Proceedings of the 11th International Coral Reef Symposium, Ft. Lauderdale, Florida, 7-11 July 2008
Session number 4

Coral rare earth element tracers of terrestrial exposure in nearshore corals of the Great Barrier Reef

S. D. Jupiter[1,2]

1) U. of Queensland, ARC Centre of Excellence for Coral Reef Studies, Brisbane, QLD 4072, Australia
2) U. C. Santa Cruz, Dept. of Ecology and Evolutionary Biology, Santa Cruz, CA 95064, USA

Abstract. Rare earth element and yttrium (REY) concentrations were measured from two nearshore *Porites* sp. corals collected from Round Top Is. and Keswick Is., at 5 km and 32 km offshore from Mackay, Queensland, on the southern Great Barrier Reef, Australia. The REY patterns from the Round Top coral differed from the Keswick coral in 5 respects: (1) greater REY concentrations; (2) preferentially enriched light rare earth elements (LREEs); (3) reduced slope across the heavy rare earth elements (HREEs); (4) more negative cerium (Ce) anomaly; and (5) lower yttrium (Y) to holmium (Ho) ratios. These patterns suggest greater terrestrial exposure and higher biological productivity at Round Top Is. Total abundance of REY in both corals increased over time between 1950 and 2002. The rate of increase at Round Top Is. was 3-fold greater than at Keswick Is., thus the innermost site was likely more influenced by weathering from rapid agricultural expansion in the adjacent Pioneer River catchment. The Y/Ho ratio decreased over time in both corals, but as the coral values were substantially higher than ambient seawater, more research is suggested to identify the cause.

Key words: Rare earth elements, yttrium, *Porites*, Great Barrier Reef

Introduction

Concentrations of rare earth elements and yttrium (REY) in coastal corals are good geochemical tracers of freshwater runoff and/or chemical weathering of continental crust because they are: (1) incorporated into coral lattices in close proportion to ambient seawater concentrations (Sholkovitz and Shen 1995); and (2) fractionated differentially in shales, river water and seawater (Elderfield et al. 1990). REY can be measured independently, or together in series, to investigate patterns that may indicate sources from local geology or land use (Lawrence et al. 2006a). Yet, the geochemical pathways from riverine transport of REY to incorporation within coral skeletons are not well studied, largely because instruments that can measure aqueous concentrations of yttrium and the monoisotopic REE with precision have only recently become available (Nozaki et al. 1997; Lawrence et al. 2006b).

River discharge is the main source of marine REY concentrations in nearshore waters (Byrne and Sholkovitz 1996). REY come from weathered topsoil and are transported in catchment waterways attached to colloidal particles within the 0.45μm fraction of the suspended sediment load (Byrne and Sholkovitz 1996). A large proportion of REY is removed in the estuarine mixing zone due to flocculation of iron-organic colloids at low salinities (Sholkovitz 1995), although large increases in REY abundances between ~5 to 10 ppt probably reflect REY release from river particles (Lawrence and Kamber 2006). Fractionation of the freshwater REY pattern also occurs within the mixing zone: light rare earth elements (LREEs) become more depleted relative to heavy rare earths (HREEs); Y fractionates relative to holmium (Ho), and a positive lanthanum (La) anomaly develops relative to its pattern in shale (Lawrence and Kamber 2006).

To identify potential terrestrial sources in marine REY, the data are typically normalized to a sediment or shale to remove the natural "saw-tooth" distribution of absolute abundances and to describe the pattern relative to a continental source (Byrne and Sholkovitz 1996). Elemental anomalies within normalized pattern, defined as departures from a smooth line predicted by extrapolation from neighboring elements (Sholkovitz 1995), can be used as "fingerprints" of biological and physical processes and/or provenance features (Akagi et al. 2004; Lawrence et al. 2006a). For example, *Porites* corals living adjacent to a soft waste dump and creek delivering runoff from an open-cut mine on Misima Island, Papua New Guinea (PNG) had positive middle rare earth element (MREE) anomalies that closely resembled those from Sepik River water (Fallon et al. 2002), suggesting that provenance information from a strong source can be preserved through the estuarine mixing zone.

In this study, REY patterns were measured from nearshore corals of the south-central Great Barrier

Reef (GBR), collected at 5 and 32 km offshore from the Pioneer River mouth and city of Mackay (Queensland, Australia). Since European settlement in 1865, there has been substantial land clearing both historically and in recent decades to support a rapidly expanding sugarcane industry (Jupiter and Marion 2008). Anomalies within REY patterns were examined to detect spatial differences in terrestrial exposure, while temporal changes in total REY load and Y/Ho ratios since the 1950s were measured to assess potential linkages to catchment land cover change.

Material and Methods

Sample preparation

Two cores (RTF, KIA) were collected from massive *Porites* colonies at reefs fringing Round Top Is. (5 km offshore) and Keswick Island (32 km offshore). Density bands from x-radiographs were used to identify years in slabs cut from each core, from which bulk samples were drilled from annual coral growth periods spanning years between 1950 and 2002. For each core, 3-5 consecutive years were analyzed from each decade. For each annual sample, approximately 5-15 µg of coral powder was diluted by 1000 with >18.2 MΩ water, HNO_3 was added to a total concentration of 2%, samples were left to digest overnight, and all solutions, including blanks, were spiked with 2 ppb of internal standard (indium (In), rhenium (Re), bismuth (Bi)).

Solution ICP-MS analyses

All samples were analyzed at the University of Queensland on a Thermo X-Series inductively-coupled mass spectrometer (ICP-MS). For instrument specifications, sensitivity and operating power, see Lawrence et al. (2006a) and Lawrence and Kamber (2006). Dilutions of USGS dolerite W-2, Mud of Queensland (MUQ; Kamber et al. 2005), and JCp-1 coral reference material (collected in 1999 from Ishigaki Island, Okinawa, Japan) were measured simultaneously with the samples for machine calibration. All REY (except promethium (Pm), which does not exist naturally in measurable concentrations; Byrne and Sholkovitz 1996), zircon (Zr) and the appropriate suite of interfering isotopes were measured. All data were corrected for drift (internal and external), oxide interferences (for europium (Eu) and heavier elements), and dilution factors.

Statistical analyses and anomaly calculations

A principal components analysis (PCA) was performed using a VARIMAX rotation to compare coral REY patterns with seawater, river water and sediment. Mean coral REY from RTF and KIA (over all years analyzed) were compared with REY data from MUQ and water samples collected from: Pioneer River mouth and estuary (Lawrence et al. 2006a); Coral Sea (Zhang and Nozaki 1996); and streams draining different regions of the Pioneer catchment (Lawrence et al. 2006a) (Fig. 1a). All REY abundances were scaled to the same value of samarium (Sm), for which anomalies are not expected, and Eu was excluded from the PCA because isobaric interference of BaO during ICP-MS analysis resulted in unreliable measurements of Eu from the Pioneer stream water samples (Lawrence et al. 2006a).

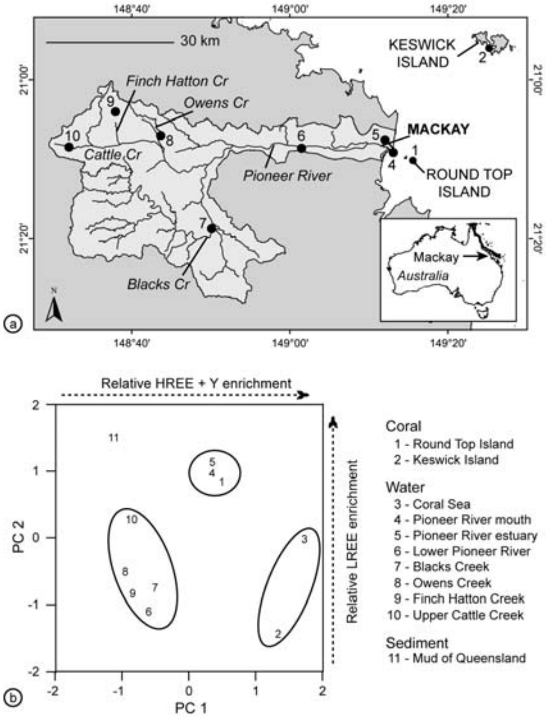

Figure 1: (a) Locations of coral core and water sample collection sites in and adjacent to the Pioneer River catchment. Inset depicts the location of Mackay within Australia. (b) Scaled REY data from coral, water and sediment samples plotted against principal components PC1 and PC2. Dashed arrows indicate directional enrichments of different groups of elements.

For assessment of deviations from the typical seawater pattern as indicators of terrestrial influence, mean coral sample REY concentrations (ppb) were normalized to those from terrestrial sediment (MUQ). To compare Mackay coral REY patterns to records from other studies, published coral REE abundances were also normalized to MUQ. The Ce anomaly was calculated using an equation from Lawrence et al. (2006b), Ce_n/Ce_n^*, where n refers to the shale-normalized abundances of Ce, praseodymium (Pr) and neodymium (Nd):

$$Ce_n^* = Pr_n * (Pr_n/Nd_n)$$

Mean differences in Ce anomalies between RTF and KIA were assessed with two-sample t-tests, after using Cochran's test to assess homoscedasticity. The ratio Lu_n/Er_n was calculated to evaluate the slope of HREE, where n refers to the shale-normalized abundances of lutetium (Lu) and erbium (Er). Because RTF and KIA had unequal variances in Lu_n/Er_n ratios, a two sample t-test with unequal variances was used to determine significance.

Multiple regressions were performed to assess changes in total REY and Y/Ho ratios from each core over time, using year and Pioneer River discharge as the independent variables. Correlations of Zr and Y/Ho ratios were checked for each core to assess detrital contamination, which would lower the Y/Ho mass ratio closer to shale values (~26) and elevate concentrations of terrestrially derived elements such as Zr (Webb and Kamber 2000). All statistical analyses were done with SYSTAT v.10.2 software.

Results

General Mackay REY patterns

When the scaled REY data were ordinated along the first two principal components, which explained 67.9% and 20.8% of the total variance respectively, the data from the most inshore coral (RTF) clustered tightly with water samples from the Pioneer River mouth and estuary (Fig. 1b). Coastal seawater, the RTF coral and terrestrial sediment (MUQ) all had high positive values along principal component 2, which are largely explained by differences in scaled LREE abundances. By contrast, the coral from further offshore (KIA) and the offshore seawater sample from the Coral Sea, had high positive values along principal component 1, which are largely explained by differences in scaled middle rare earth element (MREE) and HREE abundances. The large differences in scaled Y abundances also contribute to principle component 2, with scaled abundances of Y strongly mirroring a gradient of terrestrial influence (MUQ < Pioneer catchment streams < Pioneer River mouth < RTF < KIA < Coral Sea).

When just the coral samples were compared, RTF differed from KIA in five main respects. RTF had: (1) greater total REY abundance; (2) preferential enrichment of LREEs ; (3) flatter HREE patterns; (4) more negative Ce anomalies; and (5) smaller Y/Ho ratios (Table 1, Fig. 2). REY abundances from RTF were ~2-5 times higher than REY abundances from KIA, while LREE were preferentially enriched in RTF relative to KIA. Although shale-normalized REY from both cores were HREE enriched, RTF was less so relative to KIA, as indicated by a significantly greater (= higher slope) mean Lu_n/Er_n ratio in KIA (1.67) than in RTF (1.11) ($t = 17.41$, $df = 43$, $p < 0.001$). The mean Ce anomaly (0.502) for the RTF core was significantly lower than that (0.610) from KIA samples ($t = 6.86$, $df = 51$, $p < 0.001$). The mean Y/Ho ratio (67.3) for RTF was less than half of the mean Y/Ho (142.6) for KIA. Because there was no significant negative relationship between Zr with Y/Ho for either RTF or KIA ($r = 0.370$, $p > 0.05$ and $r = 0.045$, $p > 0.10$, respectively), these differences were not likely due to terrigenous contamination.

Temporal change

There were two major trends in the coral REY over time in both the RTF and KIA corals: (1) increased total REY; and (2) decreased Y/Ho ratios (Fig. 3a). The rate of increase in total REY abundance was approximately three times greater in RTF than in KIA, and was significantly related to both year and Pioneer River discharge: when combined they explained 49% and 46% of the total variance at Round Top and Keswick, respectively. The significance of the change in the total inshore coral REY load was more affected by river discharge at Round Top Island (partial $r^2 = 0.365$, $p < 0.002$) than at Keswick Island (partial $r^2 = 0.134$, $p < 0.025$).

The second temporal pattern in both coral records was a significant decrease of Y/Ho ratios over time, which occurred at similar rates at Round Top and Keswick islands (Fig 3b). In RTF, the trend was significantly related to year ($p < 0.001$) but not to discharge ($p < 0.059$), and together they explained 77% of the total variance. By contrast, Pioneer discharge had a more pronounced effect on the variability of Y/Ho in KIA: both year ($p < 0.002$) and discharge ($p < 0.035$) were negatively correlated with Y/Ho, but together they explained only 42% of the total variance.

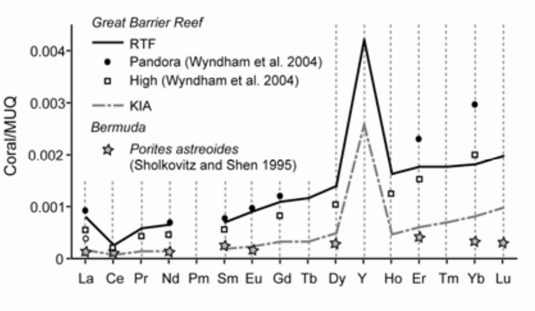

Figure 2: (a) Mean MUQ-normalized patterns in corals from Mackay (RTF: black lines; KIA: grey dashed lines) compared with other inshore GBR records (Pandora: black circles; High: white squares) and a Bermuda coral (stars).

Discussion

The presence of all of the typical marine features (La anomaly, Ce anomaly, Y/Ho fractionation, and HREE > LREE) in MUQ-normalized REY patterns from

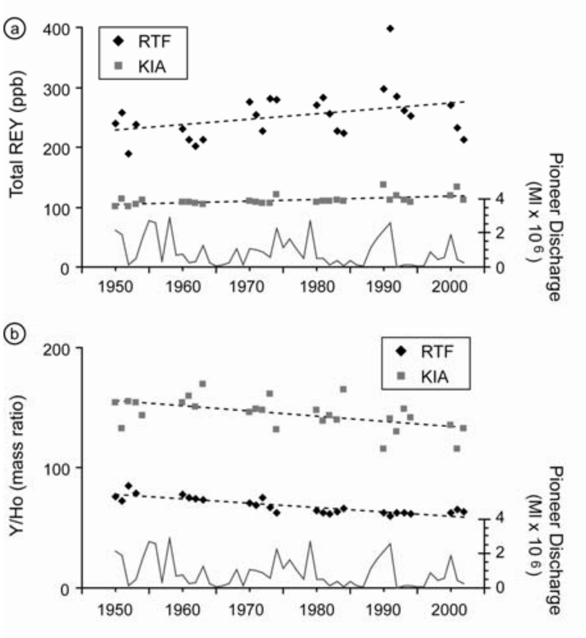

Figure 3: Temporal trends in (a) total REY concentration and (b) Y/Ho ratios between 1950 and 2002 for RTF (black diamond) and KIA (grey squares). Annual Pioneer River discharge (in megaliters) is shown with each plot.

both Mackay corals supports the assertion by previous authors that corals incorporate REY in proportion to ambient seawater concentrations (Sholkovitz and Shen 1995). However, the subtle differences in patterns between corals from Round Top and Keswick reefs likely indicate differential exposure to Pioneer River runoff and consequent differences in productivity.

The MUQ-normalized REY patterns and magnitudes from RTF were in strong agreement with other inshore GBR corals (Fig. 2) (Wyndham et al. 2004). By contrast, KIA had lower MUQ-normalized magnitudes that were similar to values from an offshore GBR reef (Wyndham et al. 2004) and values from a *Porites astreoides* collected from Bermuda (Sholkovitz and Shen 1995), suggesting reduced terrestrial influences at these sites. The underlying steady but small increase in total REY abundance over time at both sites suggests diffuse inputs of REY, possibly from greater catchment erosion coincident with agricultural expansion. Increases in REY values were most notable at Keswick in years with large floods, when plumes were more likely to reach the vicinity of the island.

LREE enrichment in the Round Top coral probably relates to greater terrestrial influence, as LREEs may be more readily mobilized by weathering than HREEs (Nesbitt et al. 1990). LREE enrichment in corals is often associated with river runoff: for example, Shioya-wan Bay (Okinawa, Japan), which receives runoff from the Taiho-o-kawa River, has flatter REY patterns (caused by LREE enrichment) and higher magnitudes of total REE in seawater and corals (including *Porites lutea*) than Sesoko-jima Island, which is distant from riverine sources (Akagi et al. 2004). When corals are sampled seasonally, LREE enrichments appear to coincide with large flood events (Wyndham et al. 2004).

The difference in the relative slopes of HREE between RTF and KIA may also be the product of terrestrial exposure. Like the water sample from the Coral Sea, the KIA coral had relative enrichments in scaled HREE abundances. While HREE enrichments are typical features of normalized oceanic seawater patterns, relative depletions in coastal waters can result from fluvial discharge, since inputs from major rivers are usually HREE depleted relative to shale (Goldstein and Jacobsen 1988). Alternatively, the flatter HREE patterns at Round Top Island may reflect differences in productivity between the two sites: Wyndham et al. (2004) noted seasonal HREE depletion in high resolution records of inshore GBR corals that they attributed to scavenging by organic (or organically coated) particles created through biological activity. Evidence of summer *Trichodesmium* blooms in the Pioneer River plume inshore from Keswick Island (Rohde et al. 2006) suggest there may be substantial differences in biological activity between the sites.

Table 1. Mean concentrations of REY in RTF, KIA, JCp-1, W-2 and MUQ. All values are in ppb, except detection limits (DL), which are in ppt (parts per trillion).

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
RTF	26.841	19.616	5.208	22.375	5.019	1.494	7.289	1.193	8.646	138.621	2.070	6.153	0.939	6.065	0.988
DL*	0.043	0.025	0.024	0.013	0.085	0.014	0.149	0.026	0.136	0.267	0.004	0.019	0.009	0.041	0.003
KIA	5.046	4.931	1.094	4.758	1.346	0.373	2.076	0.330	2.819	82.616	0.579	2.004	0.360	2.682	0.485
DL*	0.043	0.025	0.024	0.013	0.085	0.014	0.149	0.026	0.136	0.267	0.004	0.019	0.009	0.041	0.003
JCp-1	36.333	32.886	6.485	24.433	4.850	1.214	7.499	0.970	7.076	293.684	1.807	5.562	0.776	5.446	0.789
W-2	10536	23262	3032	12937	3274	1096	3714	616	3822	20186	805	2231	328	2058	302
MUQ**	32510	71090	8460	32910	6880	1570	6360	990	5890	31850	1220	3370	510	3250	490

*DL = Detection Limit. Calculated as three times the standard deviation of background levels.
**source: Kamber et al. (2005)

Differences in Ce anomalies between the two sites may also be linked to site-specific differences in biological activity. The more negative Ce anomaly from Round Top agrees with other coral (Wyndham et al. 2004) and seawater records (Nozaki et al. 2000) showing stronger Ce anomalies in coastal regions than offshore. Wyndham et al. (2004) found strong correlations between the timing of spring-summer peaks in both Mn/Ca and Ce anomalies from inshore corals. Since Ce oxidation is probably coupled with microbially-mediated Mn oxidation, Wyndham et al. (2004) suggested that Ce oxidation increased during periods of high solar radiation and temperature, and after floods, all of which increase the abundance of oxidizing bacteria.

Explanations for Y/Ho values observed in the Mackay corals may be more complex. Due to differing surface complex stabilities, Ho is scavenged approximately twice as fast as Y within the estuarine mixing zone (Bau 1996), resulting in a superchondritic marine Y/Ho mass ratio that typically varies between ~40 and 77 (Nozaki et al. 1997; Lawrence and Kamber 2006). If corals incorporate REY in proportion to seawater concentrations, and if coastal seawater REY patterns are intermediate between riverine and offshore sites, then coastal corals would be more likely to have lower Y/Ho ratios than corals from further offshore. In relative terms, the data supported this hypothesis, but in terms of absolute Y/Ho values, the coral values may not reflect surface seawater conditions. While the Y/Ho ratio (40.5) in Pioneer River mouth seawater was at the lower end of seawater range, the mean RTF Y/Ho value (67.3) was near the upper end of the range, suggesting that: (1) the distribution coefficients for Y and Ho incorporation into coral may vary, as observed for REE measured from Bermuda corals (Sholkovitz and Shen 1995); or (2) seawater fractionation between Y and Ho may change between the river mouth and sites further offshore. The mean Y/Ho value (142.6) for KIA, while similar to that (150.8) from the reference coral JCp-1, was nearly double the upper measurements of seawater Y/Ho. Such discrepancies in coral Y/Ho values compared to their local seawater Y/Ho ratios led Webb and Kamber (2000) to suggest that, in some cases, modern microbialites (with average Y/Ho = 56.1) may actually be a better proxy for seawater REY than skeletal carbonates. These results suggest that while trends of decreasing Y/Ho may be related to increasing catchment weathering and/or exposure to freshwater, further studies are needed to better determine how the elements are incorporated into coral skeletons.

Acknowledgement

Funding for this work was provided through an ARC Linkage grant (LP050896) to O. Hoegh-Guldberg and M. McCulloch, with contributions from the Mackay City Council, the Mackay Whitsunday Natural Resource Management Group, and the Great Barrier Reef Marine Park Authority. The author received additional support through Fulbright and NASA GSRP fellowships. Critical technical and analytical support was provided by M. Lawrence, B. Kamber, and A. Grieg.

References

Bau M (1996) Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf and the lanthanide tetrad effect. Contrib Mineral Petrol 123:323-333

Byrne RH, Sholkovitz ER (1996) Marine chemistry and geochemistry of the lanthanides. in Gschneider KA, Jr, Eyring L (eds) Handbook on the Physics and Chemistry of the Rare Earths. Elsevier, Amsterdam, The Netherlands, pp 497-593

Elderfield H, Upstill-Goddard R, Sholkovitz ER (1990) The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. Geochim Cosmochim Acta 54

Fallon SJ, White JC, McCulloch MT (2002) *Porites* corals as recorders of mining and environmental impacts: Misima Island, Papua New Guinea. Geochim Cosmochim Acta 66:45-62

Jupiter SD, Marion GS (2008) Changes in forest area along stream networks in an agricultural catchment of the Great Barrier Reef lagoon. Environ Manage 42:66-79

Kamber BS, Greig A, Collerson KD (2005) A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia. Geochim Cosmochim Acta 69:1041-1058

Lawrence MG, Kamber BS (2006) The behaviour of the rare earth elements during estuarine mixing--revisted. Mar Chem 100:147-161

Lawrence MG, Jupiter SD, Kamber BS (2006a) Aquatic geochemistry of the rare earth elements and yttrium in the Pioneer River catchment, Australia. Mar Freshw Res 57:725-736

Lawrence MG, Grieg A, Collerson KD, Kamber BS (2006b) Rare earth element and yttrium variability in South East Queensland waterways. Aquat Geochem 12:39-72

Nesbitt HW, MacRae ND, Kronberg BI (1990) Amazon deep-sea fan muds: light REE enriched products of extreme chemical weathering. Earth Planet Sci Lett 100:118-123

Nozaki Y, Zhang J, Amakawa H (1997) The fractionation between Y and Ho in the marine environment. Earth Planet Sci Lett 148:329-340

Nozaki Y, Lerche D, Alibo DS, Snidvongs A (2000) The estuarine geochemistry of rare earth elements and indium in the Chao Phraya River, Thailand. Geochim Cosmochim Acta 64:3983-3994

Rohde K, Masters B, Brodie J, Faithful J, Noble R, Carroll C (2006) Fresh and marine water quality in the Mackay Whitsunday region 2004/2005. Mackay Whitsunday Natural Resource Management Group, Mackay, QLD, Australia, p 91

Sholkovitz E, Shen GT (1995) The incorporation of rare earth elements in modern coral. Geochim Cosmochim Acta 59:2749-2756

Sholkovitz ER (1995) The aquatic chemistry of rare earth elements in rivers and estuaries. Aquat Geochem 1:1-34

Webb GE, Kamber BS (2000) Rare earth elements in Holocene reefal microbialites: a new shallow seawater proxy. Geochim Cosmochim Acta 64:1557-1565

Wyndham T, McCulloch M, Fallon S, Alibert C (2004) High-resolution coral records of rare earth elements in coastal seawater: Biogeochemical cycling and a new environmental proxy. Geochim Cosmochim Acta 68:2067-2080