

## **Earth Environment Introduction**

Research in the Earth Environment Group is focused on environmental change and long-term interactions between humans and our environment. Research is directed toward understanding globally significant processes within the themes of climate and sea-level change, landscape evolution, human evolution and extinctions and the impact of ongoing global change on the marine environment. Our research is based around the application of a unique group of World-class research facilities that enable analysis of a wide range of trace element and isotopic systems, with an emphasis on the timing and rate of change of major environmental and Earth surface processes. Emphasis is on developing detailed chronologic records that span a few tens to several hundred thousand years of the Earth's history, and using these as a basis for understanding past and present environmental change and predicting future trends. Earth Environment specialises in the reconstruction of high-resolution environmental records from growth banding preserved in fossil and modern corals, speleothems (cave deposits), layered sedimentary deposits and anthropologic sites of special significance.

## **ARC**

During 2005 there were a number of highlights. Academic staff continued their high level of success with ARC proposals from both Professor Grün and Dr Gagan being funded. Professor Grün's proposal is being undertaken jointly with Professor Roberts from the University of Wollongong and involves dating of a number of key archeological sites using both OSL and ESR methods. Dr Gagan will continue his important research in the Indonesian region with two projects being funded. The first project is for five years and involves the use of coral records to better constrain the recurrence interval of major earthquakes in the Sumatra region. The second project is for three years and is being undertaken jointly with Dr Zhao from the University of Queensland and Dr Drysdale from the University of Newcastle and addresses the important question of the environmental impacts of early human history in southern Australasia. This will be tackled using geochemical microanalysis of precisely dated speleothems to document climate and environmental change in southern Indonesia.

## **Coral Reef Centre of Excellence**

Earth Environment is also a key member of the newly established Coral Reef centre of Excellence where Professor McCulloch is an Associate Director. This is an ARC funded initiative and provides new opportunities to undertake and expand our research in coral reefs with a world-leading group of researchers. The centre is based at James Cook University

under the Directorship of Professor Hughes from Marine Biology together with the Marine Sciences Centre at University of Queensland led by Professor Hugh-Guldberg (Associate Director). In addition to providing additional funding for Post Doctoral positions across wide interdisciplinary fields there are also many opportunities for PhD students to undertake research utilising the combined resources and talents of the Centre.

### **New instrumentation**

New LIEF funded state-of-the-art equipment is now being installed in the Earth Environment Group to enable us to continue our cutting-edge research. This includes an ~\$2 million gas source AMS which will revolutionise our capacity to undertake  $^{14}\text{C}$  dating terrestrial materials and an ultra-short wavelength (157 nm) laser ICPMS combination to enable direct in-situ analyses of a wider variety of Geological materials with greatly enhanced sensitivity.

### **Research highlights**

The following section describes some of the research highlights of our group. Major break-throughs have been made in understanding how Australia's desert environment has responded to climate change during the past million years. On shorter timescales the effects of ENSO variability in the Philippine region has now been clarified during the Holocene period, and using new refined thermal ionisation methods, boron isotope variations in corals have been used to determine variability of seawater pH due to uptake of anthropogenic  $\text{CO}_2$  during the industrial and preindustrial periods.

# Long-term perspectives on monsoon dynamics, environmental shifts, and early human impacts in southern Australasia

## Late Holocene reconstruction of strong El Niño events

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Annually-resolved  $\delta^{18}\text{O}$  records were derived from a modern and a 2.3 ky coral acquired in Maydolong, eastern Samar, Philippines to reconstruct past El Niño events. The two records are comparable in length: the modern coral spans the past 82 years (1922 to 2003) whereas the 2.3 ky coral includes 91 years. Replicate measurements of samples milled at annual increments were made until the standard error of the mean fell below 0.05‰.  $\delta^{18}\text{O}$  anomalies were then calculated by subtracting the 7-year running mean from the average of each year.

Strong El Niño events in the past 82 years exhibited positive  $\delta^{18}\text{O}$  anomalies. The most recent events, which occurred in 1972/3, 1982/3, 1991-3 and 1997/8, registered values from 0.09 to 0.18‰ (Fig. 1). To identify strong El Niño events in the 2.3 ky coral record, we used the threshold value of 0.10‰ as weak to moderate El Niños have an average  $\delta^{18}\text{O}$  anomaly of 0.05‰. Eight events occurring at fairly regular intervals (approximately every 10 years) were identified in the late Holocene record (Fig. 1). Relative to modern-day events starting from the 1970s, the frequency as well as the amplitude of strong El Niños is similar to that of the late Holocene. The tendency for more frequent and stronger El Niño events in the late Holocene has been shown in a climate model (Clement et al., 2000) and in coral records from Papua New Guinea (Tudhope et al., 2001; McGregor and Gagan, 2004). However, persistent events (lasting more than 1 year) are more common in the late Holocene record relative to the modern. This corroborates findings of multi-year El Niño events based on coral reconstructions (Tudhope et al., 2001; McGregor and Gagan, 2004) but not captured in models.

Clement, A.C., Seager, R., and Cane, M.A., 2000. Suppression of El Niño during the mid-Holocene by changes in the Earth's orbit. *Paleoceanography*, 15: 731-737.

McGregor, H.V., and Gagan, M.K., 2004. Western Pacific coral  $\delta^{18}\text{O}$  records of anomalous Holocene variability in the El Niño-Southern Oscillation. *Geophysical Research Letters*, 31: doi:10.1029/2004GL019972.

Tudhope, A.W., Chilcott, C.P., McCulloch, M.T., Cook, E.R., Chappell, J., Ellam, R.M., Lea, D.W., Lough, J.M., and Shimmield, G.B., 2001. Variability in the El Niño-Southern Oscillation through a glacial-interglacial cycle. *Science*, 291: 1511-1517.

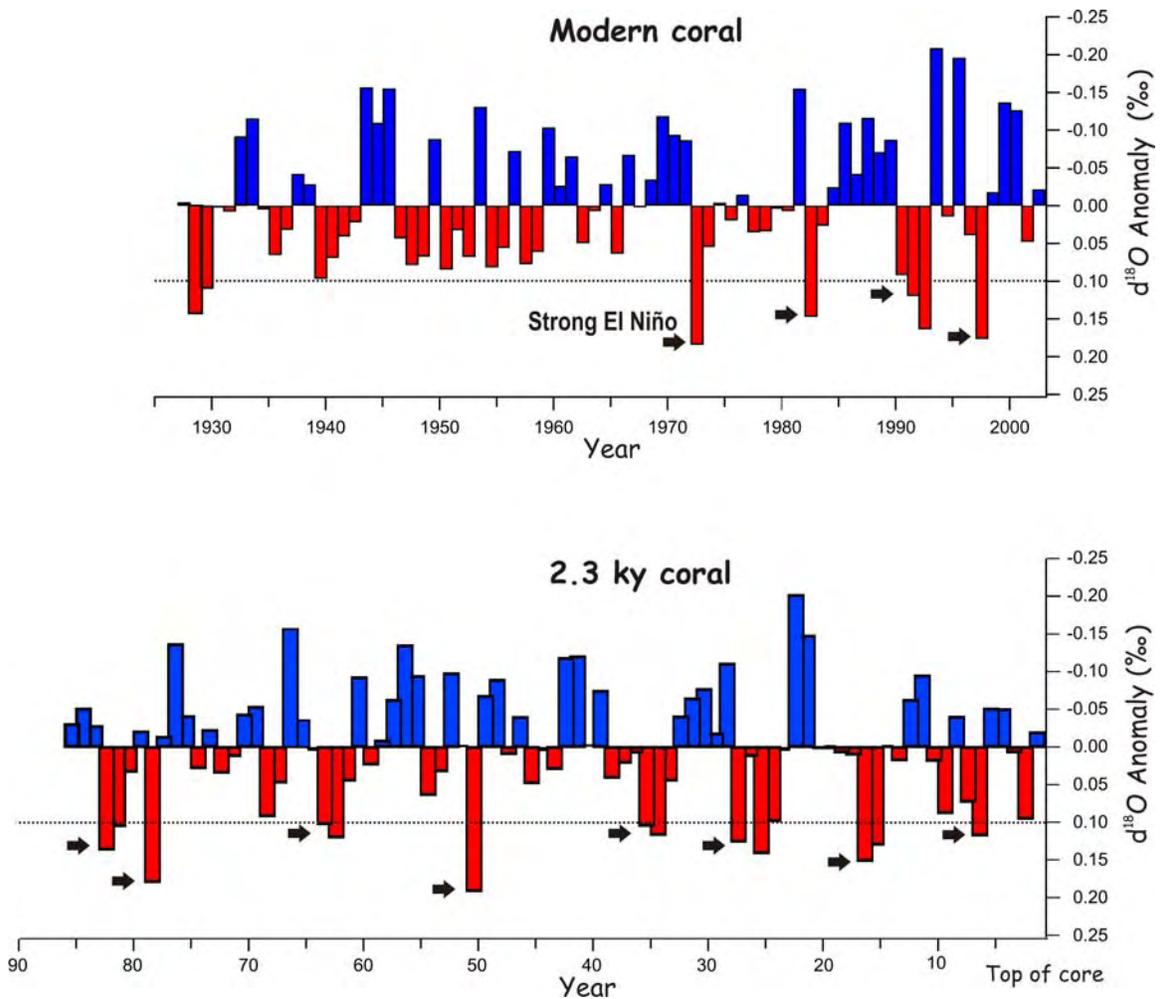


Figure 1.  $\delta^{18}\text{O}$  anomalies in the modern (top) and 2.3 ky (bottom) coral records from Maydolong, eastern Samar, Philippines. Black arrows indicate strong El Niño events. The threshold for strong events is marked by the dashed line

## Geochemical ecology of a high latitude coral: establishing high resolution records to evaluate potential as a paleoclimate archive

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Corals growing in high latitude waters are sensitive to changes in climate, especially seasonal fluctuations in sea surface temperature. The annual nature of density bands of *Plesiastrea versipora* were verified using U/Th ages derived from multi-collector ICP-MS analyses and the resulting extension rates varied from an average of 1.2 mm yr<sup>-1</sup> to 9 mm yr<sup>-1</sup> for different colonies located within the same reef. High resolution (~fortnightly) laser-ablation ICP-MS analyses of established paleo-temperature proxies including B/Ca, Mg/Ca, Sr/Ca and U/Ca and milled  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  analyses were obtained from several cores of *P. versipora* from Gulf St Vincent (34.5°S) and Spencer Gulf (35°S), South Australia. Elemental compositions were compared to *in situ* sea surface temperature (SST) and satellite (IGOSS) records. There was a significant correlation between  $\delta^{18}\text{O}$  and Ba/Ca ( $r^2 = 0.82$ ) and a significant inverse correlation was observed between  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .

Sea surface temperature linear regressions provided the following calibration equations:

$$\delta^{18}\text{O} = 0.9 - 0.16 \text{ SST } (^{\circ}\text{C}), r^2 = 0.77.$$

$$\text{Ba/Ca } (\mu\text{mol/mol}) = 8.35 - 0.13 \text{ SST } (^{\circ}\text{C}), r^2 = 0.65.$$

$$\text{Sr/Ca } (\text{mmol/mol}) = 10.55 - 0.06 \text{ SST } (^{\circ}\text{C}), r^2 = 0.62.$$

$$\text{B/Ca } (\text{mmol/mol}) = 0.96 - 0.13 \text{ SST } (^{\circ}\text{C}), r^2 = 0.55.$$

$$\text{U/Ca } (\mu\text{mol/mol}) = 2.3 - 0.16 \text{ SST } (^{\circ}\text{C}), r^2 = 0.6.$$

Barium may not have been recognised as a temperature covarying proxy in previous studies due to the smaller temperature range for lower latitude environments (~5°C versus 12°C for this study) and other factors masking the Ba signal such as terrestrially-derived or upwelled sources. However, it could not be determined whether the covariance was directly related to temperature or another factor which varies with winter periods such as phytoplankton blooms or increased oceanic mixing.

Other trace elements analysed gave an indication of both the nutrient availability (P and Mn) and terrestrially derived pollutants (V, Y, Mo, Sn and Pb) correlating strongly with luminescent bands. Several of the stronger luminescent bands coincide temporally with known oil spills at a nearby port refinery and research is ongoing to determine if this is the point source of pollution. These data taken together suggest that *P. versipora* can provide valuable paleoclimate information in high-latitude environments, recording large seasonal variation in both temperature and productivity regimes with high fidelity and may also be employed to reconstruct anthropogenic activity.

## **Regional and continental-scale erosion in the Yangtse River catchment, China, from cosmogenic nuclides**

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Regional erosion arising from land clearing undeniably has increased in wide tracts of agricultural land but human impacts on erosion are less clear for high mountain areas, where natural erosion rates are high. With a long history of intensive human occupation, the Yangtse River basin in China is an ideal test case. The river rises in the northeast Tibetan Plateau and descends through ranges of very high mountains, passing eastwards across China, collecting water and sediment from a series of tributaries, before passing through the Yangtse Delta into the East China Sea. To determine regional erosion prior to the impact of agriculture, we used measurements of cosmogenic nuclides in eroding rock surfaces and sedimentary quartz grains. These nuclides are produced by cosmic rays impacting common nuclei in surface rocks; their abundance decreases with increasing erosion, and this signature is preserved in sediment from the eroding surfaces. Results from high mountain catchments of the western Yangtse River basin are similar to rates derived from sediment gauges along the river system and range to over 700 m Ma<sup>-1</sup>, while cosmogenic determinations from headwater tributaries on the northeast Tibetan plateau gave much lower long-term rates, around 20–30 m Ma<sup>-1</sup>. For lowland and lesser mountains in the eastern reaches of the Yangtse River catchments, rates from cosmogenic nuclides were around 30 m Ma<sup>-1</sup>, which is about half the present-day regional average derived from sediment gauges. In summary, human land use has sensibly increased catchment-scale erosion in eastern China, but regionally the effect in high mountains of the western Yangtse River appears to be minor.

## The history of aridity in Australia

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Australia became progressively drier while it drifted northwards in the Cenozoic but the picture is complex and wet periods punctuated the drying trend. Regolith, groundwater and salts actively interact with the landscape and with each other, during these climatic changes. The project is a study of Upper Cenozoic climate changes in the Australian interior and their effects on the regolith. Targets include aeolian landscapes (longitudinal dunefields, source-bordering dunes and lunettes), stony desert and dissected silcrete and ferricrete landforms, surfaces with thick regolith and deep weathering with mine-pit access, and palaeochannel systems.

The broad timing of major phases of silcrete and ferricrete formation followed by landscape dissection and falling groundwater have been established by palaeomagnetic dating of ferruginous regolith dating of relict fluvial deposits. A key study concerns the age structure of major dunefields and stony deserts, which are the most widespread regolith materials in the arid zone. The ages of other arid-climate deposits including aeolian silt mantles are also being determined.

Stony deserts are durable indicators of aridity but hitherto have not been directly dated. We have successfully determined the age of the stony deserts, using <sup>21</sup>Ne and <sup>10</sup>Be produced in surface rocks by cosmic rays, and have shown that Australian stony deserts formed 2–4 Ma ago, at the time when global cooling initiated the Quaternary ice ages and intensified aridity induced major landscape changes in central Australia. To achieve this, we developed new methods for determining cosmogenic <sup>21</sup>Ne in the presence of neon components from other sources. Using our cosmogenic toolkit (<sup>21</sup>Ne, <sup>10</sup>Be and <sup>26</sup>Al), we have also found that the Simpson Desert dunefield has existed for at least the last 1.5 Ma, whereas optical dating (OSL) of drill-core samples shows that individual dunes were active during global cold episodes of the Late Pleistocene ice ages, when many dunes were extensively reworked. In short, the cosmogenic data have allowed us to determine the antiquity of Australia's most characteristic arid landforms, while OSL dating allows us to assess the degree to which arid landscape processes have been episodic.

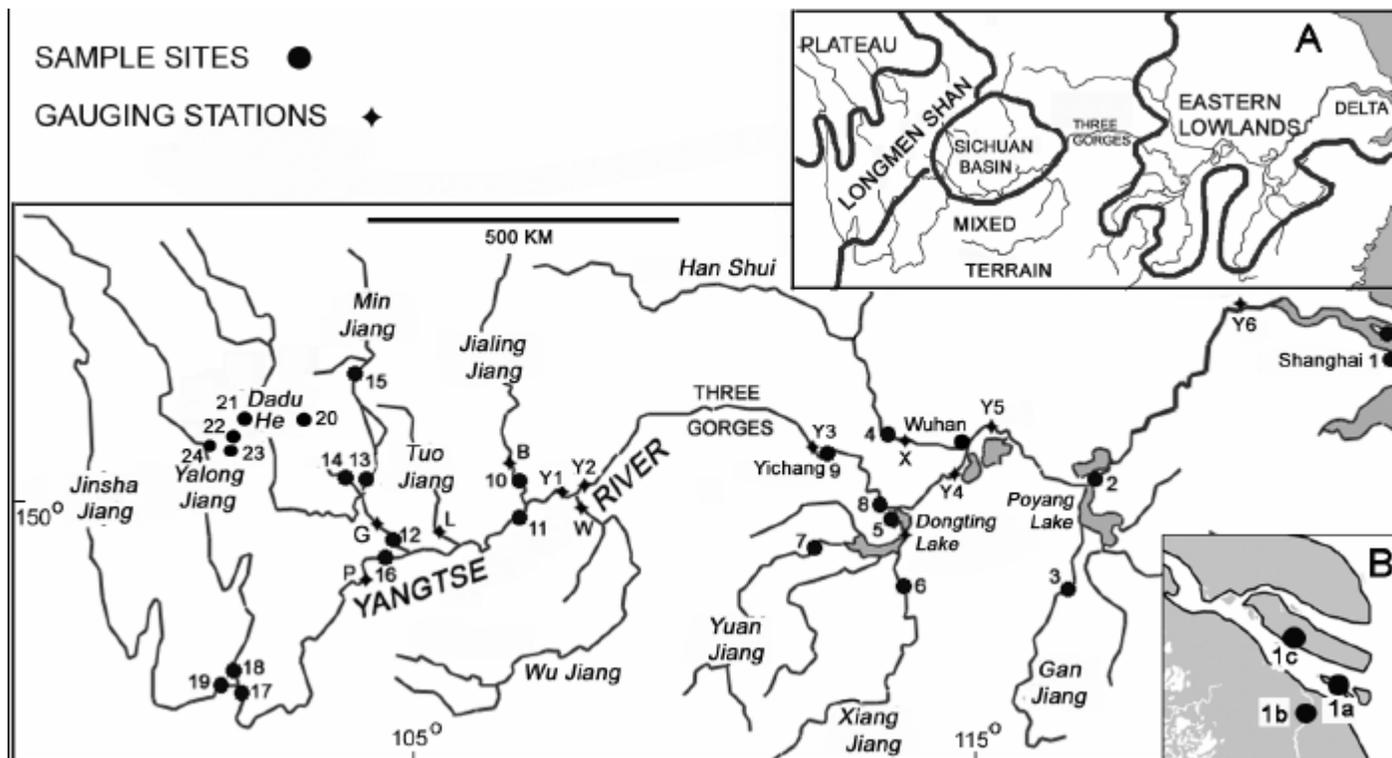


Figure 1 Regional erosion in China – major river sampling sites in China

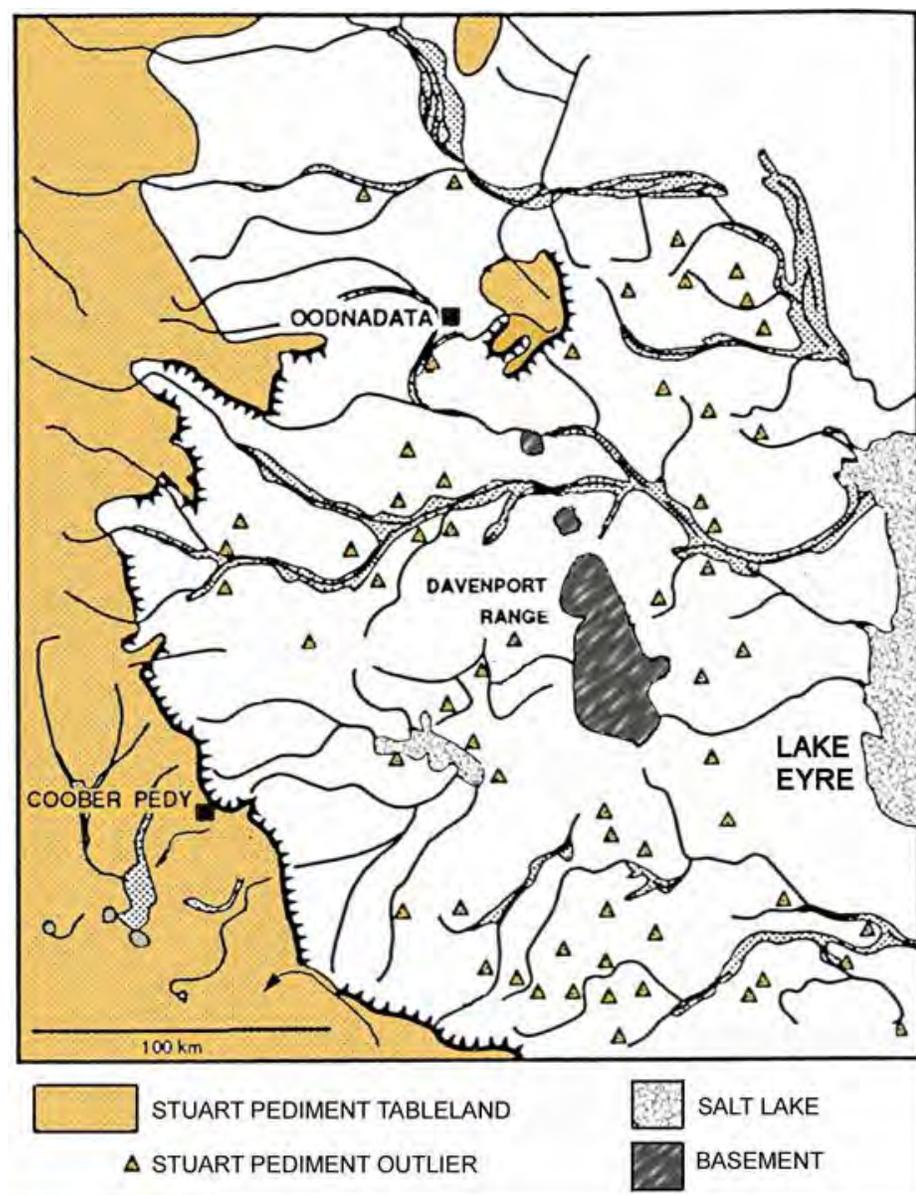


Figure 2 History of aridity: sampling site for cosmogenic determination of stony desert ages

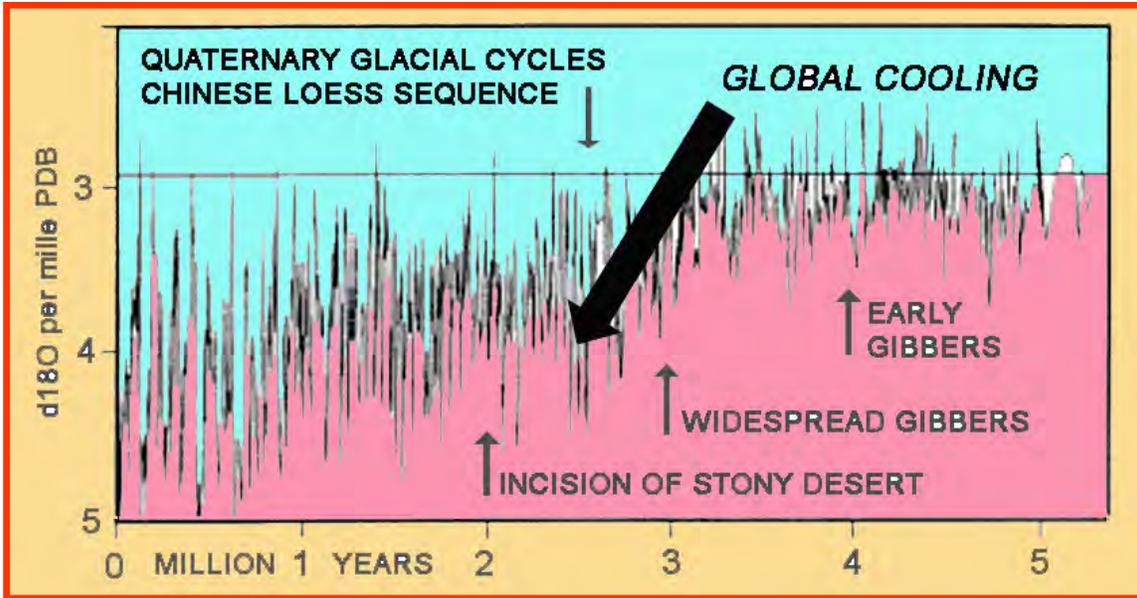


Figure 3. Timing of the formation of stony "gibber" pavements in central Australia

# Micro-sampling of skeletal mass accumulation in the tissue layer of *Porites*: implications for paleo-environmental reconstruction

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Stable isotope and trace element geochemical records obtained from *Porites* corals are an important source of quantitative paleoclimate information. The depth over which aragonite is deposited within the growing tissue layer of these corals determines the amount of biological smoothing imparted to environmental signals that are preserved in their skeletons. If these distortions are not accounted for when transforming raw data into estimates of sea surface temperature (SST) and salinity, substantial inaccuracies in paleoclimatic reconstruction may result. In order to estimate the magnitude of this problem we have measured the mass of aragonite in consecutive 200  $\mu\text{m}$  thick samples through the upper 10-12 mm of five corals from four locations and have found that growth can be characterised by two patterns: “sharp” growth when all aragonite is deposited in the upper 2mm of the coral skeleton; and, “smooth” growth when aragonite is deposited throughout the tissue layer, typically 6 to 10 mm in thickness (Fig.1). Ningaloo is the only coral that shows a smooth growth pattern in our dataset.

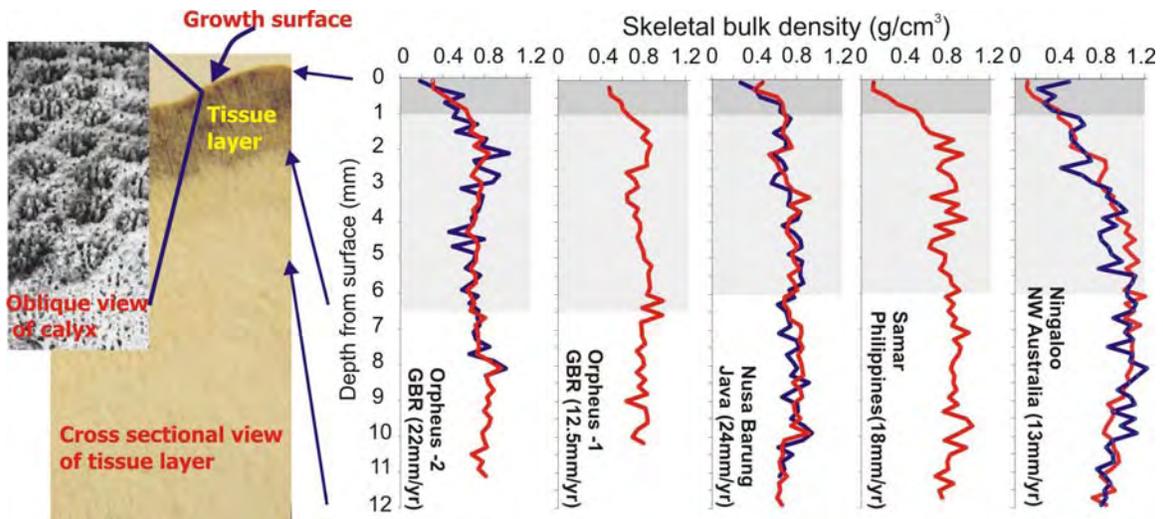


Figure 1. Plots showing variations in bulk density with depth for five corals. Where possible each milling transect was replicated (blue curves). Note that with the exception of Ningaloo, systematic increases in density are confined to the upper 2 mm of each coral.

By adopting two smoothing functions (for sharp and smooth growth measurements) to a sine wave (which approximates the kind of variability evident in many environmental signals) it is possible to model the degree of

attenuation of environmental cycles of different periods for different rates of coral growth (Fig. 2).

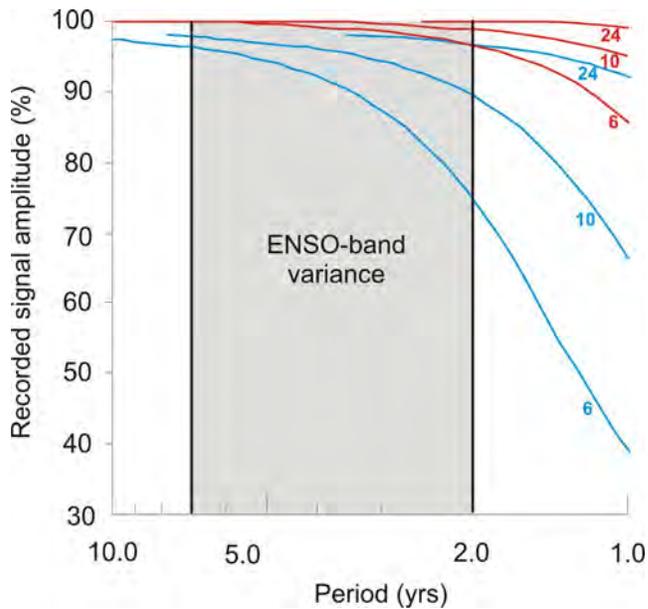


Fig. 2. The attenuation of sine waves with periods between 1 and 10 years for modelled coral growth at 6, 10 and 24 mm/yr (labelled on graph) as a result of bio-smoothing. Results are shown for “sharp” (red) and “smooth” (blue) calcification patterns as defined in the text.

This model suggests attenuation of annual and longer cycles is limited to <10% for most *Porites* corals over a wide range of growth rates, consistent with published environmental records that assume limited smoothing (e.g. Alibert & McCulloch, 1997; Gagan et al., 1994; 1998; Wellington et al., 1996). However, where aragonite deposition takes place throughout the tissue layer (“smooth” – type calcification) significant smoothing of environmental signals will occur. The difficulty for researchers is that this type of growth does not appear to be environment or species specific and cannot be determined directly in fossil corals where the outer coral skeleton is typically not preserved.

## References

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## Dating of Australian arid landforms using cosmogenic Ne/Be exposure dating

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3

In principle, the history of aridity in Australia can be determined by dating the landforms and deposits that form under arid conditions. Over 75% of Australian continent is semi-arid to arid, and stony deserts are a major feature of these regions. Stony deserts are characterized by a surface monolayer of pebble- to cobble-sized rocks (gibbers) which, once formed, tend to remain in place with little subsequent modification. Some gibbers were formed *in situ* by breakdown of their underlying parent rock; others were fluvially transported to their present positions. We propose that the age of the stony deserts can be estimated by determining the time when gibbers were formed.

In this study, we measured cosmogenic nuclides, <sup>21</sup>Ne and <sup>10</sup>Be, in silcrete gibber samples collected from stony deserts in central Australia, to determine their exposure ages (Fujioka et al., 2005). The use of cosmogenic <sup>21</sup>Ne, which is a stable cosmogenic nuclide, allows us to examine the history of gibber formation beyond the exposure dating range of <sup>10</sup>Be, which limited by radioactive decay to a few million years. We note that we have developed a reliable method for determining cosmogenic <sup>21</sup>Ne in the presence of <sup>21</sup>Ne from other sources.

Apparent exposure ages calculated from the concentrations of cosmogenic <sup>21</sup>Ne and <sup>10</sup>Be in the gibber samples from stony deserts west of Lake Eyre in northern South Australia ranged from two to five million years, but the apparent <sup>21</sup>Ne ages are significantly greater than the apparent <sup>10</sup>Be ages. The discordance indicates that the parent silcrete, from which the gibbers were derived, was buried at a shallow depth for a considerable period before being stripped and broken into gibbers. Calculations indicate that the silcrete was stripped and gibbers began to form around 4 m.y. ago, and that gibber-mantled tablelands were widely developed and dissected around 2-3 m.y. ago. These ages correspond to the time of late Cenozoic global cooling inferred from benthic oxygen isotope records in marine sediment cores (Figure).

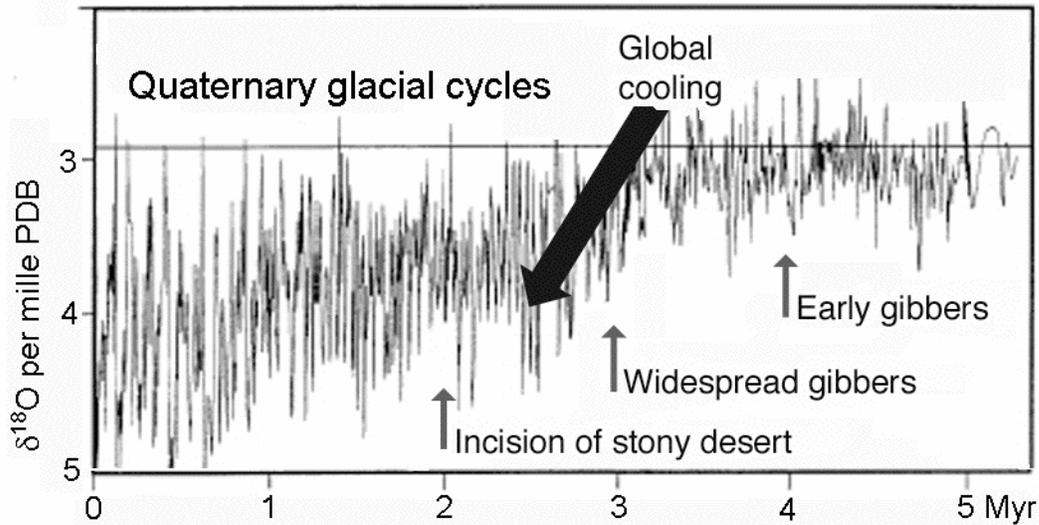


Figure. Relationship between the timing of the formation of gibber plains in Australia and benthic oxygen isotope record in marine sediment cores (east Atlantic Ocean Drilling Program Site 659; Tiedemann et al., 1994). Gibber ages (arrows) indicate that Australia's stony deserts formed during late Cenozoic global cooling as seen in marine sediments, that led to Quaternary glacial cycles. PDB: Peedee belemnite.

## References

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## Long-term perspectives on monsoon dynamics, environmental shifts, and early human impacts in southern Australasia

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The Earth Environment Stable Isotope Laboratory contributed to advances along several fronts in 2005 to improve our understanding of the late Quaternary history of the Australasian monsoon, palaeo-environmental shifts, and early human impacts in southern Australasia. Two papers describing new coral geochemical records were published in *Earth and Planetary Science Letters* (Sun et al., 2005) and *Science* (Pelejero et al., 2005). Sun et al. (2005) developed a 54-year long, high-resolution skeletal  $\delta^{18}\text{O}$  record for a massive *Porites* sp. coral from Hainan Island, South China Sea, to investigate East Asian monsoon variability during summer and winter ~4,400 calendar years ago. The East Asian monsoon is a prominent feature of the tropical general circulation that impacts the lives of ~25% of the world's population, yet its year-to-year variability is still difficult to predict. The coral record shows that ENSO-related sea-surface temperature anomalies were well established in the South China Sea by ~4,400 years ago, despite ENSO variability being significantly weaker in the Pacific region at that time. Our findings indicate that the monsoon is sensitive to forces, other than ENSO, that could act as alternative drivers of interannual monsoon variability. If this is the case, greater interannual climate variability could accompany the strengthening of the Asian monsoon predicted to occur during the 21st century as transient greenhouse warming preferentially warms Eurasia, even if ENSO perturbations remain relatively stable.

Pelejero et al. (2005) reported on a new coral record for a *Porites* sp. from Flinders Reef in the Coral Sea, which provides a continuous time-series of seawater  $\delta^{13}\text{C}$  and pH commencing in 1708 AD, well before the start of the industrial revolution. The most striking feature of the coral  $\delta^{13}\text{C}$  curve is the trend towards lower values commencing in 1800 AD. The secular decrease in coral  $\delta^{13}\text{C}$  can be ascribed to the Suess effect, which is due to uptake by the oceans of atmospheric  $\text{CO}_2$  that has been progressively depleted in  $^{13}\text{C}$  by the combustion of fossil fuels. The likely consequence of this absorption of anthropogenic  $\text{CO}_2$  is that the surface-ocean will become progressively acidic. The impact of progressive ocean acidification on marine ecosystems is unclear, but will likely depend on species adaptability and the rate of change in seawater pH relative to its natural variability. To address this issue, coral  $\delta^{11}\text{B}$  was used as a "palaeo-pH meter" to show that Flinders Reef seawater pH has varied over ~50 year cycles in tandem with the Interdecadal Pacific

Oscillation. The results suggest that natural cycles in reef-water pH will modulate the impact of future ocean acidification on coral reef ecosystems.

In 2005, the Earth Environment Group's progress and potential in the area of high-resolution coral-based palaeoclimatology was rewarded through new research funding for the next five years (2006-2010) from the Australian Research Council Discovery grants scheme. This stream of research, The Indian Ocean Dipole, Australasian drought, and the great-earthquake cycle: Long-term perspectives for improved prediction, will be driven by team-members from RSES, Indonesian Institute of Sciences, Australian Institute of Marine Science, CSIRO, University of Wisconsin, and Caltech. The team will combine cutting-edge geochemical microanalysis of recently discovered corals with world-leading palaeoclimate modelling to quantify the Indian Ocean Dipole system, and mechanistic links with Australasian drought, over the past 130,000 years. Our other primary goal is to develop an innovative submarine earthquake hindcasting technique that will improve understanding of the recurrence intervals of great-earthquakes and tsunamis in Australasia.

In addition to our contributions to the new ANU Marine Science Initiative, the Earth Environment Stable Isotope Laboratory also contributed to the production of novel terrestrial palaeoclimate records. The highlight of these was the paper published by Miller et al. (2005) in *Science* describing a unique 140,000-year time-series of dietary  $\delta^{13}\text{C}$  in fossil eggshells of the Australian emu and extinct *Genyornis newtoni*. This comprehensive data set represents the culmination of 15 years of field collecting by John Magee (DEMS, ANU) and Gifford Miller (U. Colorado) and more than 1,400  $\delta^{13}\text{C}$  analyses on a subset of over 100,000 eggshell fragments. The 140,000-year record of dietary  $\delta^{13}\text{C}$  documents a permanent reduction in food sources available to the Australian emu beginning about the time of human colonisation of Australia (55-45 ka). The unprecedented shift in dietary  $\delta^{13}\text{C}$  is best explained by human firing of landscapes and rapid conversion of a drought-adapted mosaic of trees, shrubs, and nutritious grasslands to the modern fire-adapted desert scrub. Given this profound ecosystem shift, animals that could adapt survived, while those that could not became extinct.

Johnson et al. (2005) analysed the Holocene portion of the emu eggshell  $\delta^{13}\text{C}$  record from Lake Eyre, South Australia, and found that the proportion of  $\text{C}_4$  plants in emu diets has been reduced by ~20% over the last 200 years at Lake Eyre. Probable causes of the recent reduction in  $\text{C}_4$  plants at Lake Eyre include overgrazing by both introduced and native animals, increasing drought, and a change in fire regime beginning in the late 1890s. The eggshell  $\delta^{13}\text{C}$  record provides the first evidence for major environmental change at Lake Eyre soon after Europeans settled the arid zone.

Treble et al. (2005) made significant progress in understanding the nature of seasonal-scale  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  variations in speleothems via high-resolution analysis of an 81-year old stalagmite from Moondyne Cave, southwest Australia. For this study, seasonal variations in calcite  $\delta^{18}\text{O}$  were measured in situ by ion microprobe at UCLA, whilst interannual variations of  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  were measured by gas-source mass spectrometry at RSES. The key point is that the seasonal range in speleothem  $\delta^{18}\text{O}$  at Moondyne Cave is larger than any interannual-decadal variation in  $\delta^{18}\text{O}$  observed in the record. This finding raises the possibility that even small changes in the relative masses of speleothem calcite deposited in winter and summer could produce significant shifts in mean  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  determined by "bulk sampling" of speleothems. Therefore, long-term trends in speleothem records may have a complex relation to climate, particularly those for shallow cave sites where seasonal variations in geochemical tracers are large, including most of the sub-tropical monsoon belts and mid- to high-latitudes with distinctly seasonal rainfall.

In 2005, the Earth Environment Group was awarded a 3-year Australian Research Council Discovery grant (2006-2008) to pursue the production of novel speleothem records in Indonesia. This new stream of research, Monsoon extremes, environmental shifts, and catastrophic volcanic eruptions: Quantifying impacts on the early human history of southern Australasia, will be pursued by team-members from RSES, Indonesian Institute of Sciences, University of Queensland, University of Newcastle, and NASA. The team will use novel geochemical microanalysis of precisely dated speleothems from southern Indonesia and state-of-the-art palaeoclimate modelling to document, for the first time, millennial to seasonal extremes in monsoonal rainfall, environmental shifts, and catastrophic volcanic eruptions over the past 150,000 years. These new records will provide the basis for evaluating the relative influence of natural and human-induced environmental change on early human dispersal in Australasia, including the surprisingly recent extinction of *Homo floresiensis* ("the Hobbit").

In summary, palaeo-records provide valuable insights into how climate variability and change has and could affect our marine and terrestrial environments. Readers who are interested in what Quaternary palaeo-science can reveal about climate change and its potential impacts in Australia should refer to the comprehensive report compiled by Harle et al. (2005) for the Australian Greenhouse Office.

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# In situ U-series microanalysis of fossil human remains

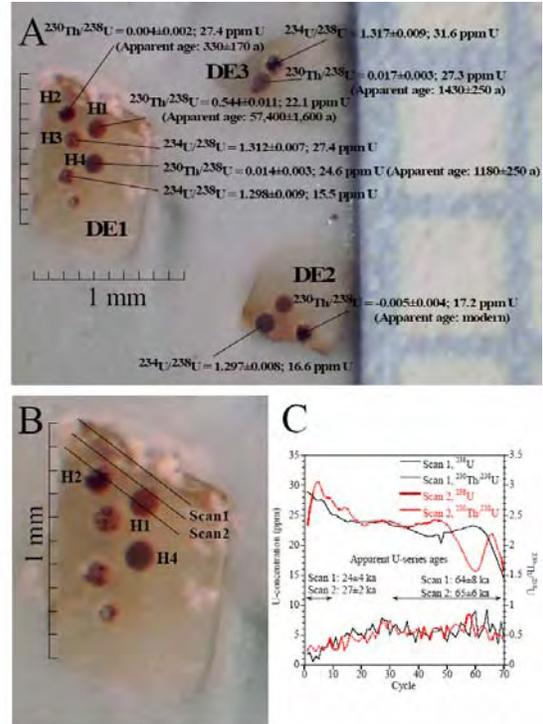
Rainer Grün<sup>1,2</sup>, Stephen Eggins<sup>1</sup> and Julia Maroto<sup>3</sup>

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When dating human remains, it is necessary to keep any destruction to an absolute minimum. During an ESR dating study on the Neanderthal Banyoles mandible, it was necessary to analyse the U-series isotopes on dentine adjacent to the enamel piece that had previously been analysed by ESR. We were able to obtain three small dentine fragments (DE1 to DE3), the largest had a maximum dimension of 1 mm (Figure 1). These were analysed for U-series isotopes by drilling holes with the laser (see Figure 6A) and subsequent analysis with the Neptune multicollector ICP MS. Because of the configuration of the Neptune with a single central ion counter, this can either be used for the measurement of  $^{234}\text{U}$  or  $^{230}\text{Th}$ . Thus the material ablated from the holes give either  $^{234}\text{U}/^{238}\text{U}$  or  $^{230}\text{Th}/^{238}\text{U}$  ratios. The



The  $^{234}\text{U}/^{238}\text{U}$  ratio is very homogeneous, four measurements yielding a mean of  $1.306 \pm 0.009$  (1- $\sigma$  s.d.). In contrast, the  $^{230}\text{Th}/^{238}\text{U}$  ratios and the U concentrations varied greatly: the  $^{230}\text{Th}/^{238}\text{U}$  ratio between virtual background and  $0.544 \pm 0.011$ , and the U-concentration between about 15.5 and 32 ppm. The large variation of the  $^{230}\text{Th}/^{238}\text{U}$  values is astonishing, particularly considering that the high U-concentrations and the extremes measured on the material ablated from holes H1 and H2 in dentine fragment DE1 are less than 0.2 mm apart. Because of the surprising small scale variation in the  $^{230}\text{Th}/^{238}\text{U}$  values, two laser ablation scans were run across the top of DE1 in the same track (the second scan ablating material from deeper into the sample). The approximate positions of the scans are indicated in Figure 1B. Note that the three-dimensional symmetry of the sample is somewhat different than can be estimated from the surface shown in Figure 1B. The first scan did not penetrate either of holes H1 and H2, while the second scan ran completely through H1 (causing the apparent drop in U-concentration in Scan 2; see Figure

1C) and just the top of H2. It can be clearly seen that the U-concentrations increase from H1 to H2, while the  $^{230}\text{Th}/^{238}\text{U}$  values decrease, confirming the observations made from the holes. The average U-concentration of the dentine is  $24 \pm 5.5$  ppm. Because of the small-scale variations in the  $^{230}\text{Th}/^{238}\text{U}$  ratio, it is difficult to estimate an average  $^{230}\text{Th}/^{238}\text{U}$  value for the dentine. All results below 0.5 mm below the surface (i.e. hole H4 and below) and the other two dentine fragments, whose exact spatial relationship to DE1 cannot be reconstructed, correspond to U-series ages of younger than about 1400 years (apparent U-series age on DE3).

The dentine clearly underwent at least two U-accumulation stages, one several tens of thousands of years ago, possibly during the initial burial phase, and a second one, perhaps starting about 1400 years ago and continuing to very recent times. This later U-accumulation phase was most likely initiated by the activation of percolating waters from historic quarrying and drainage activities. In 812, Abbot Bonitus founded the monastery of Sant Esteve on what was then waste land. To control the level of the lake, the monks laid a network of irrigation ditches which turned an uninhabitable place into an agricultural and industrial area which would soon become prosperous. In the 13<sup>th</sup> and 14<sup>th</sup> centuries, the area underwent great expansions with the establishment of varied industries.

With conventional analytical techniques we may have been able to obtain one single U-series result on the combined dentine. The micro analytical capabilities of the laser ablation system do not only allow repeated, detailed analyses of the material, they also give hitherto unobtainable insights into the mechanism of U-migration in dental material.

## **Proliferation and Demise of Deep-Sea Corals in the Mediterranean During the Younger Dryas**

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Deep-sea, cold-water corals have been recognised in the Mediterranean for some time, but it is only in the last several years that oceanographic surveys have begun to reveal their full extent and distribution. Living specimens are relatively rare, with the main reef framebuilders, the colonial *Madrepora oculata* and the solitary coral *Desmophyllum dianthus* being the most widespread, while the colonial *Lophelia pertusa* is known in only several locations. Although deep, cold-water corals are now in recession, pre-modern or sub-fossil examples were much more abundant, occurring throughout the Mediterranean basin (Figure 1) either as in situ assemblages, patch reefs, or as coral-bearing sedimentary mounds, at depths ranging from 250 to 3000 m. Many of these latter sites are now covered in a veneer of muddy sediment which together with their excellent state of preservation indicates that they were exposed on the sea-floor for only a limited time before burial. Thus in contrast to fossil occurrences in the N. Atlantic where specimens are commonly patinated by thin films of Fe-Mn, in the Mediterranean the post-LGM occurrences found on the continental shelves, still often maintain their original luster, making it difficult to discriminate between sub-fossil and modern sample.

In the Mediterranean all the major taxa (*Lophelia pertusa* *Madrepora oculata*, *Desmophyllum dianthus*,) are represented in sub-fossil and pre-modern patch reefs and coral mounds at intermediate water-depths. Specimens from the western and central Mediterranean give a surprisingly narrow range of U-Th ages, with the majority falling between 13,500 to 11,000 yrs BP, indicating that deep-sea corals flourished during the cooler more glacial-like conditions of the Younger Dryas (YD) period. Radiocarbon ages from these corals show that since the Last Glacial Maximum (LGM), the intermediate depth waters of the Mediterranean generally had similar  $\Delta^{14}\text{C}$  compositions to surface waters (Figure 2), except for a narrow period in the early YD ( $12,500 \pm 100$  yrs) when corals approached atmospheric-like compositions. This followed the peak in  $^{14}\text{C}$  production in the early YD and implies a very brief,  $\sim 200$  yr period, of extremely rapid ventilation. Prolific deep-sea coral growth ended abruptly at  $\sim 11,000$  yrs BP,  $\sim 500$  yrs after the cessation of the YD with many of the deposits being draped in a thin veneer of mud. Consequently, their demise was probably due to a combination of factors, the rapid  $6\text{-}8^\circ\text{C}$  rise in sea surface temperatures that occurred at the end of the YD, together with the unusually high sedimentation in

the Mediterranean caused by a massive increase in river discharge from glacial meltwater pulses associated with the termination of the YD.

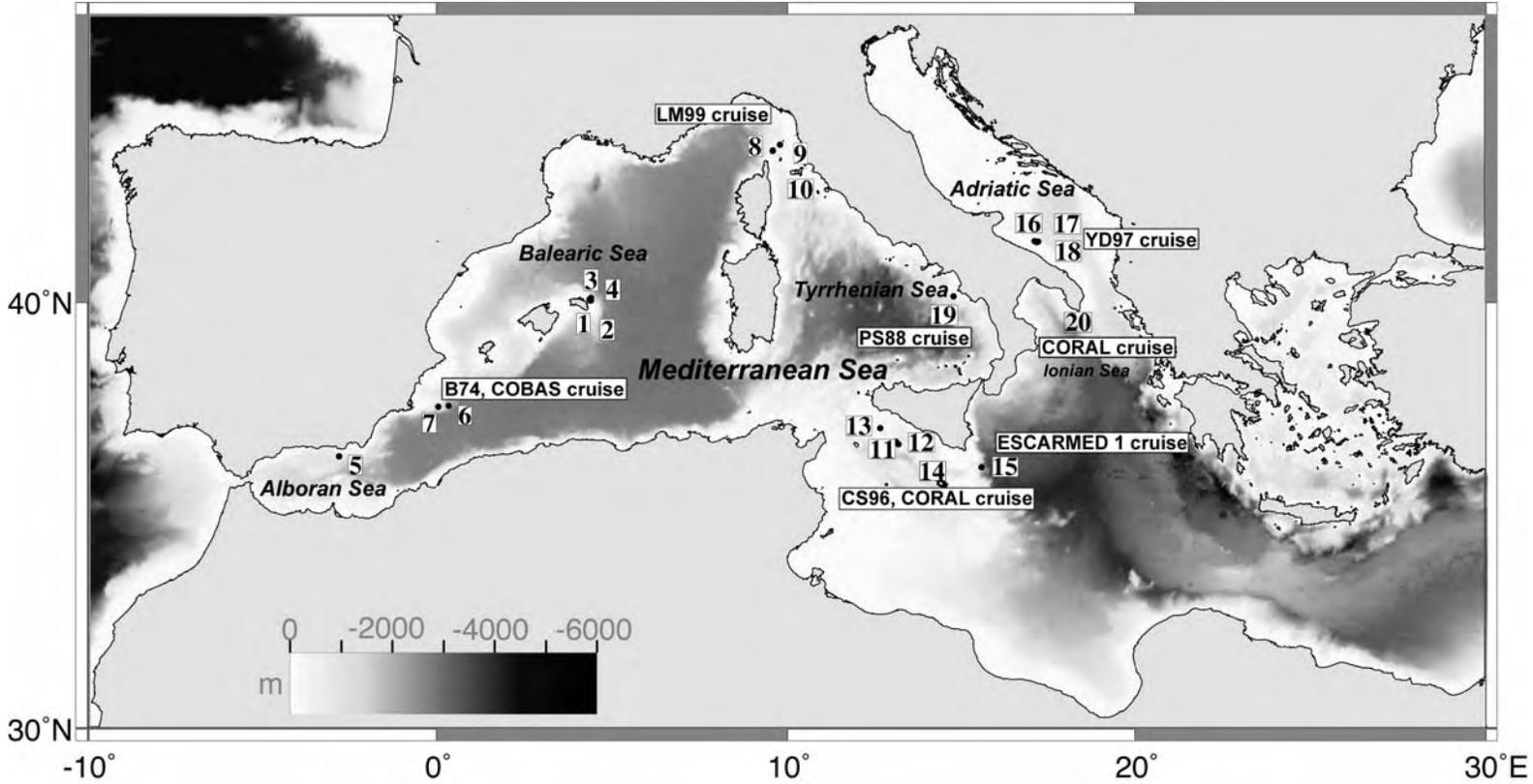


Figure 1. Map showing localities of deep-sea coral sites from the Mediterranean basin. The sample cruises are shown in closed rectangles and the number key to individual samples is given in Table 1 (supp material)

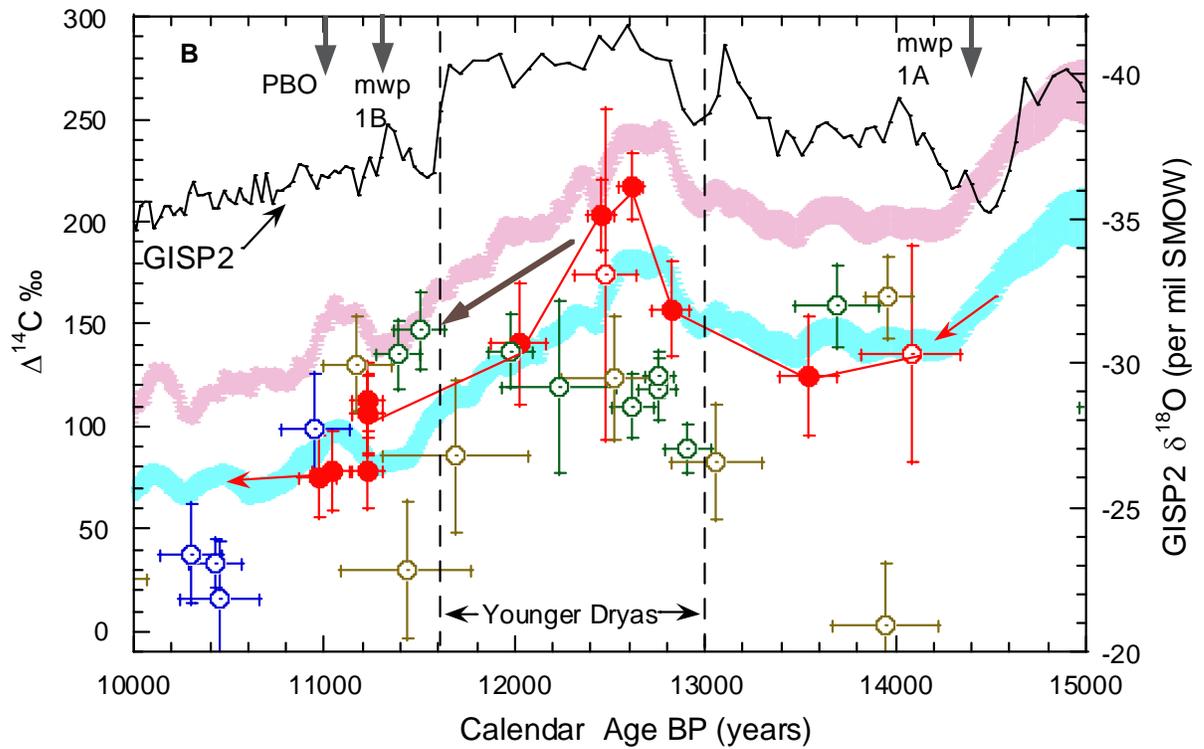
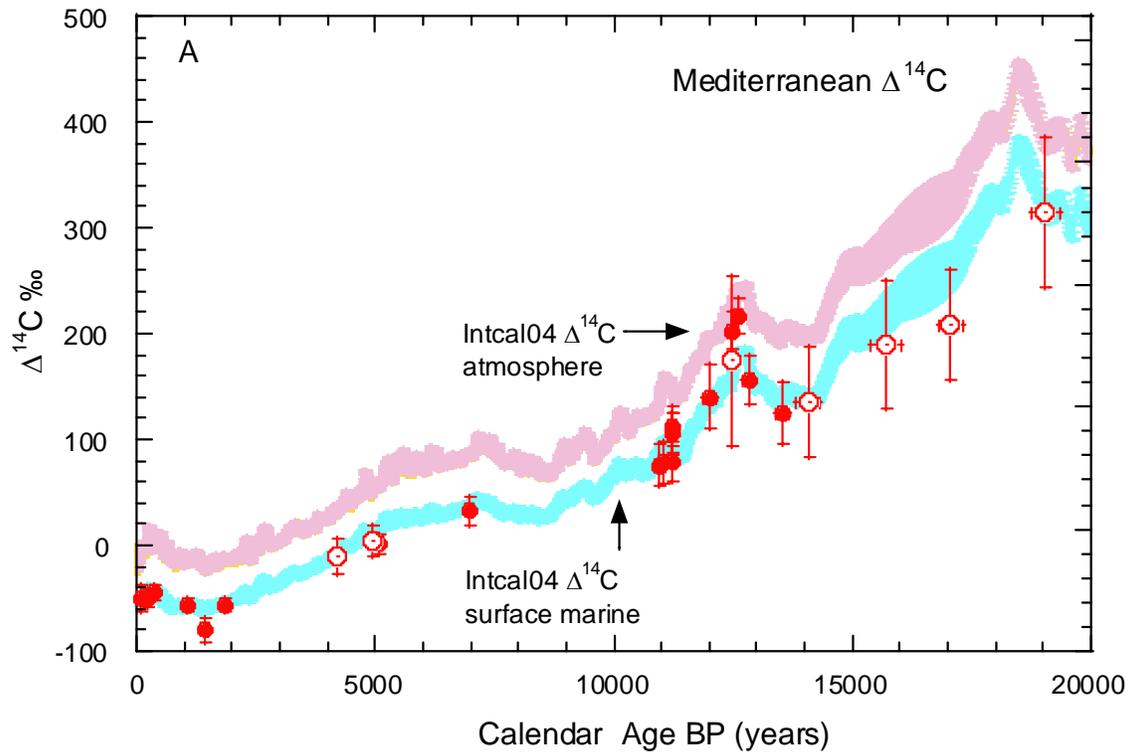


Figure 2A. Plot of  $\Delta^{14}\text{C}$  values for the Mediterranean for the last 20,000 yrs. Values determined in this study using combined U-Th and  $^{14}\text{C}$  ages are shown in solid symbols. With the exception of two samples from the early YD period which have near atmospheric  $\Delta^{14}\text{C}$  values, all deep-sea coral samples have  $\Delta^{14}\text{C}$  values within error of the Intcal04 surface marine curve<sup>13</sup>.  $\Delta^{14}\text{C}$  values determined from  $^{14}\text{C}$  ages of planktonic foraminifera and contemporaneous tepha pairs from Siani et al. are shown in open symbols and also lie error of the surface marine curve.

2B. Expanded plot showing  $\Delta^{14}\text{C}$  values of the Mediterranean compared to deep sea coral data from N. Atlantic from other workers (green, blue, olive). The increased near atmospheric-like values found in this study (solid red symbols) during the YD occur shortly after the rapid rise in  $\Delta^{14}\text{C}$  values, are coincident with a decrease in  $\Delta^{14}\text{C}$  values from GISP2. This indicates that the initiation of the YD involved a close link between cooling (lower  $\Delta^{14}\text{C}$  values) and increased  $\Delta^{14}\text{C}$  from shutdown of deep water formation in the N. Atlantic. In contrast the termination of the YD is marked by rapid warming (higher  $\Delta^{14}\text{C}$  values) without perturbation of the steadily decreasing  $\Delta^{14}\text{C}$  values suggesting that factors other than deep-water formation in the N. Atlantic were responsible for the steadily decreasing  $\Delta^{14}\text{C}$  values from ~12,500 yrs to 11,200 yrs. At ~11,400 yrs, several deep-sea corals from the N. Atlantic have atmospheric  $\Delta^{14}\text{C}$  compositions. These appear to be anomalous as they require isolation of surface water masses for over 1000 yrs. A sequence of  $\Delta^{14}\text{C}$  values (supp. Fig1) determined from a single septal element covering ~100 yrs time period for specimen LM99-124D (*D. dianthus* of age 11,230 yrs) from the Mediterranean exhibits a range of  $\Delta^{14}\text{C}$  values of from  $79 \pm 19$  ‰ (surface marine) to  $113 \pm 18$  (‰). These values overlap with the surface marine curve and approach atmospheric values, consistent with a period of rapidly fluctuating  $\Delta^{14}\text{C}$  values as previously found for an earlier period in the N. Atlantic. Solid arrow shows trajectory for decreasing  $\Delta^{14}\text{C}$  due to  $^{14}\text{C}$  decay.

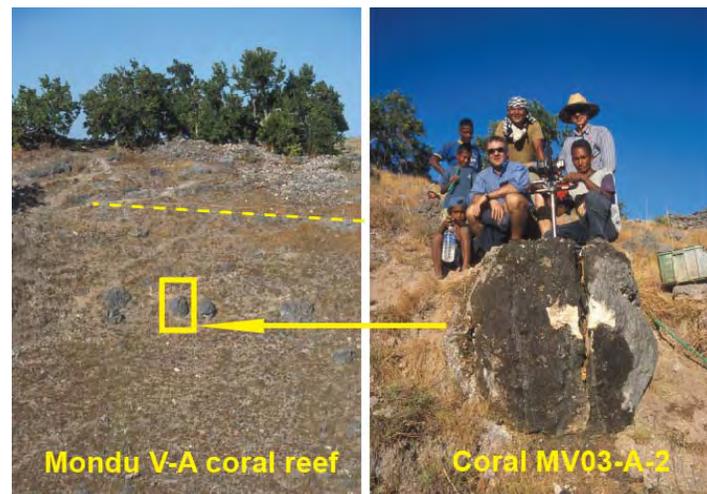
## High resolution coral record of Indo-Pacific Warm Pool climate during the penultimate deglaciation, Sumba, Indonesia

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Ocean-atmosphere interactions in the tropical Indo-Pacific Warm Pool are fundamental drivers of the global meridional Hadley and zonal Walker circulations. Recent research indicates that changes in sea surface temperatures and atmospheric convection in this region play important roles in modulating global climate on interannual, decadal, millennial, and even glacial-interglacial time-scales. Knowing the natural bounds of past ocean-atmosphere variability in the Warm Pool region will enhance our ability to predict the climate in the future. Massive, long-lived corals are one of the only paleoclimate archives capable of providing high resolution records (weekly to monthly) for periods when climate boundary conditions were different from those of the present day. Here we report a 28-year-long high resolution  $\delta^{18}\text{O}$  record for a sea-level highstand during the penultimate deglaciation (140 to 130 ka) reconstructed from a massive *Porites* coral from the Mondu raised reefs, located southwest of Cape Laundi on the island of Sumba, eastern Indonesia.



**Fig.1 A** 1.2 metre long fossil *Porites* coral core MV03-A-2c has been drilled from the Mondu V-A raised reef, 1.5 km inland from the sea. The coral is now 39 m above modern sea level. This coral has an average annual skeletal extension rate of 16 mm/yr, which is typical for modern and Holocene Sumba *Porites* corals

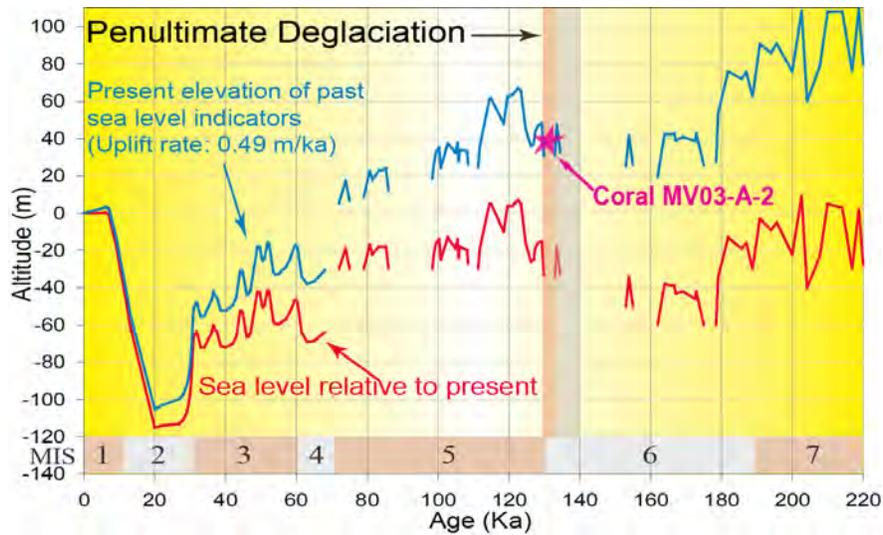


Fig.2 The present elevation of past sea level indicators in study area is shown by the blue curve based on a constant uplift rate of 0.49 m/ka (Pirazzoli *et al.* 1991). Sea level change (red curve) is based on data from John Chappell (Pers. Comm.) and Thompson and Goldstein (2005). The closed-system U/Th age for coral MV03-A-2 is  $136 \pm 1.5$  ka. However, because the  $\delta^{234}\text{U}_i$  is slightly high (158.8‰), we believe that the open-system age of 131 ka is more correct (Thompson *et al.* 2003). Both ages are in the penultimate deglaciation and are consistent with topographic surveys and stratigraphic analysis.

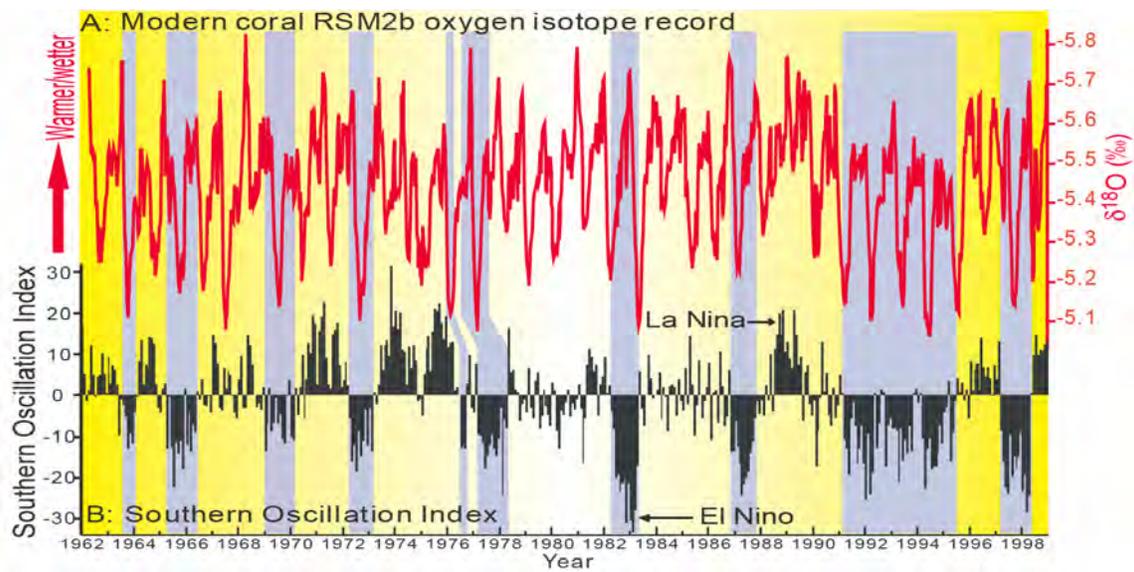
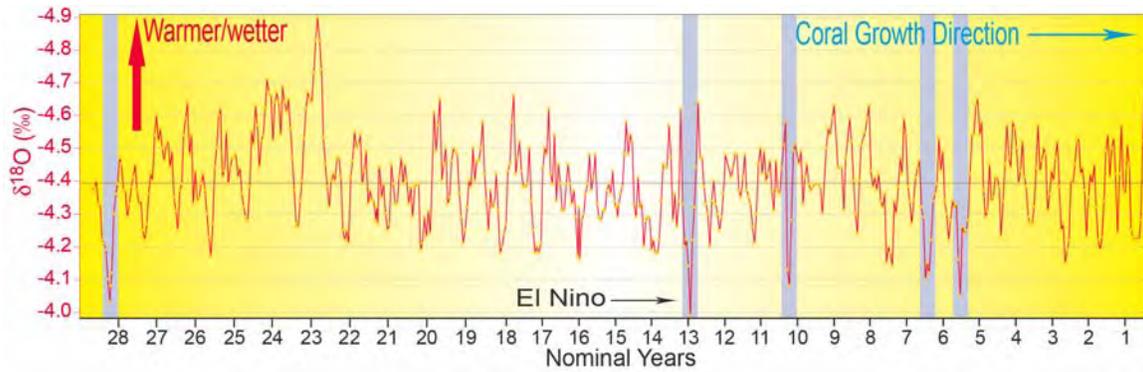
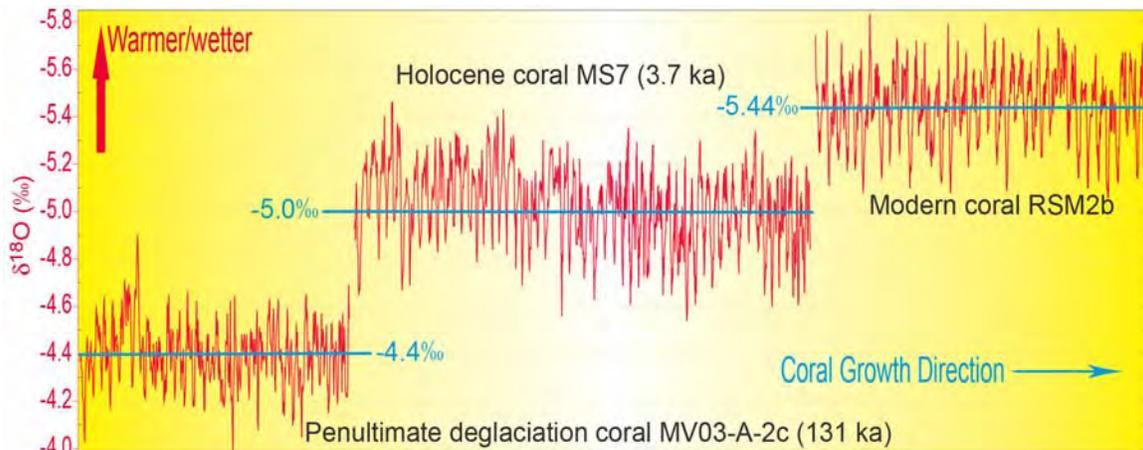


Fig.3 A modern coral was drilled from a nearby fringing reef to establish the basis of the coral climate reconstruction. The coral  $\delta^{18}\text{O}$  mostly reflects SST, with superimposition of a salinity (rainfall) signal. The Mondu coral  $\delta^{18}\text{O}$  records ENSO events very well, especially the winter values. During El Nino events, the winter is relatively dry and cool, reflected by higher  $\delta^{18}\text{O}$  values; in contrast, during La Nina events, the warmer/wetter winter climate is reflected by lower  $\delta^{18}\text{O}$  values.



**Fig.4 Coral record of the penultimate deglaciation:** This coral MV03-A-2c  $\delta^{18}O$  record covers a 28-year period of the penultimate deglaciation climate signal, showing good preservation of annual cycles, and, in many years, a double peak indicating the seasonal development of the wet/warm summer monsoon. The double peak reflects the cross-equatorial movement of the Inter-Tropical Convergence Zone, presumably during years when monsoon rainfall is strong. 5 El Nino events are recognized in this record according to the drier and cooler winters.



**Fig.5 Comparison of penultimate deglaciation and Holocene coral records:**

a. The average  $\delta^{18}O$  for the penultimate deglaciation coral is  $-4.4\text{‰}$ , which is  $0.6\text{‰}$  higher than the average value of the mid-late Holocene coral and  $1.0\text{‰}$  higher than the modern coral on the Mondu reefs. Taking into account the ice volume effect, and assuming constant surface salinity, the shift in  $\delta^{18}O$  indicates that the SST during this period of the penultimate deglaciation at 131 ka was  $2\text{ }^{\circ}\text{C}$  cooler than it is today.

b. The average annual range in  $\delta^{18}O$  between summer and winter of this penultimate deglaciation coral record is smaller than that in the Holocene and modern corals. This change might result from reduction of seasonal difference in insolation or monsoon during that time.

c. The fossil coral record also shows that the frequency of cooler/drier years, indicative of El Nino events, was lower than today.

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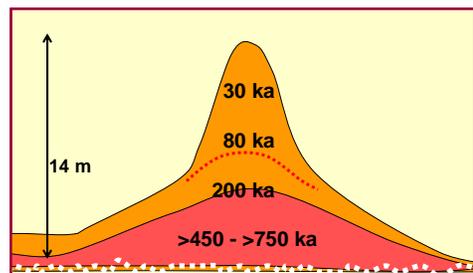
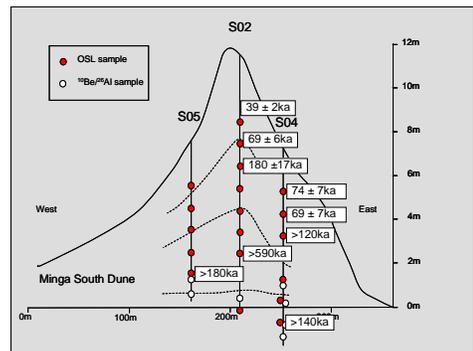
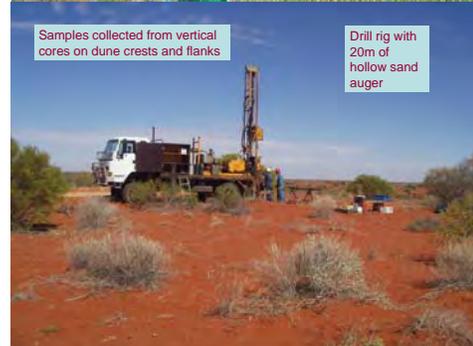
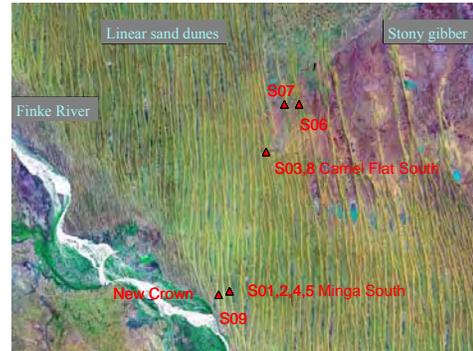
# The age of the Simpson Desert, Australia

Ed Rhodes, John Chappell

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The results of 30 luminescence dates of sand cored from the centre of several large longitudinal sand dunes in the western Simpson Desert provide evidence that these significant geomorphological features are of a surprisingly great antiquity. The sediments were dated using optically stimulated luminescence (OSL) determinations of sand-sized quartz. This method provides an age estimate for the time of burial since the grains were last exposed to daylight, during the construction of the dune by aeolian processes.

The age estimates that we have derived from dune sediments in the Simpson Desert, near the community of Finke, NT, are in stark contrast to similar dates from the Stzelecki and Tirari Deserts. DEMS PhD student Kat Fitzsimmons has measured over 80 samples from dunes at locations throughout the Stzelecki and Tirari Deserts using a similar approach, and of these, fewer than 4% provide age estimates over 150,000 years (Rhodes et al. 2003). For the Simpson dataset, more than 50% provide age estimates of beyond 150,000 years. Of those that are younger, the majority were deposited before 60,000 years ago, again, providing a contrast to the age estimates from the Stzelecki and Tirari Deserts. Many of the older sediments from the Simpson are beyond the range of conventional OSL methods, and preliminary results from novel "slow component" OSL methods provide encouragement that this method will allow us to date deposition on time scales up to one million years.



We have also measured 12 paired  $^{10}\text{Be}/^{26}\text{Al}$  cosmogenic nuclide concentrations in quartz from the Simpson dunes. This allows us to assess total burial time (possibly in multiple burial and erosion cycles) and approximate exposure time prior to burial for these bulk samples. The mean of the total burial age estimates is  $850 \pm 300$  ka, while the mean of the pre-burial exposure ages is  $210 \pm 100$  ka. We note that these exposure ages are similar to surface samples from the Macdonnell Ranges (which represents the source of sand in this region), suggesting that transport from the ranges into the desert was relatively rapid.

Rhodes E. J., Chappell, J. and Spooner N. A. 2003 Age and mobility of arid regolith: assessment by luminescence dating methods. In: Roach I. C. ed. *Advances in Regolith*, CRC LEME, 342-344.

## Characterising southwest Australia's natural rainfall variability for the past 1000 years using speleothem records

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Speleothems (cave stalagmites) have the capacity to preserve high resolution proxy rainfall records extending from recent times to tens of thousands of years. Rainfall isotopes are preserved in the speleothem calcite, as are trace elements whose concentrations reflect the amount of soil and rock weathering and vegetation activity. These geochemical signals vary between wet and dry years.

Three papers from Earth Environment were published in 2005 that investigated the potential for reconstructing rainfall records from southern Australian speleothems. Treble et al. (2005a) showed that O isotopes ( $\delta^{18}\text{O}$ ) in southern Australian rainfall vary inversely with rainfall amount and are primarily controlled by the strength and proximity of the mid-latitude low pressure systems that generate rainfall across this region. Analysing southern Australian speleothem  $\delta^{18}\text{O}$  will allow us to reconstruct how wet it was in the past and potentially, how major atmospheric circulation features varied.

Using a modern speleothem that grew on a tourist cave boardwalk in southwest Western Australia, Treble et al. (2005b) confirmed that speleothem  $\delta^{18}\text{O}$  can indeed be used to track rainfall history. Speleothem  $\delta^{18}\text{O}$  rose 0.5‰ in response to the rainfall decrease that occurred from about 1970 onwards. Treble et al. (2005c) further contributed to the understanding of trace element incorporation in speleothems by mapping their concentrations over speleothem growth layers. The maps show that Ba, Sr, U and Na concentrations coherently follow annual growth layers but that complex crystal growth affects Mg incorporation as well as influencing the number of annual cycles, their amplitude and wavelengths. These results have clear



**Stalagmite GL-S1 from Golgotha Cave, southwest Western Australia will be used to construct 1000 years of rainfall proxy data.**

implications for studies that use annual trace element cycles as chronological markers, growth rate or seasonality proxies.

The study of southern Australian speleothems continues in Earth Environment with a new grant that began in May 2005. The aim of this latest project is to reconstruct 1000 years of rainfall history to determine natural variability for the region. This study will contribute significantly to our understanding of whether the drier conditions experienced from about 1970 onwards in southwest Western Australia are driven by natural variability or signal climate change.

Treble P. C., Budd W. F., Hope P. K. and Rustomji P.K. (2005a) Synoptic-scale climate patterns associated with rainfall  $\delta^{18}\text{O}$  in southern Australia. *Journal of Hydrology* **302**, 270-282.

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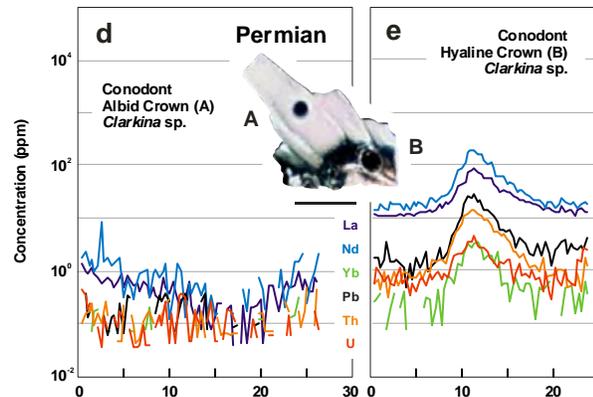
# Chemical systematics of conodont apatite determined by laser-ablation ICPMS

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Major, minor, and trace element compositions of a suite of Ordovician, Silurian, and Permian conodonts have been characterised by laser ablation-inductively coupled plasma mass spectrometry. Continuous, high-resolution chemical profiles through individual conodont elements have revealed systematic compositional differences between the component histologies (albid, hyaline, and basal body tissues). Comparative analyses of contemporaneous bio-apatites (ichthyoliths and inarticulate brachiopods), as well as Late Holocene and modern fish material, show linear relationships between their respective rare earth element, yttrium, lead, thorium, and uranium compositions, which has implications for their relative permeability and susceptibility to diagenesis. Accordingly, LA-ICPMS profiles have been assessed in the context of histology, general morphological structure, and post-depositional chemical exchange, and suggest that albid crown may be the least permeable of the conodont mineralised tissues. These data have significant implications for the interpretation of conodont geochemistry and its application to palaeoceanography.



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## Ultrastructure, permeability, and integrity of conodont apatite determined by Transmission Electron Microscopy

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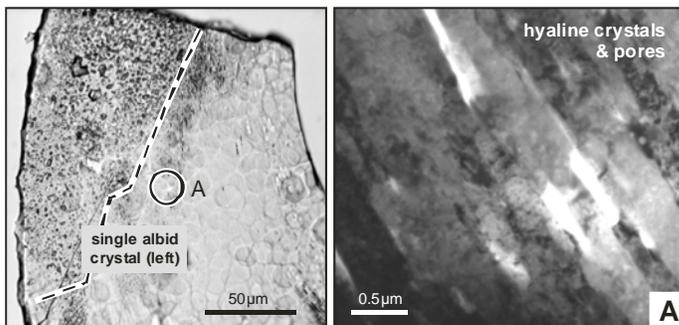
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Nanometre scale analysis of conodont apatite by Transmission Electron Microscopy has provided new insights into its crystalline structure, porosity, and inherent integrity. The component hard tissues are differentiated by crystal size, and inter- and intra-crystalline porosity. Basal body tissue typically comprises randomly oriented, isometric to elongate nanocrystals, which are commonly loosely packed causing significant intercrystalline porosity. Hyaline crown is also polycrystalline but characterised by elongate crystals typically of micron-scale that accommodate numerous spherical nanopores; the crystals are strongly aligned and typically tightly bound within a broader lamellar structure that lacks 'interlamellar spaces'. In contrast, albid crown comprises extraordinarily large crystals (100's  $\mu\text{m}$ ) with nano- to micron-sized pores that are often irregularly shaped, forming a 'cancellate' microstructure.

Large pores ( $\geq 0.5\mu\text{m}$ ) within crown tissues promote significant light scattering causing optical opacity ('albidity'), which may occur in both cancellate and polycrystalline lamellar crown. Cancellate albid and hyaline tissues are suggested to represent microstructural 'end-members' of conodont crown as some intermediate zones show 'hybrid' features and variable opacity. The range of histologies observed by TEM reveals the inadequacies of terms currently used to describe conodont crown, and are revised herein to accommodate some of these structural complexities.

The potential of conodont apatite to retain primary geochemical information



must depend upon crystal size and permeability. On this basis, cancellate albid crown probably offers the greatest potential for resisting post-mortem alteration and recording palaeomarine signatures.

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