An assessment of an environmental gradient using coral geochemical records, Whitsunday Islands, Great Barrier Reef, Australia

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Great Barrier Reef

Water quality gradient

Abstract

Coral cores were collected along an environmental and water quality gradient through the Whitsunday Island group, Great Barrier Reef (Australia), for trace element and stable isotope analysis. The primary aim of the study was to examine if this gradient could be detected in coral records and, if so, whether the gradient has changed over time with changing land use in the adjacent river catchments. Y/Ca was the trace element ratio which varied spatially across the gradient, with concentrations progressively decreasing away from the river mouths. The Ba/Ca and Y/Ca ratios were the only indicators of change in the gradient through time, increasing shortly after European settlement. The Mn/Ca ratio responded to local disturbance related to the construction of tourism infrastructure. Nitrogen isotope ratios showed no apparent trend over time. This study highlights the importance of site selection when using coral records to record regional environmental signals.

1. Introduction

A distinctive environmental and water quality gradient exists through the Whitsunday Island group of the Great Barrier Reef (GBR, Australia) where clear changes in several water quality parameters and biological assemblages have been measured (van Woensel et al., 1999; Udy et al., 2005; Cooper et al., 2007). It has been postulated that this gradient has been exacerbated by increased sediment and nutrient loads delivered from adjacent river catchments as a result of the establishment and expansion of the grazing and cropping industries in the region (van Woensel et al., 1999). In the broader context of the GBR, coral geochemical proxy records have been used to establish the presence of cross-shelf gradients (e.g. Albright et al., 2003; Fallon et al., 2003; Wyndham et al., 2004; Jupiter et al., 2008) and to quantify increased terrestrial influences since catchment clearing and land use change following European settlement (McCulloch et al., 2003; Lewis et al., 2007). However, no study has previously exploited coral core records in the Whitsunday Islands to examine the environmental and water quality gradient and possible changes over time. In addition, the collection of multiple coral cores from a number of sites across this gradient provides a means to assess the reproducibility of coral geochemical records as recorders of both local and regional environmental signals.

The Whitsunday Islands environmental and water quality gradient (see van Woensel et al., 1999; Udy et al., 2005; Cooper et al., 2007) reflects increasing distance from the river mouths of the Proserpine and O'Connell Rivers (Table 1). It is characterised by decreasing concentrations of chlorophyll a, water column suspended sediment and nutrient concentrations and increases in water irradiance depth (optimal and Secchi depth) and carbonate contents of benthic sediments (van Woensel et al., 1999; Cooper et al., 2007). This gradient has also been linked to changes in species assemblages of macroalgae, coral and benthic foraminifera as well as changes in coral morphology and photophysiology (van Woensel et al., 1999; Uthicke and Nobes, 2008; Cooper and Ulstrup, 2009), van Woensel et al. (1999) noted that some reefs (Calf Island and Pine Island) along this gradient had ‘recently’ lost their reef building capacity which was interpreted as a sign of anthropogenic impact. However, other researchers noted that many inshore fringing reefs of the wider GBR stopped accreting vertically and/or laterally well before (i.e. last 3000 years) the influence of European settlement (c. 1860), which they attributed to a lack of suitable
accommodation space for continued reef growth (Smithers et al., 2006; Perry and Smithers, 2010).

Geochemical proxy records from coral cores can provide robust indicators of changing river loads of sediments and nutrients as a result of land use change in catchments (e.g. McCulloch et al., 2003; Lewis et al., 2007; Jupiter et al., 2008). Trace element (barium – Ba, manganese – Mn, yttrium – Y) to calcium (Ca) ratios measured in coral cores provide proxies of changing sediment loads delivered to the marine environment (e.g. McCulloch et al., 2003; Fleitmann et al., 2007; Lewis et al., 2007). Barium desorbs from suspended sediments in the low salinity area of the flood plume and is then transported in the dissolved phase and substituted for Ca into the coral lattice (Sinclair and McCulloch, 2004). The $^{15}$N of coral organic material provides a record of changing nutrient fluxes to the ocean (Marion et al., 2005; Jupiter et al., 2008). However, the integrity of some of these coral proxies has been questioned as they may record other environmental influences such as upwelling, biological activity (i.e. phytoplankton and Trichodesmium outbreaks), ground-water seeps, trace metal release from mangrove reservoirs, sediment resuspension and changes in sea surface temperature (Alibert et al., 2003; Sinclair, 2005; Prouty et al., 2010).

In this study, we collected a series of coral cores from Porites colonies at eight sites across the environmental and water quality gradient of the Whitsunday Island group. These cores contained growth records spanning at least 20–30 years with three cores containing growth records of >70 years (i.e. prior to the large increase in fertiliser use in the catchment) and one of these longer cores covers the period 1820–1992 (i.e. prior to European settlement c. 1860). We show that the trace elements and isotopic proxies all record different environmental influences both locally and regionally and highlight possible changes in the gradient during the 1860s. Finally, we discuss the validity of each coral proxy as a reliable recorder of environmental change and suggest a more optimal approach in the selection of corals for geochemical analysis.

### 2. Study sites and methods

#### 2.1. Study site description

The two major rivers which regularly influence the coral reefs of the Whitsunday Island group are the Proserpine and O’Connell Rivers. The catchments of these rivers were settled by Europeans in the early 1900s before sugarcane production became the dominant industry (McClements, 1973; Kerr, 1997). Nitrogen fertilisers were used in croplands of the Proserpine and O’Connell River catchments from as early as the 1910s but, in particular, fertiliser use increased over fourfold between 1960 and 1990 (Pulsford, 1996). Other rivers that occasionally influence this region include the Pioneer River to the south and the Burdekin River to the north (Fig. 1). More localised influences on the coral reefs of the Whitsunday Island group include the introduction of grazing animals (sheep, goats and pigs) on certain islands (mainly from the 1880s to 1930s) as well as the development of tourism infrastructure on some islands (largely since the 1950s, Blackwood, 1997). The discharge of sewage may also have some localised impacts in the region such as in Pioneer Bay (see Costanzo et al., 2000). Small coastal streams discharge directly into Whitsunday Passage and may influence local areas.

#### 2.2. Coral collection and preparation

Ten short (~0.36–0.52 m) and 3 long (1.0–1.9 m) coral cores were collected from eight sites along the environmental and water quality gradient in the Mackay Whitsunday region (Figs. 1 and 2, Table 2). All replicated coral cores from individual sites were collected in close proximity to each other (within 100 m). In addition we used a long coral core collected in 1992 from AIMS’ Coral Core Archive (CID-01A). Large, massive Porites sp. coral colonies (>1 m diameter) were sampled at each site using a drill powered by either surface-supply air tanks (short cores) or by a generator-powered corer (long cores). These cores were slabsbed into approximately 7 mm thick slices, washed in freshwater and air-dried at the Australian Institute of Marine Science (AIMS) before being X-rayed. The coral slices were further cut into ~9.5 cm length, ~2.5 cm width and 0.7 cm thick blocks along the major growth axis of the coral. These blocks were then ultrasonically cleaned in mini-Q water and oven dried at 40 °C in preparation for Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS) analysis.

#### 2.3. Coral geochemical analysis

The LA-ICPMS analytical methods were identical to those reported in Jupiter et al. (2008). Briefly, the coral blocks were mounted on a stage containing standards and analysed using a Varian 820 inductively coupled mass spectrometer. The resultant data were then normalised to $^{40}$Ca using a Varian Laser Scanning analysis software program developed at the Australian National University (ANU)’s Research School of Earth Sciences (by L. Kinsley). Data were then smoothed using a 10 point running mean to reduce the influence of outliers, followed further by a 10 point mean to reduce data volume (Jupiter et al., 2008). Replicate tracks were performed on selected coral slices to confirm that features of the trace element record represented true incorporation into the coral skeleton and were not a result of surface contamination.

A reliable technique to measure the nitrogen isotopic composition of the insoluble organic fraction of the coral skeleton was developed by Marion (2007; see also Marion et al., 2005; Jupiter et al., 2008). Two coral core slices from CID Harbour Island (CID-01A and CID-71B) with a combined growth record from 1820 to 2006 were sampled at three year intervals. These samples were ultrasonically cleaned in mini-Q water and oven dried at 40 °C before being homogenised with a porcelain mortar and pestle. Around 2.5–3.5 g of each sample was then digested in ~80 ml 2 M orthophosphoric acid (H$_3$PO$_4$) to remove the carbonate fraction. Once the reaction was complete, the samples were filtered under vacuum on a Millipore manifold using Whatman GF/F glass fibre filter papers (0.7 µm nominal pore size). The filter papers (which captured the insoluble organic component of the coral skeleton) were oven dried at 60 °C for ~20 h. The filter paper was folded into a small ball and packed into a tin cup. The samples were interspersed with gelatine and alanine standards (to monitor instrumental drift) and analysed for $^{15}$N on a Carlo Erba (Milan, Italy) EA1110 CHNS machine attached to a Micromass (Middlewich, UK) Isochrom CF-IRMS at the Research School of Biology, ANU. We also used ANU cane sugar and USGS41 glutamic acid for $^{13}$C calibration. A coral from Shaw Island was homogenised

<table>
<thead>
<tr>
<th>Site</th>
<th>Secchi depth (m)</th>
<th>Chlorophyll a (µg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Repulse Island</td>
<td>4.99</td>
<td>0.60</td>
</tr>
<tr>
<td>Shaw Island</td>
<td>5.97</td>
<td>0.57</td>
</tr>
<tr>
<td>CID Harbour Island</td>
<td>6.93</td>
<td>0.55</td>
</tr>
<tr>
<td>North Molle Island</td>
<td>5.28</td>
<td>0.60</td>
</tr>
<tr>
<td>Haslewood Island</td>
<td>9.95</td>
<td>0.47</td>
</tr>
<tr>
<td>Whitsunday Island</td>
<td>8.46</td>
<td>0.52</td>
</tr>
<tr>
<td>Hook Island</td>
<td>8.44</td>
<td>0.52</td>
</tr>
<tr>
<td>Cobham Reef</td>
<td>15.07</td>
<td>0.43</td>
</tr>
</tbody>
</table>
with a porcelain mortar and pestle and six sub-samples were ana-
lysed yielding an analytical precision of ±0.35‰.

2.4. Coral luminescence analyses

The occurrence and intensity of bright luminescent lines in
nearshore corals of the GBR provide robust proxies for freshwater
flood events (Lough et al., 2002). Coral luminescence was mea-
sured on a luminometer at AIMS (see Barnes et al., 2003). Briefly,
the coral slices were placed on a table which moved at 0.25 mm
increments, illuminated under 390 nm ultra-violet light and lumi-
nescence emissions and reflections at 490 nm were recorded. The
luminescence emissions were then standardised by the reflectivity
at each sample point. The annual luminescence was calculated as
the difference between the summer peak luminescence and pre-
ceding winter minimum luminescence; this method provides the
best correlation with river discharge (see Lough, 2011).

2.5. River flow data

River flow data (daily ML) were obtained from Queensland
Department of Environment and Resource Management gauging
stations on the Proserpine River at Peter Faust Dam tailwater
(GS122003A) for 1960–1990 the Proserpine River at Proserpine
gauge (GS122005A) for 1991–present and the O’Connell River at
Caping Siding gauge (GS124001A) for 1969–present. The flow data
from the Proserpine and O’Connell Rivers were summed and pre-
sented as ‘Whitsunday discharge’.

2.6. Coral chronology

The chronology of the coral geochemical records was assigned
using prominent coral luminescent lines as markers for large
flood events in the region (e.g. 1970, 1974, 1979, 1988–1991,
2000). An intense luminescent line (linked to regional stresses in-
duced by a strong El Niño event) coinciding with 1983 coral
growth was prominent in all coral slices from the Whitsunday Is-
lands sites (excluding Cobham Reef) and was also observed in cor-
als offshore from the Pioneer River (Jupiter et al., 2008).
Geochemical proxies of sea surface temperature (Sr/Ca, U/Ca
and B/Ca ratios) were then used to match peak ratios with winter
(8th August) and trough values with summer (8th February).
These dates represent the mean of peak and trough sea surface
temperatures from the IGOSS SST dataset for the region (http://
www.iridl.ldeo.columbia.edu/SOURCES/.IGOSS/.nmc/). The combi-
nation of these proxy markers allows a robust chronology to be
established and also allows a fixed date to be assigned to the
minimum and maximum SST’s (see Jupiter et al., 2007, 2008).
The timing of the intervening data points is approximated by
assuming a uniform growth rate (i.e. by linear approximation).
We note however that due to the complex nature of coral skele-
tal growth, the trace element signal assigned to each decimal day
also represents the integration of aragonite deposition over sev-
eral weeks of growth. After depositing new aragonite skeleton
on the outer surface layer over a period of days, Porites corals
continue to thicken their skeletons through a more diffuse pro-
cess by adding layers (Barnes and Lough, 1993). This thickening
process produces a smoothing effect on trace material incorpora-
tion on at least a weekly timescale that tends to reduce the over-
all amplitude and broaden the shape of a sharp environmental
signature (e.g. river flood) (Barnes et al., 1995). In addition during
the summer months when the extension rates are greatest there
is likely to be an enhanced broadening of the summer period. To
facilitate comparisons of inter-annual variations in the trace ele-
ment geochemical tracers, annual mean values were calculated
from August to August dates.
3. Results

The results show that the corals record a variety of signals and many spikes in the trace element ratios could not be matched across sites or even with different coral colonies from the same location. Here we present the key findings in three separate sections which include evaluations of: (1) the connectivity between the coral coring sites and flood plume exposure using correlations

![Landsat 5 image](image_url)

*Fig. 2. A Landsat 5 image taken on the 28th January 2005 shows the complex movement of flood waters through the Whitsunday Islands with several island wake effects (white circles). Also shown are the coral coring sites. Image courtesy of Ken Rohde, Queensland Department of Environment and Resource Management.*

**Table 2**

<table>
<thead>
<tr>
<th>Site</th>
<th>Core name</th>
<th>Core length (cm)</th>
<th>Distance from river mouth (km)</th>
<th>Latitude (degrees south)</th>
<th>Longitude (degrees east)</th>
<th>Date of collection</th>
<th>Period of record</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shaw Island</td>
<td>SHW-82A</td>
<td>46</td>
<td>45</td>
<td>20.480</td>
<td>149.069</td>
<td>26/06/2008</td>
<td>1977–2007</td>
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<tr>
<td>Whitsunday Island</td>
<td>WHI-34A</td>
<td>52</td>
<td>75</td>
<td>20.169</td>
<td>148.907</td>
<td>30/06/2008</td>
<td>1939–2008</td>
</tr>
<tr>
<td>Hook Island (Stonehaven Beach)</td>
<td>SNH-73A</td>
<td>36</td>
<td>80</td>
<td>19.396</td>
<td>148.806</td>
<td></td>
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</tr>
</tbody>
</table>

* 135 km from mouth of the Burdekin River.
between trace elements, coral luminescence and river discharge, (2) trends of trace element ratios across the environmental and water quality gradient, and (3) longer-term (>decadal) temporal variability in trace element ratios and $\delta^{15}$N.

3.1. Comparisons of inter-annual variations between cores and Whitsunday River flow

For the common period, 1984–2004, interannual variations in individual coral cores were compared with each other and the Whitsunday discharge (Proserpine + O’Connell Rivers). For Ba/Ca, Y/Ca and Mn/Ca there were no clear patterns of significant correlations either between cores or with river flow (Supplementary Tables 1–3). Only the site of South Repulse Island which is relatively proximal to the river discharge shows a clear Ba/Ca signal that correlates with river flow. By contrast, the luminescence range is significantly correlated between individual coral cores and with interannual variations of Whitsunday discharge, with three notable exceptions (Table 3) which include cores from Haslewood, Whitsunday and Cobham that were drilled from colonies located 70, 75 and 160 km, respectively, from the river mouth. We note that while coral Y/Ca ratios were only correlated across some coring sites and only one coral core from Shaw Island (SWH-82A) displayed a significant, positive correlation between Y/Ca ratios and Whitsunday discharge, a significant positive correlation existed between the core mean coral Y/Ca ratios and coral luminescence (Table 4). We note that the Ba/Ca and Mn/Ca ratios did not display any significant correlations between sites (Table 4).

3.2. Trends across the environmental and water quality gradient

Only the Y/Ca ratios showed a notable (decreasing) trend across the environmental and water quality gradient as well as a general decreasing trend in the overall variability of the data (Fig. 3). Concentrations at the most inshore site at Repulse Island were 4 to 5-fold higher (core means of $4.7 \times 10^{-7}$ to $1.8 \times 10^{-7}$, $5.8 \times 10^{-7}$ to $1.9 \times 10^{-7}$, and $4.0 \times 10^{-7}$ to $1.7 \times 10^{-7}$ for REP-72A, REP-72B and REP-71A, respectively) than the offshore site at Cobham Reef (core mean of $1.2 \times 10^{-7}$ to $3.5 \times 10^{-7}$). However, the core Y/Ca ratios in the cross-gradient transect from North Molle Island ($1.7 \times 10^{-7}$ to $5.4 \times 10^{-8}$), Cid Harbour Island ($1.9 \times 10^{-7}$ to $5.3 \times 10^{-8}$, $2.4 \times 10^{-7}$ to $2.3 \times 10^{-7}$ and $2.3 \times 10^{-7}$ to $7.7 \times 10^{-8}$ for CID-73A, CID-71B and CID-01A, respectively) and Haslewood Island ($3.0 \times 10^{-7}$ to $1.6 \times 10^{-7}$) was the opposite to what would be expected given that North Molle Island is the closest site to the coast and is likely to experience the most ‘direct’ terrestrial influence. We note, however, that all three sites are a similar distance from the mouths of the Proserpine and O’Connell Rivers (60–70 km, Table 2). Spikes in Y/Ca did not occur with a regular seasonal periodicity and peaks occurred at different intervals throughout the year (e.g. Fig. 4).

3.3. Temporal variability in trace element ratios

The Mn/Ca ratios in the coral from Whitsunday Island showed a sustained period of enrichment (~10-fold over baseline values) between 1964 and 1967 compared to the remainder of the record (Fig. 5B) and other sites in the region. While there were elevated Mn/Ca ratios during this period at other sites in this vicinity (i.e. Cid and Shaw Islands), the elevated Mn/Ca ratios were not as high (~5-fold) or as prolonged as those measured in the coral from Whitsunday Island. Moreover, the coral sites more distal to Whitsunday Island showed little variation in Mn/Ca ratios over this period, including South Repulse Island near the mouths of the Proserpine and O’Connell Rivers and Cobham Reef on the mid-shelf (Fig. 5). Peak Mn/Ca ratios were commonly concentrated in the months of spring and summer (October to April).

The Ba/Ca ratios in all coral records display two types of signals: (1) sharp spikes of high magnitude (~3–10-fold higher than baseline values) but of short duration representing approximately 2–4 weeks of growth; and (2) ‘seasonal’ fluctuations of lower magnitude (2-fold variability) with a more gradual rise and fall in Ba/Ca. While all coral colonies in the Whitsunday region displayed high magnitude spikes superimposed on a lower amplitude variation, the occurrence of the high magnitude anomalous Ba/Ca signals was generally not regular at most sites (i.e. not occurring every year), nor were they typically correlated across sites or with large discharge events from the Proserpine and O’Connell Rivers (Fig. 6). Similar to Mn/Ca measurements, the vast majority of the Ba/Ca spikes were concentrated in the spring and summer months (October to April), though these two elemental ratios were not correlated (Table 4; see also Supplementary Table 1). In addition, shifts in baseline concentrations were also not matched across sites (Fig. 4). In fact, there was more variability in the core mean Ba/Ca ratios between the coral colonies from a single site (e.g. REP-71A = $2.44 \times 10^{-6}$ ± $8.93 \times 10^{-7}$ compared with

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>Ba/Ca</th>
<th>Y/Ca</th>
<th>Mn/Ca</th>
<th>Luminescence</th>
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<tr>
<td>Ba/Ca</td>
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<td>Y/Ca</td>
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<td>Mn/Ca</td>
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<td>$0.09$</td>
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<td>Luminescence</td>
<td>$0.19$</td>
<td>$0.91$</td>
<td>$-0.22$</td>
<td>$1$</td>
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### Table 3

Correlations ($r$ value) between annual core luminescence time series and Whitsunday discharge (Proserpine and O’Connell Rivers), 1984–2004 (i.e. $n = 20$; values in bold significant at 5% level).

<table>
<thead>
<tr>
<th></th>
<th>Rep72a</th>
<th>Rep 72b</th>
<th>Shw 82a</th>
<th>Cid 71b</th>
<th>Cid 73a</th>
<th>Nmi 73a</th>
<th>Hwd 73b</th>
<th>Whi 34a</th>
<th>Snh 73a</th>
<th>Cob 71a</th>
<th>Whitsunday discharge</th>
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<td>Rep72a</td>
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<td>0.42</td>
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<td>Cob71a</td>
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<td>0.09</td>
<td>0.39</td>
<td>$-0.13$</td>
<td>0.30</td>
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<td>Whitsunday discharge</td>
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<td>0.65</td>
<td>0.75</td>
<td>0.77</td>
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<td>$-0.07$</td>
<td>0.20</td>
<td>0.55</td>
<td>0.13</td>
<td>1</td>
</tr>
</tbody>
</table>
REP-72A = 4.69 × 10^{-6} ± 2.63 × 10^{-6}) than from the sites further offshore along the gradient (e.g. Hook Island = 4.39 × 10^{-6} ± 1.56 × 10^{-6}; Cobham Reef = 4.37 × 10^{-6} ± 2.78 × 10^{-6}).

A clear increase in baseline Ba/Ca ratios occurred at 1870 in the long coral core record from Cid Harbour Island (Fig. 7 and Fig. 8A—note that the shaded areas in Fig. 8 refer to the periods of positive Ba/Ca anomalies in the coral from Cid Harbour Island). A considerable anomaly occurs in the coral Ba/Ca ratios coinciding with 1851 which does not correlate with any known land use change (pre-settlement). In addition, peak Ba/Ca ratios increase markedly (1.25-fold in baseline and 8-fold in peak ratios) in both frequency of occurrence and concentration after 1850. The Y/Ca ratios also show a peak around this time while coral Mn/Ca ratios display no trend (Supplementary Figs. 1 and 2). The peak Ba/Ca ratios show the highest frequency of occurrence and magnitude from 1850 to 1917 before becoming less frequent and less prominent (Fig. 7). Other positive coral Ba/Ca ratio anomalies occurred in the 1950s and 1970s (shaded area Fig. 8A), approximately corresponding with increased Ba/Ca at Havannah Island and Round Top Island (Fig. 8).

The δ^{15}N analysis of the coral organic matter for the Cid Harbour Island site show good agreement between the two coral colonies for the overlapping growth periods (1961–1991: Fig. 9). With the exception of some highly anomalous δ^{15}N variations over some of the sampled 3-year time periods (1880–1883, 1931–1934, 1934–1937 and 1943–1946), δ^{15}N in the long coral core shows no trend over time and values range between 2.6‰ and 8.0‰ with a core mean of 6.1 ± 1.0‰ (excluding the anomalies). However, the δ^{15}N in the CID-71B core shows a possible decreasing trend over the last 30 years (Fig. 9). The carbon isotope ratios of the organic fraction of the coral skeleton become more variable after 1860 towards more depleted values which may indicate increasing terrestrial sourcing of carbon (Supplementary Fig. 3).

Fig. 3. Coral Y/Ca ratios from the coral coring sites along the environmental gradient (plots based on distance from the Proserpine and O’Connell River mouths) including Repulse Island (REP), Shaw Island (SHW), Cid Harbour Island (CID), North Mole Island (NMI), Haslewood Island (HWD), Whitsunday Island (WHI), Hook Island (SNH) and Cobham Reef (COB). This summary box and whisker plot presents the median value, interquartile range (containing 50% of values: box), extreme values (values more than 3 box-lengths from the 75th percentile: stars) and whiskers extending to highest and lowest values (excluding outliers).

4. Discussion

Trace elements and stable isotopes from coral core records can provide excellent archives to quantify historical environmental changes in adjacent land catchments. However, some studies including ours have reported anomalies in coral geochemical records that are not directly correlated with river discharge (Sinclair, 2005; Jupiter et al., 2007, 2008; Prouty et al., 2010). These anomalous deviations need to be described and understood so that future studies can better select sampling sites and better interpret coral geochemical data. Here we discuss the usefulness of the trace elements and isotopes in the context of our records from the Whitsunday Islands and present hypotheses that need further testing and which may explain the complexities of our dataset. We focus our discussion of these complexities on: (1) local physical and oceanographic factors limiting trace element correlations with discharge; (2) local-scale processes and disturbance producing anomalous trace element signals; and (3) local-scale processes which may mask long-term shifts related to land use change.

4.1. Coral luminescence correlations with river discharge

The coral luminescence records were mostly positively correlated across sites and with Whitsunday discharge, although the Haslewood Island, Whitsunday Island and Cobham Reef sites displayed no such correlation (Table 3). This result suggests that most sites are recording regional runoff from the adjacent river catchments. The lack of correlation between coral luminescence and Whitsunday discharge in the Haslewood, Whitsunday and Cobham sites may be due to the complex hydrodynamics of flood plume currents in the region (Fig. 5). The islands of the Whitsunday region strongly deflect ocean currents and, in particular, cause ‘island wake’ effects where flood waters are deflected around the islands and upwelling occurs along the back of the island (see Wolanski and Hammer, 1988; Wolanski et al., 1996). As such, flood plumes in the Whitsunday Islands may rarely reach some of the coral coring sites in this study. In particular, island wakes can be observed at some of the coral coring sites (e.g. Shaw Island and Haslewood Island) on the Landsat 5 image of a flood plume in January 2005 (white circles: Fig. 2). We note that the Cobham Reef site is too distant to be influenced by discharge from the Whitsunday Rivers, therefore the luminescent lines observed in the core which coincided with sizable discharge years were likely from the much lar-
ger Burdekin and Fitzroy Rivers. On occasion (e.g. 1997), the corals from Repulse Island record relatively high luminescence coupled with low discharge from the Proserpine and O’Connell Rivers (Fig. 4). This behaviour was also observed by Jupiter et al. (2008) in coral records from Round Top Island where the relatively large tidal range (~4 m) was thought to draw freshwater from the mouth of the Pioneer River. These exceptions to the generally accepted pattern that inshore coral luminescence is correlated with freshwater runoff to the Great Barrier Reef lagoon (Lough, 2011) suggest that: (1) satellite images of plume dispersion around islands from recent flood events may provide guidance on which sampling locations are more likely to be influenced by terrestrial runoff; and (2) comparisons of coral luminescence should be made with discharge records from larger nearby rivers, which have higher correlations with amount of rainfall (Lough, 2007).

The annual core mean coral Y/Ca ratio was the only geochemical proxy to display a positive correlation to coral luminescence (Table 4). This suggests that both coral luminescence and Y/Ca are reflecting the spatial gradient in freshwater inputs across the coral sites and have the most potential to record changes in terrestrial runoff from the adjacent Whitsunday catchment area. The coral Y/Ca ratio displays a cross gradient signal with higher concentrations (~5-fold) at the inshore sites (e.g. Rupulse and Shaw Islands) versus sites more distant from the river mouths (North Molle and Hook Islands and Cobham Reef: Fig. 3). This finding is in accordance with Alibert et al. (2003) who also found a 5-fold enrichment...
of Y in an inshore coral site influenced by the Burdekin River (Pandora Reef) compared with a site on the mid-outer shelf (Davies Reef) as well as Jupiter (2006) who found a three to four fold enrichment at a site (Round Top Island) influenced by the Pioneer Fig. 5. Coral Mn/Ca records between 1960 and 1976 from: (a) Cobham Reef; (b) Whitsunday Island; (c) Cid Harbour Island; (d) Shaw Island and; (e) Repulse Island. Also shown (f) is the Whitsunday discharge (Proserpine + O'Connell Rivers). Note the vast accumulation of terrigenous sediment surrounding the larger islands of the Whitsunday Island group (from Heap et al., 2002). The grey shading on the graphs highlights the elevated coral Mn/Ca ratios in the WHI-34D coral (B). The current vector data have been compiled from Blake (1994: mean current direction) and Hamner and Hauri (1977).
River compared with sites further offshore (Keswick and Scawfell islands). However, while there was a positive correlation between annual mean Y/Ca ratios and coral luminescence (Table 4), the peaks of both proxies do not match (Fig. 4), which was also observed in the coral records analysed by Jupiter (2006).

A further complication of the Whitsunday Islands is that there are large accumulations of terrigenous sediments of 10–20 m thickness deposited around the larger islands (Heap et al., 2002; Fig. 5). The middle shelf of the Great Barrier Reef lagoon (20–40 m water depth) is typically defined as ‘sediment-starved’
Fig. 7. Coral Ba/Ca ratios in the three coral records from Cid Harbour Island.

Fig. 8. The Cid Island Ba/Ca record (A) compared with corresponding records from Havannah Island (B) (McCulloch et al., 2003) and Round Top Island (C) (Jupiter et al., 2007). The data are presented as annual standardized anomalies where annual mean Ba/Ca ratios (August to August period) were subtracted from mean Ba/Ca concentration over the base period (last 20 years of record) and divided by the standard deviation (10) of the base period.
with the Whitsunday Island group a notable exception. We hypothesise that the presence of these large sediment accumulations has influenced the geochemical signatures in the corals taken from these areas and this explains why the coral from North Molle Island has lower Y/Ca concentrations than the corals from Cid and Haslewood Islands. Sites which are further offshore typically have much lower Y/Ca ratios (Wyndham et al., 2004), although the Whitsunday Island, Cid Harbour Island and Haslewood Island corals are in areas of relatively high sediment accumulation that has occurred throughout the Holocene (Heap et al., 2002).

### 4.2. Influence of local-scale processes and disturbance on Mn/Ca and Ba/Ca records

Annual peak Ba/Ca and Mn/Ca do not show a clear change across the spatial water quality gradient and are decoupled with Whitsunday flood events, suggesting that their incorporation into coral skeletons may be more influenced by other localised processes. The anomalous enrichment in Mn/Ca ratios from the Whitsunday Island coral from 1960–1975 coincides with the construction of the underwater observatory on Hook Island which is located within 1–2 km of the Whitsunday coral site. The lease for the observatory was granted in 1959, construction started in ~1965 and it was completed by 1969. During this time the sea floor was ‘blasted’ for levelling and two hundred old car bodies were emplaced for fish habitat (Blackwood, 1997). It is conceivable that the disturbance of the thick terrigenous-rich seafloor (Fig. 5; Heap et al., 2002) around this site resulted in higher local turbidity levels and as a result caused Mn to be desolved from the sediments via photoreductive processes (i.e. reduction of Mn-IV to Mn-II: see Alibert et al., 2003; Wyndham et al., 2004; Lewis et al., 2007). Alternatively release of relatively soluble Mn may have occurred from the somewhat anoxic sediment pore waters or possibly, the chemical breakdown of the car bodies. In any case, the construction of the underwater observatory is the only explanation available that closely coincides with the timing of the highly localised Mn enrichment measured in the coral from Whitsunday Island. The regular seasonal fluctuations in coral Mn/Ca are possibly due to either photoreductive dissolution of suspended particulate Mn oxides to the soluble Mn (II) species or a diagenetic release of Mn at the seawater–sediment interface by reducing conditions induced by decay of organic matter (Alibert et al., 2003; Wyndham et al., 2004). Similarly, the bacterial decay of Mn-enriched organic matter also reduces Mn to the soluble (Mn-II) species (Addy et al., 1976). These mechanisms (photoreductive dissolution and organic decay) explain the timing of the peak Mn levels in the Whitsunday corals which coincide with spring and summer.

Anomalous Ba/Ca spikes (i.e. not correlated with river discharge) have been previously reported for a coral colony from Cow and Calf Islands (Fig. 1), also in the Whitsunday region (Sinclair, 2005), and the magnitude, occurrence and timing of these spikes are similar to those observed in this study. The Ba/Ca spikes in the corals from this study represent typically ~2 data points (corresponding to 2–4 weeks of growth) and both points have each been smoothed to a 10-point mean during the initial filtering process. Despite this rigorous filtering of the data, we could not determine whether the spikes observed in our study are reproducible as the paired/duplicated samples (replicate tracks) did not contain the spikes, although the broader seasonal trends were highly reproducible.

It has been postulated that these anomalous Ba/Ca ratios may be linked with phytoplankton blooms, *Trichodesmium* outbreaks or coral spawning although no firm conclusion has yet been reached (Sinclair, 2005). Sinclair (2005) suggested that anomalous Ba/Ca spikes are likely related to micro-geographic features which only affect specific locations. Such features in the Whitsunday Island group are likely to be common given the complex dynamics of the region including strong currents, island upwelling, resuspension and relatively high tidal ranges (up to 4 m). Other potential Ba sources may include sediment resuspension especially during high tide, sediment trapping and episodic Ba release (see Prouty et al., 2010), local runoff/groundwater discharge from the islands or from small coastal streams (Swarzenski et al., 2001), weathering of Ba-rich rocks in the Whitsunday Islands and release/desorption of Ba from the large terrigenous-rich sediment accumulations around the Whitsunday Islands (see Heap et al., 2002; Fig. 5). Future studies should couple coral geochemical records with time series satellite imagery to examine potential environmental influences such as *Trichodesmium* outbreaks, phytoplankton blooms and sediment resuspension.

### 4.3. Potential influence of changing land use practices and local-scale processes on long-term trace element and isotope records

The increase in the baseline Ba/Ca ratio in the long coral record from Cid Harbour Island after 1860 (and other positive anomalies in the 1950s and 1970s) coincides with the increase observed by McCulloch et al. (2003) in a coral from Havannah Island and also observed by Jupiter et al. (2007) in a coral record from Round Top Island (Fig. 8). Thus it appears that this increase reflects a regional change in Ba/Ca ratios coinciding with the period of early
European settlement in the GBR catchment area and also with the period of higher river discharge in the 1950s and 1970s (Lough, 2007). The increase in the frequency and magnitude of the Ba/Ca spikes after 1850 is also similar to that found by McCulloch et al. (2003). The increase in Ba/Ca in the coral from Hannah Island was interpreted to reflect an increase in the suspended sediment load from the Burdekin River (McCulloch et al., 2003). Similarly, the clearing of land in the Proserpine and O’Connell River catchments for grazing and cropping (see McClements, 1973; Kerr, 1997) may have resulted in an increase in sediment erosion. A considerable amount of the sugar grown in the neighbouring Pioneer River catchment in the earlier years was cultivated on relatively small areas of land (60 km from the river mouth) compared to Round Top Island being considerably diluted by the time they reach Cid Harbour Islands (Fig. 7). This result may imply that either the mobile surface sediment had been more or less exhausted or, that the establishment of crop lands stabilised the landscape and caused an overall reduction in erosion. Other indicators of sediment discharge such as the Y/Ca ratio (see Lewis et al., 2007) also show a corresponding increase after 1850–1860 in the Cid Harbour Island coral (Supplementary Fig. 1) which suggests an increased terrestrial influence at this time.

The $\delta^{15}\text{N}$ record of the coral particulate, insoluble organic matter from the Cid Island corals shows no apparent trend over the combined 186 year record at a 3 year sampling resolution (Fig. 9). In contrast, Jupiter et al. (2008) found large positive deviations (>9‰) in $\delta^{15}\text{N}$ in corals from Round Top and Keswick Islands (Fig. 1) which they interpreted to reflect an enriched source from the Pioneer River. The $\delta^{15}\text{N}$ record in Jupiter et al. (2008) was measured at higher sampling resolution where large individual flood years were targeted whereas our record would dilute the influence of these larger flood years. While an unmodified fertiliser nitrogen source would reflect more atmospheric $\delta^{15}\text{N}$ values (i.e. 0‰), it has been postulated that the nitrogen source may be enriched and highly fractionated by microbial denitrification and remineralisation in stagnant, nutrient-enriched waters behind weirs (i.e. in the freshwater zone) that are released into the nearshore zone during flood pulses (Marion, 2007; Jupiter et al., 2008). However, unlike the Pioneer River which is somewhat regulated by three weirs and a dam, there are no dams on the Proserpine and O’Connell Rivers that would influence the coral $\delta^{15}\text{N}$. The Peter Faust Dam on the Proserpine River was completed in 1990 but had not overflowed until December 2010.

The $\delta^{15}\text{N}$ records from corals directly offshore from Round Top Island were used to suggest that fertiliser runoff had increased by as much as 10 to 15-fold since the 1950s (Marion, 2007; Jupiter et al., 2007). The lack of correlation between the coral records from Round Top and Cid Harbour Islands may be due to the flood waters being considerably diluted by the time they reach Cid Harbour Island (60 km from the river mouth) compared to Round Top Island (5 km). However, three coral records from Repulse Island (20 km from river mouth) returned lower $\delta^{15}\text{N}$ of 4.7 ± 1.7‰ (not shown) compared with the Cid Harbour Island record (6.1 ± 1.0‰) and the Round Top corals (8.15 ± 1.29‰). Moreover, the strong and complex currents through Whitsunday Passage as well as a gyre feature in Repulse Bay (see Fig. 5; Hamner and Hauri, 1977; Blake, 1994; Stewart et al., 2000) would probably result in relatively fast flushing times in this region and thus nitrogen may not accumulate in the system. Another possibility for the lower coral $\delta^{15}\text{N}$ at the Repulse Island site compared to Cid Island and Round Top Island may be due to the consistently lower light levels (see Heikoop et al., 1998) due to the higher and chronic turbidity levels and lower optimal depth in Repulse Bay (van Woesik et al., 1999; Cooper et al., 2007). Previous studies have established a correlation between coral tissue $\delta^{15}\text{N}$ and light conditions where the $\delta^{15}\text{N}$ was lower in corals growing in deeper waters which receive lower light (Muscatine and Kaplan, 1994; Heikoop et al., 1998).

Conversely, *Trichodesmium* blooms in the region may also influence the $\delta^{15}\text{N}$ of the corals in the Whitsunday Islands. Corals have potential to incorporate and trap detrital matter within their skeletal pore spaces (e.g. see Marion et al., 2005) and in turbid water environments corals can also feed on plankton (Grottoli and Wellington, 1999; Houlbreque et al., 2004). *Trichodesmium* has the ability to fix nitrogen from the atmosphere and is thus limited by other nutrients such as phosphorus, iron and dissolved organic matter (Bell et al., 1999). The rivers of the Mackay Whitsunday region drain a large volcanic province (Bryan et al., 1997) and due to this geology, the rivers export elevated levels of phosphorus relative to other parts of the GBR catchment area (Brodie et al., 2010). Indeed, *Trichodesmium* blooms are more prolific in the central GBR (Bell et al., 1999) and since they fix atmospheric nitrogen ($\delta^{15}\text{N} = 0\%$) it is possible that coral $\delta^{15}\text{N}$ could become depleted as a result of the increased frequency and magnitude of these blooms. *Trichodesmium* blooms have been observed in flood plumes from the Whitsunday Rivers and with the higher dissolved phosphorus concentrations near the river mouths (Brodie et al., 2010), coral $\delta^{15}\text{N}$ may be expected to be lower at the Repulse Island site. Lower $\delta^{15}\text{N}$ in coral tissues has been reported on the mid-shelf of the GBR which has been linked to higher amounts of nitrogen fixation (Sammarco et al., 1999).

5. Conclusion

Geochemical records from a series of coral cores collected over an environmental and water quality gradient through the Whitsunday Island group of the Great Barrier Reef show that the corals respond to different environmental influences. The Y/Ca ratio was the only proxy to record a decreasing terrestrial influence along a gradient from the Proserpine and O’Connell Rivers, while the Ba/Ca and Y/Ca ratios indicated historical changes to the gradient shortly after European settlement in the adjacent Proserpine and O’Connell catchments. Mn/Ca ratios coincided with the timing of local influences related to infrastructure development for the tourism industry and specifically to the preparation and installation of the underwater observatory on Hook Island. There was also no significant correlation between inter-annual variations in Ba/Ca, Y/Ca or Mn/Ca and adjacent river flow variations. This contrasts with the luminescence signature which clearly indicates that freshwater flood plumes are reaching those reef sites <60 km from land. Coral $\delta^{15}\text{N}$ analyses show no apparent change before or since the time of European settlement. While the application of multi-proxy coral geochemical records can successfully reconstruct local and regional environmental changes, we caution that further research is required to understand how these trace elements and isotopes are incorporated into the coral skeleton and the environmental variables that control their changing abundances. This knowledge will allow more quantitative estimates to be made relating to environmental change. We recommend that a series of replicated cores from different sites within one region provide the best approach to separate and to reconstruct regional and local environmental changes. The results from this study imply that site selection is important to produce high quality regional-scale environmental records. We recommend that an examination of coral luminescence records and their correlation to river discharge be undertaken coupled with available data on current movements (to understand more localised influences) before corals are selected for geochemical analysis. The use of daily satellite imagery to select sites is also beneficial to identify and avoid areas of complex currents and the effects of island wakes. Moreover, the use of time ser-
ies satellite imagery can help identify possible environmental influences on coral geochemical records including Trichodesmium blooms and resuspension events. Our study highlights the complexity of interpretation of coral geochemical records in areas such as the Whitsunday Islands, where the presence of a large island network produces environments where local conditions (i.e. currents) may have more significance on the coral records than regional influences.

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Appendix A. Supplementary data


References


