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The effects of early marine aragonite, Mg-calcite and vadose-zone calcite diagenesis on reconstructions of coral calcification rate and the oceanic Suess effect

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Abstract Our observations show that early marine cements, in the form of secondary aragonite or secondary Mg-calcite, and also vadose-zone calcite are commonly precipitated from pore waters at the basal portions of coral skeletons. The focus of this paper is on the implications of the presence of such diagenetic cements on records of calcification rates, which at least for calcite $\delta^{13}\text{C}$, have not previously been explored. If undetected, the presence of these cements could bias the results toward an apparent nonlinear reduction in coral calcification rate towards the present. Both the progressive addition of early diagenetic inorganic aragonite and calcite toward the base of massive corals would produce an apparent decrease in skeletal density towards the present, which for one of our recent corals misleadingly matches the nonlinear twentieth century decrease in coral calcification rate predicted by recent modelling and experimental studies. However, while the effects of both types of cements on calcification rates are similar, their effects on the $\delta^{13}\text{C}$ values of coral skeletons differ. Secondary marine aragonite and Mg-calcite cements are enriched in ^{13}C relative to coral aragonite, resulting in a nonlinear decrease in $\delta^{13}\text{C}$ towards the present that mimics, for one of our 20th century corals, the decrease expected from the oceanic Suess effect. In contrast, the vadose-zone calcite shows a wide range of depleted $\delta^{13}\text{C}$ values. These values would either obscure or reduce the magnitude of the oceanic Suess effect recorded in the coral. The isotopic composition of the vadose-zone calcite is strongly dependant on local environmental conditions, which further complicates the interpretation of $\delta^{13}\text{C}$ records from coral cores with this type of diagenesis.

Keywords carbonate saturation state, coral calcification rate, reef growth, surface-ocean $^{13}\text{C}/^{12}\text{C}$, massive coral, early marine diagenesis, vadose-zone diagenesis, oceanic Suess effect

Introduction

Multi-century records of skeletal calcification rates and $\delta^{13}\text{C}$ values extracted from massive corals have the potential to reconstruct the progressive effect of anthropogenic changes in carbonate saturation state, and CO_2 storage of the ocean, on coral reefs. Although studies of calcification parameters in massive coral skeletons have provided evidence for changes in coral reef growth over the past few centuries, some of the findings are still controversial; have rates of coral calcification already declined, and will they further decline, in response to the 20th century build-up of atmospheric CO_2 (Gattuso et al. 1999, Kleypas et al. 1999, Langdon et al. 2000, Leclercq et al. 2000, Marubini et al. 2001), and will any decline be countered by global ocean warming, leading to an increase in coral calcification rates (McNeil et al. 2004)?

A composite record from 35 *Porites* sp. coral cores from the Australian Great Barrier Reef showed a significant decline in skeletal density and calcification rates over the period 1934-1982 (Lough and Barnes 1997) and would confirm the results of some of the above modelling and experimental studies, which have suggested that calcification rates have declined (Gattuso et al. 1999, Kleypas et al. 1999, Langdon et al. 2000, Leclercq et al. 2000, Marubini et al. 2001). Analyses of several multi-century coral cores from the Great Barrier Reef, however, shows a significant increase in calcification rates in the late 20th century relative to the previous two centuries (Lough and Barnes 2000). Analysis of a long coral core from French Polynesia also shows increased calcification rates through time (Bessat and Buiges 2001). Both of these studies attributed the rise in calcification rates to increased seawater temperatures. In contrast, a recent study of coral calcification trends, based on density measurements, suggested that declining density and calcification trends may be caused by early marine diagenesis rather than a response to a change in the carbonate saturation state of the surface ocean (Müller et al. 2004).

The combustion of fossil fuels, deforestation, and the reduction of soil carbon reservoirs releases CO₂ with δ¹³C values ~20% lower than the δ¹³C of atmospheric CO₂ (Quay et al. 1992). Following the industrial revolution, the δ¹³C of atmospheric CO₂ decreased, and this trend is called the "Suess effect". The Suess effect results in changes in the δ¹³C of dissolved inorganic carbon (DIC) in the surface-ocean, due to the air-sea equilibration of CO₂ (Gruber et al. 1999). This equilibration and the resulting decrease in δ¹³C values of the surface ocean DIC have been recorded by corals (Nozaki et al. 1978, Druffel and Griffin 1999). The study by Müller et al. (2004) showed, however, that the trend in the δ¹³C of their coral was not necessarily related to the oceanic Suess effect but was a result of secondary aragonite precipitation during early marine diagenesis.

Recent studies have investigated the distortion of coral paleo-environmental signals by a variety of diagenetic processes (McGregor and Gagan 2003, Müller et al. 2004). McGregor and Gagan (2003) found that sub-aerially exposed fossil coral from Papua New Guinea (PNG) were affected by vadose-zone calcite diagenesis (the vadose zone is the zone above the watertable not permanently saturated with water). The vadose-zone calcite altered the coral δ¹³C values and would also affect density and calcification measurements (McGregor and Gagan 2003). Sub-aerially exposed fossil corals, traditionally used to quantify climate change during the Holocene and Pleistocene (Tudhope et al. 2001, Cobb et al. 2003, Woodroffe et al. 2003, McGregor and Gagan 2004, Gagan et al. 2004), could also potentially be used to examine calcification changes over longer periods than is possible with multi-century corals. Thus diagenesis, occurring in a variety of settings, is potentially a major source of error in reconstructions of calcification rates and the oceanic Suess effect, and it is essential that the impact of diagenesis on records of calcification rates and δ¹³C values be investigated.

In this paper, we compare the diagenetic effects in corals from a range of different environmental settings to explore the variability of diagenetically induced changes in density, calcification rates and δ¹³C values, and what apparent trends in global change could be derived. We compare records of coral calcification rates, derived from skeletal density and extension rate, and δ¹³C values for a well-preserved (pristine) coral and a coral containing secondary marine aragonite at its base. These coral cores came from Ningaloo Reef Marine Park, Western Australia and span the period from ~1840 to 1994 AD. In addition, we also discuss the likely impact of secondary vadose-zone calcite precipitation using results from two diagenetically altered *Porites* sp. fossil corals collected from two different locations on Muschu Island, PNG. Our results show that diagenesis, regardless of type, can produce artifacts in calcification rates and δ¹³C values. We compare the nature of the artifacts produced and the implications for interpreting multi-century coral records of calcification rates and the Suess effect.

Methods

By combining a number of methods we were able to rigorously establish the evidence of the importance of early diagenesis in coral skeletons for paleoceanographic and paleoclimatic reconstructions. We drilled two cores from live coral colonies at two different locations in Ningaloo Reef Marine Park, Western Australia, where one showed evidence of diagenetic alteration whereas the other one did not. One was located in Tantabiddi Lagoon (21°54.3'S, 113°57.9'E) and the other off South Muiron Island (21°41.9'S, 114°18.8'E), and the distance between the two cores within the same reef was less than 50 km (Fig. 1A). Vadose-zone calcite was investigated in two fossil *Porites* sp. corals drilled from uplifted reefs at Rebiew (FM19) and Morock (FM08) Bays, Muschu Island, PNG (03°25'S 143°35'E; Fig. 1B).

The coral cores were all sawn to remove one 6-7 mm thick slice from each core. On the Ningaloo cores, density was measured directly on these coral slices using gamma-ray densitometry (Chalker and Barnes 1990). Using X-ray prints, gamma densitometry data and UV fluorescence light, peaks in density defining annual growth increments were successively counted backwards from the outermost (youngest) peak. The following time series were obtained from the density measurements for each core: (1) mean annual density (g cm⁻³); (2) annual extension rate (cm yr⁻¹) as the distance between high-density peaks; and (3) annual calcification rate as the product of mean annual density and annual extension rate (g cm⁻² yr⁻¹).

All coral slices were ultrasonically cleaned before sample collection. Samples were then collected for stable isotope geochemistry and XRD along the growth axis from the slices, along transects from pristine to altered skeleton. While the transition from pristine to altered coral skeleton with secondary aragonite precipitates was not visible in hand specimen and with X-radioigraphy in the Ningaloo coral, the transition from aragonite to calcite was clearly observed in hand specimen and with X-radiography (Fig. 2A) in the PNG coral. While these PNG corals may show relatively extreme levels of vadose-zone diagenesis, they were chosen on purpose so as to quantify the changes in δ¹³C due to vadose-zone diagenesis, and thus avoid any ambiguity associated with XRD detection limits. Petrographic thin sections were prepared from areas as close as possible to the sampling sites. This strategy allowed geochemical and 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 transects.

X-ray diffraction was carried out to detect any secondary calcite or Mg-calcite. The Ningaloo corals were analysed with a Siemens D501 diffractor, using Cu Kα radiation (40 kV, 40 mA), equipped with a curved graphite monochromator and a scintillation detector. The diffraction data were recorded over a range of 20° to 70° 2θ using a step width of 0.02 degrees per minute at a scan speed of 0.5° per minute. The detection limit was 1%. The PNG corals were analysed on a Sietronics

Diffractometer with the Cobalt X-ray tube on 90% loading (30 mA, 50 mV) and scanned from 2θ of 20° to 60° . The percent aragonite and calcite in each sample was estimated using SIROQUANT v.2.5 software. Errors on estimates of percent calcite are ~2%.

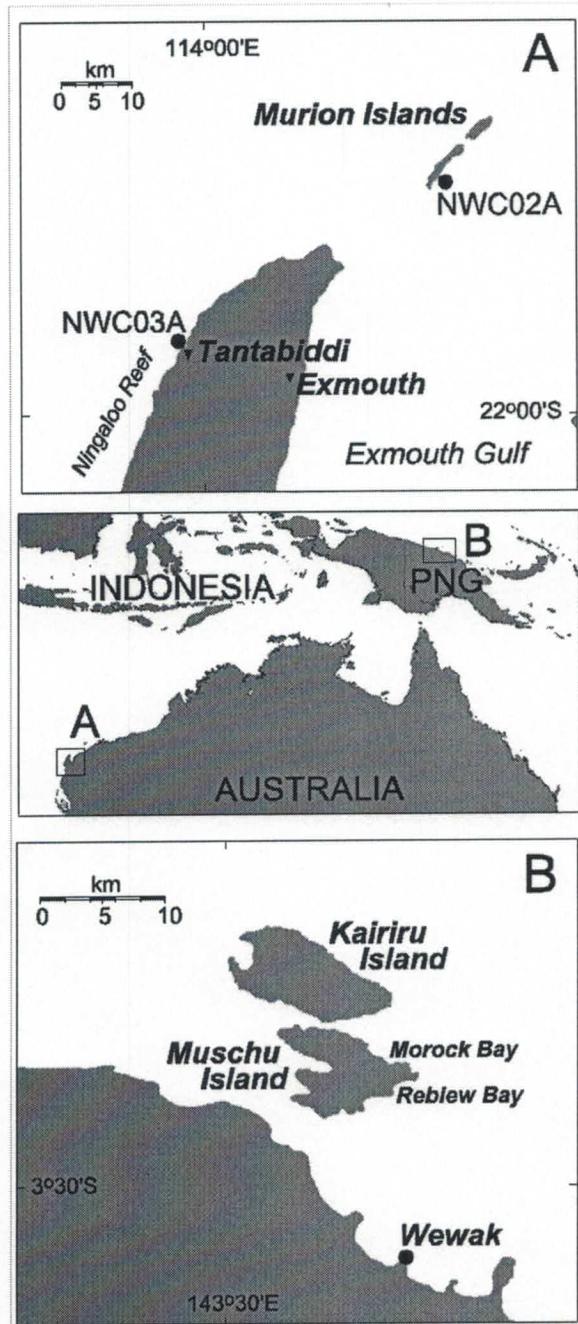


Fig. 1. Location of coral study sites (A) Tantabiddi and South Muiron Island, in Ningaloo Reef Marine Park, Western Australia, (B) Morock Bay (coral FM08) and Rebiew Bay (coral FM19), Muschu Island, Papua New Guinea.

Surfaces of the Ningaloo coral slabs were cleaned before sampling by removing 1 mm deep by 2 mm wide grooves cut continuously along the maximum growth axis. Five-year increments 2 mm wide and 2 mm deep were then milled within this groove using a 2 mm diameter end-mill bit rotating at 170 RPM. Aliquots of 150- μg of coral powder were analysed, some in duplicate, for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. For the PNG corals, $200 \pm 20 \mu\text{g}$ aliquots were taken from the same powders as used for the XRD measurements and analysed for stable isotopes. All samples were initially dissolved in 105% H_3PO_4 at 90°C in an automated carbonate (Kiel) device, coupled with a Finnigan-MAT 251 mass spectrometer. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values were calculated as per mil (‰) deviations relative to the Vienna PeeDee belemnite (VPDB), and were calibrated via the NBS-19 ($\delta^{18}\text{O} = -2.20\text{\textperthousand}$, $\delta^{13}\text{C} = 1.95\text{\textperthousand}$) and NBS 18 ($\delta^{18}\text{O} = -23.00\text{\textperthousand}$, $\delta^{13}\text{C} = -5.00\text{\textperthousand}$) standards. Average reproducibility for duplicate Ningaloo samples was $\pm 0.04\text{\textperthousand}$ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (2σ , $n=14$). The PNG coral samples were measured in duplicate, with average standard errors of $0.02\text{\textperthousand}$ for FM08 and $0.07\text{\textperthousand}$ for FM19.

Results and Discussion

Thin Section Observations of Diagenesis

Petrographic investigation showed that the secondary aragonite in the Ningaloo coral NWC02A (South Muiron Island) could be recognised by the changes that occurred throughout the altered core, from pristine skeleton at the top to altered skeleton and secondary precipitation at the base (Fig. 2B). Abundant secondary aragonite fibres were observed in skeletal pores exposed in thin section. These aragonite needles filled the skeletal pores almost completely in some areas near the base of the core, where the secondary aragonite accounted for ~30% of the total aragonite (primary and secondary aragonite). Secondary aragonite could not be seen in core NWC03A (Tantabiddi; Fig. 2C).

Petrographic observations clearly showed the secondary vadose-zone calcite was present in the PNG corals. In thin section the dark patches observed in X-ray (Fig. 2A) were identified as large single crystal calcite spar (Fig. 2D). The FM08 coral XRD sample that included one of the calcite patches indicated that the area contained 40% calcite. Further increases in percent calcite correspond with more void-filling by secondary calcite spar and with neomorphic replacement of the coral skeletal material. In thin section, areas containing 3-5% calcite (close to the XRD detection limits), were characterised by early leaching and void-filling calcite rims of ~0.1mm thick (Fig. 2E). This low level of calcite can be difficult to detect in hand specimen. Pristine aragonite located away from the diagenetic areas appeared similar to the pristine aragonite in the unaltered Ningaloo coral (Fig. 2B).

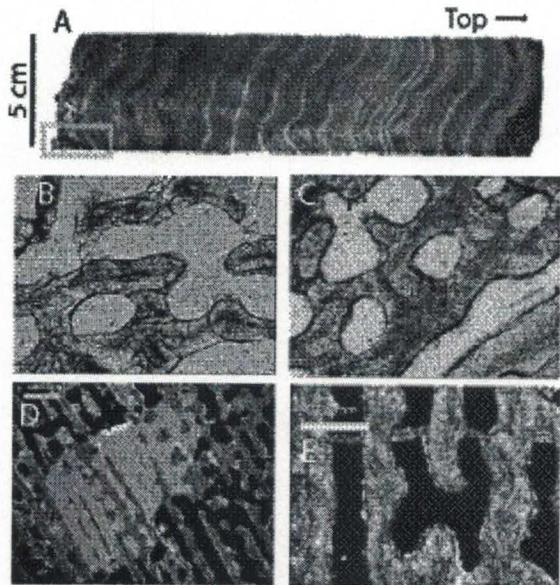


Fig. 2. X-ray and microscopic images of PNG and Ningaloo corals. (A) X-ray positive of PNG coral FM08. Light and dark couplets represent low and high density banding respectively. Dark patches (1-3 mm) at the right margin of the image are secondary single calcite spar. The grey box indicates the sampling location for this coral. (B) Plain polarized light thin section image of pristine coral skeleton of core NWC03A from Tantabiddi. (C) Plain polarized light thin section image of secondary aragonite rims on primary coralline material, indicating diagenetically altered coral skeleton in basal part of core NWC02A from South Muiron Island. (D) Cross polarized light thin section image of secondary single crystal calcite spar found in the diagenetically altered PNG corals. (E) Cross polarized light thin section image of secondary calcite rims precipitated on original coral aragonite. The secondary calcite textures in images D and E are characteristic of vadose-zone diagenesis. Images B and C are from Müller et al. (2004).

Skeletal Density and Calcification Rates

We find the pristine coral density record from Ningaloo Reef shows no significant trend in skeletal density for the period from ~1840 to 1994. In contrast, progressive addition of early marine inorganic aragonite toward the base of the altered Ningaloo coral produces an ~25% decrease in skeletal density towards the present over the same period. We derived the above decrease of ~25% by comparing the density at the altered base with that of the pristine top of the altered core (Fig. 3).

The decreased density in the altered Ningaloo coral record misleadingly matches the 20th century decrease in calcification rates predicted by recent modelling and experimental studies (Fig. 4). The slope of the trend in the altered coral agrees most closely with the experimental study of Langdon et al. (2000), who suggest a decline in coral reef calcification of ~40% between 1880 and 2065 A.D. Consequently, the results

of this study demonstrate that a long-term decline in skeletal calcification rate over the life of a coral colony may be purely an artifact of early marine diagenesis in the older part of the coral skeleton.

Similar trends in density may also be produced by the addition of secondary calcite, precipitated in either a marine environment (Mg-calcite) or in a vadose-zone setting (calcite), to the basal parts of the coral skeleton. Calcite has almost the same density as aragonite (2.71 cf 2.93 g cm⁻³), and thus the addition of similar amounts of secondary calcite as for the altered Ningaloo Reef coral would produce the same artificial density increase towards the present. This can also be seen qualitatively in the X-ray of coral FM08 (Fig. 2A), where the calcite appears as darker (and therefore higher density) patches in the coral X-ray positive.

Diagenesis and $\delta^{13}\text{C}$ Values in Recent and Fossil Corals

Clearly, while not all changes in carbon isotopes are caused by diagenesis, we have found evidence that many of them are, and that this aspects needs to be taken into account when interpreting coral $\delta^{13}\text{C}$ records. Inorganic aragonite is enriched in ^{13}C , relative to coral aragonite. The $\delta^{13}\text{C}$ results from our altered Ningaloo Reef coral show this enrichment in the basal sections, where secondary aragonite has been added to the skeleton (Fig. 5). Over the length of the coral, the $\delta^{13}\text{C}$ results show a 1.6‰ decrease in $\delta^{13}\text{C}$ toward the present (Fig. 5). In addition, two Holocene-aged fossil corals from PNG, FM08 and FM19 collected from within the vadose zone, were analysed for $\delta^{13}\text{C}$ along transects from 100% coralline aragonite to 100% vadose-zone calcite. The vadose-zone calcite produced generally lower $\delta^{13}\text{C}$ than coralline aragonite (Fig. 6). An important finding of our study is that the $\delta^{13}\text{C}$ of the vadose-zone calcite varied strongly in magnitude, ranging from -2.5 to -10.4 ‰ for FM08 and FM19, respectively. Pristine fossil and modern corals from PNG have $\delta^{13}\text{C}$ ranging from 0.02 to -1.55‰.

The decrease in the altered Ningaloo coral $\delta^{13}\text{C}$ mimics the decrease in $\delta^{13}\text{C}$ expected from the oceanic Suess effect (Fig. 5). While this shift is twice as large as that expected in the subtropical surface ocean (~0.8‰, Gruber et al. 1999), the trend is similar to that observed for the $\delta^{13}\text{C}$ of atmospheric CO₂. Taken together, the diagenetic changes in skeletal density, calcification rate and $\delta^{13}\text{C}$ values seen in the Ningaloo Reef coral could be misinterpreted to reflect changes in surface-ocean aragonite saturation state driven by the 20th century build-up of atmospheric CO₂. It is also important to note that the $\delta^{13}\text{C}$ in the pristine coral from Ningaloo Reef does not show any change over time and thus does not show the expected response in $\delta^{13}\text{C}$ to the oceanic Suess effect. This suggests that at some coral sites local environmental factors can be dominant over the global oceanic Suess effect.

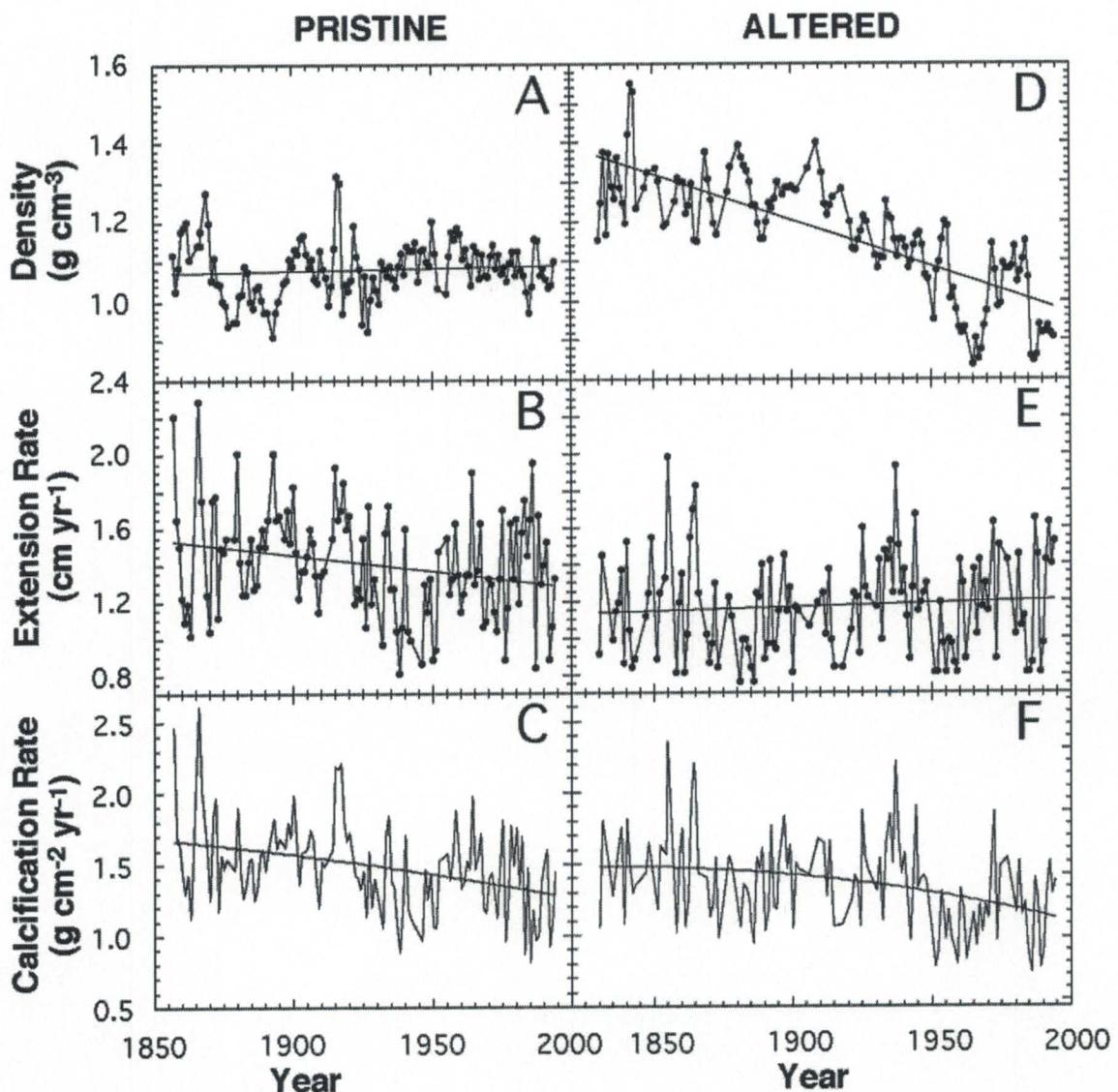


Fig. 3. Average annual skeletal density, linear extension rates and calcification rates for pristine coral from Tantabiddi (left-hand plots) and diagenetically altered coral from South Muiron Island (right-hand plots), Ningaloo Reef. Linear regression lines are given for each series of the mean annual density and extension rates. Second order polynomial fit curves are given for each of the calcification rate series. The record of mean annual density for pristine coral NWC03A remained relatively constant at $\sim 1.1 \text{ g cm}^{-3}$ (A). In contrast, the mean annual density for the altered coral NWC02A was $\sim 1.3 \text{ g cm}^{-3}$ from 1830-1910 AD, where secondary aragonite filled pores in the coral skeleton. The effect of this infilling was to produce a significant decrease in skeletal density toward the top of the core (D). Pristine coral NWC03A showed a decline in extension rate from $\sim 1.5 \text{ cm yr}^{-1}$ to $\sim 1.3 \text{ cm yr}^{-1}$ toward the present (B), whereas extension rates in the altered coral were slightly slower and relatively constant at $\sim 1.2 \text{ cm yr}^{-1}$ (E). Since calcification rate is a product of mean density and linear extension rate, trends of decreasing calcification rates toward the present occurred in both coral cores (C, F). Images from Müller et al. (2004).

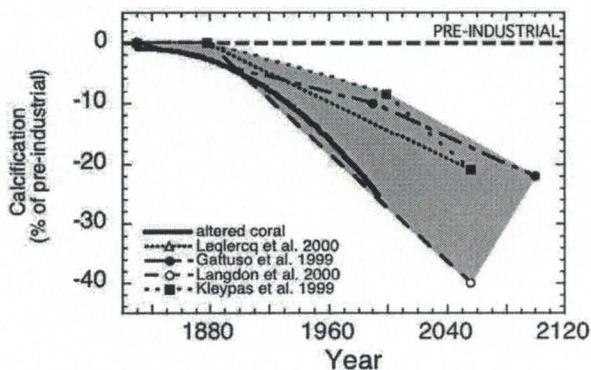


Fig. 4. Second order polynomial curve fit for calcification rates expressed as % decrease after 1880 of pre-industrial values for the diagenetically altered coral from Ningaloo Reef (Müller et al. 2004). The mean value for calcification rate for the diagenetically altered coral before 1880 ($1.50 \text{ g.cm}^{-2}.\text{yr}^{-1}$ for 1830-1879) is used as an estimate of 'pre-industrial' calcification rate (i.e. 100%). Also shown are experimental and modelling estimates of decline in coral calcification due to projected changes in ocean aragonite saturation state from Gattuso et al. (1999), Kleypas et al. (1999), Leclercq et al. (2000) and Langdon et al. (2000).

Although the diagenesis in the PNG corals was located in the midsections of the coral cores, we have also observed fossil corals with the majority of the secondary vadose-zone calcite occurring in the basal sections of the coral. Thus, based on our PNG coral $\delta^{13}\text{C}$ records, vadose-zone calcite, added to the base of a coral, would produce a positive $\delta^{13}\text{C}$ trend towards the present (Fig. 5). This is opposite to the $\delta^{13}\text{C}$ trend produced by secondary aragonite in the Ningaloo Reef coral. For an equivalent amount of secondary material to the Ningaloo Reef coral, the vadose-zone calcite could give changes of $\delta^{13}\text{C}$ between 1840 and 1994 of 0.3‰ to 2.6‰, depending on $\delta^{13}\text{C}$ of the vadose-zone calcite (Fig. 5). Variability in $\delta^{13}\text{C}$ of vadose-zone calcite, both in our PNG corals and in general, reflects the degree of soil formation in the vadose environment. This is because soil CO_2 contributes ^{13}C -depleted carbon to the meteoric waters from which the vadose-zone calcite is precipitated, and the precipitating fluid in turn, is the primary controller of the calcite $\delta^{13}\text{C}$ (Gross 1964, Allan and Matthews 1982). For example, fossil coral FM19 comes from a more vegetated site, with a soil horizon above the corals, giving low $\delta^{13}\text{C}$ calcite values. In contrast, FM08 was exposed from beneath beach sand, thus percolating waters would dissolve very little soil-gas CO_2 and $\delta^{13}\text{C}$ should show minimal changes from coralline aragonite.

The positive $\delta^{13}\text{C}$ trends towards the present, produced by the addition of vadose-zone calcite, would contradict the theory that the oceanic Suess effect is recorded in coral skeletons. Furthermore, the effect of the addition of vadose-zone calcite is far less predictable

than the addition of secondary aragonite, potentially introducing further sources of error into the 20th century coral calcification debate. Moreover, the effects of secondary aragonite and vadose-zone calcite are unlikely to cancel each other out since these forms of diagenetic material form in vastly different environments.

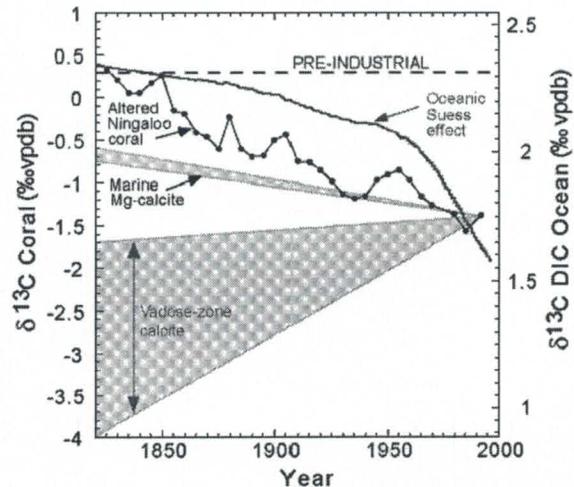


Fig. 5. Annual average $\delta^{13}\text{C}$ values for the diagenetically altered coral from Ningaloo Reef (solid line with dots) compared with $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) caused by the Suess effect for the surface ocean (Gruber et al. 1999) and pre-industrial (dashed line). Thin shaded area shows the predicted impact of the addition of 25% marine Mg-calcite, rather than aragonite, to the base of the Ningaloo Reef coral, and takes into account changes in ^{13}C fractionation with Mg content (Deines 2004). Thick shaded area shows the impact of 25% vadose-zone calcite on $\delta^{13}\text{C}$, if the calcite is added to the base of the Ningaloo Reef coral. The values are calculated using regression equations based on $\delta^{13}\text{C}$ versus % calcite along transects from calcite to aragonite in Muschu Island corals FM08 and FM19. The FM08 $\delta^{13}\text{C}$ regression is $\delta^{13}\text{C} = -1.3(\pm 0.2) - [0.012(\pm 0.007) \times \% \text{ calcite}]$. The FM19 $\delta^{13}\text{C}$ regression is $\delta^{13}\text{C} = -0.1(\pm 0.3) - [0.103(\pm 0.007) \times \% \text{ calcite}]$ (cf Fig. 6). The impact of vadose-zone calcite is presented as a shaded area to show that vadose-zone calcite $\delta^{13}\text{C}$ calcite can have a wide range of values reflecting the variability of $\delta^{13}\text{C}$ of vadose-zone waters.

It is worth noting however, that secondary marine Mg-calcite is often precipitated along with secondary aragonite during early marine diagenesis (Longman 1980). Indeed, secondary marine Mg-calcite has been reported in a number of modern corals (Houck et al. 1975, MacIntyre and Towe 1975, Naqvi 1994). Like secondary marine aragonite, secondary marine Mg-calcite precipitated in equilibrium with seawater is enriched in ^{13}C relative to pristine coral aragonite (Aharon 1991, Deines 2004), though the enrichment is not to the same extent as for secondary aragonite. The ^{13}C enrichment of secondary marine Mg-calcite however,

is in contrast to the $\delta^{13}\text{C}$ depletion of vadose-zone calcite. If 25% marine Mg-calcite were precipitated at the base of the altered Ningaloo coral (instead of secondary aragonite), then the $\delta^{13}\text{C}$ would still show a decrease towards the present ($\sim 0.7\text{\textperthousand}$), which is very close to the $\sim 0.8\text{\textperthousand}$ decrease expected for the subtropical surface ocean (Gruber et al. 1999). Overall, secondary calcite (Mg or otherwise), of whatever origin, can induce positive or negative trends in coral $\delta^{13}\text{C}$.

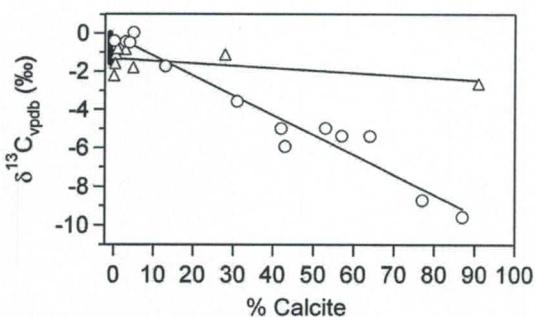


Fig. 6. Comparison of $\delta^{13}\text{C}$ in coral FM08 (triangles) and coral FM19 (circles). Solid lines show least-squares regressions for FM08 and FM19. The FM08 $\delta^{13}\text{C}$ regression is $\delta^{13}\text{C} = -1.3(\pm 0.2) - [0.012(\pm 0.007) \times \% \text{ calcite}]$. The FM19 $\delta^{13}\text{C}$ regression is $\delta^{13}\text{C} = -0.1(\pm 0.3) - [0.103(\pm 0.007) \times \% \text{ calcite}]$. Vertical black bar shows the range of values for pristine modern and fossil coral aragonite samples from PNG. Regression lines give 100% calcite $\delta^{13}\text{C}$ values of $-2.5 \pm 0.6\text{\textperthousand}$ for FM08 and a much lower value of $-10.4 \pm 0.5\text{\textperthousand}$ for FM19.

Conclusions

Both secondary aragonite and calcite added to coral skeletons in the marine and vadose-zone environments cause apparent decreasing trends in skeletal density and calcification rate. While the trends for density are similar for both types of cements, the trends for $\delta^{13}\text{C}$ show considerable variability. Both secondary aragonite and Mg-calcite formed in the marine zone are enriched in ^{13}C relative to pristine coral aragonite, though the enrichment for the Mg-calcite is not to the same extent as for secondary aragonite. Both types of cements would result in a decrease in $\delta^{13}\text{C}$ values towards the present. This trend would mimic the oceanic Suess effect and appear to reflect the changes in the $\delta^{13}\text{C}$ of the DIC of the surface ocean. In contrast to the above two cements, secondary calcite formed in the vadose zone is depleted in ^{13}C which results in an apparent increase in $\delta^{13}\text{C}$ values of the coral skeleton towards the present. Thus, the presence of vadose-zone calcite would obscure the oceanic Suess effect or, in case of minor diagenesis, considerably change its magnitude in the coral record. The interpretation is further complicated by the fact that vadose-zone secondary calcite shows a wide range of $\delta^{13}\text{C}$ values, depending on the fluids it precipitated from. Clearly, in the case of the latter cement, environmental

settings play a major role as the $\delta^{13}\text{C}$ of the original fluids are strongly influenced by land-sea interaction in the coastal zone. Overall, our results show that diagenesis, of both marine and vadose-zone origins, has the potential to produce artifacts in coral $\delta^{13}\text{C}$, and care should be taken to ensure that only coral records free of such alteration are used for interpreting 20th century changes in coral calcification rates and $\delta^{13}\text{C}$ values.

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