequentially shaving a series of 5 mm wide cuts on both sides, until the 8 mm thick slice has
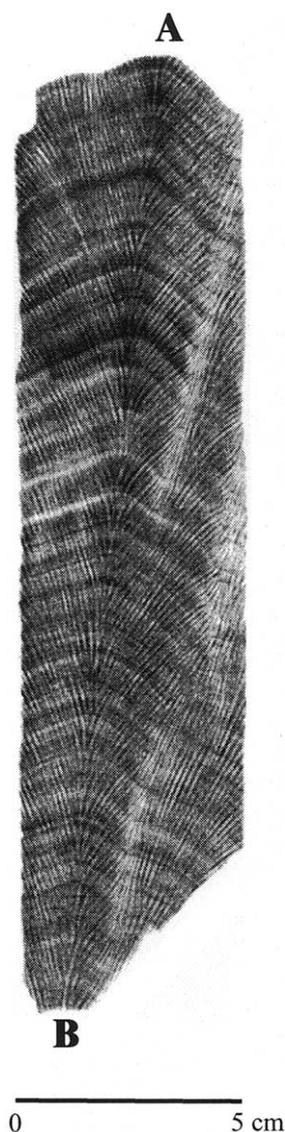
Fig. 2. A positive print of an X-radiograph of the *Porites lutea* coral Myr-2. The coral was sampled along the major growth axis, shown as A–B in the figure.

been reduced to 2 mm along the growth axis. The slice is cleaned thoroughly in an ultrasonic bath partly filled with 18 MΩ water, changing the water frequently, until no cuttings from the mill are discernable. Particular attention is paid to thoroughly cleaning the ledge.

After drying, the coral slice is once more mounted on the computer-controlled milling table. The table can be programmed to mill sequential samples at either 0.25 or 0.50 mm intervals, using a 2 mm diameter drill bit rotating at slow speed (100 rpm). At each sample interval the table is moved automatically so that the ledge comes into contact with the bit and mills into the ledge for a distance of 2.5 mm. The powdered sample is allowed to fall onto a small square of weighing paper placed beneath the ledge. The sample is placed into a 1.5 ml polypropylene microcentrifuge tube and capped. The drill then makes a clearing cut of another 1 mm, before moving the set

sampling interval distance to the next sample. This process is continued *ad infinitum*, until the length of coral desired has been fully sampled. The sampling interval is varied, depending on the growth rate of the coral, but a coral growing at 1.2 cm yr^{-1}, and sampled every 0.25 mm will produce 48 samples per year of coral growth or nearly weekly resolution.

3.2. Analytical Methods

For each Sr/Ca analysis, 80–150 μg of the milled powdered coral is weighed and transferred to an acid-cleaned 1.5 ml polypropylene microcentrifuge tube for wet chemical preparation. The sample is dissolved in 0.775 ml of 0.5N HCl, and a volume equivalent to 4 μg Ca is pipetted into a clean 1 ml Teflon beaker containing 4–5 drops of mixed Ca–Sr isotope spike and 1–2 drops of dilute phosphoric acid. After evaporation of the solution to a small phosphoric acid "bead," the sample is loaded without any further chemical separation onto an outgassed Ta filament, oxidized at dull red heat in air, and loaded into the mass spectrometer. The isotope dilution analysis is conducted automatically in static mode on a Finnigan MAT 261 mass spectrometer with 7 faraday cups, allowing Sr and Ca to be analyzed sequentially, without needing to adjust the cup settings.

Several spikes were used throughout the course of this study. The first 50 mm of the modern Myrmidon Reef coral (Myr-2) was analyzed with a ^{42}Ca–^{43}Ca–^{84}Sr mixed spike prepared from standard inventory items from the Oak Ridge National Laboratory, Tennessee after removal of ^{86}Sr from the ^{43}Ca using Sr spec.™, a Sr-specific ion exchange ElChrom resin. Instrumental mass fractionation in the Ca analysis is corrected with reference to the ^{42}Ca–^{43}Ca double spike, and mass fractionation in the Sr analysis with reference to the natural $^{86}Sr/^{88}Sr$ of 0.1194, both using a power law. This is the same spike used by McCulloch et al. (1994); Alibert and McCulloch (1997); and Gagan et al. (1998). The remainder of Myr-2 and all of St-1 were analyzed using a ^{43}Ca–^{84}Sr mixed spike. This differs from the original in that ^{42}Ca is omitted and the mass fractionation correction is made relative to natural $^{42}Ca/^{44}Ca = 0.31221$ (Russell et al., 1978) using an exponential law. Measurements by Nelson and McCulloch (1989) on the RSES MAT 261 yielded a very similar Ca isotope composition to Russell et al. (1978). Analytical precision is 2–3 times better with the ^{43}Ca–^{84}Sr spike, mainly because the mass fractionation correction is applied over two mass units, compared to a single mass unit for the original spike.

Before routine analysis began, each spike is calibrated for its isotope composition and concentration with respect to gravimetric standard solutions. The primary laboratory standard is MIX-3, prepared from Johnson & Matthey Specpure $CaCO_3$ and NBS-987 $SrCO_3$ assay standard. The Sr/Ca ratio in MIX-3 is 0.01827, similar to that in a typical coral. An independently prepared standard MIX-4, similar to MIX-3, confirms calibrations using MIX-3 to within 0.1%. The spikes are directly loaded into the MAT 261 and their isotope compositions measured. Instrumental mass fractionation in these direct measurements is assessed by also measuring mixtures of the spikes and the MIX-3 gravimetric standard and back-calculating the end-member isotope compositions.

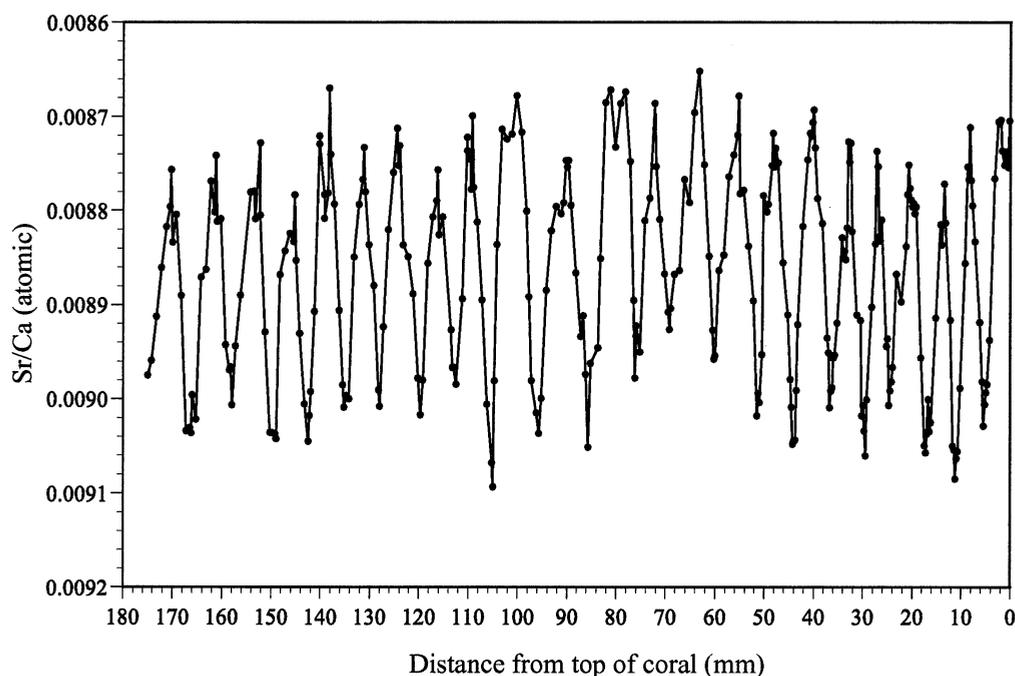The spike concentrations are monitored at regular intervals

Fig. 3. Plot of Sr/Ca vs distance for the top of the *Porites lutea* core Myr-2.

by measuring the gravimetric standard solution and other laboratory standards prepared from certain corals. Dilutions of these into 30 or 60 ml polypropylene bottles are available in the laboratory for routine use. Throughout the present study a standard was usually measured during each mass spectrometer analytical session.

4. RESULTS

4.1. Core Myr-2

The top 175 mm of core Myr-2 was analyzed for Sr/Ca using ID–TIMS. X-radiography of this coral shows well-defined annual growth bands with a prominent major growth axis at a slight angle to the core (Fig. 2). The X-radiography indicates that this particular head of *Porites lutea* has a growth rate of 7.5–10.5 mm yr^{-1}, although most of the coral has an average rate of around 8.0 mm yr^{-1}. A ledge was cut along the prominent growth axis shown in Figure 2, and the coral was milled at 0.25 mm intervals. At the rate of growth indicated from the x-ray, it was considered that the resolution at this sampling interval would be better than fortnightly.

The results from some 300 individual Sr/Ca measurements are shown in Figure 3. The Sr/Ca values for the top 2.5 mm of the coral (roughly equivalent to the thickness of the tissue layer) show a lack of variation over that growth interval. It has been noted previously that Sr/Ca ratios in the vicinity of the tissue layer can produce anomalous results. In several corals from Davies Reef, Alibert and McCulloch (1997) report anomalous Sr/Ca ratios in the tissue layer, which they attributed to remnants of organic material within this zone. However, while they recorded high Sr/Ca ratios at the top, the Sr/Ca ratios from Myr-2 are uniformly low. The cores from both sites were sampled during the austral winter/spring, July at Myrmidon

Reef and October at Davies Reef. At this time of year, it would be expected that the Sr/Ca ratio would be relatively high, so the low Sr/Ca ratios in the top 2.5 mm at Myrmidon Reef are somewhat difficult to explain. It could be that the Sr/Ca ratio of the organic material is highly variable, and capable of masking skeletal Sr/Ca.

Elsewhere, the Sr/Ca results display an extremely good and fairly regular cyclical pattern, that has been shown previously to be an annual SST signal (e.g., Alibert and McCulloch, 1997). From the number of analyses per cycle, it is obvious that the resolution of the sampling is of the order of monthly, although most data points are centered around the peaks and troughs of the curve, where the resolution is as high as fortnightly. While only two samples were repeated, the reproducibility is considered to be better than 0.25% ($<$ 0.15 °C). From the distance between Sr/Ca maxima, the annual extension rate is shown to vary between 5–11 mm yr^{-1} over a period of 21 years, with an average extension rate of 7.7 mm yr^{-1}. The highest annual extension rate occurs for the 3 years, between 75 and 105 mm (Fig. 3).

4.1.1. Calibration

In order to calibrate the Sr/Ca record against the instrumental SST, the maxima and minima of the measured SST were overlain and matched with the Sr/Ca ratio. The resulting plot is shown in Figure 4. Here, the Sr/Ca record for the first 60 mm is matched against the weekly instrumental SST for Myrmidon Reef for the period 1988–1997. The fit is particularly good, with general matching of both the amplitude and wavelength of both data sets. The Sr/Ca plot shows a lower temperature response in the summer of 1994, which amounts to a variation of about 1 °C. We can find no obvious reason for this discrep-
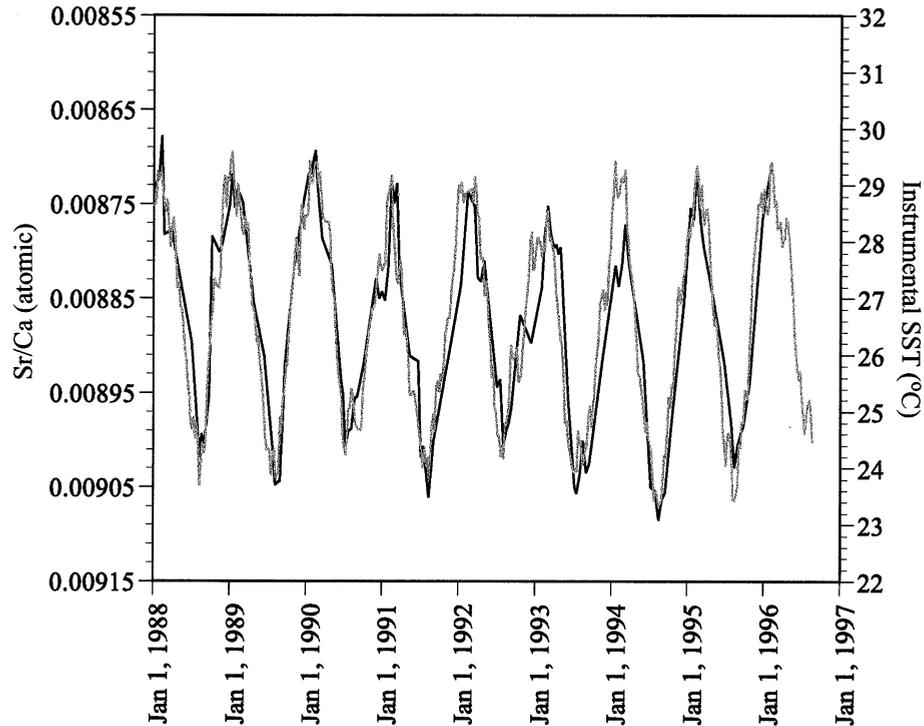
Fig. 4. Best fit of Sr/Ca ratio for Myr-2 (black) with the instrumental SST (grey) for Myrmidon Reef.

ancy; several repeat analyses of the Sr/Ca ratios on this part of the coral produced similar results, and comparison of the *in situ* instrumental SSTs with satellite SSTs did not show any difference.

To derive the calibration equation, a Williamson regression, identical to that used by Alibert and McCulloch (1997), was carried out for the time equivalent Sr/Ca ratio and instrumental SST. A total of 112 out of 122 data points were analyzed; those data points omitted were from the mismatch in 1994. For the regression analysis, the Sr/Ca error was set at 0.000005 (2σ) which is equivalent to <0.2 °C, while the error on the instrumental SST is considered to be 0.1 °C. From the total number of data points analyzed, a calibration equation of

$$Sr/Ca \times 10^3 = 10.40 \ (\pm 0.016) - 0.0575 \ (\pm 0.0005) \times T \quad (2)$$

was derived. This is very close to the calibration calculated for Davies Reef (Alibert and McCulloch, 1997) of

$$Sr/Ca \times 10^3 = 10.48 \ (\pm 0.01) - 0.0615 \ (\pm 0.0004) \times T. \quad (3)$$

4.1.2. Myrmidon Reef climatology

Using Eqn. 2 to convert the Sr/Ca ratio to SST and tying it to a common chronology with the instrumental SST, we can see a distinct temperature pattern for the past 24 years at Myrmidon Reef (Fig. 5). The total SST variation from 1973 to 1996 is from 22.7 °C (winter of 1982) to 30.4 °C (summer of 1986–1987). The average summer SST maximum is 29.0 °C, while the average winter minimum is 23.8 °C (Fig. 5). The SST pattern shown in Fig. 5 indicates a warming trend from 1973 to 1987, followed by a cooling trend from 1987 to 1994, and a

possible warming trend in 1995–1996. Although the latter warming trend is not that apparent in Figure 5, the instrumental data shows that this warming trend continued into 1998. The earlier warming trend is reversed slightly in 1983–1984, with the cool El Niño winter of 1982 being repeated in 1983 and 1984, while the 1983–1984 summer is 1.2 °C cooler than those immediately before and after (Fig. 5). Between 1973 and 1987 the summer maximum SST increased by 1.7 °C, while the corresponding winter minimum SST increased by 1.8 °C. This is somewhat greater than the 1.3 °C warming recorded at Davies Reef for the same period (Alibert and McCulloch, 1997). Conversely, between 1987 and 1994 there is a 1.8 °C and 2.4 °C cooling in summer and winter, respectively (Fig. 5).

One of the major consequences of this warming/cooling cycle is that between 1982 and 1991 the maximum summer SST exceeded the average value on 9 out of 10 occasions (Fig. 5). During this period, the maximum SST reached or exceeded 30 °C on four occasions. According to Lough (1999) this temperature represents the threshold for coral bleaching in this region. In Fig. 5 the 30 °C threshold is 1 °C higher than the average summer maximum, a figure that is often used as a minimum condition for the onset of bleaching (Hoegh-Guldberg, 1999). On the basis of temperature alone, one would have expected bleaching of the more susceptible *Acropora* and *Pocillopora* species to have occurred definitely during the summer of 1986–1987, probably in 1982–1983 and 1984–1985, and possibly in 1987–1988, but not in 1981–1982. This is exactly the opposite of what happened, with no signs of bleaching at Myrmidon Reef during the 1986–1987 summer (Berkelmans, private communication, 2000), and no reports of bleaching in
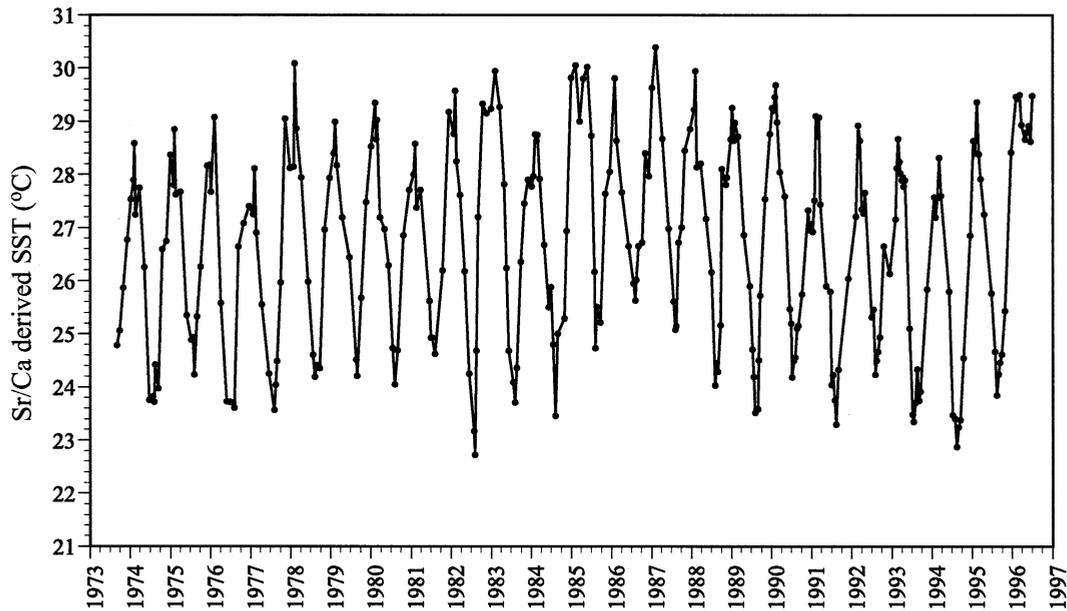
Fig. 5. Plot of the Myrmidon Reef Sr/Ca derived SST (°C) against time for the period 1973–1996.

the other years except for 1981–1982 (Berkelmans and Oliver, 1999).

One of the major factors that can affect SST in the GBR is the onset of an El Niño event. While the largest effect of the El Niño cycle is the variability in rainfall along the coastal region of Queensland, there does tend to be a typical SST signal associated with that phenomenon. According to Lough (1994), there are two components to the SST signal associated with El Niño. One is the cooler than average SST for the winter prior to the onset of El Niño, and the other is the warmer than average SST during the following summer when the El Niño is fully active. It is considered that SSTs during La Niña years stay relatively warm during winter.

The major El Niño events during the period of growth of Myr-2 occurred in 1976–1977, 1982–1983, 1986–1987, and there was a prolonged El Niño event between 1991 and 1994. As with other corals analyzed by the Sr/Ca TIMS method in the central Great Barrier Reef [e.g., Pandora Reef (McCulloch et al., 1994) and Davies Reef (Alibert and McCulloch, 1997)], there is a distinct cooling in the winter of 1982 at Myrmidon Reef associated with the intense El Niño event of 1982–1983 (Fig. 5). At Myrmidon Reef the Sr/Ca derived SSTs show a drop of around 7 °C at the end of summer in 1982, compared to the average summer–winter SST range of 5.5 °C, followed by an even larger rise from the winter of 1982 to the late summer in 1983 (Fig. 5). However, apart from this extreme event there does not appear to be the precise SST signal, as outlined by Lough (1994), for the other El Niño events. The 1976–1977 event shows neither unusual cooling nor warming; in fact, it shows the coolest summer for the whole period of the coral record (Fig. 5). The 1986–1987 event is almost the exact opposite to the 1976–1977 event, with the warmest winter of the period followed by the warmest summer. The 1991–1992 event shows winter cooling, but only moderate summer warming (Fig. 5).

4.2. Core St-1

The top 75 mm of this *Porites* sp. was analyzed for Sr/Ca using ID-TIMS to derive a calibration for a modern Stanley Reef coral in order to calculate SST values for a mid-Holocene coral from the same reef. X-radiographs of the coral show reasonably good annual banding, with the low density band accounting for about two-thirds of the annual width. The width of the density banding suggests that the growth rate of this coral is of the order of 15–18 mm yr^{-1}. Under fluorescent light, the coral shows only one thin bright band for the entire core. Judging from the position of the band and the growth rate of the coral, this appears to be the equivalent of the 1974 flood, which is the largest on record for the Queensland coast.

A ledge was cut along the most prominent growth axis, and the coral was milled at 0.25 mm intervals. At the rate of growth indicated from the x-ray, it was considered that the resolution at this sampling interval would be better than weekly. A total of 115 individual Sr/Ca measurements were carried out on this coral, producing a 4.5 year annual cycle, with estimated growth rates of 16.2 to 17.0 mm yr^{-1}. The frequency of Sr/Ca analyses is better than fortnightly. While every second sample, in general, was analyzed, consecutive samples were analyzed for the peaks and troughs.

4.2.1. Calibration

The Sr/Ca record was matched against the instrumental SST from Davies Reef; the closest site with *in situ* temperature recording (Fig. 1). The instrumental data was reduced from daily to weekly to better match the Sr/Ca data. Because the station at Davies Reef did not record SST data between 3 October 1994 to 21 May 1996, it was only possible to match the two records from June 1996 to February 1999, with two small breaks of about one month during this period. This is about the
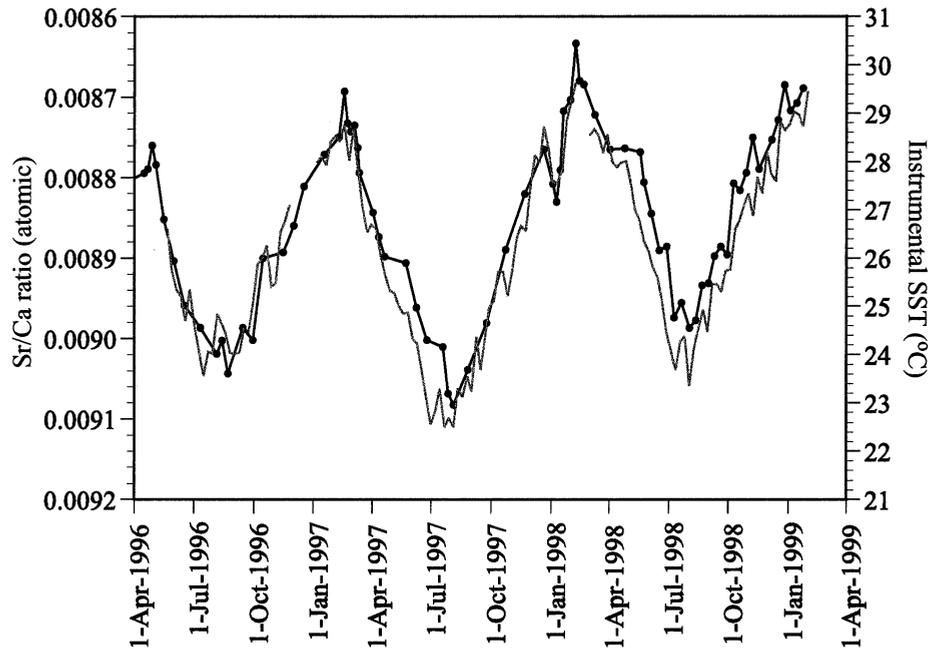
Fig. 6. Comparison between Sr/Ca data from Stanley Reef (black) and the instrumental data from nearby Davies Reef (grey).

same length of time against which the Davies 2 coral was calibrated (Alibert and McCulloch, 1997). The resulting fit (Fig. 6) is very good, and both large-scale and fine-scale detail can be seen to match in many parts of the curves.

A least squares regression analysis was carried out for the time equivalent Sr/Ca ratio and instrumental SST, similar to that used for Myr-2, with a total of 66 data points being analyzed. The error limits used were the same as for the Myrmidon Reef calibration. From the total number of data points, a calibration equation of

$$Sr/Ca \times 10^3 = 10.40 \, (\pm 0.018) - 0.0587 \, (\pm 0.0005) \times T \quad (4)$$

was derived.

The calibrated SST plot is shown in Figure 7. While summer SSTs reach 29 °C in the previous 3 years, during the summer of the 1997–1998 El Niño, temperatures reach 30 °C. It is noteworthy that during the 1997 winter, SSTs were only moderately low, and the typical El Niño signal of cool winter followed by warm summer as outlined by Lough (1994) is not as apparent as during the 1982–1983 event. Of some note is the 1 °C drop in temperature at the beginning of 1998 (Fig. 7). A similar drop over much of the GBR is present in the instrumental data in early January of the same year, which Lough (1999) attributed to short-term cooling following the passage of a tropical low that produced extensive flooding on the central Queensland coast. This 1998 cooling event also appears in the Sr/Ca record of a coral from Pandora Reef.

4.3. Comparison of Calibrations from the Central GBR

Including the results presented here for Myrmidon and Stanley Reefs, to date, six reefs in the central GBR off Townsville have provided Sr/Ca–SST records measured on cored *Porites*

sp. at one or several sites on each reef. These include Pandora Reef (McCulloch et al., 1994) and Orpheus Island (Gagan et al., 1998) on the inner shelf (Fig. 1), and Davies and Wheeler Reefs on the mid-shelf (Alibert and McCulloch, 1997). It is the intention here to compare the TIMS-derived Sr/Ca–SST calibrations for all these reefs; the SSTs for Wheeler Reef were derived using the Davies Reef calibration, and are not discussed further.

While the calibration for Davies Reef is that derived by Alibert and McCulloch (1997) from *in situ* instrumental data, the original paper on the Pandora Reef Sr/Ca record (i.e., McCulloch et al., 1994) used the revised calibration of Beck et al. (1992) from New Caledonia and the *Porites lobata* calibration of de Villiers et al. (1994) from Hawaii. Although the summer SST values from these two calibrations are similar, they can diverge by more than 2 °C in the winter. Recently, Alibert et al. (1999) calibrated a modern *Porites* sp. head collected at Pandora Reef in October 1998 against *in situ* SSTs measured at nearby Orpheus Reef. Their calibration of

$$Sr/Ca \times 10^3 = 10.3 \, (\pm 0.01) - 0.0542 \, (\pm 0.0005) \times T \quad (5)$$

is similar to the revised calibration of Beck et al. (1992), but very different from that of de Villiers et al. (1994). It is also within the error limits of the Davies Reef (Alibert and McCulloch, 1997) and the Myrmidon and Stanley Reef calibrations.

Five separate Sr/Ca–SST calibrations have now been derived for the central GBR (Fig. 8). Two of these (Davies and Myrmidon Reefs) are based on *in situ* SST measurements, two (Pandora and Stanley Reefs) are based on *in situ* SST measurements from nearby reefs, and one (Orpheus Island) is based on satellite SST data. Four of the calibrations are within the error limits of each other, whereas one, that from Orpheus Island
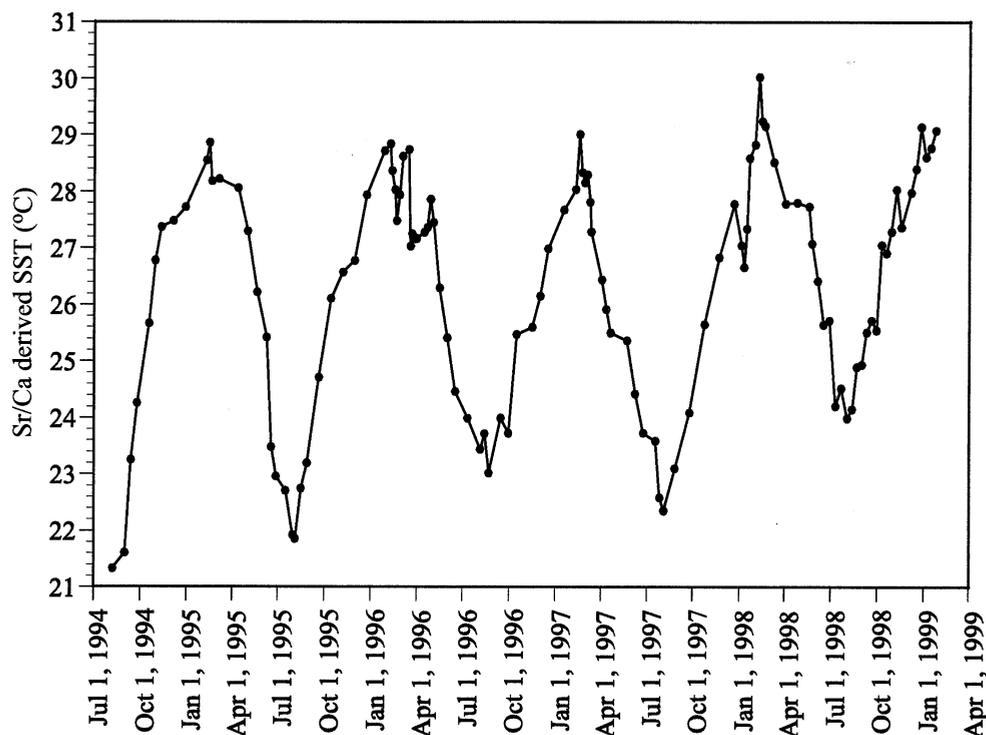
Fig. 7. Plot of Sr/Ca derived SSTs from 1994 to 1999 for Stanley Reef showing the warm El Niño summer of 1997–1998 and the 1 °C drop in temperature in January 1998.

(Gagan et al., 1998), shows a difference of some 3 °C from the others (Fig. 8). Again, the reason for the difference is not obvious. Even though the Orpheus calibration used satellite SSTs, there are no significant errors between satellite data and *in situ* SSTs that are currently being acquired for all these sites. The calibration from Orpheus Island is also very similar to calibrations derived for Java and Dampier, Western Australia by Gagan et al. (1998). Davies, Stanley and Myrmidon Reefs occur on the outer half of the shelf and do not appear to be affected by freshwater discharge from the coast, whereas in-shore reefs, such as Orpheus and Pandora are enveloped, during periods of high rainfall, by the freshwater plume from the Burdekin River to the south of Townsville. Lowering of salinity on these inner reefs during these discharge events is evident from the δ ^{18}O signal of the corals (Gagan et al., 1998; McCulloch et al., 1994). However, the Sr/Ca activity ratio for inshore seawater does not appear to be adversely affected on an annual basis (Chantal Alibert, private communication, 1997), presumably because the discharges are relatively short lived.

5. DISCUSSION

5.1. Strontium Incorporation into Hermatypic Corals

As outlined in the Introduction, the incorporation of Sr into the lattice of coralline aragonite is believed to be controlled mainly by the Sr/Ca activity ratio of seawater and the Sr/Ca distribution coefficient between aragonite and seawater (Beck et al., 1992). However, the mechanisms that control trace element incorporation into the coral skeleton remain imperfectly understood. Simple inorganic models predict that trace element partitioning is dependent upon the ionic composition of the calcifying fluid, the calcification rate, and the temperature (Sinclair, 1999). Of these three factors, the coral has the ability to control, at least partly, the first two. While corals partition most trace elements at close to inorganic values, they do not calcify in equilibrium with seawater. For strontium this disequilibrium is relatively minor (e.g., $D_{Sr}^A \approx 1.06$ for *Porites* sp. and ≈ 1.13 for inorganic aragonite), but it does indicate that physiology does play a significant role in its uptake.

If corals are not calcifying in equilibrium with seawater, then to be a reliable temperature proxy it has to be assumed that the amount of disequilibrium is constant, if not for all corals, then at least at the generic or species level. The range of distribution coefficients for all corals is relatively small. Weber (1973) calculated an average D_{Sr}^A of 1.01 ± 0.03 for 47 genera of shallow water hermatypic corals, whereas Smith et al. (1979), on a more limited range of corals, suggested a value of 1.06. For *Porites* sp. corals from Taiwan, D_{Sr}^A averages 1.056 ± 0.003 (Shen et al., 1996), while for the central GBR the value is 1.052 (S. Fallon, private communication). There also appears to be little difference in D_{Sr}^A for the more common species of *Porites*, in particular *P. lobata* and *P. lutea* (Shen et al., 1996). While the data is limited, it seems reasonable to assume that this disequilibrium is constant for the genus most commonly used for Sr/Ca derived SST records in the Indo-Pacific region.

Corals also exert a fair degree of physiological control over their calcification rates. It has long been established that calcification in zooxanthellate corals is faster during the day than at night (e.g., Goreau, 1959), and several hypotheses have been advanced to explain how zooxanthellae can affect calcification
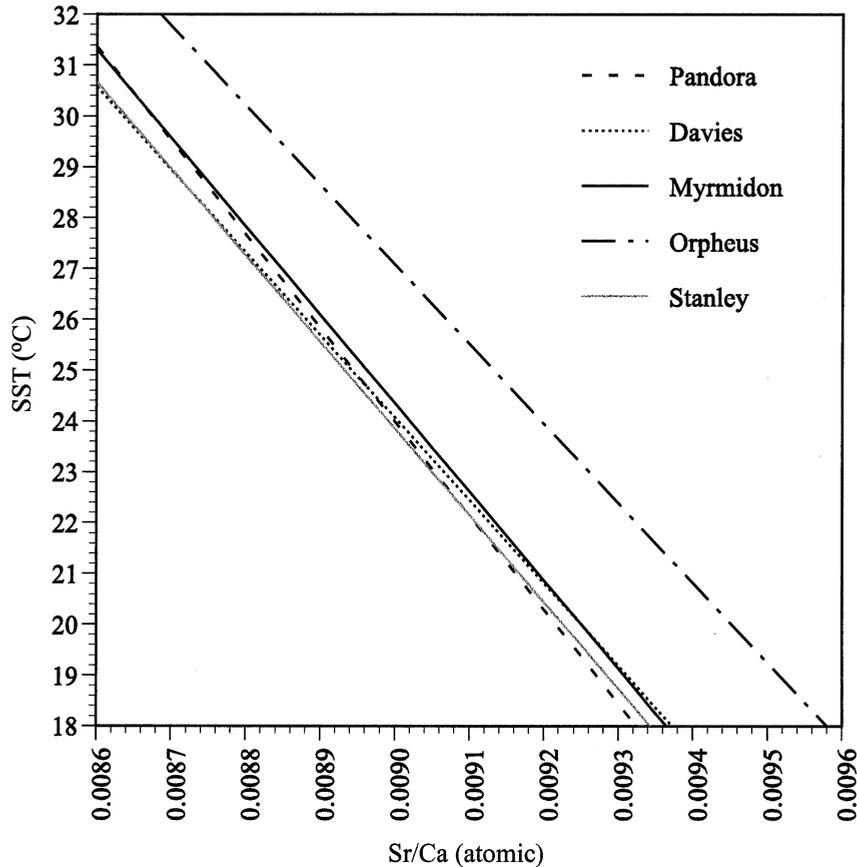
Fig. 8. Sr/Ca vs SST calibrations derived from the central GBR.

(Johnston, 1980; Krishnaveni et al., 1989). It is thought that as part of their symbiosis the zooxanthellae produce low molecular weight organic molecules that are readily metabolized by the coral to generate energy and enhance calcification. The zooxanthellae may also help the coral by removing waste products, such as PO_4^{3-}, SO_4^{2-}, and NO_3^- (Goreau, 1959), all of which can have an inhibiting effect on calcification. It has also been proposed that removal of CO_2 by photosynthesis may also aid the calcification process (McConnaughey and Whelen, 1997) by maintaining a neutral pH in the calcifying fluid. On the other hand, Marshall (1996) has suggested that, rather than enhance day time calcification, zooxanthellae actually suppress night time calcification.

The most serious objections to date regarding the reliability of the Sr/Ca method with regard to calcification rate have been raised by de Villiers et al. (1994, 1995). Their results from a *Pavona clavus* coral from the Galapagos Islands indicated that a change of annual extension rate from 6 to 12 mm yr^{-1} produced an apparent offset in SST of 1 °C–2 °C, with higher Sr/Ca values associated with the slower extension rate. The conclusion from this experiment was that variable extension rates do affect the amount of Sr uptake by the coral. Similarly, Alibert and McCulloch (1997) conducted experiments where they measured Sr/Ca ratios along both the growth axis and off axis. They found that off axis, the lack of space and less optimal conditions for growth result in small corallites and lower skeletal density, which shifted the Sr/Ca ratios by a

variable amount toward high values, corresponding to a temperature shift of −1 °C to −3 °C. Whether the apparent temperature offset is caused by a real change in the Sr/Ca ratio in these off axis situations or by an overlap of corallites that have grown at different times of the year is hard to discern. However, it seems that the only way to overcome this disparity is to sample exclusively along the major growth axis. Because they did not do so, as indicated in Figure 11 of de Villiers et al. (1994), appears to invalidate the de Villiers et al. (1994, 1995) argument regarding calcification rate. As pointed out earlier, subsequent work by Shen et al. (1996) and Alibert and McCulloch (1997) has shown a lack of change in Sr/Ca as a result of changes in calcification rate.

While there does appear to be an obvious physiological control on the uptake of Sr into the lattice of coralline aragonite, and that corals are not calcifying in equilibrium with seawater, the above arguments would suggest that, provided only a single genus such as *Porites* sp. is used and that the coral is sampled along a major vertical growth axis, the Sr/Ca ratio should vary uniformly with the remaining variable—temperature.

5.2. The Constancy of the Sr/Ca Activity Ratio of Seawater

Both the spatial and temporal constancy of the Sr/Ca content of seawater is seen as a necessary requisite to the reliability of

the Sr/Ca technique as a proxy for both modern and palaeo SSTs. It has been pointed out previously that there is a spatial difference in Sr/Ca in modern seawater of 2–3% globally, with the deep ocean more enriched relative to the surface (de Villiers, 1999). Although this variability is very small, it does equate to an uncertainty of 2 °C–3 °C for Sr/Ca derived SST measurements. However, the Sr/Ca proxy in corals necessitates that records can only be obtained in the tropics, in seawater that is normally oligotrophic and is not usually susceptible to constant or intense upwelling. In such waters the average Sr/Ca$_{seawater}$ value is considered to be 8.5 ± 0.1 mmol mol^{-1} (de Villiers et al., 1994), and reported Sr/Ca$_{seawater}$ measurements in coral reef areas only vary between 8.464 and 8.551 mmol mol^{-1} (Alibert and McCulloch, 1997; Beck et al., 1992; Shen et al., 1996). If the somewhat higher values of Shen et al. (1996) are ignored (this is a coastal site where the corals are growing in the water intake pond to a nuclear power plant), this converts to a temperature difference of 0.8 °C. On a regional basis, the difference between Sr/Ca$_{seawater}$ for Davies and Myrmidon Reefs in the central GBR (Alibert and McCulloch, 1997) equates to a temperature difference of 0.42 °C. So while there are variations in Sr/Ca$_{seawater}$ that produce a temperature difference of 2 °C–3 °C on a global basis, in most coral reef areas the difference is much smaller, and is within the error limits of the ID–TIMS method.

Of greater consequence for the use of the Sr/Ca thermometer in palaeoceanographic research is the apparent 1–2% change in Sr/Ca$_{seawater}$ as a result of Sr release from shelf carbonates during low sea level events (Stoll and Schrag, 1998). This increase has the ability to produce a negative shift of 2 °C–3 °C, which would account for the extremely low tropical SSTs reported by the Sr/Ca method during the LGM and ensuing transgression (Beck et al., 1997; Guilderson et al., 1994), compared to other methods (e.g., Bard et al., 1997; Crowley, 2000; Curry and Oppo, 1997) which indicate a relatively milder tropical cooling during the LGM.

While the Stoll and Schrag (1998) model accounts for the loss of Sr from shelf carbonates during low sea levels, it fails to predict the long term cumulative effects of adding additional Sr to the ocean during repeated glacial cycles. In relation to the shelf carbonates, the amount of Sr that is added to the ocean during each glacial event is not matched by an equivalent input of Ca; the latter is immobilized as the stable polymorph of CaCO$_3$, low-Mg calcite. Consequently, the removal of Ca from seawater during the ensuing interglacial, in the form of shelf aragonite deposits, will leave an excess of Sr in the ocean because the distribution coefficient (D_{Sr}^A) for corals and *Halimeda* will maintain the removal of Sr and Ca at a constant rate, meaning that the excess Sr that was added to the ocean during the glacial will not be removed. Over successive glacial/interglacial events this would result in an incremental increase in the Sr/Ca activity ratio of seawater. This does not appear to be the situation, however, because reported Sr/Ca ratios for the last interglacial corals from areas such as the Huon Peninsula and Western Australia are similar to modern values (McCulloch and Esat, 2000; McCulloch et al., 1999). This suggests that there is some other mechanism for removing the excess Sr during the deglaciation. One possibility is an increase in dissolution of deep-sea carbonate sediments at this time, adding excess Ca and lowering Sr/Ca$_{seawater}$ (Hodell et al., 2001).

However, both the model results of Stoll and Schrag (1998) and the foraminiferal Sr/Ca ratios (Martin et al., 1999; Stoll et al., 1999) do indicate that Sr/Ca$_{seawater}$ can change by several percent during glacial/interglacial events. On this basis it can be argued that Sr/Ca derived SSTs for the LGM may be overestimated.

5.3. Corals Under Stress—Do they Obey the Rules?

Radiochemical studies (Ip and Krishnaveni, 1991) have found that the incorporation of ^{90}Sr into the coral skeleton is linearly dependent on the Sr concentration and is not affected by inhibitors such as potassium cyanide (KCN), darkness or the photosynthetic inhibitor 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU), whereas the Ca concentration becomes quickly saturated and is inhibited by all of the above. This suggests that some or all Ca ions are transported through the coral tissue to the calcifying site by a different pathway than Sr ions (Ip and Krishnaveni, 1991; Ip and Lim, 1991). Under normal conditions this would mean that the Sr/Ca ratio in the calcifying fluid would be lower than inorganic aragonite. However, Sinclair (1999) has proposed that if temperature conditions become more extreme, the enzymes that transport Ca ions would become less efficient, resulting in a lowering of the active Ca^{2+} transport and a decreasing calcification rate. Because Sr is not affected to the same degree, it would be possible for the Sr/Ca ratio to shift upwards towards inorganic values.

Sr/Ca derived SSTs for a coral from Pandora Reef in the central GBR (McCulloch et al., 1994) show an extreme cooling of about 3.5 °C during the El Niño winter of 1982 compared to other minimum temperatures during previous and subsequent years. However, in comparison to the Sr/Ca derived SSTs, ship and satellite data recorded a negative SST anomaly of only 2 °C. At the time it was considered by McCulloch et al. (1994) that the exceptionally cold temperatures of the 1982 winter led to a breakdown of the biological control on Sr/Ca fractionation, and the coral system moved more towards inorganic fractionation. While this conclusion has remained largely unsupported, new and more convincing evidence is provided for a shift in the Sr/Ca ratio, this time at high temperatures, from another coral from Pandora Reef (Fig. 9). This *Porites* sp. was sampled soon after the 1998 bleaching event when 87% of the inshore reefs of the GBR were affected (Berkelmans and Oliver, 1999). This particular coral shows that during 1997, Sr/Ca ratios declined steadily into the summer of 1997–1998 as the El Niño took effect. This trend was slightly reversed in early January 1998 when a tropical low entered the area, and depressed temperatures momentarily. Subsequently, the Sr/Ca ratio fell to a low of 8.62 mmol mol^{-1} as the SST rose to 30.5 °C by early February, but had risen rapidly to 9.13 mmol mol^{-1} (equivalent to 21.6 °C) by the beginning of March, after which no growth was recorded (Fig. 9).

The Sr/Ca-temperature record indicates that this particular coral was subjected to temperatures of nearly 32 °C, some 2 °C higher than the normal bleaching threshold, and warm enough to affect even a more resistant coral such as *Porites*. The implication here is that once the coral becomes thermally stressed there is inhibition of the Ca transport enzyme (Ca^{2+} ATPase) to some extent, whereas Sr continues to be transported into the calcifying fluid at the normal concentration. The Sr/Ca
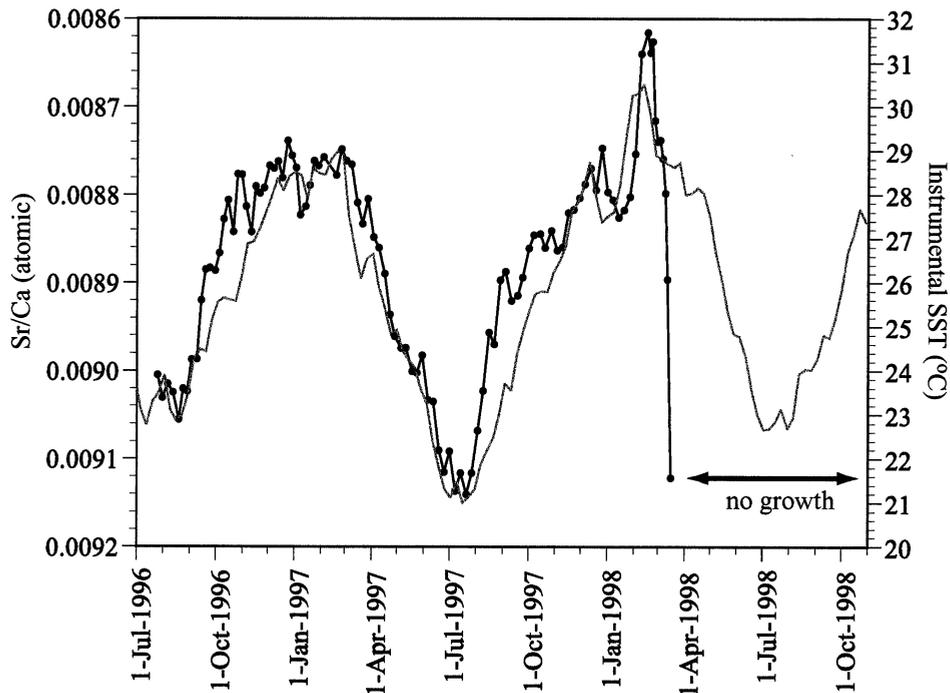
Fig. 9. Plot of Pandora Reef Sr/Ca ratio (black) against instrumental SST record from nearby Orpheus Island (grey) for the period July 1996 to November 1998 showing the effects of bleaching on the Sr/Ca ratio in February/March 1998.

ratio does not appear to be affected until a particular temperature threshold is reached. However, once bleaching is underway, the coral rapidly records an increase in the Sr/Ca ratio as relatively less Ca is made available to the calcifying fluid. Within a month the system has completely broken down and the coral stops calcifying.

The control that physiology and/or environment may have over the differences in transport behavior of Ca and Sr mentioned above may also be affected by variables other than extreme temperatures. According to Sinclair (1999), "if Ca^{2+} transport is energy dependent, but Sr^{2+} transport is not, then anything that influences the energy budget of the coral will result in a change in the relative rates at which the two ions are transported to the calcifying fluid." This could include variations in such parameters as light intensity and nutrients. In a study of a coral from Christmas Island in the eastern Indian Ocean (Marshall, 2000), it was considered that either a decrease in light intensity (as a result of increased macroalgal production) and/or an increase in nutrients might have affected the Sr/Ca ratio because the coral was growing in the same location as a phosphate loading terminal. The stress generated by either could have been enough to affect the transport behavior of Sr and Ca, resulting in an upward shift in the Sr/Ca ratio and hence lower apparent SSTs. In contrast, several corals from nearby Cocos (Keeling) Atoll appear to have experienced stress that resulted in only partial breakdown in the transport behavior of Sr and Ca, although it is obvious that periodically the situation has been serious enough to bring about a complete halt to calcification (Marshall, 2000). The reports of fish kills and coral mortality, seen from time to time in the lagoon, appear to be a result of algal blooms (Woodroffe and Berry, 1994). The corals sampled at Cocos are all exposed to open

water, so the stresses so evident in the lagoon might only be partially affecting them. However, it is quite clear that corals under stress do not obey the rules.

5.4. Differences in Sr/Ca–SST Calibrations and Potential Causes

One of the most contentious issues of using the Sr/Ca ratio in corals as a proxy for SST has been the calibration of the Sr/Ca ratio with measured SST. If the Sr/Ca ratio of seawater and the Sr/Ca distribution coefficient between aragonite and seawater are sufficiently constant to be within the error limits of the TIMS method, then it could reasonably be expected that one calibration would suffice for all *Porites* sp. Unfortunately, just about every study of the Sr/Ca proxy for modern corals published so far using TIMS has produced a different calibration (Fig. 10). The spread in the calibrations equates to temperature differences of up to 4 °C to 6 °C for the normal range of Sr/Ca ratios.

What is apparent in Figure 10, and the list of calibrations shown in Table 1, is that, with several exceptions, the slope of the calibration equation is similar, whereas the intercepts are not. This not only applies to TIMS-derived calibrations, but to others that have used techniques such as ICP–MS, ICP–AES, and HR–ICP–MS by solution, and LA–ICP–MS [e.g., Crowley et al. (1999); Fallon et al. (1999); Schrag, (1999); Correge et al. (2000)]. On this basis, it can be argued that calibrations by de Villiers et al. (1994) and Shen et al. (1996) are incorrect because their slope is either higher or lower than the rest (Fig. 10).

Some of the calibrations shown in Table 1 can be dismissed as not being precise enough, either with respect to the Sr/Ca
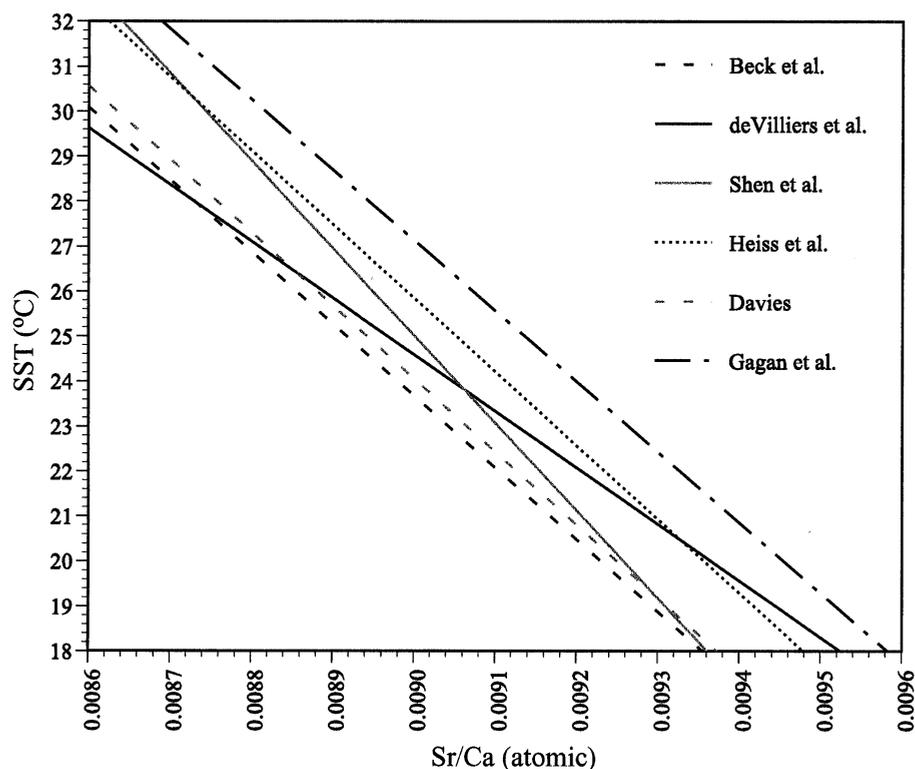
Fig. 10. Plot of previously published calibrations showing their lack of uniformity.

measurement or the instrumental SST. For instance, the calibration of Smith et al. (1979) can be discarded on the basis of imprecise Sr/Ca measurements because they used AAS, with errors of the order of 10 times that of TIMS. The precision of some of the ICP instruments are quoted to be as low as ±0.05% (e.g., Schrag, 1999), compared to ±0.1% for ID–TIMS, and others quote <±0.3% (e.g., Crowley et al., 1999). Typically, LA–ICP–MS precision for Sr/Ca is ±1.5% (e.g., Fallon et al., 1999), which equates to a temperature of ±1.2 °C.

The normal procedure for converting the Sr/Ca ratio to temperature has been to match the former with some form of temperature measurement, whether it be *in situ* instrumental SST, blended ship and satellite SST, or even another temperature proxy [e.g., $\delta^{18}O$ (Beck et al., 1992)]. Of the 15 calibrations shown in Table 1, only five are actually based on *in situ* SST measurements at the actual site itself (i.e., Amedee Lighthouse, New Caledonia and Davies and Myrmidon Reefs, central GBR). The Sr/Ca ratios of de Villiers et al. (1994) were calibrated against an SST station more than 100 km distant. The calibrations of Heiss et al. (1997); Gagan et al. (1998) and

Table 1. List of published and unpublished Sr/Ca–SST calibrations. AAS, atomic absorption spectrophotometry. ID–TIMS, isotope dilution thermal ionisation mass spectrometry. HR–ICP–MS, high-resolution inductively coupled plasma mass spectrometry. LA–ICP–MS, laser ablation inductively coupled plasma mass spectrometry. ICP–AES, inductively coupled plasma atomic emission spectrophotometry. ICP–MS, inductively coupled plasma mass spectrometry.

|	Calibration	Source	Method
1	$Sr/Ca \times 10^3 = 10.94 - 0.070 \times SST$	Smith et al. (1979)	AAS
2	$Sr/Ca \times 10^3 = 10.479 - 0.062\ 45 \times SST$	Beck et al. (1992)	ID–TIMS
3	$Sr/Ca \times 10^3 = 10.956 - 0.079\ 52 \times SST$	de Villiers et al. (1994)	ID–TIMS
4	$Sr/Ca \times 10^3 = 10.286 - 0.0514 \times SST$	Shen et al. (1996)	ID–TIMS
5	$Sr/Ca \times 10^3 = 10.577 - 0.061 \times SST$	Heiss et al. (1997)	ID–TIMS
6	$Sr/Ca \times 10^3 = 10.48 - 0.0615 \times SST$	Alibert and McCulloch (1997)	ID–TIMS
7	$Sr/Ca \times 10^3 = 10.731 - 0.0638 \times SST$	Gagan et al. (1998)	ID–TIMS
8	$Sr/Ca \times 10^3 = 10.30 - 0.0542 \times SST$	Alibert et al. (1999)	ID–TIMS
9	$Sr/Ca \times 10^3 = 10.375 - 0.0593 \times SST$	Marshall and McCulloch (2001)	ID–TIMS
10	$Sr/Ca \times 10^3 = 10.40 - 0.0575 \times SST$	Myrmidon Reef (this study)	ID–TIMS
11	$Sr/Ca \times 10^3 = 10.40 - 0.0587 \times SST$	Stanley Reef (this study)	ID–TIMS
12	$Sr/Ca \times 10^3 = 10.383 - 0.0587 \times SST$	Crowley et al. (1999)	HR–ICP–MS
13	$Sr/Ca \times 10^3 = 10.76 - 0.063 \times SST$	Fallon et al. (1999)	LA–ICP–MS
14	$Sr/Ca \times 10^3 = 10.55 - 0.0514 \times SST$	Schrag (1999)	ICP–AES
15	$Sr/Ca \times 10^3 = 10.73 - 0.065\ 67 \times SST$	Correge et al. (2000)	ICP–MS
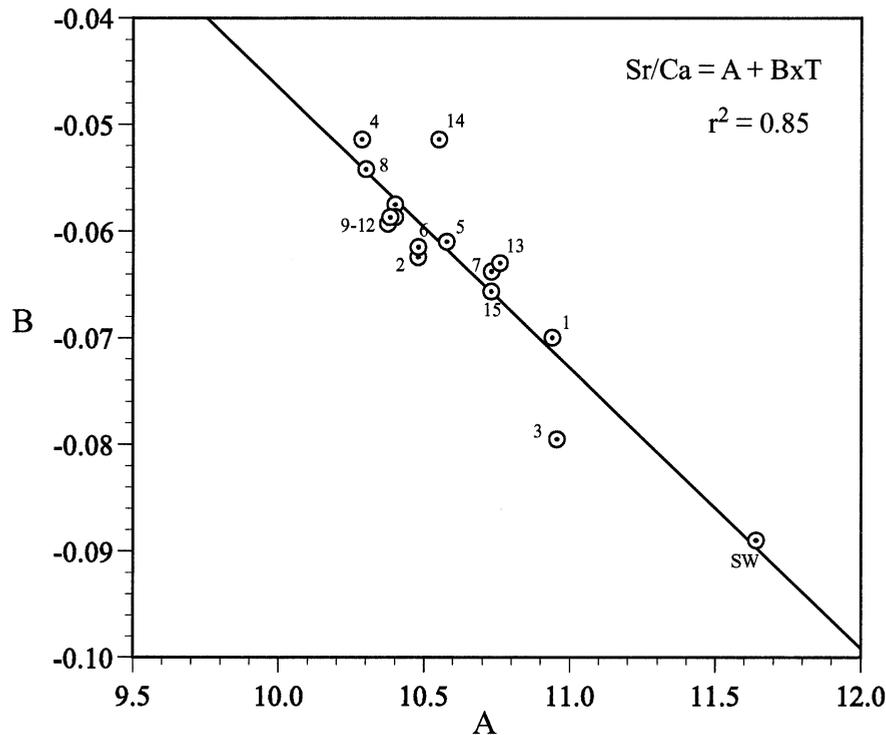
Fig. 11. Plot of calibration slope against intercept for all calibrations listed in Table 1 (SW = seawater value).

Christmas Island (Marshall and McCulloch, 2001) were derived from blended ship and satellite data. While this may not be as accurate as *in situ* measurements on the reefs, it does seem to have some veracity. However, the 1° × 1° spatial smoothing does mean that relatively small scale, but significant anomalies, such as related to upwelling as seen at Christmas Island or narrow boundary currents as at Myrmidon Reef, are seldom measured with sufficient accuracy. Notwithstanding these problems, Gagan et al. (1998) were able to derive calibrations from three widely spaced sites that were in very good agreement with each other.

One potential method of checking a calibration is to plot the slope of the calibration equation against the intercept. (This idea, communicated to us by both Dan Schrag and Tom Guilderson, is attributed to Harry Elderfield). Figure 11 shows a plot of the 15 calibrations listed in Table 1 together with the seawater value. A linear best fit of the data shows most calibrations lying along the line or within the error limits of the calibration, with only two of the calibrations, that of de Villiers et al. (1994) and Schrag (1999), offset. The reason for this linear spread in the calibrations, and its tie-in with the seawater value is not immediately clear. The implication is that corals from different localities around the world are responding to their own particular environment or that certain types of environment exert a control on the corals' physiology.

5.5. Does Coral Size (Age) Matter?

It was mentioned previously that separate calibrations were derived for five *Porites* sp. from Davies Reef (Alibert and McCulloch, 1997), and that within the error limits three corals

(Davies 2, 8, 11) produced similar calibrations (±0.5 °C), whereas two others (Davies 3 and Davies A) showed errors of up to ±1.5 °C. In fact, there is a greater spread in the calibrations for the five Davies Reef corals than there is for the combined calibrations for Davies, Pandora, Stanley, and Myrmidon Reefs (Fig. 8). At Davies Reef both Davies 3 and Davies A are small heads. A similar situation is apparent for Holocene corals from Myrmidon and Stanley Reefs (Marshall et al., 2002 submitted). These produce results that are not in agreement with each other, indicating that the calibration derived from the modern coral is not appropriate to some (or all?) of them. From the core logs it is obvious that these are small heads, probably no longer than 20 cm. The suggestion here is that younger corals produce calibrations that are less reliable than larger, older heads, but why?

At this stage there is no obvious reason, but some insight might be derived from stable isotopes. In a study by Gagan et al. (1996) on supposed enrichment of ^{13}C during spawning events, the small, 15 year old head of *Porites lobata* from Ningaloo Reef shows no annual δ ^{13}C variation for some 6 years, and, when it does so, it is out of phase with the δ ^{18}O signal. This contrasts with the top of the larger, 300 year old colony from Pandora Reef, where both the δ ^{13}C and δ ^{18}O produce an in phase annual signal. The inference here is that immature or juvenile coral heads are somehow physiologically different from their more mature counterparts, and this is reflected in their intake of trace elements and isotopes. While this is highly conjectural at this stage, it needs to be confirmed by measuring both stable isotopes and Sr/Ca ratios on a suite of small and large heads which have grown preferably side by side.

The reason for suspecting the size (age) of the *Porites* sp. is that, while in many papers the size of the coral is not mentioned, there is a distinct suspicion that the heads are small and were collected by hand rather than by drilling. In most cases only 1 to 6 years of growth is analyzed. It is significant that of the most seminal and/or critical papers on the Sr/Ca method (i.e., Beck et al., 1992; de Villiers et al., 1994, 1995; McCulloch et al., 1994; Shen et al., 1996), only one (Alibert and McCulloch, 1997) refers to the size of the coral heads, although the coral from Pandora Reef measured by McCulloch et al. (1994) is the same 300 year old head measured by Gagan et al. (1996). From this it can be surmised that the lack of agreement for some calibrations (Fig. 10), compared say to the excellent agreement for the central GBR (Fig. 8), where only large heads (>25 years) were cored, is due to the size of the coral. Again, this concept awaits to be tested.

5.6. The Sr/Ca Ratio in Corals as an Accurate Palaeothermometer

While the calibration issue can be seen as a major drawback to the use of the Sr/Ca ratio in corals as a proxy for SST, it has been the estimation of palaeotemperatures using the Sr/Ca method that has perhaps engendered most discussion from palaeoceanographers. In particular, it has been the estimation of palaeo SSTs for the LGM and deglaciation that has raised the most controversy. As discussed earlier, Sr/Ca-based palaeotemperature estimates of corals indicate that tropical SSTs in the Atlantic Ocean during the LGM were some 5 °C–6 °C cooler than today (Guilderson et al., 1994), and that SSTs rose some 6 °C during the deglaciation phase between 8–14 kyr in the south western Pacific Ocean (Beck et al., 1997; Gagan et al., 2000). These results are at odds with a variety of palaeoceanographic techniques.

In a recent paper, Crowley (2000) argues that a decrease in SST in the tropics of −5 °C during the LGM would indicate that climate sensitivity is relatively high; in which case a doubling of CO_2 in the atmosphere by the next century would lead to a temperature increase of the order of 4.5 °C. While Crowley (2000) takes to task other cool SST estimates for the LGM, such as those based on tropical snowlines and groundwater estimates, he refutes coral palaeotemperature-based estimates on the grounds that the calibrations should be derived from a regional gridded field, and must be validated against early 20th century instrumental records. While these may be seen as relatively minor issues compared to those mentioned above, it only applies to $\delta^{18}O$/SST calibrations and not necessarily to Sr/Ca-based SST estimates (Crowley et al., 1999). With regard to trace element incorporation into corals, Crowley (2000) maintains that if the SST was some 5 °C cooler, then corals during the LGM would be living under stressed conditions. As seen in the earlier part of the discussion, stress, particularly in the form of high and low SSTs, does result in an increase in the Sr/Ca ratio that can produce anomalously cooler temperatures.

On the other hand, if SSTs were cooler by 5 °C, all but a few of the present-day coral reefs of the world would not survive. Crowley (2000; Fig. 5) attempted to show this, suggesting that for 95% of present-day coral reef sites it would be too cold. While he was trying to show that corals could not exist at

−5 °C lower than present, but could at −2.5 °C, there is, indeed, very little evidence to suggest that coral reefs did develop during the LGM. The only site documented in any detail is Barbados (Fairbanks, 1989). One has to take into account that sea level was some 120 m lower than present, meaning that many LGM coral reefs would have had to establish themselves on the steep slopes of atolls or on the upper continental slope. While other factors, such as lack of substrate, increased sedimentation, etc., may have been deleterious to reef growth, it would be expected that LGM reefs would have grown in most parts of the tropics if SSTs dropped only by 2 °C–3 °C. This does not appear to be the case. Other areas where late Pleistocene/early Holocene (ca. 10 000 year old) reefs have been drilled, such as New Guinea and Vanuatu, would also be able to support reef growth at −5 °C, according to Crowley's (2000; Fig. 5) estimation. It is ironic that here too the Sr/Ca SST estimate is also −5 °C cooler than present.

So while there are pertinent arguments to suggest that Sr/Ca derived SSTs for LGM corals are overestimated because of changes to the Sr/Ca ratio of seawater or as a result of thermal stress, the almost total lack of coral reefs, except for a few areas in the tropics, indicates that it was too cold for them to develop during the LGM. In other words, by turning Crowley's (2000) argument around, if SSTs in the tropics were −5 °C relative to present, then only 5% of coral reefs would survive. This does appear to have been the situation during the LGM.

6. CONCLUSIONS

Although the precise determination of the Sr/Ca ratio in corals provides a potent tool for measuring SSTs in both modern and fossil corals, serious doubts have been raised as to its reliability. Much of this stems from the fact that corals are not calcifying in equilibrium with seawater. While corals do not calcify exactly in equilibrium with seawater, their distribution coefficient is sufficiently close, and this disequilibrium appears to be constant at the generic level. It has also been established that corals, through their symbiotic zooxanthellae, can exert a fair degree of physiological control over their calcification rate. While some objection has been raised regarding the reliability of the Sr/Ca method with regard to calcification rate (e.g., de Villiers et al., 1994, 1995), much of this can be discarded due to poor sampling techniques. Notwithstanding the obvious physiological control on the uptake of Sr into the lattice of coralline aragonite, it is suggested that, provided only a single genus or species is used, and that sampling occurs along a major vertical growth axis, then the Sr/Ca ratio should vary uniformly with temperature. The fact that most of the world's coral reefs occur in low productivity areas would appear to reduce the variability of $Sr/Ca_{seawater}$ to less than ±0.4 °C; well within the error limits of ID–TIMS or ICP–AES. At the temporal level, the modelled loss of Sr from shelf carbonates during low sea levels fails to predict the long term effects of adding additional Sr to the ocean during every glacial event. This would lead to an increase in $Sr/Ca_{seawater}$ over successive glacial periods, but last interglacial corals show no such increase, suggesting that other mechanisms, such as carbonate dissolution during each deglaciation, may be important in maintaining relatively constant Sr/Ca ratios.

Evidence from several corals in this study suggests that

stress may be a major cause in the breakdown in the Sr/Ca–SST relationship. Thermal stress, resulting from either extremely warm or cool temperatures, is considered to lead to a reduction in Ca^{2+} transport to the calcifying fluid, whereas Sr does not appear to be similarly affected, and an upward shift in the Sr/Ca ratio occurs. Evidence from Pandora Reef in the central GBR shows that both excess (bleaching) and extremely cool (<18 °C) temperatures produce anomalously low Sr/Ca derived SSTs as a result of this breakdown of the biological control on Sr/Ca fractionation. It is considered that other stresses, such as increased nutrients and changes in light intensity, can also lead to a breakdown in the Sr/Ca–SST relationship.

This study suggests that while some of the previously published calibrations can be dismissed on the basis of inaccuracies in the Sr/Ca and SST measurements, there still appears to be sufficient evidence to suggest that the Sr/Ca–SST calibration is not constant. While many calibrations appear to be based on measurements from small (young) coral heads, the central GBR calibrations are based on cores of large (old) heads, and these seem to give the most reliable results. The fact that tropical LGM palaeotemperature estimates using the Sr/Ca method are 2 °C–3 °C cooler than other climate proxies is a cause for serious concern. However, it is argued here that the overall lack of evidence for reef growth during the LGM suggests that SSTs were too cold in most parts of the tropics for reefs to develop. This would lend support to the idea that tropical SSTs were much cooler than that proposed by CLIMAP data. Those arguments which suggests that Sr/Ca derived SSTs for LGM corals are overestimated because of changes to the Sr/Ca ratio of seawater or as a result of thermal stress need to be evaluated in more detail.

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