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Sentinels of the Marine Environment: High Resolution LA-ICP-MS Trace Element Analyses of Corals from the Great Barrier Reef

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The Great Barrier Reef (GBR) of Australia extents for over 2500 km along the northeastern coastline of Australia. Like most of the worlds reefs there is growing concern over the impact that humans are having on these sensitive coastal environments where enhanced loads of sediments and nutrients from terrestrial erosion, acting together with climatic stress, is often proving to be a lethal combination. Colonies of Porites corals can normally live for many hundreds of years depositing continuous layers of calcareous skeleton. Trace elements are co-precipitated with the skeletal aragonite at concentrations determined by ambient seawater compositions as well as environmental factors such as sea surface temperature and salinity. In the central GBR a number of sites representing inner, mid and outer reef locations have been used to evaluate temperature proxies such as U/Ca, B/Ca, Mg/Ca and U/Ca as well as Sr/Ca. Measurements have been undertaken using an excimer (193 nm) LA-ICP-MS configured with a large aperture (500x50 microns) to minimize noise from the coral structure. Elemental ratios have been calibrated with an in-house standard prepared from finely crushed coral whose concentrations had been independently determined using isotope dilution TIMS and/or solution ICP-MS. For Sr/Ca it is also possible to compare measurements of larger milled samples (~ 200 ug) with those determined by LA-ICP-MS. There is generally excellent agreement between the two methods, although the LA-ICP-MS exhibits higher frequency response consistent with the ~x1000 smaller sample size. A good correlation also exists between Sr/Ca and B/Ca ($r > -0.8$) consistent with a sea surface temperature (T) calibration of: $1000Sr/Ca = 10.5 - 0.06T$. For Mg/Ca and U/Ca there is also good agreement between the mid and outer reef sites but temperature calibrations differ for the inner reef. This may reflect differing seawater compositions, salinity effects or other environmental parameters. It is also shown that inshore corals from the central GBR provide quantitative records of both the volume of freshwater river discharge as well as suspended sediment load. Coastal rivers adjacent to the GBR experience highly episodic flows due to flooding from cyclones or occasionally intense monsoonal depressions. During these high intensity events there are massive discharges of freshwater and suspended sediment into the near-shore GBR lagoon. These low salinity, high turbidity nutrient rich flood plumes are usually advected northwards along the coast and depending on hydrodynamic conditions can persist over the near-shore reefs for many weeks. Ba/Ca ratios and oxygen isotope compositions have been examined in corals at several sites impacted by coastal rivers. There is a close correlation between the timing of Ba/Ca peaks in the coral and the initiation of flood plume events. At Pandora and Havannah Reefs both of which are subject to flood plumes from Australia's second largest river the Burdekin, an exquisite record of flood plume events is preserved for the past ~300 years. For example during the 1974 flood event, the largest flood this century, Ba/Ca ratios of up to 18 umolar were recorded compared to background levels of ~4 umolar. Interestingly the previous 1970 flood event had only a slightly lower Ba/Ca ratio of ~14 umolar although the river discharge was more an order of magnitude lower (4.9 million megalitres for 1970 compared to 54 million megalitres for 1974). Prior to 1970 there was a period of major drought which made the semi-arid catchment susceptible to increased soil erosion during subsequent floods. These observations suggest that Ba acts as a proxy for suspended sediment rather than freshwater volume. This is consistent with the well known behaviour of Ba in river/estuarine systems; i.e. Ba is desorbed from riverine particulates as a result of increasing salinity adding significantly to the total dissolved Ba pool and thereafter Ba acts as a conservative element undergoing simple mixing with seawater. Using these assumptions an effective Ba river end member (given by extrapolation of the linear conservative Ba mixing regime to zero salinity) can be calculated for the 1974 and 1970 flood events of 313 and 1160 nm/l respectively. This indicates significant increases in suspended sediment load following periods of drought. The geochemistry of corals thus provides a means to determine long-term changes in riverine suspended sediment loads and thus nutrients (phosphorus) that are entering coral reefs and to quantify the impacts of more intensive land-use practices that have been adopted following European settlement.