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## **Diagenesis and geochemistry of Porites corals from Papua New Guinea: implications for Paleoclimate reconstruction**

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## Diagenesis and geochemistry of *Porites* corals from Papua New Guinea: Implications for paleoclimate reconstruction

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**Abstract**—Coral proxy records of sea surface temperature (SST) and hydrological balance have become important tools in the field of tropical paleoclimatology. However, coral aragonite is subject to post-depositional diagenetic alteration in both the marine and vadose environments. To understand the impact of diagenesis on coral climate proxies, two mid-Holocene *Porites* corals from raised reefs on Muschu Island, Papua New Guinea, were analysed for Sr/Ca,  $\delta^{18}\text{O}$ , and  $\delta^{13}\text{C}$  along transects from 100% aragonite to 100% calcite. Thin-section analysis showed a characteristic vadose zone diagenetic sequence, beginning with leaching of primary aragonite and fine calcite overgrowths, transitional to calcite void filling and neomorphic, fabric selective replacement of the coral skeleton. Average calcite Sr/Ca and  $\delta^{18}\text{O}$  values were lower than those for coral aragonite, decreasing from 0.0088 to 0.0021 and  $-5.2$  to  $-8.1\text{‰}$ , respectively. The relatively low Sr/Ca of the secondary calcite reflects the Sr/Ca of dissolving phases and the large difference between aragonite and calcite Sr/Ca partition coefficients. The decrease in  $\delta^{18}\text{O}$  of calcite relative to coral aragonite is a function of the  $\delta^{18}\text{O}$  of precipitation. Carbon-isotope ratios in secondary calcite are variable, though generally lower relative to aragonite, ranging from  $-2.5$  to  $-10.4\text{‰}$ . The variability of  $\delta^{13}\text{C}$  in secondary calcite reflects the amount of soil  $\text{CO}_2$  contributing  $^{13}\text{C}$ -depleted carbon to the precipitating fluids. Diagenesis has a greater impact on Sr/Ca than on  $\delta^{18}\text{O}$ ; the calcite compositions reported here convert to SST anomalies of  $115^\circ\text{C}$  and  $14^\circ\text{C}$ , respectively. Based on calcite Sr/Ca compositions in this study and in the literature, the sensitivity of coral Sr/Ca-SST to vadose-zone calcite diagenesis is  $1.1$  to  $1.5^\circ\text{C}$  per percent calcite. In contrast, the rate of change in coral  $\delta^{18}\text{O}$ -SST is relatively small ( $-0.2$  to  $0.2^\circ\text{C}$  per percent calcite). We show that large shifts in  $\delta^{18}\text{O}$ , reported for mid-Holocene and Last Interglacial corals with warmer than present Sr/Ca-SSTs, cannot be caused by calcite diagenesis. Low-level calcite diagenesis can be detected through X-ray diffraction techniques, thin section analysis, and high spatial resolution sampling of the coral skeleton and thus should not impede the production of accurate coral paleoclimate reconstructions. Copyright © 2003 Elsevier Science Ltd

### 1. INTRODUCTION

Paleoclimate reconstruction in the tropics has emerged as an important tool for exploring the natural bounds of climate variability. Long-lived, massive corals provide valuable natural archives of tropical climate and fossil corals provide “windows” into climates of the past. However, the extent of sea surface temperature (SST) cooling during glacial episodes appears to be over-estimated by coral Sr/Ca (Guilderson et al., 1994; Beck et al., 1997; McCulloch et al., 1999), at least when compared to other marine temperature proxies, such as foraminiferal assemblages (CLIMAP, 1981), foraminiferal Mg/Ca (Lea et al., 2000) and alkenone unsaturation ratios (Bard et al., 1997). Although some of this variability may be accounted for by variations in seawater Sr/Ca during glacial-interglacial cycles (Stoll and Schrag, 1998; Martin et al., 1999; Stoll et al., 1999), discrepancies still remain (Lea et al., 2000).

There has been concern that coral proxy records may be affected by diagenesis (Guilderson et al., 1994; McCulloch et al., 1996; Esat et al., 1999; Hughen et al., 1999; Woodroffe and Gagan, 2000; Guilderson et al., 2001; Tudhope et al., 2001). For corals, diagenesis refers to the precipitation of secondary aragonite or calcite in skeletal voids, or the replacement of

skeletal aragonite, usually with calcite (Bathurst, 1975). During this transformation, isotopes and trace elements are exchanged and removed, thus changing the geochemistry of the coralline matrix.

An increasing number of proxy climate records are being produced from subaerially exposed corals of Holocene and Last Interglacial age, which may be subject to diagenesis, primarily in the vadose zone (McCulloch et al., 1996; Hughen et al., 1999; McCulloch et al., 1999; Corrège et al., 2000; Woodroffe and Gagan, 2000; Tudhope et al., 2001). If diagenesis occurs in the vadose zone, corals are most likely to transform to calcite. Several authors have stated screening methods, involving X-ray diffraction (XRD) and petrographic analysis, to avoid diagenesis in corals (Guilderson et al., 1994; McCulloch et al., 1996; Esat et al., 1999; Hughen et al., 1999; Woodroffe and Gagan, 2000; Guilderson et al., 2001; Tudhope et al., 2001). However, only a limited number of studies quantify the effect of diagenesis on coral climate proxies. Most of the numerous studies on diagenesis focus on geochemical changes in carbonate stratigraphic sequences, from a variety of facies, which have often undergone several phases of diagenesis (Bathurst, 1975; Arthur et al., 1983; Schroeder and Purser, 1986). Of those works that have examined diagenetic effects on coral proxies, most investigated diagenetic processes, rather than exploring the paleoclimatic implications of these diagenetic transformations (Sie-

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gel, 1960; Harris and Matthews, 1968; Martin et al., 1986; Zhu et al., 1988; Zhu, 1990; Stein et al., 1993; Zhu et al., 1994).

Inclusion of even a small amount of diagenetic material in a coral used for climate reconstruction has the potential to render the results inaccurate. To quantify the paleoclimatic implications of diagenesis in vadose zone fossil corals, we have measured stable isotopes and Sr/Ca in aragonite-to-calcite transects from two mid-Holocene *Porites* sp.. These corals were periodically subaerially exposed in the intertidal zone of Muschu Island, Papua New Guinea (PNG). XRD and petrographic analysis of thin sections have been used to match diagenetic textures and the percentage of calcite with geochemical results for the corals. The results show that diagenesis gives lower Sr/Ca and stable isotope ratios. By converting these ratios to SST, we have explored the consequences of this type of diagenesis for paleotemperature estimates.

### 1.1. Geological Setting

Fossil corals from Muschu Island (03°25'S 143°35'E), PNG, were chosen for geochemical and petrographic analysis of diagenesis due to their obvious transition from aragonite to calcite, seemingly good preservation of aragonite away from the transition zone, and contrasting preservation environment. The two *Porites* sp. corals were drilled from uplifted reefs at Rebiev (FM19) and Morock (FM08) Bays (Fig. 1) during Leg 6b of Project TROPICS (Tropical River-Ocean Processes In Coastal Settings) from 24 May to 19 June, 1998. A modern *Porites lutea* coral (J. True, private communication) from Cape Saum, Muschu Island (MS01), was used for comparison with the fossil corals. The climate of the Muschu Island region is equatorial, with an average annual rainfall of 2000 mm/yr (McAlpine et al., 1983). Mean annual SSTs are typically  $29 \pm 0.7^\circ\text{C}$ .

Corals from Rebiev Bay, on the southern side of the island (Fig. 1), range in age from 1360 to 1870 yr BP (oceanic  $^{14}\text{C}$  reservoir correction 410 yr) and are located in the intertidal zone, ~20 m from the beach. They are almost completely exposed and stand as isolated coral heads. Behind the beach, more corals are eroding from under a vegetated area, with a mixture of sandy soil and coral rubble covering and surrounding these corals. Coral FM19 is ~2 m high and ~1.5 m in diameter. Halfway down the 1.1 m core is an 80 mm-transition zone from aragonitic to calcitic material (Fig. 2).

Corals from Morock Bay, on the northeastern side of the island (Fig. 1), are older, ranging in age from 6110 to 4680 yr BP (oceanic  $^{14}\text{C}$  reservoir correction 410 yr). Morock Bay corals have only their tops exposed at low tide and are eroding out from a sandy beach. A 0.2 m long core was drilled from specimen FM08, a 1.3 m high coral with a diameter of 1.6 m. The base of the core was calcitised with 1 to 3 mm patches of calcite visible from 30 mm above the base of the coral (Fig. 2).

## 2. METHODS

Seven millimeter thick slices were taken from coral cores FM08 and FM19 along the main growth axis. A dentist drill with a stainless steel circular bit was used to collect samples for geochemistry and XRD from the 7 mm slices, along the aragonite-to-calcite transects (Fig. 2). The mirror image face of one side of the slice, on the off-cut of the core, was used to prepare standard 50 to 100  $\mu\text{m}$  thick,  $60 \times 20$  mm petrographic thin sections. This strategy allowed geochemical and

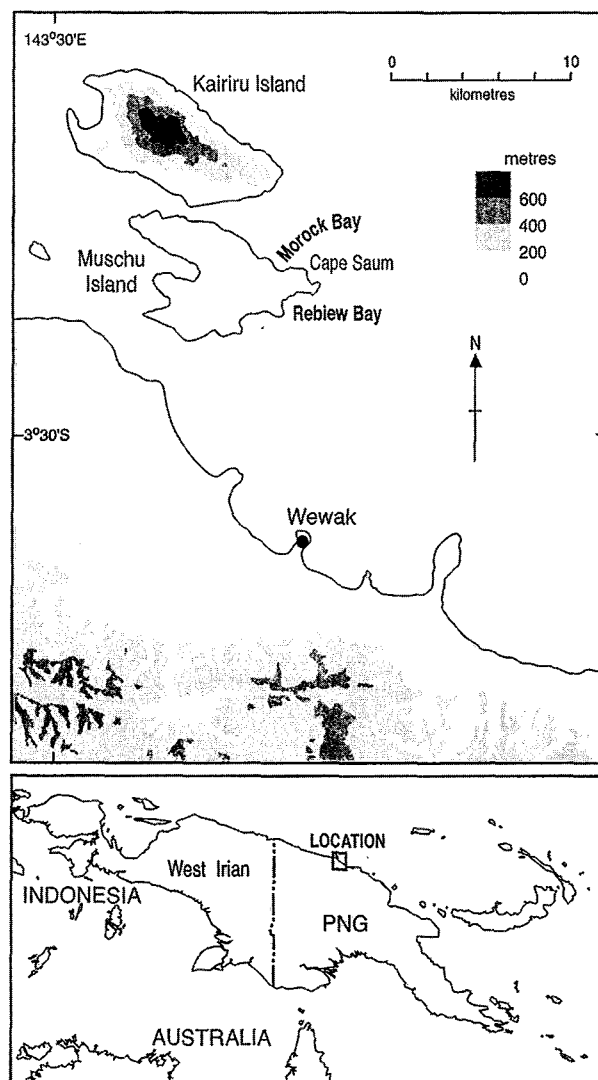


Fig. 1. Location of the coral collection sites Morock and Rebiev Bays, Muschu Island, Papua New Guinea (PNG).

XRD results to be compared as closely as possible to petrography. Additional ~100% aragonite and ~100% calcite samples were collected from each coral, with these samples located away from the original transect. All slices were ultrasonically cleaned before sample collection.

A second 7 mm thick slice was cut from FM08 and yearly samples were collected, with years defined by the transition from a high to a low density band, as seen in the coral X-ray (Fig. 2). XRD and thin section analysis of five of these samples, along with the X-ray prints and visual inspection, revealed traces of calcite. Four of these five samples were milled at near-weekly resolution (0.25 mm per sample) using the automated micro-milling system described in Gagan et al. (1994).

Approximately 100 to 200 mg of coralline powder from each sample was used for XRD analysis. Samples were ground under ethanol to approximately 25  $\mu\text{m}$  and smeared onto a glass slide. The slides were analysed on a Sietronics Diffractometer with the Cobalt X-ray tube on 90% loading (30 mA, 50 mV) and scanned from  $2\theta$  of  $20^\circ$  to  $60^\circ$ . The percent aragonite and calcite in each sample was estimated using SIROQUANT v. 2.5 software utilising the Rietvelt method for analysing diffraction peaks. Errors on estimates of percent calcite are  $\pm 2\%$ .

A separate aliquot of each sample was analysed for Sr/Ca using thermal ionisation mass spectrometry. 60 to 150  $\mu\text{g}$  of coral powder

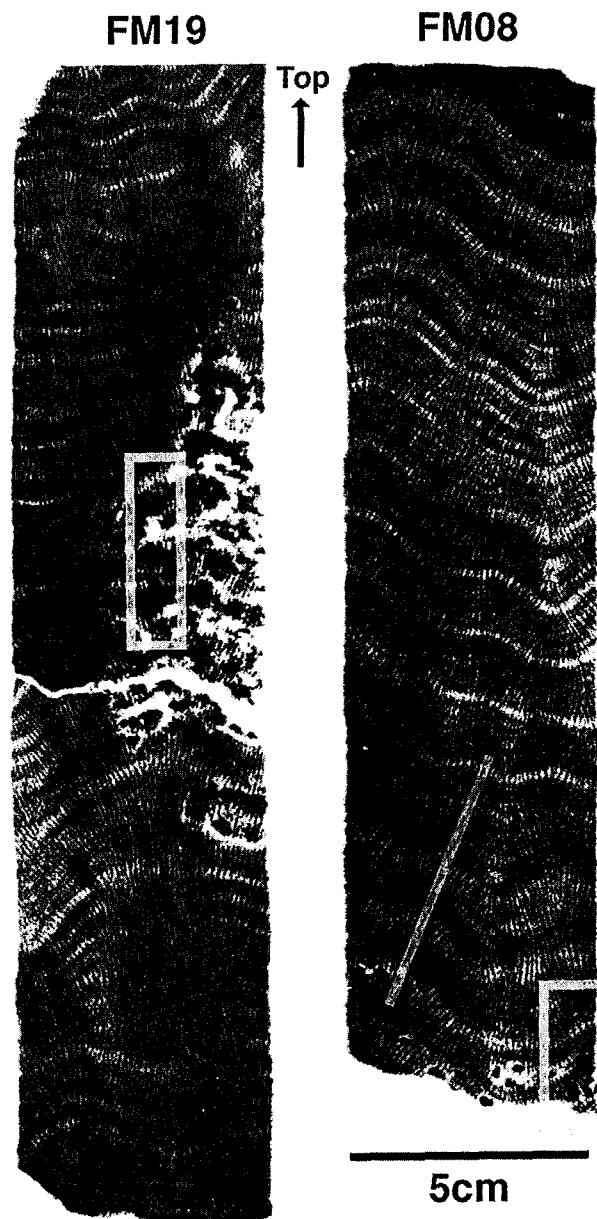


Fig. 2. X-ray positive images showing diagenesis in corals FM08 and FM19. Dark high-density patches indicate the presence of secondary calcite. Calcite patches are 1 to 3 mm in diameter in FM08 and, in FM19, the calcite forms a distinct zone. Grey boxes show sampling transects used for geochemical analysis. Grey line on FM08 shows the location of high-resolution sampling transect. Note the faded density band halo around the calcitic area in FM19.

was weighed into acid washed vials and dissolved in 0.5N HCl. Four  $\mu\text{g}$  Ca subaliquots were then added to phosphoric acid, along with a  $^{43}\text{Ca}$ - $^{84}\text{Sr}$  spike, giving a mix with  $^{43}\text{Ca}/^{44}\text{Ca}$  and  $^{84}\text{Sr}/^{86}\text{Sr}$  of approximately one. Following evaporation to near dryness, the aliquots were loaded onto single Tantalum filaments and Sr/Ca was determined by isotope dilution mass spectrometry on a Finnigan MAT 261 thermal ionisation mass spectrometer. An exponential fractionation law based on  $^{42}\text{Ca}/^{44}\text{Ca}$  was used to correct for Ca mass fractionation during analysis. Corrections for Sr mass fractionation during analysis used a power law based on  $^{88}\text{Sr}/^{86}\text{Sr}$ . The spike is calibrated against a Research School of Earth Sciences mixed Sr/Ca standard solution, based

on high purity  $\text{CaCO}_3$  and  $\text{SrCO}_3$ , prepared gravimetrically. Measurement of internal standards gives precision of  $\pm 0.08\%$  ( $2\sigma$ ).

Oxygen and carbon isotope ratios were measured on a Finnigan MAT 251 mass spectrometer. For each sample aliquot,  $200 \pm 20 \mu\text{g}$  of powder was initially dissolved in 105%  $\text{H}_3\text{PO}_4$  at  $90^\circ\text{C}$  in an automated carbonate (Kiel) device. Isotope results were calibrated relative to the Vienna Pee Dee Belemnite (v-pdb) using the NBS 19 ( $\delta^{18}\text{O} = -2.20\text{‰}$ ,  $\delta^{13}\text{C} = 1.95\text{‰}$ ) and NBS 18 ( $\delta^{18}\text{O} = -23.00\text{‰}$ ,  $\delta^{13}\text{C} = -5.00\text{‰}$ ) standards. Duplicate samples were measured except for the high-resolution samples. The average standard error on duplicate samples was  $0.02\text{‰}$  for FM08 and  $0.07\text{‰}$  for FM19.

### 3. RESULTS

In thin section, well preserved fossil corals should show all the skeletal features of modern corals, as well as an absence of void filling or cement formation by calcite or secondary aragonite (Constantz, 1986). An example of good preservation in a fossil coral is presented in crossed polarised light in Figure 3b. For comparison, a modern *Porites lutea* coral (MS01) is included (Fig. 3a). All images show excellent preservation of centers of calcification (central thin dark line in crossed polarised light), with no evidence of replacement by calcite. The radiating fans of the sclerodermites are clearly visible, as are the dissepiments. No borings, sediment infillings or cements are present and there is minimal leaching. These images show that it is possible to find well preserved coral from these Muschu Island sites.

Fossil corals FM19 and FM08 show a variety of textures as they convert from aragonite to calcite (Fig. 3c and 4). As the amount of calcite increases (measured by XRD), the thin section textures observed for each coral change in similar and characteristic ways. With 3 to 5% calcite, the corals develop "chalky" zones and show increased leaching (black patches, Fig. 3c), particularly at the centers of calcification. Calcite material is precipitated as a void-filling rim  $\sim 0.1$  mm thick. At 10 to 30% calcite (Fig. 4a), leaching is more extensive to the point where calcification centers have been removed. Thin micritic rims are present, and some voids are filled with single crystal calcite spar. With 40 to 60% calcite (Fig. 4b), aragonite is replaced with calcite without destroying the gross coral morphology (neomorphism). This replacement occurs at a diagenetic front, a zone where the transformation of aragonite to calcite occurs across a thin film of water separating the two minerals. In addition, a mosaic of calcite spar may also replace the skeletal material. This spar is likely to be filling the space left by the dissolution of the coral. Micritic calcite rims are present where voids have not been filled with single crystal calcite spar. At 75 to 100% calcite (Fig. 4c), complete replacement of the aragonite skeleton has occurred and almost all voids are filled with single crystal calcite spar. Primary skeletal elements are preserved as "ghosts" of the original texture.

Sr/Ca for corals FM08 and FM19 decreased systematically as a function of the amount of calcite present in the sample (Fig. 5a). This trend holds true irrespective of the site from which the corals were collected. Least-squares regressions for both corals give similar slopes (Fig. 5a) and high correlation coefficients ( $r = -0.99$ , both corals). The similarity of the Sr/Ca-calcite slope relationships suggests that the composition of the calcite is essentially the same at both sites. The weighted mean regression for the Sr/Ca-calcite relationship in Figure 5a is

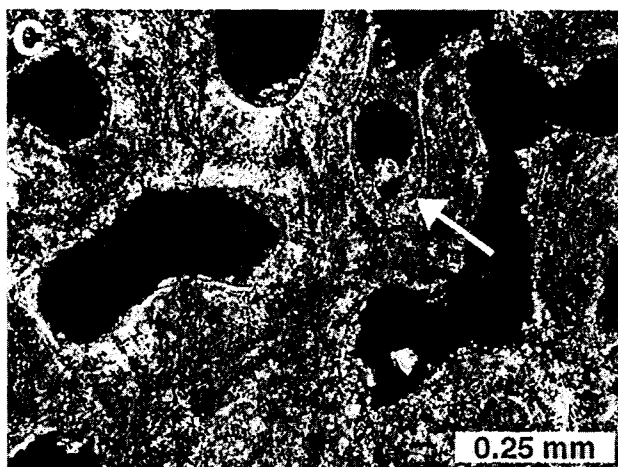
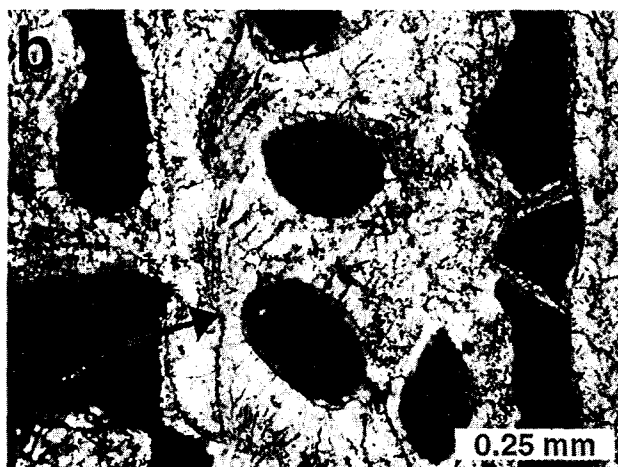
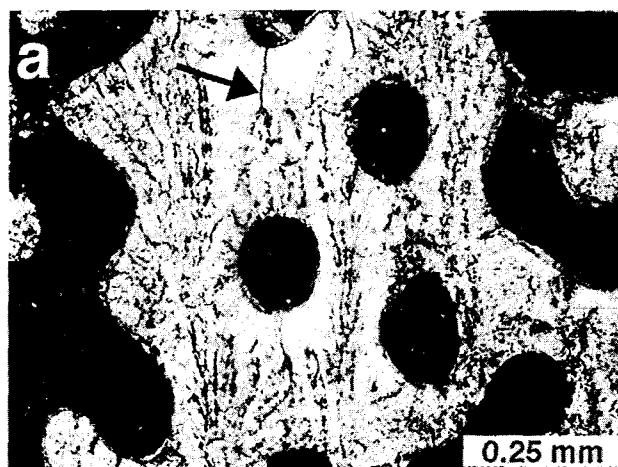


Fig. 3. Comparison of (a) well preserved modern coral, (b) well preserved fossil coral and (c) fossil coral containing 3 to 5% calcite. All images are of corals under crossed polarised light. Arrows in (a) and (b) point to centers of calcification. Arrow in (c) shows calcite rims growing into voids. The darker color of the coralline aragonite in (c) is due to dissolution. Dissolution is most obvious along the centers of calcification.

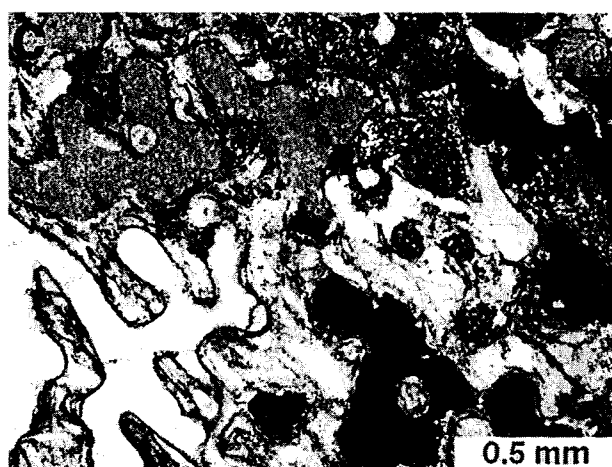
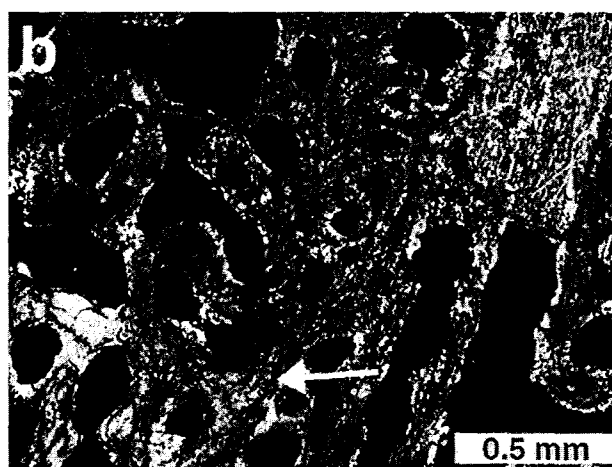
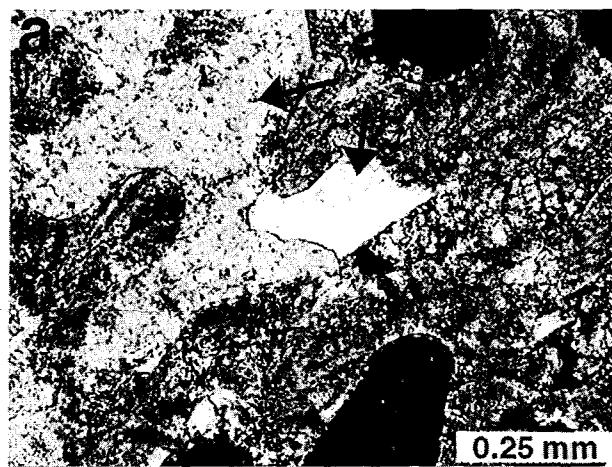


Fig. 4. Comparison of fossil coral with (a) 10 to 30% calcite, (b) 40 to 60% calcite and (c) 75 to 100% calcite. All images are of corals under crossed polarised light. Arrows in (a) indicate single crystal void filling calcite. Arrow in (b) shows a neomorphic calcite front. Note the single calcite crystal in the top right and the dissolution of remaining aragonite. (c) Near complete neomorphic transformation of skeletal aragonite to calcite and calcite void filling.

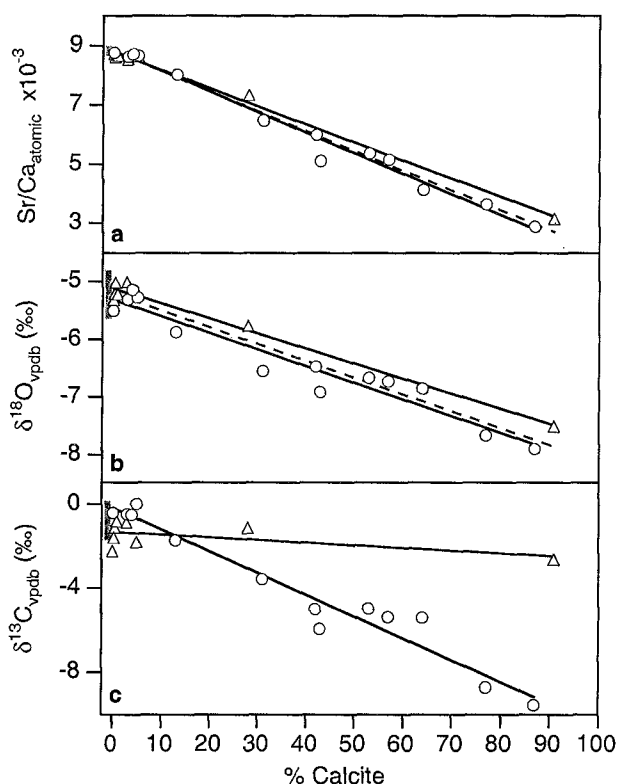


Fig. 5. Comparison of Sr/Ca (a),  $\delta^{18}\text{O}$  (b), and  $\delta^{13}\text{C}$  (c) in coral FM08 ( $\Delta$ ) and coral FM19 ( $\circ$ ). Solid lines show least-squares regressions for FM08 and FM19; dashed line indicates weighted mean regression for Sr/Ca and  $\delta^{18}\text{O}$ . The Sr/Ca weighted mean regression is  $\text{Sr/Ca}_{\text{atomic}} \times 10^3 = 8.79(\pm 0.0817) - [6.69(\pm 0.00193) \times \% \text{ calcite}]$ , ( $r = -0.99$ ,  $p < 0.001$ ,  $n = 21$ ). The  $\delta^{18}\text{O}$  weighted mean regression is  $\delta^{18}\text{O} = -5.2(\pm 0.07) - [0.029(\pm 0.002) \times \% \text{ calcite}]$ , ( $r = -0.97$ ,  $p < 0.001$ ,  $n = 21$ ). The FM08  $\delta^{13}\text{C}$  regression is  $\delta^{13}\text{C} = -1.3(\pm 0.2) - [0.012(\pm 0.007) \times \% \text{ calcite}]$ , ( $r = -0.61$ ,  $p < 0.1$ ,  $n = 8$ ). The FM19  $\delta^{13}\text{C}$  regression is  $\delta^{13}\text{C} = -0.1(\pm 0.3) - [0.103(\pm 0.007) \times \% \text{ calcite}]$ , ( $r = -0.98$ ,  $p < 0.001$ ,  $n = 13$ ). Grey stippled bar shows the range of values for modern and fossil coral aragonite samples from PNG.

$$\text{Sr/Ca}_{\text{atomic}} \times 10^3 = 8.79 (\pm 0.0817) - [6.69 (\pm 0.00193) \times \% \text{ calcite}] \quad (1)$$

( $r = -0.99$ ,  $p < 0.001$ ,  $n = 21$ ). Extrapolation to 100% calcite gives a Sr/Ca of  $0.0021 \pm 0.00015$ .

$\delta^{18}\text{O}$  values for both corals are negatively correlated with the percentage of calcite ( $r = -0.97$  for FM08 and  $r = -0.99$  for FM19), and the  $\delta^{18}\text{O}$ -calcite slopes are similar (see Figure 5 for weighted mean regression). As for Sr/Ca, this trend is independent of coral location. Extrapolating to 100% for calcite gives a  $\delta^{18}\text{O}$  value of  $-8.1 \pm 0.1\text{‰}$ . Some samples with up to 5% calcite have  $\delta^{18}\text{O}$  values that are similar to those of non-diagenetic fossil and modern corals. This occasional overlap is attributed to variability in the  $\delta^{18}\text{O}$  values of coral aragonite, as indicated by the grey bar on each graph (Fig. 5), and to the uncertainty in the XRD measurements at low calcite percentages.

There is also a strong relationship between  $\delta^{13}\text{C}$  and the percentage of calcite in corals FM08 and FM19, however,

unlike Sr/Ca and  $\delta^{18}\text{O}$ , the  $\delta^{13}\text{C}$  signals differ between the two coral sites (Fig. 5c). FM19 shows a negative trend in  $\delta^{13}\text{C}$  with increasing calcite, whereas the calcite in FM08 gives essentially the same  $\delta^{13}\text{C}$  as the primary aragonite. The correlation coefficient for  $\delta^{13}\text{C}$  and percent calcite is much stronger for FM19 ( $r = -0.98$ ,  $p < 0.001$ ,  $n = 13$ ) than for FM08 ( $r = -0.61$ ,  $p < 0.1$ ,  $n = 8$ ). FM08 shows a particularly large spread in  $\delta^{13}\text{C}$  values for samples with less than 5% calcite, as large as that for non-diagenetic modern and fossil corals. Regression lines give end-member calcite  $\delta^{13}\text{C}$  values of  $-2.5 \pm 0.5\text{‰}$  for FM08 and a much lower value of  $-10.4 \pm 0.5\text{‰}$  for FM19.

## 4. DISCUSSION

### 4.1. Vadose-Zone Diagenesis

Diagenetic textures in carbonates can give clues regarding the physical and geochemical environment in which diagenesis has occurred. Petrographic analysis of fossil corals is an effective way of recognising diagenesis, identifying the diagenetic setting and assessing the potential geochemical implications of the diagenesis. For the Muschu Island corals, the early leaching identified in thin sections probably occurs through interaction with meteoric water under-saturated with respect to  $\text{CaCO}_3$  (Longman, 1980). "Chalky" aragonite is a dissolution texture often developed in association with precipitation of single-crystal calcite (e.g., James, 1974; Pingitore, 1976; Marshall, 1983). The texture is thought to occur in areas saturated with water, such that dissolution occurs at a greater rate than calcite precipitation (e.g., James, 1974; Pingitore, 1976; Marshall, 1983). The "chalky" zones in the Muschu Island corals are interpreted as small-scale water saturation in localised zones within the coral, in a vadose setting, rather than diagenesis occurring in a meteoric phreatic environment.

Precipitation of calcite into voids, fabric selective replacement of aragonite skeletal material and neomorphism are all characteristic features of coral undergoing diagenesis in a vadose environment (James, 1974; Bathurst, 1975; Longman, 1980; Martin et al., 1986). Longman (1980) notes that in the vadose zone cement distribution and morphology reflects the patchy distribution of water within the available pore spaces, with the calcite sourced from aragonite dissolution in the surrounding coral (James, 1974; Bathurst, 1975; Longman, 1980). The Muschu coral cements are usually large single crystals bounded by dissepiments and skeletal walls (Fig. 4), suggesting that dissolution of surrounding aragonite has occurred. Water has probably been present in these areas for a significant period, though the corals have not necessarily been completely saturated. Our interpretation of coral diagenesis in a meteoric vadose environment is consistent with field observations of the corals eroding from onshore environments on Muschu Island. This simplified diagenetic environment should facilitate interpretation of the geochemical results.

### 4.2. Geochemistry

On average, the Sr/Ca in the Muschu Island corals decreased from 0.0088 to 0.0021 as the calcite content increased from 0 to 100%. The Sr/Ca of inorganic carbonate depends on the Sr/Ca partition coefficient,  $D_{\text{Sr}}$ , and the Sr/Ca of the precipi-

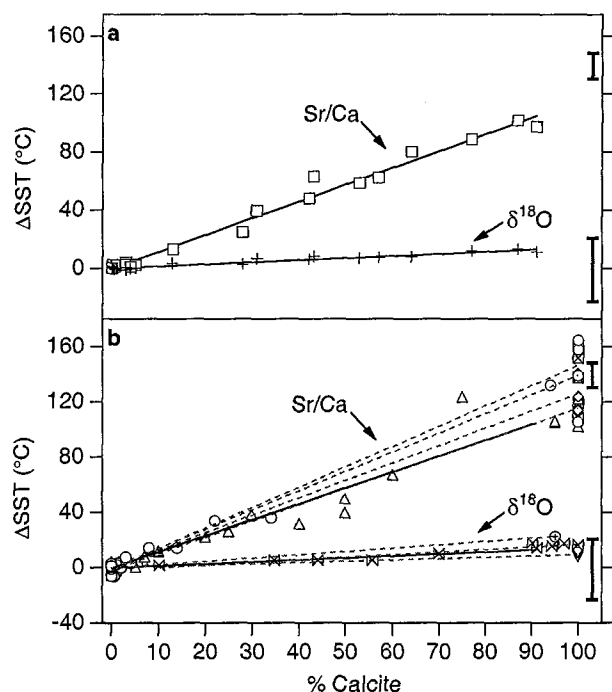


Fig. 6. Diagenetic changes in  $\delta^{18}\text{O}$  and Sr/Ca expressed as a change in SST. All data were converted to SST using the average of published Sr/Ca and  $\delta^{18}\text{O}$  SST slopes (see text). (a) Weighted mean linear regressions for  $\delta^{18}\text{O}$  (+) and Sr/Ca (□) data from corals FM08 and FM19 at Muschu Island. Regression lines are Sr/Ca- $\Delta \text{SST (}^{\circ}\text{C)} = 1.15 (\pm 0.03) \times \% \text{ calcite}$ , ( $r = 0.99$ ,  $p < 0.001$ ,  $n = 21$ );  $\delta^{18}\text{O}$ - $\Delta \text{SST (}^{\circ}\text{C)} = 0.14 (\pm 0.01) \times \% \text{ calcite}$ , ( $r = 0.97$ ,  $p < 0.001$ ,  $n = 21$ ). (b) Comparison of SST regressions for this study (solid lines) with those for various coral species with varying percentages of vadose-zone calcite (dashed lines).  $\delta^{18}\text{O}$ - $\Delta \text{SST}$  regression for Martin et al. (1986,  $\nabla$ ), Stein et al. (1993,  $\oplus$ ), and Wei et al. (1998,  $\times$ ). Sr/Ca- $\Delta \text{SST}$  regression for Seigel (1960,  $\Delta$ ), Zhu (1990,  $\circ$ ), Zhu et al. (1988,  $\boxtimes$ ), and Zhu et al. (1994,  $\diamond$ ). Bars at 100% calcite represent the range of calculated end-member Sr/Ca- $\Delta \text{SST}$  (upper vertical line) and calculated end-member  $\delta^{18}\text{O}$ - $\Delta \text{SST}$  (lower vertical line).

tating solution (Kinsman and Holland, 1969; Veizer, 1983) as follows:

$$\text{Sr/Ca}_{\text{carbonate}} = D_{\text{Sr}} \times \text{Sr/Ca}_{\text{solution}} \quad (2)$$

The partition coefficient for Sr in carbonate varies with temperature, the carbonate phase and kinetic factors such as precipitation rate (Kinsman and Holland, 1969; Veizer, 1983). Reported values of  $D_{\text{Sr}}$  for calcite vary from 0.016 to 0.14 (Kinsman and Holland, 1969; Katz et al., 1972; Lorens, 1981; Veizer, 1983; Morse and Bender, 1990; Tesoriero and Pankow, 1996). The reported value for  $D_{\text{Sr}}$  for aragonite to calcite transformations is 0.05 (Katz et al., 1972).  $D_{\text{Sr}}$  for aragonite precipitation is 0.9 to 1.2 (Veizer, 1983). Thus, regardless of the absolute value of the calcite  $D_{\text{Sr}}$ , calcite will have lower Sr/Ca than the water from which it precipitates and aragonite precipitated in equilibrium with the same water.

The Sr/Ca of meteoric waters is a function of the Sr/Ca of dissolving carbonate and the degree of closure of the diagenetic system. In a closed diagenetic system, initially the meteoric water will take on the Sr/Ca of the first carbonate material dissolved. The resulting calcite will have a ratio given by Eqn.

2. With time, and continued dissolution and precipitation, the excess Sr relative to Ca from each precipitation will accumulate in the meteoric water, because the  $D_{\text{Sr}}$  for calcite is less than unity. When equilibrium is reached, the maximum Sr/Ca in calcite will be that of the dissolving carbonate phase (Kinsman, 1969; Veizer, 1983). In open systems such as coral reefs, however, the fluid flow is high so there is no accumulation of Sr/Ca in the meteoric water and Sr/Ca of calcite is likely to be the same as that of the initial closed system (Kinsman, 1969). Given the porous nature of the Muschu Island corals examined in this study, and the high regional rainfall, calcite is unlikely to be precipitating in a completely closed system.

The  $\delta^{18}\text{O}$  of diagenetic calcite is determined by the ratio of moles of oxygen derived from dissolving carbonate (aragonite) and from the meteoric water (Gross, 1964; Allan and Matthews, 1982). However, the water flow rate is generally much greater than the rate of dissolution, thus the  $\delta^{18}\text{O}$  of carbonate precipitated in vadose environments reflects the  $\delta^{18}\text{O}$  of the meteoric water. Using the inorganic calcite equilibrium precipitation equation of O'Neil et al. (1969), the  $\delta^{18}\text{O}$  for the meteoric water from which the Muschu Island coral calcite was precipitated was approximately  $-6.3\text{‰}_{\text{SMOW}}$ , which is similar to the average  $\delta^{18}\text{O}$  values of  $-7.1\text{‰}_{\text{SMOW}}$  for modern precipitation in PNG (Rozanski et al., 1993).

The change in calcite  $\delta^{13}\text{C}$  during the aragonite to calcite alteration process is dependent on the  $\delta^{13}\text{C}$  of the meteoric water from which the calcite is precipitated (Gross, 1964; Allan and Matthews, 1982).  $\delta^{13}\text{C}$  is dependent on the ratio of the moles of carbon from the dissolving coralline aragonite and, if covered with soil, the  $\delta^{13}\text{C}$  of soil-gas  $\text{CO}_2$  derived from plant respiration and organic matter decay (Gross, 1964; Allan and Matthews, 1982). Soil-gas  $\text{CO}_2$  is depleted in  $^{13}\text{C}$  relative to marine dissolved inorganic carbon so calcite derived from this source has a lower  $\delta^{13}\text{C}$  value than the original marine carbonate (Allan and Matthews, 1982). Thus, the variability in  $\delta^{13}\text{C}$  of calcite in Muschu Island corals reflects the degree of soil formation in their respective environments. Rebiev Bay (FM19) is a more vegetated site, with a thin soil horizon above the corals before they are exposed. In contrast, fossil corals from Morock Bay (FM08) are exposed from beneath beach sand, thus percolating waters would dissolve very little soil-gas  $\text{CO}_2$  and  $\delta^{13}\text{C}$  should show minimal changes. This explains why the  $\delta^{13}\text{C}$  values for 100% secondary calcite in coral FM19, from the well-vegetated Rebiev Bay, are much lower ( $-10.4\text{‰}$ ) than that for calcite in coral FM08 from Morock Bay ( $-2.5\text{‰}$ ).

#### 4.3. Diagenesis, Paleothermometry and Paleoclimate Reconstruction

When converted to a paleotemperature signal using the average slope of several calibrations for coral Sr/Ca (Beck et al., 1992; Min et al., 1995; Shen et al., 1996; Alibert and McCulloch, 1997; Gagan et al., 1998) and  $\delta^{18}\text{O}$  (McConnaughey, 1989; Leder et al., 1996; Quinn et al., 1996; Wellington et al., 1996; Müller et al., 2001), diagenesis in the two Muschu Island corals has a greater impact on estimates of SST from Sr/Ca (Sr/Ca-SST) than on those derived from  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}$ -SST) (Fig. 6). Based on results from both Muschu corals, the apparent change in temperature for the aragonite-calcite transformation



is  $\text{Sr/Ca-}\Delta\text{SST} = 1.15 (\pm 0.03)^\circ\text{C}$  ( $r = 0.99$ ,  $p < 0.001$ ,  $n = 21$ ) and  $\delta^{18}\text{O-}\Delta\text{SST} = 0.14 (\pm 0.01)^\circ\text{C}$  ( $r = 0.97$ ,  $p < 0.001$ ,  $n = 21$ ) per percent calcite (Fig. 6a). The smaller shift in  $\delta^{18}\text{O-SST}$  reflects the smaller impact of differences in  $\delta^{18}\text{O}$  between meteoric water, dissolved aragonite and precipitated calcite. The large shift in  $\text{Sr/Ca-SST}$  is due to the  $D_{\text{Sr}}$  of calcite giving much lower  $\text{Sr/Ca}$  relative to aragonite. Thus, calcite diagenesis in the vadose environment will always produce  $\text{Sr/Ca-SST}$  estimates that are warmer than those derived from original coral aragonite, assuming an open system. SSTs estimated from  $\delta^{18}\text{O}$  values may be warmer or colder depending on the  $\delta^{18}\text{O}$  of meteoric water, which is in turn dependent on the  $\delta^{18}\text{O}$  of tropical rainfall, with regional differences in isotopic composition.

To judge the potential impact of vadose-zone diagenesis on coral paleothermometry, we calculated the potential range of values for  $\text{Sr/Ca}$  in vadose-zone calcite (Fig. 6). The range in calculated end-member  $\text{Sr/Ca-}\Delta\text{SST}$  accounts for the range of reported  $D_{\text{Sr}}$ , and for the calculation the initial meteoric water  $\text{Sr/Ca}$  was assumed to be 0.0088, the average  $\text{Sr/Ca}$  of modern corals from Muschu Island. The end-member  $\text{Sr/Ca-}\Delta\text{SST}$  ranges from 130 to 149°C, which is somewhat warmer than the 100% calcite  $\text{Sr/Ca-}\Delta\text{SST}$  of 115°C for the Muschu data. This is most likely due to an underestimate of the  $\text{Sr/Ca}$  for meteoric water in the calculated end member, as the Muschu Island meteoric water may have picked up additional Sr from other carbonate sources in the overlying soil and beach sand. There may also have been some degree of system closure in the corals.

A range of end-member  $\delta^{18}\text{O}$  calcite values was calculated using the maximum  $\delta^{18}\text{O}$  range of  $1\text{‰}_{\text{SMOW}}$  to  $-8\text{‰}_{\text{SMOW}}$  for tropical rainwater (Rozanski et al., 1993) (Fig. 6).  $\delta^{18}\text{O}$  calcite was calculated using the calcite precipitation equation of O'Neil et al. (1969). This gave a  $\delta^{18}\text{O}$  calcite range of  $-0.8\text{‰}$  to  $-9.8\text{‰}$ . The calcite  $\delta^{18}\text{O}$  value for Muschu calcite ( $-8.1\text{‰}$ ) falls near the lower end of this range, which is to be expected given that PNG rainfall is highly depleted in  $^{18}\text{O}$  (Rozanski et al., 1993). This result confirms that the main factor controlling the  $\delta^{18}\text{O}$  of diagenetic calcite at Muschu Island is the  $\delta^{18}\text{O}$  of rainfall. From the range of calculated  $\delta^{18}\text{O}$  calcite values,  $\delta^{18}\text{O-SST}$  values relative to modern Muschu Island coralline aragonite were determined (end-member  $\delta^{18}\text{O-}\Delta\text{SST}$ ). The end-member  $\delta^{18}\text{O-}\Delta\text{SST}$  ranges from  $-23^\circ\text{C}$  to  $21^\circ\text{C}$  (Fig. 6).

The trends in the Muschu data and the calculated end-member values were also compared to those reported in the literature for corals undergoing diagenesis in the vadose zone (Fig. 6b). The literature data are from Huon Peninsula, PNG (Zhu et al., 1988; Zhu, 1990; Stein et al., 1993; Zhu et al., 1994), Florida Keys (Siegel, 1960; Martin et al., 1986) and Nansha Islands, China (Wei et al., 1998). Despite the variety of locations, ages and species of coral examined in the literature studies, alteration of coralline aragonite to calcite always gives lower  $\text{Sr/Ca}$  (warmer SST) and there is minimal variability in the slopes. All literature  $\delta^{18}\text{O-}\Delta\text{SST}$  data show similar results to the Muschu data. These data plot at the upper end of the range defined by the calculated end-member  $\delta^{18}\text{O-}\Delta\text{SST}$ . All the locations of these studies receive isotopically light monsoon rainfall (Rozanski et al., 1993) and the calcite  $\delta^{18}\text{O-}\Delta\text{SST}$ s reflect this.

Based on all the data presented in Figure 6b, the range of

slopes for the change in  $\text{Sr/Ca-SST}$  is 1.1 to  $1.5^\circ\text{C}$  per percent calcite. The range in slopes for the change in  $\delta^{18}\text{O-SST}$  is  $-0.2$  to  $0.2^\circ\text{C}$  per percent calcite, depending on the  $\delta^{18}\text{O}$  of the water from which the calcite is precipitated.  $\text{Sr/Ca-SST}$  is at least five times more sensitive to diagenetic changes than  $\delta^{18}\text{O-SST}$ . The relationship presented for  $\text{Sr/Ca-}\Delta\text{SST}$  per percent calcite can be used to correct  $\text{Sr/Ca-SST}$  paleo-data and, if a precipitation  $\delta^{18}\text{O}$  value for a given location is assumed, the same can be done for  $\delta^{18}\text{O-SST}$ .

Several recent studies (Gagan et al., 1998; Hughen et al., 1999; McCulloch et al., 1999; Tudhope et al., 2001) have reported warmer than present SSTs for Holocene and Last Interglacial corals, based on  $\text{Sr/Ca}$  thermometry (Fig. 7a). These studies have also reported changes in  $\delta^{18}\text{O}$ . To investigate the potential impact of diagenesis on these results, we have assumed a scenario where all the warmer  $\text{Sr/Ca-SST}$ s have resulted from calcite diagenesis rather than actual warming due to climate change. The  $\text{Sr/Ca-}\Delta\text{SST}$ s were converted to an equivalent percent calcite, and, using a two end-member mixing equation, the range of  $\delta^{18}\text{O}$  deviations due to diagenesis was calculated (Fig. 7b). Relative to the observed  $\delta^{18}\text{O}$  data, the diagenetic  $\delta^{18}\text{O}$  deviations are negligible (Fig. 7c). The measured  $\delta^{18}\text{O}$  in fossil corals are too large to be due to diagenesis alone and climate variability is the most likely explanation. Thus, although  $\text{Sr/Ca-SST}$ s may be highly susceptible to diagenetic changes and questions remain over the calculation of mean SSTs from this proxy,  $\delta^{18}\text{O}$  is a robust paleoclimatic tracer not easily affected by calcite diagenesis.

#### 4.4. Diagenesis and Sampling Resolution

One of the goals of coral paleoclimatology is to reconstruct climate on seasonal scales to understand climatic processes. From this viewpoint, the absolute SSTs are often less important than the preservation of detail in the seasonal cycle itself. The data presented thus far show that small amounts of calcite may give erroneous mean SSTs, however it is unclear whether high-resolution (subannual sampling) reconstructions of seasonal cycles from corals with 1 to 2% calcite can also be erroneous.

To explore this issue, we have sampled at near-weekly resolution four annual growth increments from coral FM08, where XRD and thin sections show that two  $\leq 1$  mm diameter patches of calcite are present, and  $\sim 1\%$  calcite is distributed throughout the section. The 1% calcite is distributed as irregular rims around skeletal voids and occasionally replaces the coralline aragonite. Three years of coral growth were analysed for  $\delta^{18}\text{O}$  and  $\text{Sr/Ca}$  at approximately 26 samples per year, and for one year, (HR-year), approximately 52 samples were analysed. The HR-year was chosen for additional analysis due to its close proximity to one of the calcite patches, allowing comparison of geochemical signals from areas of high and low calcite. For the HR-year, the data were averaged to simulate fortnightly and monthly sampling to examine the effect of different sampling resolutions superimposed on low level diagenesis. All data were plotted in terms of SST to assess the impacts of diagenesis on  $\text{Sr/Ca-SST}$  relative to  $\delta^{18}\text{O-SST}$  at high resolutions. Records were calibrated using the SST relationships of Gagan et al. (1998).

The presence of diagenetic calcite in coral FM08 can be seen

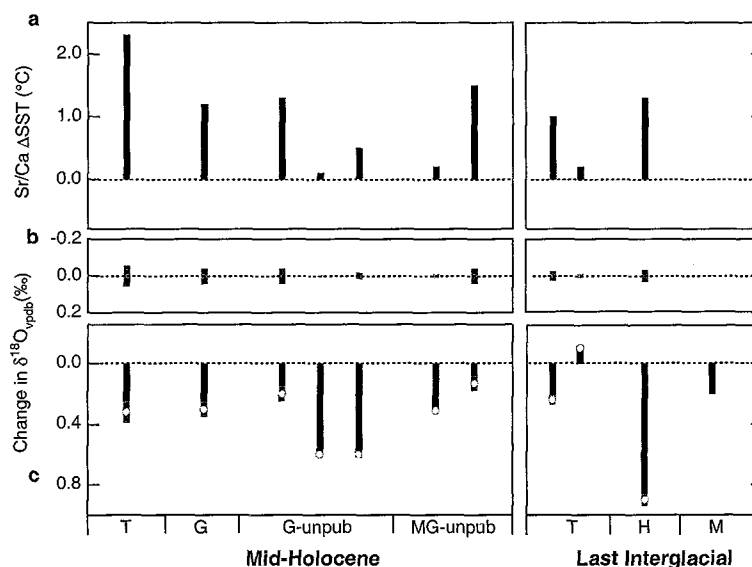


Fig. 7. Impact of diagenesis on coral Sr/Ca ratios and  $\delta^{18}\text{O}$  values reported for mid-Holocene and Last Interglacial corals. T = Tudhope et al. (2001); G = Gagan et al. (1998); G-unpub = Gagan unpublished results; MG-unpub = McGregor unpublished results; H = Hughen et al. (1999); M = McCulloch et al. (1999). (a) Difference in Sr/Ca-SST between modern and fossil corals from the same location, as stated in the studies listed above.  $\Delta\text{SSTs}$  are calculated using the quoted calibrations or, for unpublished results, using the calibration of Gagan et al. (1998). (b)  $\delta^{18}\text{O}$  deviations due to diagenesis, assuming the warming indicated by coral Sr/Ca is due to secondary calcite in the sample. Firstly, from the Sr/Ca- $\Delta\text{SST}$  in panel (a) an equivalent percentage of calcite was calculated, using the mean of the range of end-member Sr/Ca- $\Delta\text{SSTs}$  in Figure 6 ( $1^\circ\text{C}:0.7\%$  calcite). Then a two end-member mixing equation, between modern coral aragonite  $\delta^{18}\text{O}$  values and the calculated end-member  $\delta^{18}\text{O}$  range for secondary calcite ( $0.8\%$  to  $-9.8\%$ ), was used to determine the range of likely  $\delta^{18}\text{O}$  deviations due to diagenesis. (c) Published changes in  $\delta^{18}\text{O}$  relative to modern (black bar with open circle) with effect of diagenesis (from panel b) superimposed (grey shading). The change in  $\delta^{18}\text{O}$  due to diagenesis is significantly less than the changes in coral  $\delta^{18}\text{O}$  reported in the literature.

in the high-resolution  $\delta^{18}\text{O}$  and Sr/Ca-SST records (Fig. 8). The calcite patches are clearly defined in both Sr/Ca-SST and  $\delta^{18}\text{O}$ -SST (Fig. 8a). The magnitude of the change in SST for the Sr/Ca proxy is much greater than that for  $\delta^{18}\text{O}$  and the relative response of the two tracers is similar to that predicted from the calculated end-member values. Seasonal cycles in both Sr/Ca-SST and  $\delta^{18}\text{O}$ -SST are evident, though the uneven contribution of diagenesis to the Sr/Ca signal introduces variability of approximately  $0.5^\circ\text{C}$  relative to the  $\delta^{18}\text{O}$  signal (Fig. 8b). When the high-resolution data are smoothed to monthly resolution the seasonal cycle is preserved in both Sr/Ca-SST and  $\delta^{18}\text{O}$ -SST. Similar results were obtained when every fourth micro-sample was plotted, as opposed to averaging four samples.

The results suggest that meaningful paleoclimate records of the seasonal cycle can still be obtained from corals with low percentages of calcite, given sufficient smoothing of the Sr/Ca-SST signal. However, estimates of mean SSTs from such calcite-affected data will still be in error. Sr/Ca and  $\delta^{18}\text{O}$  analysis of 1 to 2 yr of coral growth at near-weekly resolution may be a good way to reveal significant calcite diagenesis and to estimate the errors in mean SST. An additional crosscheck would be to compare short records from two corals with similar ages.

Many coral paleoclimate studies state that corals have been screened for diagenesis (Guilderson et al., 1994; McCulloch et al., 1996; Esat et al., 1999; Hughen et al., 1999; Woodroffe and Gagan, 2000; Guilderson et al., 2001; Tudhope et al., 2001).

Two in particular (Hughen et al., 1999; Tudhope et al., 2001) cite the preservation of details of the seasonal cycle as evidence for a lack of significant diagenesis. This assumption seems to be valid based on results of this study, which show that at low percentages of calcite seasonal cycles are recorded in the corals.

## 5. CONCLUSIONS

1. Changes in skeletal texture and geochemistry for mid-Holocene corals from raised reefs at Muschu Island, PNG, suggest that calcite diagenesis occurred in the vadose environment following uplift to the high intertidal zone.
2. Sr/Ca in corals decreases dramatically when subject to calcite diagenesis in the vadose zone. In the Muschu Island environment,  $\delta^{18}\text{O}$  also decreased, though, in general, the magnitude and direction of diagenetic changes in coral  $\delta^{18}\text{O}$  will vary regionally as a function of the mean  $\delta^{18}\text{O}$  value of precipitation.  $\delta^{13}\text{C}$  in vadose calcite also tends to be lower than  $\delta^{13}\text{C}$  in coral aragonite and depends on the moles of  $^{13}\text{C}$ -depleted carbon derived from soil-gas  $\text{CO}_2$ .
3. When converted to temperature using published calibration equations, the Sr/Ca and  $\delta^{18}\text{O}$ -SSTs of vadose-zone calcite in the Muschu Island corals gives anomalously warm temperature estimates of  $115$  and  $14^\circ\text{C}$ , respectively. The range of slopes for Sr/Ca- $\Delta\text{SST}$  reported in the literature, and shown in this study, are  $1.1$  to  $1.5^\circ\text{C}$  per percent calcite and are at least five times more sensitive to diagenetic changes

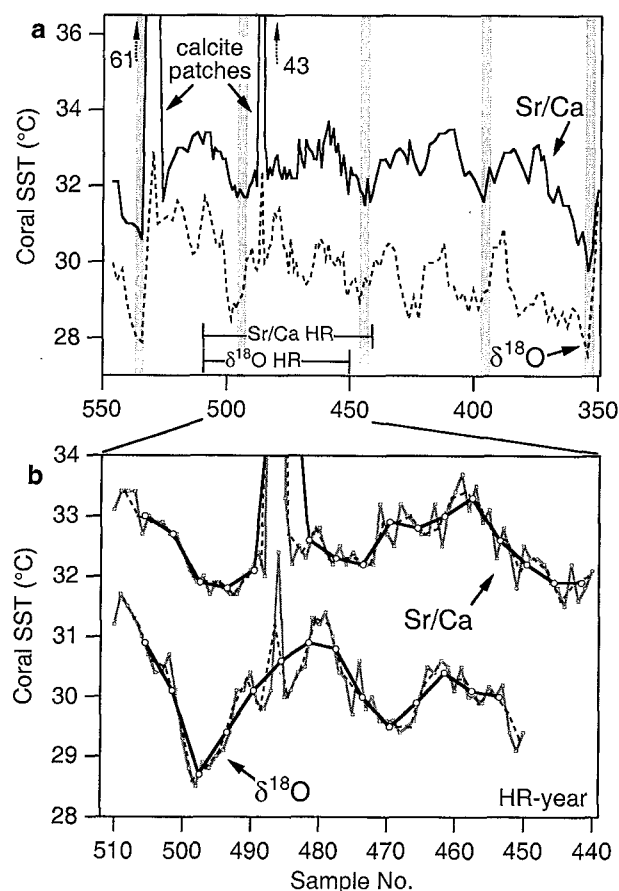


Fig. 8. (a) High resolution Sr/Ca and  $\delta^{18}\text{O}$ -SST data for four growth years from coral FM08 as an estimate of the impact of  $\sim 1\%$  calcite on paleotemperature estimates. Vertical shading marks the start and finish of each year, as defined by X-radiography. Samples were milled at near-weekly resolution and every second sample was analysed. Horizontal bars (marked Sr/Ca HR and  $\delta^{18}\text{O}$  HR) indicate sections where every sample was analysed. (b) Comparison of sampling resolutions for resolving climate signals from  $\delta^{18}\text{O}$  and Sr/Ca-SST data, where calcite is present. From the original near-weekly data (grey line) two and four samples were averaged to simulate fortnightly (dashed line) and monthly sample resolution (black line, open circles), respectively.

than  $\delta^{18}\text{O}$ -SSTs ( $-0.2$  to  $0.2^\circ\text{C}$  per percent calcite). The slope relationships can be used to correct Sr/Ca-SST paleo-data with low percent calcite, and if a site-specific  $\delta^{18}\text{O}$  value for precipitation is assumed, the same can be done for  $\delta^{18}\text{O}$ -SST. The difference in the response of Sr/Ca and  $\delta^{18}\text{O}$  to vadose diagenesis was exploited to show that  $\delta^{18}\text{O}$  signals in corals are robust when subject to small amounts of calcite diagenesis.

4. Sr/Ca and  $\delta^{18}\text{O}$  in corals with low concentrations of secondary calcite can still be used to investigate seasonal and interannual climatic variability, although mean temperature estimates may be erroneous. In addition to detailed XRD and thin-section petrography, analysing Sr/Ca for 1 to 2 yr of coral growth at near-weekly resolution should reveal noise in the record, and the magnitude of potential errors, due to low concentrations of calcite. Checking the reproducibility of climate signals in corals of similar age can also reduce errors in paleoclimate reconstruction.

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