Earth Environment Introduction

In the past year public awareness of climate and associated global change issues has grown markedly, such that this is now the number one issue of public concern. The wide range of research undertaken by the RSES Earth Environment Group is highly relevant as we are addressing current issues of concern such as the frequency and longevity of droughts in Australia, as well as questions of longer term relevance, such as the effects of climate change on terrestrial and marine systems and its impacts on human evolution.

Our research draws upon a unique group of World-class research facilities that enable the 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 placed on developing diagnostic environmental proxies within an absolute chronologic framework that spans a few tens to several hundred thousand years of the Earth's history, and to use 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.

The Earth Environment group maintained success in obtaining ARC funding through both discovery as well as linkage grants. Successful strategic planning rounds in 2005-2006 resulted in the joint RSES/DEMS appointment of Dr Mike Ellwood and the RSES/RSPhysEngS appointment of Dr Stewart Fallon, adding unique expertise and sorely needed critical mass to our marine sciences initiative. Likewise Dr Steve Eggins's appointment to the tenure track staff ensures that our group will maintain our world leading abilities in marine geochemistry.

We also welcome new Post Doctoral Researchers, Dr Linda Ayliffe, Maxime Aubert and Dr Stacy Jupiter who are funded by ARC grants to Professor Grün and Dr Gagan and via support from the Coral Reef Centre of Excellence to Professor McCulloch, respectively. There has also been a talented cohort of graduating students who completed their PhD theses in an exemplary manner and we wish Drs Ayling, Fraser, Trotter and Wyndham continued success in their future endeavours.

During 2006 academic staff continued their high level of success with ARC proposals with Professors Grün, Chappell and Dr Ellwood being funded. Dr Mike Ellwood was extraordinary successful in his first time applications having both of his ARC grants funded, one being jointly with Dr Eggins. These proposals focus on the role of nutrients and atmospheric CO2 in the Southern Oceans by examining the biogenic silica cycles as well as patterns of Ge/Si fractionation in sponges and diatoms. Professor Grün’s Linkage proposal on the Willandra Lakes World Heritage Area ranks is especially important for documenting Australia's unique cultural and environmental history. This project is being undertaken jointly in a strategic alliance between the custodians and managers of the area and leading Australian research institutions to build a picture of the continent’s human and environmental history before this evidence is irretrievably lost.

Installation of new LIEF funded state-of-the-art equipment is now essentially complete in the Earth Environment Group enabling us to continue our cutting-edge research. This includes an ~$2 million gas source AMS which will revolutionise our capacity to undertake 14 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.
Researchers Highlights

Seasonal structure of Holocene El Niños: high-resolution reconstruction from coral skeletal stable isotopes
Rose D. Berdin

Oceanic germanium/silicon fractionation: evidence from oceanic profiles, diatom cultures and sediment opal.
Michael J Ellwood

In situ Sr analysis of a Neanderthal tooth
Rainer Grün

Ultrastructure and in-situ geochemistry of conodont mineralised tissues
Julie A. Trotter

In-situ oxygen isotope compositions of Ordovician conodonts using SHRIMP II and laser ablation MC-ICPMS
Julie A. Trotter

Coral Reefs and Global Change

Permo-Carboniferous inheritance in Australian landscapes
Malcolm McCulloch

Routine penetration of South Java Current into the Savu Sea recorded by a Porites coral
Brad Pillans

Diurnal origin of Mg/Ca banding in Orbulina universa and effects of cleaning on test composition
Dingchuang Qu

Variability in the uranium isotopic composition of the oceans over glacial-interglacial timescales
Eggins S.M

From Cane to Coral Reefs: Ecosystem Connectivity and Downstream Responses to Land Use Intensification
Tezer M. Esat

Evidence for past climates and environmental response from sediment archives in central and eastern Australia
Stacy D. Jupiter

Initiation of Australian longitudinal dunefields, revealed by cosmogenic burial dating on dune-sand quartz from the Simpson Desert, central Australia
Ed Rhodes

Understanding climate change: Speleothems as archives of natural rainfall variability and rapid climate events
Toshiyuki Fujioka

Pauline C. Treble
Stable isotope ratios of oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) were analyzed at bi-weekly resolution for two modern and three Holocene Porites corals from eastern Samar, Philippines. Previous low-resolution $\delta^{18}O$ analysis of the Holocene corals revealed extraordinarily strong droughts (typically longer than three years) for specimens with uranium series ages between 7.6 – 2.3 ka. The purpose of the new high-resolution $\delta^{18}O$ records presented here is to investigate the nature of these protracted droughts, and to compare their seasonal structure with present-day droughts produced by El Niño events. The modern coral $\delta^{18}O$ records clearly track the cooler sea-surface temperatures and droughts associated with the prolonged El Niño event in the early 1990s, the severe 1997/98 El Niño, and the moderate 2002/03 El Niño.

To allow direct comparison of the coral records, annual growth increments in the coral skeletons were determined using the annual cycle of $\delta^{13}C$, which is regular and well-defined. The records were then re-sampled to 26 points per year using Analyseries and stacked to determine the mean annual cycle. El Niño events were identified from $\delta^{18}O$ anomaly plots, derived by subtracting the mean annual cycle from the $\delta^{18}O$ records. Positive $\delta^{18}O$ anomalies in the modern coral records are indicative of cool/dry periods produced by El Niño-like events in the past.

Composite analysis of these El Niños was performed by stacking annual cycles of $\delta^{18}O$ for each event. The El Niño $\delta^{18}O$ composites for the modern coral records show markedly higher $\delta^{18}O$ from late boreal fall to early summer. The timing of this anomaly compares well with El Niño’s signature in stacked bi-weekly records of rainfall and SST, and is consistent with the regional rainfall anomaly in the western Pacific, where rainfall is greatly reduced from November to May during the mature phase of El Niños (Ropelewski and Halpert, 1987).

Modern and Holocene El Niño composites show differences in terms of magnitude and timing of the peak $\delta^{18}O$ anomaly, which corresponds to the period of maximum cooling/drying (Fig. 1). The older Holocene records exhibit peak $\delta^{18}O$ anomaly values that are approximately 0.2‰ higher than the younger records. Furthermore, the timing of the maximum cooling/drying appears to occur progressively later in the calendar year: late winter for present-day events, early fall at 2.3 ka, and late fall at 7.3 – 5.8 ka. These differences in timing might be a response to orbitally-driven changes in the seasonal cycle of solar radiation, which, based on a climate model by Clement et al. (2000), is thought to influence the behavior of ENSO in the past.
Figure 1. Modern and Holocene El Niño δ¹⁸O composites standardized relative to the mean δ¹⁸O February of each record. Numbers along the X-axis correspond to a fortnight starting from January. Arrows indicate the coolest/driest period in each record, which occurs progressively later in the calendar year in the Holocene records.


Oceanic germanium/silicon fractionation: evidence from oceanic profiles, diatom cultures and sediment opal.

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The cycling of inorganic germanium in the ocean closely resembles that of silicon. Profiles of dissolved germanium concentration versus depth are almost identical to that of silicon, and when the two are plotted against each other a near linear relationship is obtained ($r^2 = 0.997$) (Figure 1). This correlation between germanium and silicon indicates that the uptake and regeneration of inorganic germanium by diatoms dominates its oceanic cycle. Although germanium mimics silicon in the ocean, differences in biogeochemical behaviour occur. Small diatoms (10-40 mm) appear to faithfully record the germanium/silicon (Ge/Si) ratio of seawater, whereas large diatoms (> 40 mm) do not. Large diatoms isolated from the same sediment horizons as their smaller counterparts tend to have lower Ge/Si ratios. This result suggests that larger diatoms discriminate against germanium during silicon uptake and frustule formation. This interpretation is supported by the fact that the global germanium versus silicon relationship has a small but significant positive intercept suggesting that germanium is discriminated against during silicon uptake and frustule formation (Figure 1).

In an effort to further understand the possible mechanism(s) that might lead to germanium fractionation we cultured the fast growing diatom Minutocellus polymorphus under controlled Ge/Si conditions. Results from the culture work showed that at low silicon concentrations significant discrimination of germanium occurred leading to lower Ge/Si ratios within diatom opal and increased Ge/Si ratios of culture medium. This pattern suggests that the positive intercept in the global germanium versus silicon relationship results from germanium discrimination by diatoms during silicon uptake. Short-term Michaelis-Menten uptake experiments were also conducted to understand processes leading to germanium discrimination. Results from these experiments showed that the half saturation constants for silicon and germanium were 0.87 m mol/L and 2.70 m mol/L, respectively.

This confirms that the uptake of germanium is slower than that of silicon and that this is the primary mechanism leading to Ge/Si fractionation in diatoms. This result was incorporated into a simple partitioning model to describe diatom opal Ge/Si fractionation. Utilising this model, we show the interglacial-glacial fluctuations in Ge/Si opal record reflects changes in the surface ocean silicon concentration (Figure 2). This interpretation has major implications for paleo-nutrient reconstructions utilising Ge/Si, the silicon isotope and the germanium isotope signatures of diatom opal.
Figure 1.

Figure 2.
In situ Sr analysis of a Neanderthal tooth

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The present day $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in bedrock depends on its geological age and initial $^{87}\text{Sr}/^{86}\text{Sr}$ and Rb/Sr ratios. Soils have closely similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as their source-rocks. Some of the soil Sr enters the food chain via plants and it has been shown that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain virtually unchanged during the various biochemical processes, and when Sr replaces Ca in the mineral phase of skeletal tissues. Therefore, skeletal Sr isotopic composition reflects the geographic range during tissue formation. The measurement of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in bones and teeth has been increasingly used for the reconstruction of residential mobility and migration among ancient human and animal populations.

We have applied in situ laser ablation ICP-MS analysis on a Neanderthal tooth from the site of Payre, which is located in a limestone overlooking the western bank of the Rhone, near Valence. Bedrocks in that area vary from the metamorphic and granitic rocks of the Massif Central, via the sediments of the Rhone and its flood plains to the sedimentary sequences of the Western Alps.

Figure 1: A Neanderthal tooth from Payre (left). The tooth is cut in the middle (middle) and all analyses are carried out in situ on the interior enamel surface (right).

The tooth was cut in halves and the analysis is carried out on the internal cuts of the tooth enamel (Figure 1). Initial results looked very promising, showing variations in the Sr isotopic composition (Figure 2, left), which could perhaps be explained by seasonal migrations. However, when comparing these isotopic variations with Sr concentrations (Figure 2, middle), a broad mixing line is observed (Figure 2, right), perhaps indicating post-depositional Sr uptake with different isotopic composition compared to the physiologically incorporated Sr.

To address the problem of post-depositional Sr uptake, we have mapped the Sr concentrations in a large part of the tooth with laser ablation (Figure 3). Figure 4 shows the resulting Sr map along with two selected tracks. In the dentine, there is a clear gradient from the root towards the enamel. It is interesting to note that at the dentine/enamel boundary, the Sr concentration does not show a very sharp drop (about cycle 400 to 550 in Line 1, Figure 4, lower left), as is usually observed for other mobile elements, such as uranium. There is also a clear gradient in the Sr concentration in the enamel.
At the moment it is difficult to conclude whether this gradient is a primary signature or whether it is a diagenetic over-print. Work is continuing to measure Sr-isotope maps, which will give further insights into the Sr-systematics of fossil teeth. We have also mapped a series of other elements, such as Ca (to check Sr/Ca ratios), Al, Ba, Mg, Th and U (for dating). Particularly the latter showed that it has absolutely no intentions to adhere to simplified diffusion models. On the same tooth, the work on in situ oxygen isotope measurements with the SHRIMP 2 is continuing.

Figure 2: Sr isotope (left) and Sr concentration (middle) variations along the laser track shown in Figure 1, right. Sr isotopes versus Sr concentration (right).

Figure 3: Cross section of the tooth with light area indicating the location of the laser tracks.

Figure 4: Map of Sr concentrations in the area indicated in Figure 3. Top: angled and vertical views, below left: U-concentration along laser track 1, right: U-concentration along laser track 11.
Ultrastructure and *in-situ* geochemistry of conodont mineralised tissues

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Novel approaches integrating both histological and *in-situ* geochemical analyses of conodont apatite have been investigated to identify primary crystalline structures and compositions of the component tissues. In the context of diagenesis, it is important to recognise the complex relationship between sample histology and geochemistry, as the permeability and integrity of conodont apatite is partly controlled by its crystalline structure. The component histologies have thus been examined by transmission electron microscopy (TEM), which for the first time has been conducted on Ar ion-milled conodonts. TEM analyses have revealed near pristine structures and most significantly, resolution of the component crystallites of all histologies (Trotter *et al.*, in press). Of particular note, electron patterns show that albid crown comprises very large (100’s µm) crystal domains, which provides a meaningful platform to interpret the respective geochemistry of conodont tissues that have been characterised *in-situ* by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Continuous compositional depth profiles through discrete conodont elements reveal systematic differences between the component tissues in their rare earth and heavy element contents especially (Trotter and Eggins, 2006). The U-shaped depleted profiles of albid crown contrast markedly to the enriched and typically equilibrated profiles of hyaline and basal tissues, their concentrations following a linear relationship with albid, basal (together with coeval ichthyoliths and phosphatic brachiopods), and hyaline tissues representing low-, high- and intermediate concentrations. These data collectively provide insights into the relative uptake of chemical species post-mortem, and clearly suggest that albid crown is the least permeable histology (ie. large crystal domains and U-shaped profiles) hence is less susceptible to diagenetic alteration. This work has significant implications for interpreting the geochemistry of conodont apatite, and identifying the most suitable components for palaeoseawater studies.


In-situ oxygen isotope compositions of Ordovician conodonts using SHRIMP II and laser ablation MC-ICPMS

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Given the potential utility of conodonts as geochemical tracers, new and developing technologies have been investigated to assess the feasibility of extracting isotopic records by in-situ analysis. Reconnaissance work has shown that ion microprobe (SHRIMP II) and laser ablation multi-collector ICPMS offer considerable potential to determine the oxygen and strontium compositions of conodont apatite. The benefits of analysing marine bio-apatites rather than less chemically stable carbonates, together with the capability of utilising high spatial resolution techniques, provide an opportunity to target specific components that are most likely to retain primary compositions. Accordingly, this work has significant implications for better characterising the evolution of seawater chemistry throughout the Palaeozoic.

Preliminary Sr isotope datasets of discrete conodont elements determined in-situ by laser ablation MC-ICPMS fall within similar ranges of existing Ordovician records based on labour intensive conventional TIMS analyses of both calcitic brachiopod and conodont samples. Further, LA-MC-ICPMS analyses of conodont albid tissue have yielded less radiogenic 87 Sr/86 Sr ratios than hyaline tissue for coeval samples, suggesting that there may be systematic differences between the compositions of the component conodont histologies.

Reconnaissance in-situ oxygen isotope analyses using SHRIMP II have yielded considerably higher and more realistic δ18O values (~16 to 19‰ V-SMOW) than conventional GIRMS data based on calcitic brachiopods (~10 to 25‰ V-PDB) reported in the literature (e.g. Shields et al., 2003), the integrity of which has been the focus of much scepticism. Although the initial SHRIMP results have an analytical error of ±1‰, a temporal shift during the Arenig is apparent. Better constraining this shift as well as the well-known Late Ordovician δ18O excursion is the focus of further work, which given the recent progress in technique development promises to yield higher external precision for conodont apatite, and thus a significantly improved δ18O seawater curve for the Ordovician.


Coral reefs are subject to increasing threat from the degradation of their marine environment which is occurring at an unprecedented rate, on both local and global scales. Locally, landuse changes in river catchments, wetlands and estuaries is leading to increased supplies of sediment and nutrients to coral reefs, which together with pressures from activities such as trawling and overfishing, can lead to an evolutionary trajectory that may ultimately result in an abrupt phase shift from a coral to a macroalgae dominated ecosystem. On global scales, extreme climatic events caused by increased sea surface temperatures together with rising carbon dioxide levels from fossil fuel burning is resulting in an increased frequency of mass coral bleaching such as occurred in 1998, and increasing ocean acidity which will ultimately lead to a decrease in the rates of coral calcification. Understanding the complex array of interacting processes (see Figure) that are driving changes at both local as well as global scales is thus essential for the development of optimal strategies to ensure the long-term sustainability of coral reefs.

The approach taken at the RSES node of the ARC Centre of Excellence for Coral reef Studies is that knowledge of the past improves our ability to understand both the present as well as to help predict future consequences of human impacts, and rapid climate change. Studies of coral reef systems and their environments prior to the impact of human civilisations provides a ‘natural’ baseline against which anthropogenic changes can be compared and assessed. Our group is thus developing novel methods for studying past environments and assessing rates of evolutionary changes in coral reefs. We are identifying the mechanisms via which local and global changes in the marine and adjacent terrestrial environments are causing reductions in coral reef biodiversity and ecosystem function. Together with ecological and physiological studies of processes underlying reef stress, this broad approach provides the Centre with a unique perspective on environmental change and how it impacts community structure and longer term evolutionary dynamics of coral reefs on timescales that ranges from centuries to millennia.

Ecological Response of Coral Reefs to Global Change

![Figure 1. Schematic diagram showing both global and local impacts on coral reef systems.](image)
Permo-Carboniferous inheritance in Australian landscapes

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During the late Carboniferous and Early Permian (~320–280 Ma), Australia was part of the Gondwana Supercontinent, which included Antarctica, India, Africa, New Zealand and South America. Gondwana was situated at mid to high latitudes in the Southern Hemisphere. Evidence for glaciation is widespread and includes glacial tills and striated pavements in all states of Australia, as well as the other Gondwana continents. Although the timing, character and distribution of glacial events and deposits are debated (Jones & Fielding 2004 and references therein), most reconstructions show a large ice cap covering much of southern and western Australia in the Early Permian, with glacio-marine sedimentation in the adjacent Canning Basin. In contrast, in eastern Australia the evidence indicates discrete, short-lived episodes of localized mountain glaciation, with substantial non-glacial intervals in between. Just how much of Australia was covered in ice is unclear, but a large ice sheet, probably several kilometers thick, was likely centred over the Yilgarn Craton in Western Australia. Glacial till and tunnel valleys, dating from this time, are preserved at Lancefield on the eastern margin of the ice sheet, where glacial meltwater drained into the Officer Basin (Eyles & de Broekert 2001). Relict Early Permian landforms including ice-scoured channels, U-shaped valleys, rock drumlins and striated pavements are also common along the northeastern margin of the Pilbara Craton (Playford 2001). However, significant areas of Australia must have been ice free, at least for long periods of time (millions of years) during the major interval (280–320 Ma) of Gondwana glaciation, because paleomagnetic dating of giant (60 m+) weathering profiles in the Tanami and Yilgarn regions, as well as at Northparkes mine in New South Wales (Pillans 2005), indicates widespread deep oxidation of the regolith (Figure 1). K-Ar dating of illitic clays in weathered volcaniclastics within Jenolan Caves, some 200 km ESE of Northparkes, yields a cluster of ages in the range 342–335 Ma (Early Carboniferous), and a zircon fission track age of 345 Ma on one sample is consistent with the K-Ar ages (Osborne et al. 2006), making Jenolan Caves among the oldest currently open cave system in the world. The entry of the volcaniclastic sediments and the morphology of the caves mean that they must have been relatively close to the surface in the Early Carboniferous. Paleokarst features of Early Permian age are also preserved in the northern Canning Basin in Western Australia. In summary, Permo-Carboniferous glacial landforms, weathering profiles and caves at or near the present landsurface, in diverse parts of the Australian continent, suggest a significant Late Paleozoic inheritance in the modern landscape. The survival of ancient landforms and weathering profiles in Australia is usually explained as being a consequence of prolonged tectonic stability and postulated low rates of weathering and erosion. However, while measured rates of long-term (10 5–10 7 yr timescales) weathering and bedrock erosion in Australia may indeed be low by world standards, they are not low enough to explain the continuous subaerial survival of pre-Cenozoic landforms and weathering profiles. Burial and exhumation must therefore be significant contributing factors in the preservation of ancient features in the Australian landscape, a conclusion that is supported by apatite fission-track thermochronology (e.g. Kohn et al. 2002).
Figure 1. Permo-Carboniferous deep oxidation of Proterozoic rocks exposed in Redback pit (~60 m deep), Tanami gold mine, Northern Territory.


Routine penetration of South Java Current into the Savu Sea recorded by a Porites coral

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Even though early studies have noticed that the eastward flow of the South Java Current could significantly reduce the transport of the Indonesian Throughflow (ITF), it had not been confirmed if the Indian Ocean water enters into the Indonesian seas through the Sumba Strait which is one of the main exits of the ITF until a couple of recent observations during 1995 to 1998 using current meters. Here we report a high resolution Sumba modern Porites coral $d^{18}O$ which recorded routine penetration of remote forced Indian Ocean Kelvin wave into the Savu Sea and the resulting distinct freshening during the austral autumn (March to May) during 1962 to 1998. Strong interannual variability with a 3-year period for the Kelvin wave input has been observed and spectral analysis has indicated that intrinsic process within the Indian Ocean basin dominantly controls this variability. The high resolution Sumba coral $d^{18}O$ seems to reflect the fluctuation of the direction and source of the surface currents flowing through the Sumba Strait during November to May and also suggests the occurrence of eastward flowing during November to March, even though the frequency and intensity might be much weaker than that of the austral autumn Kelvin wave passage (Figure).
Diurnal origin of Mg/Ca banding in *Orbulina universa* and effects of cleaning on test composition

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Culture experiments have been performed on the algal symbiont-bearing planktonic foraminifera *Orbulina universa*, using juvenile foraminifera collected by plankton net off the south coast of NSW. Individual foraminifera were grown at fixed temperature in a day-night lighting cycle (12 hour day + 12 hour night) through the full adult-stage of their life-cycle, which involved final spherical chamber formation, gametogenesis and death over a period of up to 10 days. The number and composition of Mg/Ca bands formed in the wall of the final spherical chamber of individual foraminifers was investigated using both electron microprobe and laser ablation ICPMS. The number of high- and low-Mg/Ca band pairs developed was found to accord with the number of diurnal light cycles over which the individual foraminifers calcified their final chamber. This result confirms the proposed diurnal origin for Mg/Ca banding in *Orbulina universa* proposed by Eggins et al. (2004), and points to a significant role for algal symbionts in determining the Mg/Ca composition of foraminiferal calcite, most likely through influence on [CO$_3$]$^{2-}$ concentration and calcite saturation state (cf. Wolf-Gladrow et al., 1999).

The impact of a range of cleaning methods upon the Mg/Ca compositional banding developed in fossil and live-collected *Orbulina universa* has also been investigated, inclusive of the widely used oxidative and reductive cleaning protocols. Characterisation of test fragments taken from the same *Orbulina universa* tests were analysed by LA-ICPMS both prior to and following cleaning. Results reveal significant differences in the ability of the different procedures to remove Mg-rich outer surfaces and attached organic material (where present). The internal Mg/Ca banding resists chemical modification and is unchanged by any of the cleaning procedures.


Variability in the uranium isotopic composition of the oceans over glacial–interglacial timescales

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Uranium-series mass spectrometric analyses of corals from the uplifted last glacial terraces at Huon Peninsula, Papua New Guinea, that grew from 50,000 years ago to 30,000 years ago show systematically low values of 234 U/238 U, at the time of coral growth, compared with modern corals. When combined with coral data from other studies a systematic trend emerges indicating shifts in the 234 U/238 U ratio at times of major glacial–interglacial transitions that involve large variations in sea-levels. From last glacial to Holocene, the rate of change in d 234 U is approximately 1‰ per thousand years. The variations in the U budget of the oceans appear to be due to accumulation of excess 234 U in near shore areas in anoxic and suboxic sediments, in salt marshes and mangroves, in estuaries, and in continental margins during periods of warm climate and high sea-levels. These near-shore areas are exposed during periods of low sea level resulting in rapid oxidation of U into highly soluble phases. The subsequent release of 234 U-enriched uranium into the oceans occurs over a sustained period, in step with rising sea-levels.

Fig. A compilation of d 234 U values in U-series dated corals from the Last Interglacial, the last glacial, and the Holocene. For each data set representative uncertainties are as shown. The sea-level curve is intended only as a guide for the eye in contrasting the trend in d 234 U with changes in sea-level. The shaded band represents the uncertainty in sea-level estimations. The Last Interglacial sea-level was 3–5 m above the current sea-level and we have placed it at d 234 U ~ 153‰. The general resemblance of the d 234 U variations to the sea-level curve for this period is remarkable. In living coral d 234 U = 149 ± 2‰. There is a systematic rise in d 234 U from a low of 132‰, during the last glacial, up to about 153‰ at the start of the Holocene, corresponding to an extra ~20 Mmol of 234 U. There is considerable variability during the 30–60 ka period over a range of 10‰ in d 234 U. The prominent sea-level high-stands around 80–110 ka display a large range of low to high values of d 234 U. The Last Interglacial is represented by a mass of points that appear randomly distributed, and may reflect increased variability in measurements due to older ages and digenesis in comparison to samples from the Holocene.
Clearing of catchments draining into the Great Barrier Reef Lagoon (Queensland, Australia) has increased sediment and nutrient loads in river runoff. The extent of land cover change and the intensification of land use were analyzed for the Pioneer River catchment near Mackay (from Landsat images, 1972-2004), and for the estuary (from aerial photographs, 1948-2002), to determine whether and how loss of natural vegetation has affected sediment delivery to nearshore waters and adjacent coral reefs. Geochemical proxy records of weathering and sediment delivery to the sea, deposited in skeletons of living *Porites* corals from inshore (5 km from Pioneer mouth) and midshelf (32-51 km offshore) reefs, were analyzed to determine the spatial and temporal extent of terrestrial impacts. High-temporal resolution (~weekly) concentrations of barium (Ba), yttrium (Y) and calcium (Ca) were measured by laser ablation inductively-coupled mass spectrometry (LA-ICP-MS), while annual samples of rare earth elements and yttrium (REY) were measured by solution ICP-MS. Major trends emerging from integration of contemporaneous terrestrial changes, marine geochemical proxies and climate records include: 1. A 33% net decline (1972-2004) of forests on alluvial plains as farms encroached into riparian zones; and a 22% net decline (1948-2002) of tidal mangroves in the estuary. 2. Ba/Ca correlations with Pioneer River discharge were influenced by wind direction and strength; but there was no apparent temporal change in Ba/Ca since 1946. The absence of enrichment in mean inshore Ba/Ca ratios (versus midshelf reefs) may be due to biological recycling by phytoplankton, which may restrict Ba availability. 3. Mean Y/Ca ratios from inshore (5 km) corals were 3.1 and 3.6 times higher than from midshelf (32 and 51 km) corals, and inshore REY abundances were ~2-5 times higher than from midshelf reefs. Inter-annual REY variation on both inshore and midshelf sites was correlated significantly with year and discharge, while long-term temporal trends in maximum annual Y/Ca, normalized to Pioneer River discharge, appear to reflect both agricultural expansion and changing management practices. 4. The combination of high turbidity and high nutrient discharge from the Pioneer River may be affecting benthic community composition on both inshore and midshelf reefs.
Evidence for past climates and environmental response from sediment archives in central and eastern Australia

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We have made significant advances in the dating of quartz from wind and water-deposited sediments from Australia. These advances operate at several different levels, providing improved information for both large and small scale processes.

Optically Stimulated Luminescence (OSL) dating relies on the trapping of electrons in the crystal lattices of quartz and feldspar grains, when they are subject to natural environmental radiation. When grains are exposed to light or heat, the electrons in some trapping sites are emptied, effectively resetting the luminescence clock. This method has been used to date wind and water-deposited sediments, as well as the heating of archaeological artefacts and hearths.

A significant issue in OSL dating relates to the completeness of the zeroing process prior to and during the deposition of sediments. Based on theoretical expectation and the dating of modern surface samples, wind-blown sediments from desert environments have been assumed to be well-zeroed, while water-lain deposits may contain grains with significant residual signals. We have dated a large number of aeolian desert samples, and note that a significant proportion demonstrate signal patterns indicating incomplete zeroing at deposition; basically repeat determinations provide varying apparent ages, caused by the influence of non-zeroed grains. To understand how these age distributions are produced in multi-grain aliquots or sub-samples, numerical simulations were undertaken based on measured single grain OSL sensitivity data from real samples. The modelling results demonstrate that natural variations in OSL signal intensity allow the recognition of incomplete zeroing in multi-grain aliquots, and for some samples, this may represent the optimum means to detect this effect. This work also highlights how OSL data may be used to reconstruct conditions at the time of deposition, in particular the rapidity of deposition and the nature of the sediment sources.

Perhaps our most exciting findings relate to this use of OSL variation to determine depositional conditions. Work in two catchments in eastern Australia has demonstrated that single grains from fluvial deposits can retain information about their depositional history, and past sediment storage events. In both longitudinal dunes and lunettes (source-bordering dunes around ephemeral lakes) we also find significant evidence for the rapid reworking of earlier deposits, some of which occurred at night. While we must quantify these effects to determine reliable age estimates for these deposits, we can also start to develop detailed sediment transport models for their construction. In the Simpson desert, we have combined OSL age estimates from dunes with triple nuclide cosmogenic dating based on 10 Be, 20 Ne, 26 Al, to construct large scale models of dunefield initiation and reworking in response to climate changes on timescales of 1,000,000 to 1,000 years.
We find that many dunes retain a high degree of detailed palaeoenvironmental information, and that most dunes were constructed in a relatively small number of significant dune-building events which occur across the areas studied. This has very significant implications for understanding the nature of the environmental response to climate change in vulnerable parts of central Australia.

Figure 1: Active dune in the Strzelecki Desert near Camerons Corner, SA.
Initiation of Australian longitudinal dunefields, revealed by cosmogenic burial dating on dune-sand quartz from the Simpson Desert, central Australia

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Fields of longitudinal dunes are most extensive and a major feature of Australian sandy deserts that cover ~40% of the continent (Mabbutt, 1988). Chronological studies of the Australian longitudinal dunes, however, have been sparse owing to the lack of suitable dating method; conventional radiocarbon is of limited use owing to both the lack of organic materials and to the restricted age range (<50ka). Development of luminescence dating, notably optically stimulated luminescence (OSL), opened way to date sand deposits up to ~300 ka, but, because of the nature of the dating, luminescence ages tend to represent "stabilisation ages" rather than formation ages of dunefields (e.g., Nanson et al., 1992). Cosmogenic burial dating offers a way of dating deposits up to 5 Ma in the case of 10 Be and 26 Al pair, in which the degree of radioactive decay of cosmogenic nuclides, produced prior to burial, in a deposit can be interpreted as depositional age of the material (Granger and Muzikar, 2001).

In this study, a total of 69 sand and rock samples were collected from longitudinal dune fields at the western margin of the Simpson Desert, near Finke, central Australia, including sand samples, 20 for cosmogenic burial and 46 for OSL dating, together with three sets of gibber samples from adjacent gibber plains, in order to determine the timing of dune building episodes in central Australia. Nine drill holes from the crest to base of five longitudinal sand ridges identified paleosol horizons within the dunes, indicating that the dune formation was episodic. OSL measurements, outlined in Rhodes' annual report, from lower stratigraphic units in the dunes gave minimum ages ranging from >590 ka to >110 ka, suggesting that the depositional age of the earliest dunefields in the study area is older than 500 ka, beyond the age limit of luminescence dating. Cosmogenic burial ages were calculated from the cosmogenic 10 Be and 26 Al concentrations in the dune-core samples, showing consistently older ages from ~360 ka to ~1600 ka. The amounts of cosmogenic 21 Ne in the samples were also determined by evaluating non-cosmogenic neon components such as crustal and in situ nucleogenic 21 Ne, and the burial ages calculated from pairs of 10 Be-21 Ne and 26 Al-21 Ne were generally consistent with the 10 Be-26 Al burial ages, indicating that the non-cosmogenic 21 Ne components were successfully corrected.

The cosmogenic burial ages indicate that the first dune building episode at the west Simpson Desert occurred at least ~1200-1300 ka ago, and that mobile sand became available for the early dune building about ~1600 ka ago, which could have been earlier up to ~2000 ka. These ages are much older than any dune dates reported previously, and suggest that dry-out of rivers, and thus onset of aridity, in central Australia occurred immediately after cessation of widespread gibber formation, ~2 Ma ago, in this region (Fujioka et al., 2005). The earliest dune building episode at the west Simpson Desert, ~1200-1300 ka ago, indicates deepened aridity in Australia.
Figure 1. Summary of the measured burial ages, calculated from cosmogenic 10 Be and 26 Al in the dune-core samples, and OSL ages for a longitudinal dune, near Finke, in the west Simpson Desert. Internal dune units were defined based on the paleosol (brown curves) and carbonate (orange curve) horizons, identified during drilling. Ages with asterisk represent samples with accordant 10 Be–26 Al–21 Ne burial ages.


The need for high resolution paleoclimate records is evermore apparent in times of changing climate and an increased demand on Australia's water resources. Long, detailed records of natural rainfall variability are required to understand the impact of climate change on our water resources. 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.

Current research in Earth Environment includes reconstruction of long-term natural rainfall variability for sites in southern Australia by Dr Treble and colleagues. A key strength in this research is the detailed investigation being carried out on very young speleothems whose growth overlaps the instrumental record permitting calibration of speleothem geochemical trends to climate change. Speleothems from southwest WA, southeast SA, Tasmania and the Australian Alps are being used to develop calibrations over the 20th century which can be extended back in time. These young speleothems and drip water monitoring programs offer an excellent opportunity to explore new potential environmental proxies preserved in speleothems. These geochemical data are being used to extend the climate record back 1000 years.

Research was also carried out on a speleothem that grew during the last glacial period when the Earth's climate was remarkably unstable. At this time, Greenland ice core records show repeated and rapid temperature variations of almost the same magnitude of a full glacial-interglacial cycle. These rapid climate events have been recorded in paleoclimate archives in many other places across the world. One such archive are speleothems from Hulu Cave, China, which show large abrupt O isotope (δ18O) shifts at the time of the North Atlantic events (Wang et al., 2001). High-spatial resolution SIMS O isotope analyses were carried out across the δ18O shift corresponding to Heinrich event 1 increasing the temporal resolution of the previously published data by approximately tenfold providing yearly resolution. These new data demonstrate that the East Asian monsoon underwent a major change and that the majority of this transition took place in as little as 1-2 years (Treble et al., in press). This rapid shift marked a significant change in mean climate that persisted for approximately 500 years.
Figure 1. O isotope record of Hulu Cave at the time of Heinrich event 1. The two overlapping SIMS O isotope transects demonstrate that 75% of the rapid change in the East Asian monsoon climate at 16.07 ka took place in less than 2 years.
