REPORT

River runoff reconstructions from novel spectral luminescence scanning of massive coral skeletons

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Abstract Inshore massive corals often display bright luminescent lines that have been linked to river flood plumes into coastal catchments and hence have the potential to provide a long-term record of hinterland precipitation. Coral luminescence is thought to result from the incorporation of soil-derived humic acids transported to the reef during major flood events. Corals far from terrestrial sources generally only exhibit dull relatively broad luminescence bands, which are attributed to seasonal changes in coral density. We therefore tested the hypothesis that spectral ratios rather than conventional luminescence intensity provide a quantitative proxy record of river runoff without the confounding effects of seasonal density changes. For this purpose, we have developed a new, rapid spectral luminescence scanning (SLS) technique that splits emission intensities into red, green and blue domains (RGB) for entire cores with an unprecedented linear resolution of 71.4 μm. Since humic acids have longer emission wavelength than the coral aragonite, normalisation of spectral emissions should yield a sensitive optical humic acid/aragonite ratio for humic acid runoff, i.e., G/B ratio. Indeed, G/B ratios rather than intensities are well correlated with Ba/Ca, a geochemical coral proxy for sediment runoff, and with rainfall data, as exemplified for coral records from Madagascar. Coral cores also display recent declining trends in luminescence intensity, which are also reported in corals elsewhere. Such trends appear to be associated with a modern decline in skeletal densities. By contrast, G/B spectral ratios not only mark the impact of individual cyclones but also imply that humic acid runoff

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increased in Madagascar over the past few decades while coral skeletal densities decreased. Consequently, the SLS technique deconvolves the long-term interplay between humic acid incorporation and coral density that have confounded earlier attempts to use luminescence intensities as a proxy for river runoff.

Keywords Luminescence spectra · Soil runoff · Coral carbonate · Humic acids · Core scanning

Introduction

Understanding the impact of global warming on present-day rainfall patterns and river discharge requires constraints on long-term 'natural' climate variability and hence the need for climate records extending back for at least several hundred of years. Unfortunately such records are rare, and in some locations such as Madagascar, even present-day weather data remains scarce (Dewar and Wallis 1999; Dewar and Richard 2007). This lack of continuous long-term instrumental data highlights the importance of climate proxy records such as those preserved in the massive annually banded coral *Porites* sp. (McCulloch et al. 1994; Felis and Pätzold 2003; Lough 2004; Grottoli and Eakin 2007 and references therein). Various skeletal properties have been employed to trace past climate change using coral records, yet their ability to be used as environmental proxies is compromised by our limited mechanistic understanding of their origin (Lough 2004; Corrège 2006; Jones et al. 2009 and references therein).

When placed under ultraviolet (UV) light, some coral cores show bright luminescence patterns that are related to freshwater flood events and thus past river flow and rainfall dynamics in tropical environments (Isdale 1984; Boto and Isdale 1985; Scoffin et al. 1989; Lough et al. 2002). Pioneered by Isdale (1984), a number of techniques have been developed to measure the varying intensity of luminescence in coral skeletons (Barnes et al. 2003 and references therein; electronic supplemental material, ESM). Variability in emission intensities was first thought to be caused by the incorporation of luminescent humic acids and soil-derived organic compounds introduced by seasonal river runoff (Isdale 1984; Susic and Boto 1989; Susic et al. 1991; Matthews et al. 1996; Isdale et al. 1998; Wild et al. 2000). Changing coral density and architecture has been proposed as another cause since massive corals form a skeleton of luminescent aragonite (MacRae and Wilson 2008), and banded luminescence is also found in corals in oceanic environments devoid of terrestrial inputs (Barnes and Taylor 2001a, b). Barnes and Taylor (2005) introduced a classification of skeletal luminescence patterns discriminating between faint bands and bright lines. Faint luminescent banding is attributed to the annual skeletal density banding, while the brighter narrow luminescent lines (linked to runoff) are considered to be associated with another component, e.g., humic acids, relating to skeletal chemistry (Barnes and Taylor 2005). Therefore, the hypotheses formulated for this research paper are (1) both humic acids and aragonite density determine luminescence intensities in corals and (2) that their deconvolution is required in order to reconstruct river runoff accurately.

This study introduces a novel scanning technique that quantifies luminescence intensities by splitting the total emission spectrum into different spectral domains. Measured luminescence intensities and calculated spectral luminescence ratios are analysed from coral cores drilled in Madagascar to investigate the potential for normalising the episodic bright (humic acid) emission bands to the overall aragonite skeleton emission, thus generating normalised luminescence data using spectral luminescence ratios. Recently, Cobb et al. (2008) addressed various sources of uncertainties in coral luminescence-based paleorecords. Firstly, the cause of luminescence in corals is not fully understood (Barnes and Taylor 2001a, 2005; Jones et al. 2009), and secondly, there is some evidence that luminescence intensities show an unexplained long-term declining trend that could compromise runoff reconstructions (Isdale et al. 1998; Lough JM pers comm). The aim of this research is to improve the robustness of luminescence as a proxy for humic acid runoff, while resolving the uncertainties addressed by Cobb et al. (2008).

While banded luminescence seems to reflect the organic flux carried by seasonal variability in river runoff (Isdale 1984), coral Ba/Ca also provides a highly sensitive tracer of suspended sediment fluxes (Alibert et al. 2003; McCulloch et al. 2003) and in some regions, upwelling (Fallon et al. 1999). Suspended sediments (clays) carry adsorbed barium and other river-born trace elements that are desorbed in the low-salinity estuarine mixing zone and subsequently behave as conservative dissolved constituents of the ambient seawater in which the corals thrive (Sinclair and McCulloch 2004). Consequently, Ba/Ca and luminescence are used to reconstruct sediment and humic acid runoff, respectively in tropical catchments, where both have been shown to co-vary with the changing magnitude of precipitation and river flow (Fleitmann et al. 2007). As Madagascar weather data are scarce (Dewar and Wallis 1999; Dewar and Richard 2007), novel spectral luminescence ratios and conventional luminescence intensities are paired with Ba/Ca to validate the method, supported by rainfall data from a nearby weather station. Finally, differences in luminescence between corals from reef environments near and distant from terrestrial inputs will be evaluated.

Materials and methods

Spectral luminescence scanning (SLS) was developed to quantify skeletal emissions in different spectral domains from coral cores (Grove et al. 2009). Below, we describe how spectral emission intensities are quantified for entire core slabs and the modifications undertaken of the Avaatech core-scanner, conventionally used for analysing the changing element composition of entire sediment cores by X-ray fluorescence (Jansen et al. 1998; Richter et al. 2006). The Avaatech XRF core-scanner is equipped with a line-scan camera that yields high-resolution images using visible light to establish digital core archives and to assist in interpreting element stratigraphy data. It is the line-scan camera in combination with the core-scanning technology that makes this technique unique. A summary of the techniques advantages can be found in the electronic supplementary material (ESM) together with a detailed description of the method.

Method summary

The standard light source of the Avaatech core-scanner was replaced by two long-wave UV-A tubes in the 350–450 nm range (Fig. 1). The light source and camera progress down the sample slab as a single unit when the scan is initiated, constantly scanning multiple lines, resulting in a continuous core image. A 450-nm light cut-off filter is optionally placed beneath the camera lens to eliminate reflected light from the UV source and record luminescence intensities in the blue domain (Fig. 1). Luminescence emission is recorded by a Line Scan Camera. Incoming light passing through the lens is split into three wavelength ranges (Red, Green and Blue) by a Dichroic RGB beam splitter prism and recorded by separate sensors (Fig. 1). As the camera moves over the slab, it continuously collects a single cross-core line image of 2048 × 1 pixels for each spectral range. The current set-up gives a spatial resolution of 140 pixels per cm, each pixel therefore yielding a linear resolution of 71.4 μm. Three data points are produced for each individual pixel in the R, G and B range.

The specifically designed software (Avaatech) enables linear transects to be manually drawn from the luminescence image to retrieve intensity profiles for any specified area and direction (Fig. 2). Once the areas of interest are identified, transects are created up to 150 cm in length and 15 cm in width, however, usually limited to shorter transects depending on sample size, changes in the direction of growth axes or breaks and/or visual discrepancies in the sample. Connecting transects is achieved by transferring quantified intensity data into a separate program used for data management. Multiple transects can be created for any length, in any direction, at any required width from just a
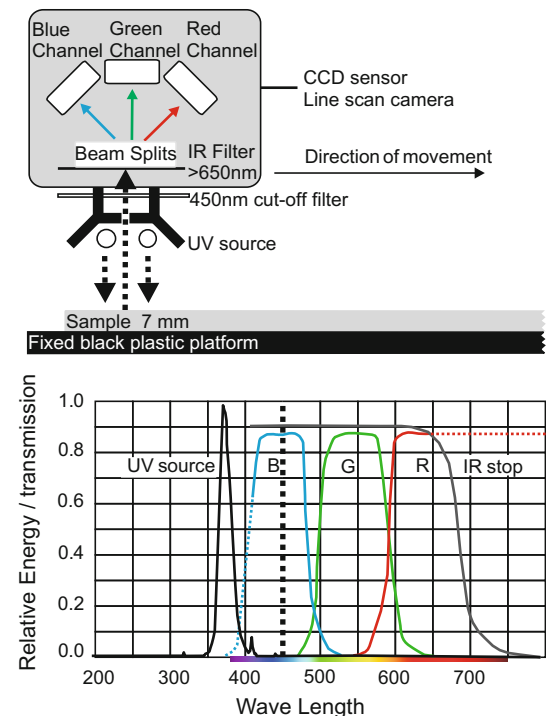

Fig. 1 Schematic diagram of the modified Avaatech core-scanner used for spectral luminescence imaging (*upper panel*) and the spectral distribution and sensitivity of the light source and camera sensors (*lower panel*). The UV light source efficiently emits in the range of 315–450 nm. The 450-nm cut-off filter (*black dotted line*) removes all UV source emissions (*reflected light*) before splitting into *red*, *green* and *blue* fractions by a dichroic RGB beam splitter. A 650-nm infrared cut-off filter prevents light of greater wavelengths from entering the three separate CCD sensors

single scan taking up to 1 h. Uranyl glass with homogenous luminescent properties is mounted on the platform and used as a standard reference for all intensity measurements. Line transects drawn through the entire length of the standard material using the image and software are used to correct for any drift in either the light source intensity or camera recording sensitivity. Subsequently, the resulting sample intensities are corrected for any drift to allow direct inter-comparisons between cores to be made over time. Importantly, SLS provides fast, non-destructive quantified data that allows for matching and comparing coral carbonate skeletons with little sampling effort.

Core collection and sample preparation

A total of five coral cores drilled from *Porites* sp. colonies, four from Antongil Bay (E 49°, S 15°) and one off St Marie island (E 49°, S 17°), Northeast Madagascar (Fig. 3), were used to test this new technique, with a more detailed coral climate analysis being given elsewhere. The four cores from Antongil Bay are all influenced by seasonal river plumes occurring in the wet season between December and
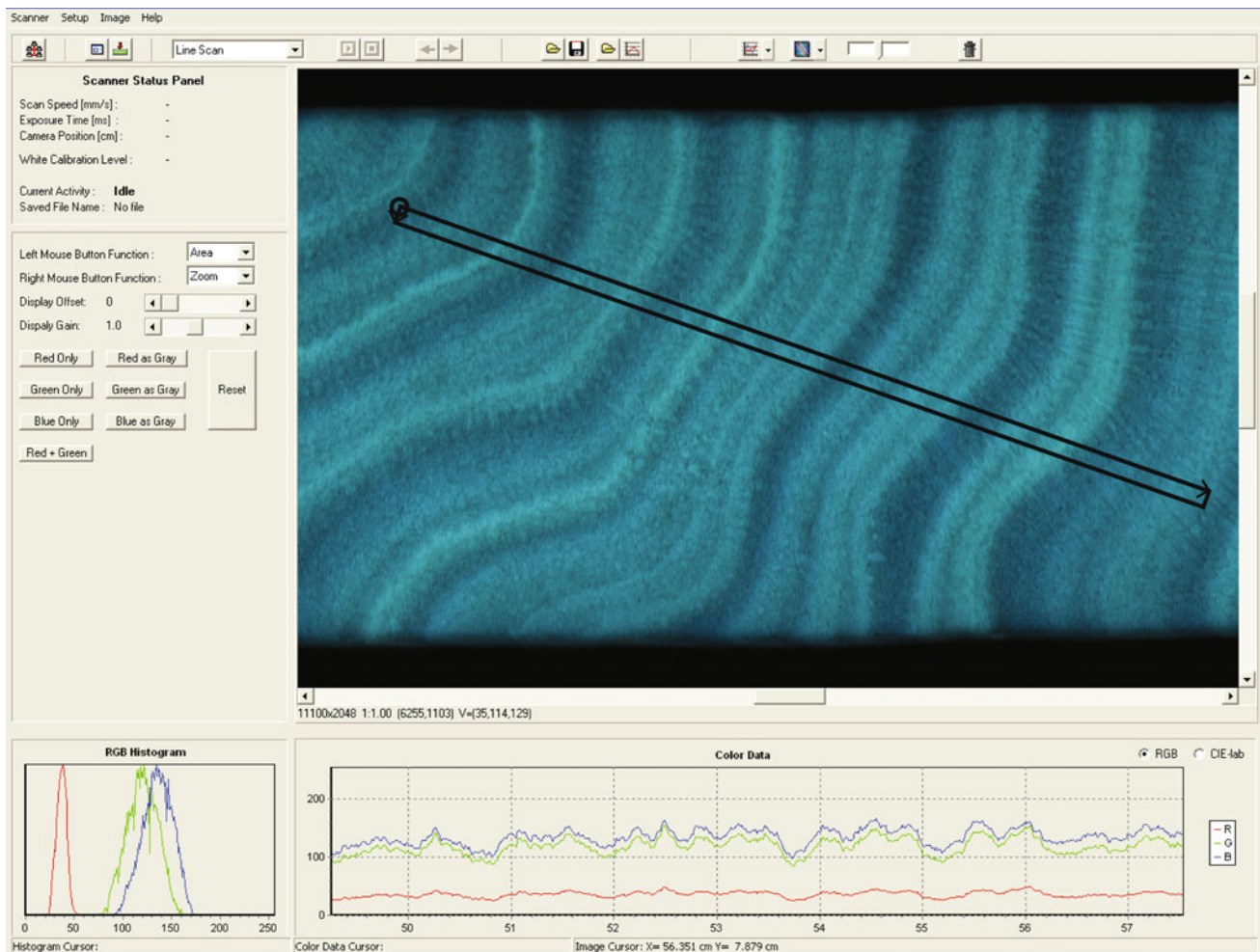
Fig. 2 Screen shot of the software used to analyse UV luminescence imaging. The image shows a section of the coral core ANDRA, with a black transect drawn onto the image parallel to the growth axis. Multiple transects can be manually selected on the digital image in any direction for any width after a single scan

April. The other core from St Marie is not influenced by any river. All cores were collected in March and April 2007 between the depth ranges of 4–6 m and are dated between 27- and 129-years-old (Table 1). A detailed description of the research area and climate setting is provided in the ESM. Coral chronologies were developed by counting density bands using digitalised X-rays, complemented by counting luminescence intensity bands (Hendy et al. 2003).

All coral cores were cut into 7-mm-thick slabs and ultrasoniced three times in ultrapure 17 Ω water for 10-min periods, removing all surficial particles. For luminescence measurements, coral slabs must have a smooth surface and be of uniform thickness. The slabs were also cleaned with compressed filtered air between ultrasonicing to remove all remaining loose particles and dried for 24 h in a laminar flow hood. It is essential to clean cores identically in order to prevent changes in emissions through the addition or removal of luminescent substances between cores

(Carricart-Ganivet et al. 2007). Particularly for the most recent years, intensities decrease due to the quenching signal by residual organic matter associated with the coral tissue layer and/or endolithic algae. Oxidative cleaning for 24 h with sodium hypochlorite (NaOCl, 10–13% reactive chloride; Sigma–Aldrich Company, St. Louis, MO) removes these contaminating organics yet may also affect the chemistry of the skeletal lattice compromising climate reconstruction (Boiseau and Juillet-Leclerc 1997; Watanabe et al. 2001; Grottoli et al. 2005). Therefore, cores were first sampled for geochemical analysis and then scanned for spectral luminescence before and after treatment with NaOCl.

Luminescence intensities generated by the SLS technique were also compared to the emission produced using an argon-ion laser-beam as an excitation source and an Ocean-Optics linear diode array detector via an optical fibre at the VU University, Amsterdam. Laser-Ablation ICP-MS profiles were undertaken to determine Ba/Ca
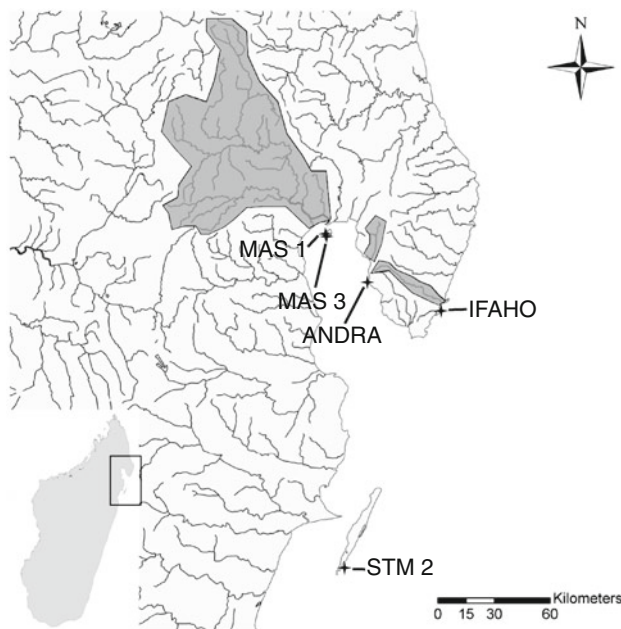
Fig. 3 Map of the region where cores MAS1, MAS3, ANDRA, IFAHO and STM2 were drilled. Coral locations (*stars*) and their corresponding rivers and watersheds (*grey shaded areas*) are marked accordingly in and around Antongil Bay. The largest river is the Antainambalana, influencing MAS1 and MAS3; the river influencing ANDRA is the Ambanizana, flowing south westward into the bay; and the river influencing IFAHO is the Anaovandran flowing eastward outside the bay. The coral core STM2 is not influenced by any river and is located to the south east of the island St Marie

ratios at a sub-weekly resolution on the coral core MAS1 at ANU Canberra following the method of Sinclair et al. (1998) and Fallon et al. (2002). Geochemical analysis yielded Ba/Ca ratios, a well-established proxy for sediment runoff, used here to cross-validate the luminescence results (McCulloch et al. 2003). Density profiles were measured using the CoralXDS program, where X-ray images were digitalised, uploaded and calibrated using an aragonite wedge (Helmle et al. 2002; Carricart-Ganivet et al. 2007).

Rainfall and river discharge time series are not available for Antongil Bay and are generally scarce across Madagascar (Kremen 2003). However, for calibration of coral luminescence data, we use Tamatave (WMO code 67095), the nearest weather station with rainfall data (18.15°S, 49.37°E), 293 km south of Antongil Bay, which also provides the most continuous time series for northeast Madagascar covering the period 1889–1985 (data available at http://www.ncdc.noaa.gov/oa/climate/ghcn-monthly/).

Results

Technique and resolution

Line-scanning achieves a linear resolution of 71.4 μm, generating detailed luminescence intensity profiles of coral skeletons. This equates to a temporal resolution of 2.6 days for corals growing at a rate of 1 cm/year. The resolutions achieved by SLS are among the highest found in coral proxy analysis and comparable to Laser-Ablation ICP-MS, used for element composition in palaeo-reconstructions (Sinclair et al. 1998; Fallon et al. 2002). The performance of the new SLS technique was also compared to that obtained from an argon laser excitation, coupled with a linear diode array detector via an optical fibre (Milne and Swart 1994). Intensity profiles appear very similar for both methods, considering the lower linear resolution of 0.1 mm achieved with the laser method (Fig. ESM1).

Coral luminescence intensities

Digital images generated using visual and UV light are displayed for the top section of the MAS1 coral core, a 15.8-cm slab covering the years 1991–2006 (Fig. 4). Luminescence scanning displayed seasonal variability in relative intensities, with a gradual decline observed since

Table 1 A summary of the five coral cores drilled in Madagascar, applied in a manner that demonstrates the potential of the SLS technique and the application of spectral luminescence ratios. In some cases, only sections of cores were used for this study

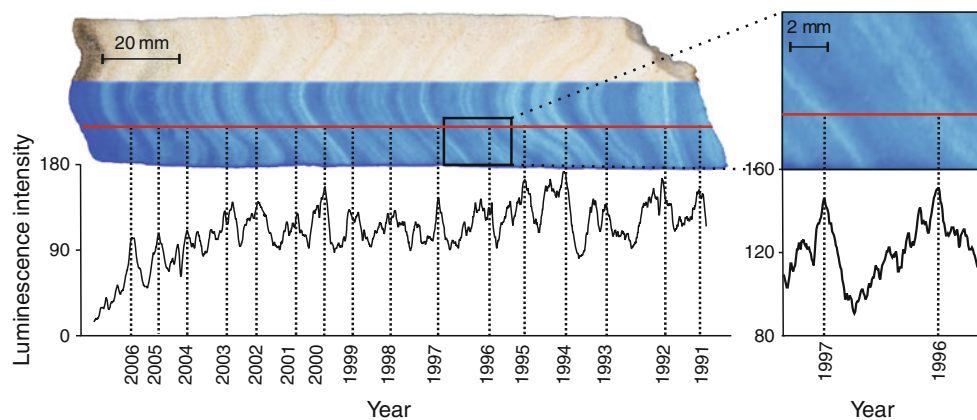| Coral name	Location	Length (cm)	Age (years)	Distance to closest river source (km)	Average growth rate (cm/yr)
MAS1 (Antongil Bay)	S 15°30,566 E 49°45,437	120.78	102	7	1.18
MAS3 (Antongil Bay)	S 15°30,578 E 49°45,456	142.97	129	7	1.11
ANDRA (Antongil Bay)	S 15°41,17 E 49°57,419	119.82	94	7	1.27
IFAHO (Antongil Bay)	S 15°51,968 E 50°18,73	37.95	27	4.5	1.41
STM2 (St Marie)	S 17°05,685 E 49°51,483	168	115	40	1.45

Fig. 4 An example of the digital images generated by the line-scan camera using the top section of the coral core MAS1, scanned under visible light (*top half*) and UV light (*bottom half*). The *red transect line* marks the area of which *green* luminescence intensity (G) is measured, with annual cycles assigned to the raw data by designating peak values from 1991 to 2006. The *black box* marks an enlarged section of relative photoluminescent intensities (G) for the years 1996 and 1997 (*right*). A separate transect of a smaller size was created on the zoomed image (*red*), identifying fine-scaled fluctuations in intensities

2003 (Fig. 4). Treated with NaOCl, the intensity of luminescence for the most recent bands increases (Fig. ESM2). MAS1 shows periodic yellow bands within the skeleton under visual light that correlate temporally with increased luminescence intensities (Fig. 4). As illustrated for the years 1996 and 1997, high magnification of the digital image improves the ability to identify and avoid physical discrepancies within cores and enables the precise selection of sampling tracks (Fig. 4).

Luminescence assists with the construction of age models by analysing the green luminescence intensity profiles, exemplified for a 9-year section of each core drilled within Antongil Bay (Fig. 4). In addition to counting annual bands down-core, there are singular sections within the profiles that each displays a distinct pattern shared by all corals (Fig. 5). These provide reference points independent of the annual banding leading to robust age models. As expected, the most similar intensity profiles were found for the two nearby cores influenced by the same watershed (MAS1 and MAS3; Figs. 3, 5). For the complete monthly intensity time series, correlations of MAS1 with MAS3 ($R = 0.65$, $P < 0.001$, $n = 1,234$) are higher than with ANDRA ($R = 0.63$, $P < 0.001$, $n = 1,112$) and IFAHO ($R = 0.52$, $P < 0.001$, $n = 305$).

Application of spectral luminescence ratios

In all cores from Antongil Bay, intensity values in the green domain (G) were higher than in the red (R), whereas the green and blue (B) intensities were similar with the 450-nm filter fixed below the camera (Fig. ESM3). To validate luminescence as a proxy for river runoff, we first correlated luminescence intensity (hereafter G) with Ba/Ca ratios, an established proxy for sediment runoff (McCulloch et al.

2003). Although temporally aligned, there is little agreement between G and Ba/Ca in terms of seasonal amplitudes and the long-term trend (Fig. 6). Spectral ratios are applied to optically remove the assumed density and architectural effect and to retrieve the luminescence signal emitted by the humic acids incorporated from soil runoff (Fig. 6b). As the spectral emissions of humic acids and aragonite cluster at similar wavelengths, it is difficult to separate the two using traditional fluorescence spectroscopy (Matthews et al. 1996; Wild et al. 2000). Although both are within the green–blue range, humic acid emission wavelengths are slightly longer towards the green end of the spectrum (Ramseyer et al. 1997). Hence, the green/blue (G/B) spectral ratio is a measure of the humic acid concentration relative to the aragonite density of the coral.

Correlations of Ba/Ca with the spectral G/B ratio improve compared to G, exemplified by core MAS1 (Fig. 6b). A marked peak in G/B ratios not observed in G now appears, matching a significant spike in Ba/Ca for the year 2000 (Fig. 6b). Indeed, for the total length of the MAS1 core, correlations of G/B ratios with Ba/Ca are higher and statistically significant ($R = 0.60$, $P < 0.001$, $n = 1,234$) compared to G alone ($R = 0.09$, $P < 0.005$, $n = 1,234$). For yearly averages, correlations between G/B ratios and Ba/Ca remain robust ($R = 0.61$, $P < 0.001$, $n = 102$), whereas G and Ba/Ca are negatively correlated ($R = -0.42$, $P < 0.001$, $n = 102$; Fig. 7). Correlations of monthly MAS1 G/B with MAS3 ($R = 0.69$, $P < 0.001$, $n = 1,234$) are higher than with ANDRA ($R = 0.67$, $P < 0.001$, $n = 1,112$) and IFAHO ($R = 0.64$, $P < 0.001$, $n = 305$). Indeed, correlations of G/B between all cores relative to MAS1 are now similar in contrast to G, testifying that G/B identifies an environmental signal of regional significance.
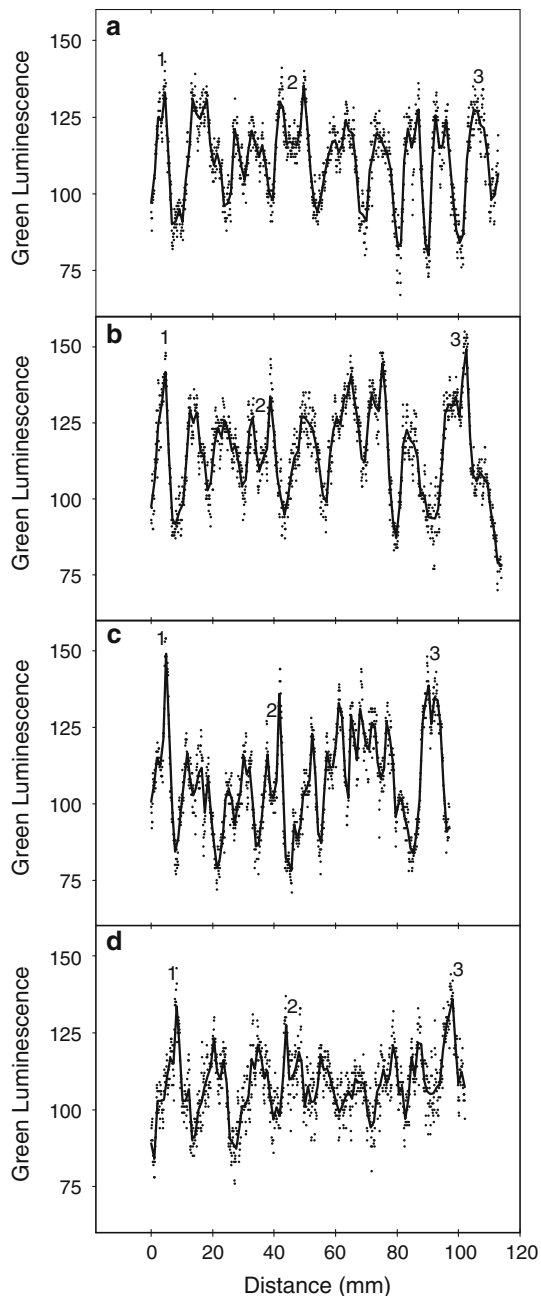
Fig. 5 A 14-point moving average (*solid*) applied to the raw (*dots*) luminescence intensity profile data in the green spectral domain (G) for 9-year sections of the Antongil Bay cores MAS1 (**a**), MAS3 (**b**), ANDRA (**c**) and IFAHO (**d**). Points 1 and 3 mark exceptionally high luminescence intensities, and point 2 a clear double spike within a yearly cycle. MAS1 (**a**) and MAS3 (**b**) are located closest to each other (<1 km) and show the most observed similarities. ANDRA (**c**) is 30 km from both MAS1 and MAS3, and IFAHO (**d**) is a further 40 km away

Fig. 6 MAS1 monthly resolved Ba/Ca (*black*) compared with **a** the monthly averaged G (*green*) and **b** the G/B ratio (*red*). While the variability in green luminescence and Ba/Ca-runoff (**a**) is aligned, seasonal amplitudes and long-term trends are in poor agreement with each other. The correlation coefficient of G/B improves with Ba/Ca ($R = 0.69$, $P < 0.001$, $n = 185$; **b**) compared to G ($R = 0.5$, $P < 0.001$, $n = 185$; **a**), revealing a significant spike in the year 2000 corresponding to cyclone Hudah. To physically remove architectural effects, monthly sections of the coral sampling transect were powdered and compressed into micro-pellets (**c**). Green luminescence intensities (*green*) of micro-pellets also show an observed coherence with Ba/Ca (*black*), including the 2000 spike, testifying to the effect of skeletal architecture on absolute luminescence

In order to further assess the effect of density and architecture on luminescence, samples were manually crushed from the same section of the MAS1 core. Crushing removed the large-scale architecture and was achieved by
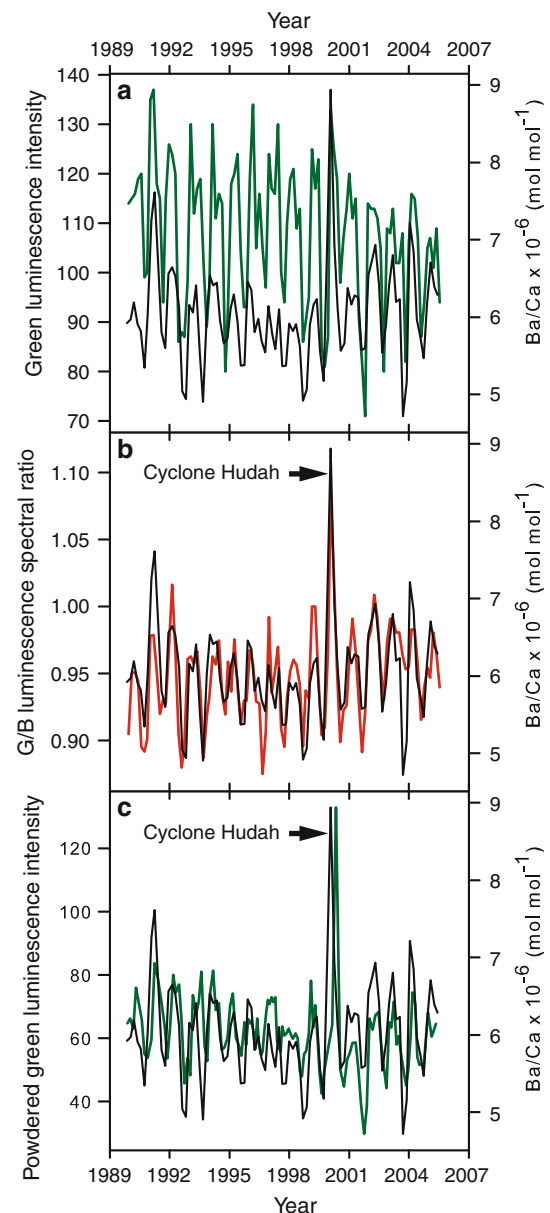
drilling sub-samples along the coral growth axis parallel to the optical measurement track, homogenising the extracted powder and pressing them into pellets. Each pellet
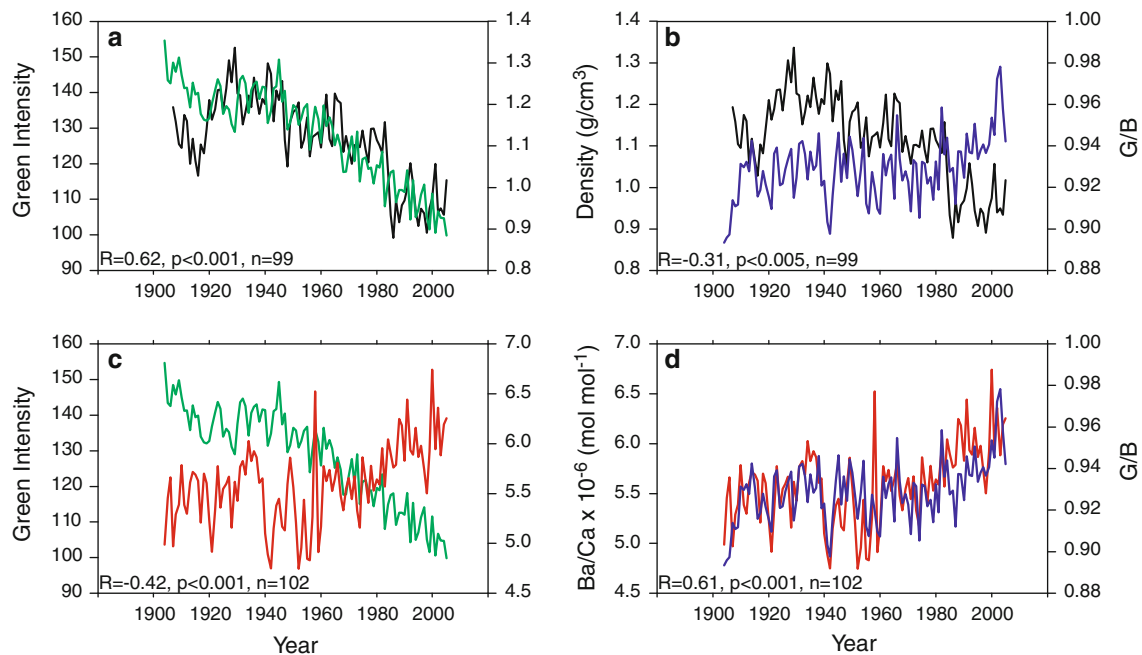
Fig. 7 Time series plots for the annual means of MAS1 G (*green*), density (*black*), Ba/Ca (*Red*) and G/B (*Blue*). The last 3 years of the X-ray image were distorted and were not used, therefore $n = 99$. All parameters were scaled by calculating yearly averages. Correlation coefficients and significance levels are shown at the bottom of each graph; luminescence intensity vs. density (**a**), density vs. G/B (**b**), luminescence intensity vs. Ba/Ca (**c**) and Ba/Ca vs. G/B (**d**). Note the highly significant annual mean correlation of G/B with Ba/Ca and G with density, while negative correlations exist for G/B with density and G with Ba/Ca

approximately represented 1 month and was measured using the same SLS technique. Difference in resolution between the crushed samples and scanned cores hinders the perfect alignment of the two time series (Fig. 6c). Nevertheless, crushed sample luminescence intensities show a much improved coherence with Ba/Ca (Fig. 6c), as, e.g., the marked peak of 2000 becomes apparent. Consequently, manual crushing confirms that G/B spectral ratios effectively normalise the humic acid signal to the aragonite signal in a manner conceptually similar to normalising elemental proxy concentrations against aragonite, i.e., Ba/Ca, Sr/Ca. This provides the opportunity for tracing humic acid runoff in coral records without interference from density and architectural effects.

Coral STM2, from a reef devoid of terrestrial influences, typically shows very low luminescence intensities in the green domain, as exemplified for a 7-year section (Fig. 8). Both skeletal and powder intensities are considerably lower than MAS1, a core strongly affected by soil runoff (Fig. 6). Crushed samples from STM2 show no annual cycles and little variance, unlike the intensities in the intact core (Fig. 8). Removal of the density and architecture by crushing yields a low and stable intensity signal in the green domain without any trend, as opposed to the intact core which shows a declining luminescence intensity trend towards the core top.
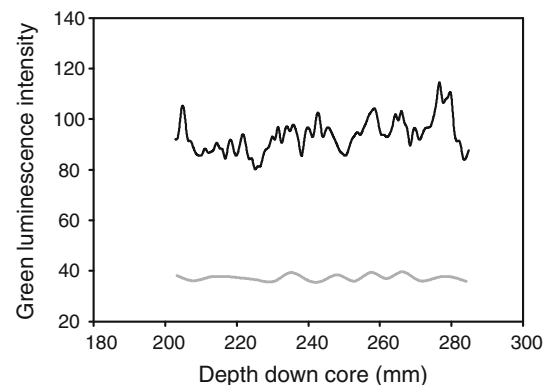

Fig. 8 A 14-point moving average applied to G data (*black*), corresponding to a 7-year section (measuring 80 mm) from the coral core STM2. The core shows weak annual banding with relatively low amplitudes. By powdering and compressing monthly sections of the coral, we physically removed the architecture. Pellets were then scanned to analyse luminescence intensities (*grey*), showing little variance and low relative intensities

Declining luminescence intensities were observed for all three long corals from the Antongil Bay region (Fig. 9a), in concert with declining density (e.g., MAS1; Fig. 7). The decreasing trends over the period 1905–2006 in both luminescence intensities (-40.92/100 years; $r^2 = 0.42$, $P < 0.001$) and density (-0.24 g/cm³/100 years; $r^2 = 0.30$,

Fig. 9 Luminescence intensities are shown in the green spectrum (G) for the three cores MAS1 (*red*), MAS3 (*blue*) and ANDRA (*green*). An observed decline from approximately 1950 is followed by a further sharp decline from 1980 till present (**a**). G/B spectral luminescence ratios reveal an observed increase since 1980 (**b**). A long-term comparison of G/B (*red*) and Ba/Ca (*black*) is shown for the core MAS1 (**c**). G/B ratios and Ba/Ca show a good match (see Fig. 7 for correlations) for long-term trends and inter-annual variability. All data were normalised and smoothed using a 21-month filter
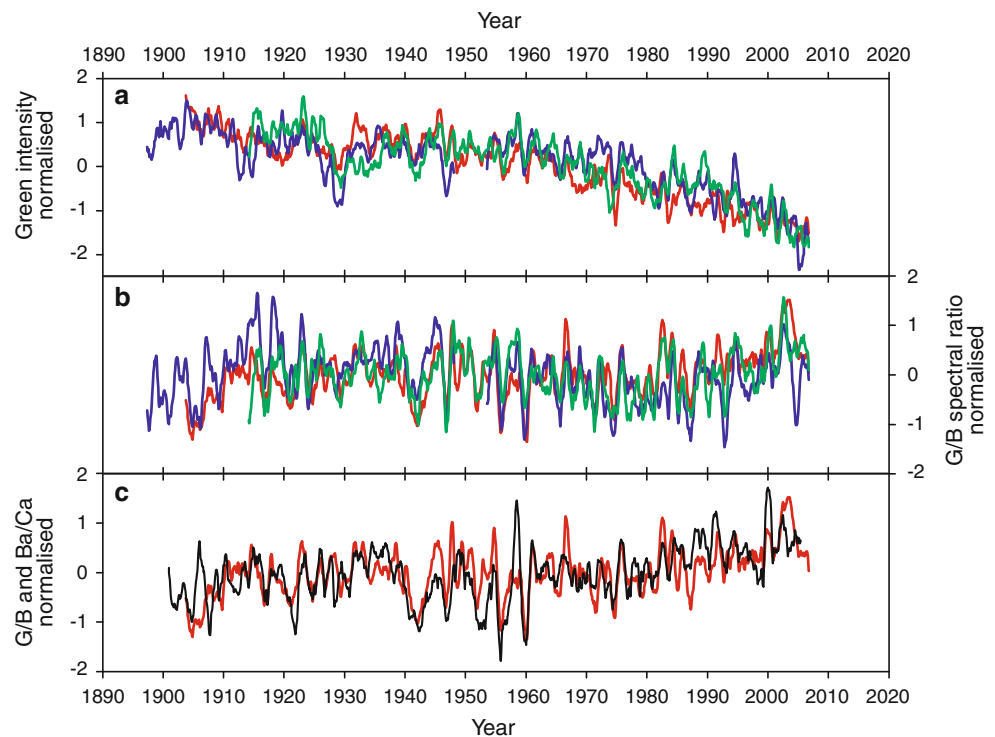
$P < 0.001$) are statistically significant. Both show an accelerated decline since the 1950s. The decreasing trend over the period 1950–2006 in luminescence intensity and density is -33.77 ($r^2 = 0.37$, $P < 0.001$) and -0.26 g/cm^3 ($r^2 = 0.37$, $P < 0.001$), respectively. Thus, the declining trends are most apparent after the 1950s. By contrast, spectral luminescence ratios show a different long-term pattern with significant increases since approximately 1980 (Fig. 9b). For the MAS1 core, the long-term trends in G/B and Ba/Ca ratios correlate well, indicating a modern increase in humic acid and sediment runoff, respectively, in northeast Madagascar (Figs. 9c, 7). As a corollary, G is negatively correlated with Ba/Ca and positively correlated with density (Fig. 7). Correlations of MAS1 and MAS3 annual average G/B are statistically significant ($R = 0.62$, $P < 0.001$, $n = 102$) and higher than G ($R = 0.44$, $P < 0.001$, $n = 102$), again testifying that G/B identifies an environmental signal of regional significance.

To validate the G/B ratio in coral MAS1, results are compared against precipitation data from the nearest weather station (WMO code 67095) in Tamatave (18.15°S, 49.37°E) which yields the most continuous rainfall time series available for northeast Madagascar for the period 1889–1985 (http://www.ncdc.noaa.gov/oa/climate/ghcn-monthly/). MAS1 is used since this coral is influenced by the largest watershed. Annual means were computed for September to August (water year) rainfall and G/B ratios (Fig. 10). As a tracer of humic acid runoff, G/B ratios track the interannual and decadal variability in Tamatave rainfall,
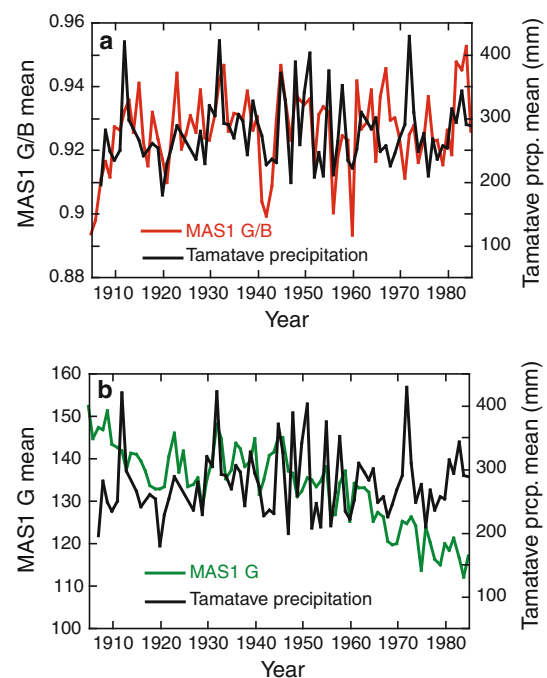

Fig. 10 A comparison of annual mean G/B (**a**) and G (**b**) with precipitation data from Tamatave; the most continuous rainfall time series for northeast Madagascar (WMO code 67095; 18.15°S, 49.37°E) covering the period 1905–1985 (data available at http://www.ncdc.noaa.gov/oa/climate/ghcn-monthly/). Annual means were calculated by averaging 'water year' monthly values, September to August. The correlation between MAS1 G/B and rainfall (**a**) is statistically significant ($R = 0.30$, $P = 0.01$, $n = 74$). There is no significant correlation between MAS1 G and rainfall ($R = 0.01$, $P = 0.98$, $n = 74$; **b**)

which have a statistically significant correlation ($R = 0.30$, $P = 0.01$, $n = 74$; Fig. 10). No significant correlation was observed between G and rainfall ($R = 0.003$, $P = 0.98$, $n = 74$; Fig. 10), further testifying that G/B ratios are a true measure of humic acid runoff and not overprinted by coral density effects.

Discussion

The coral skeleton is a complex structure reflecting seasonal and long-term changes in growth. The principle component of the aragonite skeleton is $CaCO_3$, and therefore quantification of geochemical proxies has been achieved by normalising the tracer element to calcium, e.g., Sr/Ca, Ba/Ca (Alibert et al. 2003; McCulloch et al. 2003). Our results show that spectral luminescence ratios (G/B ratios) offer a quantified signal of humic acid incorporation (Isdale 1984; Susic and Boto 1989; Susic et al. 1991; Matthews et al. 1996; Isdale et al. 1998; Wild et al. 2000) when normalised against density (Barnes and Taylor 2001a, b, 2005). The coral aragonite and humic acids it incorporates are both luminescent and have emissions in the green–blue domain (Matthews et al. 1996; Ramseyer et al. 1997; Wild et al. 2000; Nyberg 2002; Sierra et al. 2005). As humic acid emissions have slightly longer wavelengths than aragonite (Ramseyer et al. 1997), dull and bright luminescent intensity bands in coral skeletons have often been referred to as blue and yellow–green bands, respectively (Matthews et al. 1996; Wild et al. 2000).

SLS separates the humic acid signal from the density signal by normalising two grouped intensity values in the green and the blue domain, rather than extracting the humic acid wavelength emission from the skeleton using traditional fluorescence spectroscopy (Matthews et al. 1996; Wild et al. 2000). Although part of the humic acid signal will reside in the blue domain and part of the aragonite signal in the green (and vice versa), it is the relative increase in one compared to the other that reflects compositional changes. Indeed, Wild et al. (2000) divided the spectral emission matrix of a bright band by a dull band and found enhanced bright band emissions at longer wavelengths in ratios between 0.9 and 1.25, a range replicated by the G/B ratio. Following up from Wild et al. (2000), compositional changes are quantified by SLS, thus providing a means to reconstruct humic acid runoff at a linear resolution of 71.4 μm. The G/B ratio therefore renders a normalised humic acid signal equivalent to a humic acid/aragonite ratio, which is comparable to the geochemical trace element/Ca proxies. Spectral ratios provide more accurate measurements than luminescence intensities for identifying changes in humic acid runoff/erosion within

tropical marine environments by normalising for the effects of skeletal density and architecture.

The majority of techniques employed to reconstruct humic acid runoff from coral luminescence have previously focused on intensities alone (Boto and Isdale 1985; Matthews et al. 1996; Isdale et al. 1998; Wild et al. 2000; Barnes and Taylor 2001a). Corals produce high and low annual density bands; consequently conventional luminescence intensity measurements result in an indirect density measurement as proven by SLS (Fig. 7). High concentrations of humic acids locked into a low density (g/cm^3) section of coral skeleton would result in a weak luminescence intensity signal, as the area measured is significantly porous. In this situation, both green and blue intensities will be low while the G/B ratio will be relatively high, given the high proportion of humic acids locked within the aragonite. This may explain the occurrence of 'anomalous barium peaks' in coral records, i.e., that are not matched by a similar peak in luminescence intensities (Sinclair 2005). Indeed, for a similar anomaly found in our Madagascar cores for the year 2000, spectral ratios now identify that the 'anomalous barium spike' was caused by an extreme runoff event, rather than caused by any of the multiple biological mechanisms inferred by Sinclair (2005). It coincides with the landfall of Tropical Cyclone Hudah, which caused massive destruction in and around Antongil Bay, and catastrophic sediment and humic acid runoff (Birkinshaw and Randrianjanahary 2007). Consequently, spectral ratios rather than luminescence intensities should be taken to reconstruct humic acid runoff. Luminescence intensity profiles remain important, however, for the construction of age models by counting bands down-core and connecting corresponding marker points (Hendy et al. 2003). Cores possessing individual luminescence intensity traits are likely created by localised intra- and inter-colony variability in density (Felis et al. 2003; Suzuki et al. 2005). Spectral ratios remove this inter-colony variability in density, reflecting predominantly the regional humic acid runoff.

In tropical catchments influencing the Great Barrier Reef, seasonal variability in rainfall was shown to control river flow (Finlayson and McMahon 1988; Furnas and Mitchell 2001). For Madagascar, river discharge time series are extremely scarce hindering further calibration of coral luminescence other than by rainfall data from the nearest weather station Tamatave. The MAS1 time series shows a statistically significant correlation between G/B ratios and Tamatave rainfall for September to August annual means (Fig. 10). The coral G/B time series tracks the interannual to decadal variability in Tamatave rainfall rather well and adds confidence to our results. The relatively low correlation coefficient ($R = 0.30$, $P = 0.01$, $n = 74$) most probably results from Tamatave rainfall not

precisely replicating the local rainfall variability of the Antainambalana river catchment influencing coral MAS1. However, the green luminescence intensity shows no correlation with rainfall testifying that spectral ratios are the more reliable proxy for river flow carrying soil-derived humic acids. Hydrological modelling of river discharge including gridded rainfall products and land-use change data are still required to calibrate spectral ratios for reconstructing river discharge.

Corals far from terrestrial inputs exhibit dull luminescent bands resulting from the high- and low-density aragonite structure (Barnes and Taylor 2001a; Barnes and Taylor 2005). Skeletal pores can amplify or quench luminescence intensities (Barnes and Taylor 2001a). Indeed, by removing the architecture through crushing left little variance in the baseline signal of aragonite (Fig. 8). Since corals devoid of terrestrial inputs only carry a single luminophore (aragonite), internal light reflections caused by the complex skeletal architecture create fluctuating G/B signals, rather than the uniform response from humic acid runoff. Estuarine corals affected by humic acids possess two luminophores normalised by applying G/B spectral ratios. Internal reflections therefore cause both humic acid and aragonite G/B signal to shift in proportion to one another but do not affect the significant correlation between G/B and Ba/Ca.

As density also affects luminescence intensity, long-term declining luminescence trends are likely a result of common declining coral densities (De'ath et al. 2009). Since the 1950s, luminescence intensity and density both declined in all the Madagascar cores, and correlations are statistically significant as exemplified for the coral core MAS1. Spectral luminescence ratios combined with long-term Ba/Ca now confirm the role of density by revealing similar trends, resolving the question as to what causes the marked decline in luminescence intensities shown by some coral luminescence records (Isdale et al. 1998; Cobb et al. 2008; Lough JM pers comm); e.g., 14 out of 20 coral cores sampled from inshore reefs from the Great Barrier Reef display a significant declining luminescence intensity trend (Lough JM pers comm).

In conclusion, declining density trends are responsible for the marked decrease in absolute luminescence intensities rather than humic acid runoff. Indeed, Barnes and Taylor (2005) found that chemical reduction in skeletal density caused a decline in luminescence intensities. Declining luminescence trends has likely affected the interpretation of past erosion records. Nyberg et al. (2007) show multiple cores with declining luminescence intensity trends, which they relate to a decreasing trend in hurricane activity. The findings presented here suggest that such declining trends may alternatively reflect declining coral densities, perhaps in response to the same cause.

Wild et al. (2000) highlighted the importance of comparing neighbouring bright and dull bands to normalise for varying background luminescence which we now relate to changing aragonite density. A method designed to account for the declining luminescence trends is currently being developed, subtracting annual luminescence minimum intensity from the maximum intensity to calculate the annual range (Lough JM pers comm). All luminescence intensity records from NE Madagascar show declining trends, but when spectral ratios are applied they reveal that soil-derived humic acid runoff increased as opposed to decreased. This could be related to either increases in precipitation or land-use activity both promoting soil erosion and extracting humic acids from the watershed (Fig. 9). Based on this new understanding of coral luminescence, spectral luminescence ratios are proposed as a novel robust proxy for humic acid runoff as recorded by inshore corals, improving on the uncertainties of climate interpretation as addressed by Cobb et al. (2008). In summary, (1) both humic acids and aragonite density determine luminescence intensities in corals and (2) normalisation is required for their deconvolution in order to reconstruct river runoff accurately.

Soil erosion is a major problem in developing countries, with a number of amplifying factors such as land development, cyclone impact and increased seasonal rainfall patterns associated with the monsoon. Coral reefs are presently in a vulnerable state, with increasing sedimentation rates reducing photosynthetic activity of their endosymbiotic algae (Anthony and Connolly 2004). Accurate long-term records of erosion can identify changing rates over time, which coupled with other proxies will assist in identifying potential causes, whether climatic (rainfall) or anthropogenic (land-use change). Spectral luminescence ratios of massive corals can provide such records for tropical marine catchments, identifying where and when runoff is changing. As humic acids are not significantly affected by biological activity within the marine system, high-resolution spectral luminescence ratios provide a reliable proxy for humic acid runoff related to changes in hinterland precipitation and soil erosion. On a local scale, multiple coral core records should identify locations most influenced by changing runoff and erosion into inshore reef systems, e.g., by deforestation. Prior to any future development plans to specific regions, SLS may be considered to assess potential environmental impacts. SLS offers a rapid continuous and cost-effective monitor of river discharge, providing valuable information that will assist in reef conservation efforts and understanding past climate change.

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