Summary of Previous Methods Employed

Pioneered by Isdale (1984), a UV source used for excitation together with a spectrophotometer, were first employed to measure light emissions via an optic fibre. Although a UV light still remains popular, a wide variety of other sources have since been used, such as a nitrogen laser (Milne and Swart 1994), a mercury arc lamp (Isdale et al. 1998) and a quartz-halogen lamp (Barnes et al. 2003). Other techniques employed to retrieve luminescence information from corals include light filters (Boto and Isdale 1985; Matthews et al. 1996; Isdale et al. 1998; Wild et al. 2000; Barnes and Taylor 2001), visual categorisation or photography of coral slabs exposed to UV light (Scoffin et al. 1989; Lough et al. 2002; Lough 2007) and image-analysis of grey scale intensity profiles (Sinclair and McCulloch 2004; Sinclair 2005). A more detailed summary of the various techniques employed are described in Barnes et al (2003).

Spectral Luminescence Scanning Methodology

UV Light Source

The standard light source of the Avaatech core-scanner was replaced by two long-wave UV-A tubes in the 350-450nm range (FPL36BLB, SANKYO DENKI). The bulbs were switched on at least 15 minutes prior to measurements in order to stabilise output. One high frequency electronic ballast (45 KHz) was connected to the UV light source to avoid 50 Hz flickering associated with the mains frequency. Both UV tubes were fitted into a specifically designed black holder to eliminate the back scatter of reflected light. A 5 mm narrow slit in the middle of the UV-tube holder allows the camera lens located above to acquire line-scan images, capturing the emitted light from the underlying sample (Fig. 1). When the scan is initiated the light source and camera progress down the sample slab as a single unit while constantly scanning multiple lines, resulting in a continuous core image. A 450nm 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.

Camera Sensor

Luminescence emission is recorded by the Jai CV-L105 3 CCD RGB 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). Each sensor has 2048x1 pixels and the alignment between the three sensors is +/- 1 pixel. The distance between the light source, the sample slab surface and the sensors is kept constant to ensure that incident and detected intensities can be standardised. 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 distance between the camera and the slab will determine the area scanned and thus the resolution of the image. The current setup gives a spatial resolution of 140 pixels per cm, each pixel therefore yielding a linear resolution of 71.4µm. Three data points are produced for each individual pixel in the R, G and B range. Depending on the intensity of luminescence for specific carbonate materials, the appropriate camera settings are chosen (exposure time and lens aperture). Increasing the exposure time enhances the intensity, and thus the sensitivity for samples with low luminescence. In order not to over-saturate the coral carbonate signal, an exposure time of 40ms was used, generating optimal intensities. The aperture size is adjusted to gain maximum light intensity without saturating the signal as recorded by the camera. The maximum core length that can be measured in one continuous scan is 150cm, and full scans are routinely completed within an hour. As long as the exposure time and aperture width of the camera setup remains the same, line-scanning provides

fast, non-destructive quantified data that allows for matching and comparing carbonates with little sampling effort.

Data and Standardisation

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 150cm in length and 15cm 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 single scan taking up to one hour. A customised platform for positioning the sample slabs was built from a non-luminescent black plastic (polymethyl metacrylaet - PMMA). 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 will identify any drift in either the light source or camera recording. Comparing relative intensities of all spectra to previous scans indicates spectral shifts in the standard. Subsequently the resulting sample intensities are corrected for any drift to allow direct inter-comparisons between cores to be made over time.

Method Summary

- Quantitative photoluminescence data is produced with a linear resolution of 71.4µm (pixel length); compatible for coupling with other high resolution analysis e.g. LA-ICP-MS, ion-microprobe.

- Such a resolution is ideal for calibration purposes, identifying short-term (flood/cyclones) events that will remain unresolved by existing methods.
- Plotting transects adjacent to previous sampling tracks is a major advantage of the technique, useful for combining datasets and keeping scales consistent.
- The RGB scanning system obtains data from the Red and Green spectra without filters, and the Blue with the use of a 450nm filter.
- Spectral ratios indicate changes in the amount of soil organics incorporated in carbonate skeletons and/or changes in mineralogy.
- High quality normalised photoluminescence images are obtained using a line-scan camera, creating digital archives.
- Establishing a number of physical properties by visual assessment is useful in selecting the optimum elemental sampling track line, e.g., growth axes, compositional changes, physical discrepancies, relative intensities.
- Cross comparison of carbonates is possible as long as preparation methods are consistent.
- Scans take no more than 1 hour per 1.5m to produce the photoluminescence image.
- Once an image is produced, photoluminescence images can be re-sampled without the need for re-scanning.
- Software allows any transects to be manually selected from the image along or across growth axes for any length in any direction, for any width, for multiple transects in a single sample, from a single scan.
- Widths of transects created can be optimised. Long term trends may require averaging of pixels, ridding of sub-millimeter variability.

- For long-term temporal paleoclimate analysis, it may be appropriate to widen transects on the UV image, averaging the cross-core pixels perpendicular to the skeletal growth axis. This provides a smoothened time series record by eliminating cross-core sub-millimetre variability, while retaining a down-core linear resolution of 71.4µm (Fig. ESM4).
- The exposure time can be optimised to the specific photoluminescence intensity yield of the carbonate, i.e., low intensity requires a high exposure time.

Research Area and Climate Setting

Antongil Bay is located in the NE of Madagascar, covering an area of 2800 km^2, with a mean depth of 41.5 m and a coastline of 270 km extending 80 km inland (Ersts and Rosenbaum 2003). Two protected forest areas are found in the vicinity of the bay, the Makira Forest and the Masoala Peninsula National Park (Birkinshaw and Randrianjanahary 2007). One of the largest rivers draining into Antongil Bay is the Antainambalana, running through the Makira Forest Area from a source 1450 m above sea level (Goodman and Ganzhorn 2004). Its watershed covers an estimated 4000 km^2 (estimated with: http://www.acme.com/planimeter) and the river mouth is located in the city of Maroansetra (Fig. 3). The MAS1 and MAS3 coral cores were collected next to the island Nosy Mangabe, ca. 7 km from the river mouth (Fig. 3). The ANDRA coral core was collected 30 km from MAS1/3 on the east side of the bay, ca. 7 km from the Ambanizana river mouth (Fig. 3). The Ambanizana has a much smaller watershed (ca. 160 km^2) and runs southwest towards Antongil Bay through a mountainous region with dense forest cover. IFAHO is situated ca. 4.5 km from the mouth of the river Anaovandran (watershed: ca. 180 km^2) outside of Antongil Bay (Fig. 3). The river originates from the same mountains as the Ambanizana, but flows

eastwards away from Antongil Bay. For the last ca. 11 km it flows through a plain before entering the ocean. One coral core was obtained off the island of St Marie (E 49º, S 17º; Northeast Madagascar; Fig. 3). This coral site experiences fully oceanic conditions devoid of terrestrial influences.

The climate in Madagascar can be divided into a August-December cold-dry season and a January-July warm-wet season. Air temperatures peak in December and January and are lowest between July and September (Kremen 2003). Highest rainfall occurs between January and March, while lowest rainfall occurs between September and November (Kremen 2003). Highest runoff occurs between February and April, one to two months after peak rainfall (Kremen 2003).

References

Ersts PJ, Rosenbaum HC (2003) Habitat preference reflects social organization of humpback whales (Megaptera novaeangliae) on a wintering ground. J Zool 260:337-345

Goodman SM, Ganzhorn JU (2004) Biogeography of lemurs in the humid forests of Madagascar: the role of elevational distribution and rivers. J Biogeogr 31: 47-55

Figures

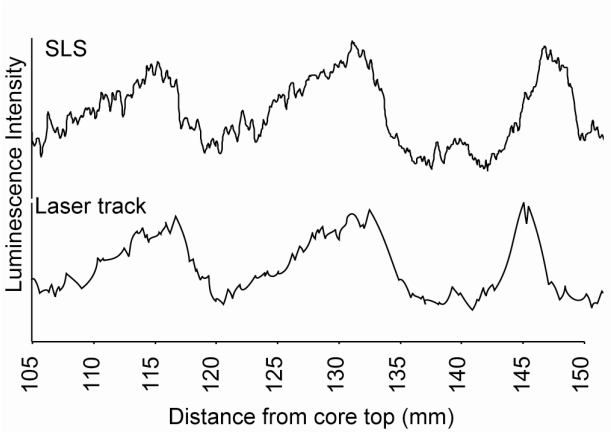

Figure 1. Comparison of luminescence intensities between the SLS technique (above), and the argon-ion laser technique (below) measured on the same coral section. The slight offset in timing of the intensity changes between methods was caused by difficulties in defining a fixed transect using the argon-ion laser technique.

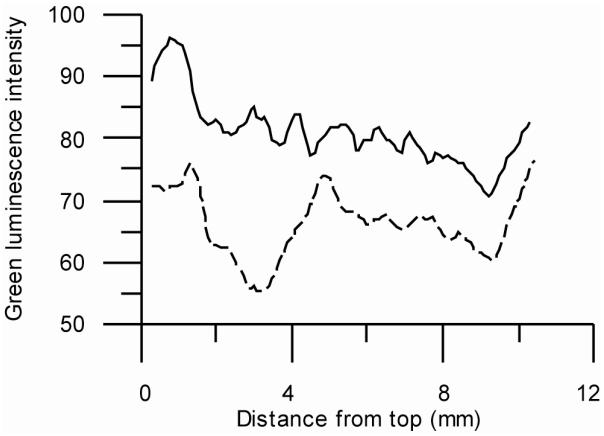

Figure 2. Comparison of luminescence intensities measured in the green domain for a coral top measuring 11mm before (dashed) and after (solid) treatment with sodium hypochlorite. The coral section represents approximately 1 year of growth.

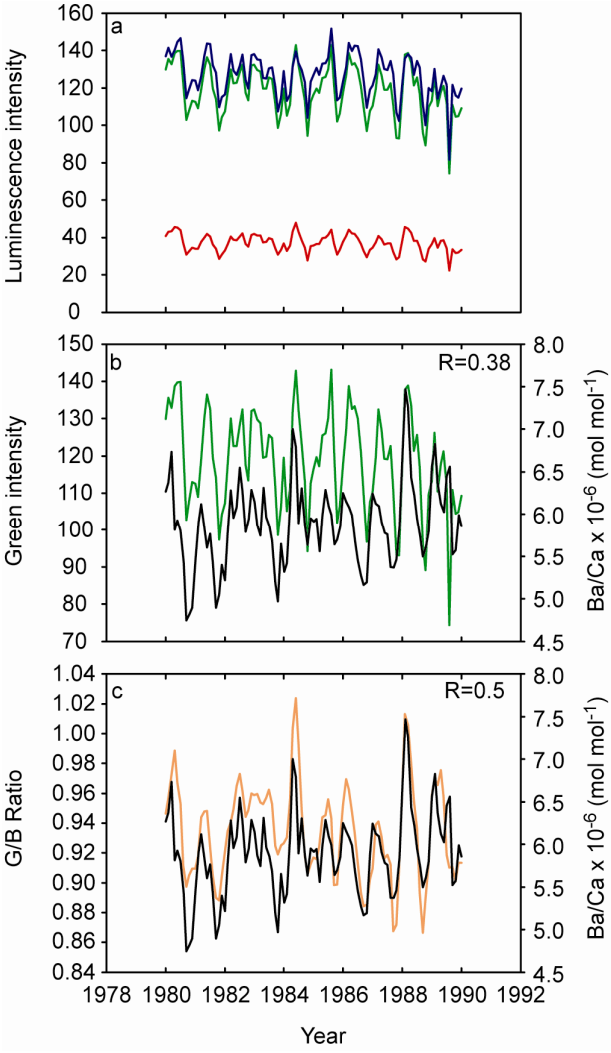

Figure 3. The photoluminescence emissions of the MAS1 core between the years 1980 and 1990 (a) for all three emission spectra R (red) G (green) and B (blue); (b) the G (green) plotted against Ba/Ca (black); and (c) the G/B ratio (orange) plotted against Ba/Ca (black). The correlation coefficient value R is given for testing the relationship of G against Ba/Ca (b) and G/B against Ba/Ca; and is shown in the top right corner of the corresponding plot. Correlations of Ba/Ca with G/B are significantly higher, with an improved correlation ($R=0.5$, $p<0.001$, $n=132$) compared to G alone ($R=0.38$, $p<0.001$, $n=132$).

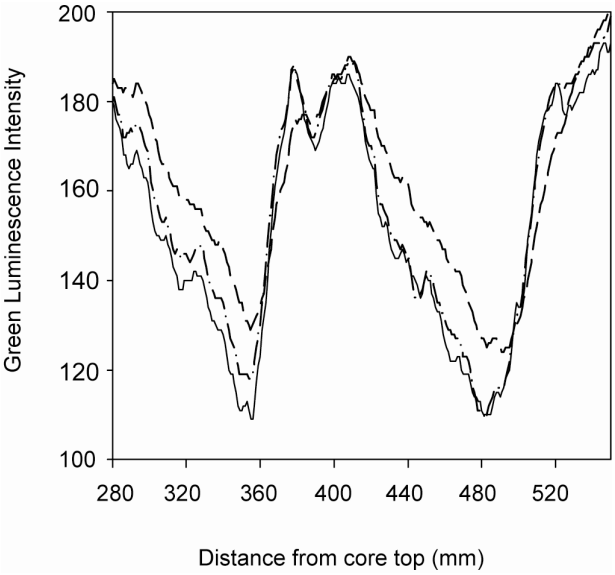

Figure 4. Measured luminescence intensities of three equally long transects with widths of 0.25mm (solid), 0.5mm (dotted) and 1mm (dashed). The width of transect determines the number of pixels averaged perpendicular to the growth direction, with the number of pixels parallel to the growth axis remaining constant.