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

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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 Woesik 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 Woesik 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. Alibert 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 Woesik 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 Woesik 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 Woesik et al., 1999; Uthicke and Nobes, 2008; Cooper and Ulstrup, 2009). van Woesik 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

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**Table 1**
WQ variables (Secchi depth & chlorophyll) from (http://e-atlas.org.au/; see De'ath and Fabricius, 2010).

| Site | Secchi depth (m) | Chlorophyll *a* ($\mu gL^{-1}$) |
|---|---|---|
| Repulse Island | 4.99 | 0.60 |
| Shaw Island | 5.97 | 0.57 |
| CID Harbour Island | 6.93 | 0.55 |
| North Molle Island | 5.28 | 0.60 |
| Haslewood Island | 9.95 | 0.47 |
| Whitsunday Island | 8.46 | 0.52 |
| Hook Island | 8.44 | 0.52 |
| Cobham Reef | 15.07 | 0.43 |

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 $\delta^{15}N$ 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), groundwater 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 isotope 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 1860s which saw the development and expansion of the sheep and cattle grazing industries. Bananas, sugarcane, corn and pumpkins were grown in the catchment during a period from the 1880s to 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 slabbed 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 milli-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 $^{43}Ca$ 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 milli-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 ($H_3PO_4$) 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 $\delta^{15}N$ 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 $\delta^{13}C$ calibration. A coral from Shaw Island was homogenised