

# 12<sup>TH</sup> AUSTRALASIAN ENVIRONMENTAL ISOTOPE CONFERENCE

10<sup>th</sup>-12<sup>th</sup> July 2013  
University of Western Australia  
Perth, Australia

## Programme and Abstracts



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Volume designed, compiled and edited by: Kate Bowler, Paul Greenwood, Sara Lock and Grzegorz Skrzypek. We gratefully acknowledge Jo Lock and Alexandra Rouillard for Front Cover design and photography.

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# Welcome

**Dear Colleagues,**

It is a great pleasure to welcome you to the University of Western Australia for the 12<sup>th</sup> Australasian Environmental Isotope Conference (AEIC). We are expecting more than 70 participants, including several international researchers, and have ahead an exciting programme of 33 oral and 12 poster presentations. The guiding principle of the meeting is to encourage presentation, communication and discussion of isotope related research results carried out in academia and industry which address significant environmental or paleo-environmental questions. The isotopes of many different elements represent key tracers of hydrological, geochemical and biophysical processes in atmospheric, terrestrial and aquatic environments. This meeting is exclusively focussed on isotopic environmental research issues, breaking from the formal association with the Australian Hydrological Conference which has been run in parallel with the AEIC in recent years, on account of the 40<sup>th</sup> IAH International Congress to be held in Perth September, 2013 (<http://iahcongress2013.org/>). We hope you enjoy the meeting and your visit to Perth and UWA.

Conference organizing committee:

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# Conference Arrangements

## Conference Venue:



**University Club, UWA** - Situated just eight minutes drive from the Perth CBD on the banks of the Swan River, The University Club is located on campus at The University of Western Australia on Hackett Drive in Crawley (Hackett Entrance 1).

**Conference mixer - Wednesday 10<sup>th</sup> July (5.30 – 7.30 pm)**, Ground Floor Terrace, UWA Club.

**Formal Programme - Oral and Poster presentations** (Thursday, Friday) - will be held in the South Banquet Room, UWA Club. Lunch and Morning/Afternoon Teas will be held in the Banquet Hall Foyer.

**Registration** – available at the Conference mixer (Wed Eve) or prior to commencement of formal programme (Thurs, Fri).

**Conference Dinner – Thursday 11<sup>th</sup> July (6 - 9 pm)**, JoJo's Restaurant, Nedlands Bath Marina (located on the jetty at the river end of Broadway, Nedlands; ~20 min walk from UWA)

**Sponsor Representatives** – will be displaying product information in the Banquet Hall Foyer.

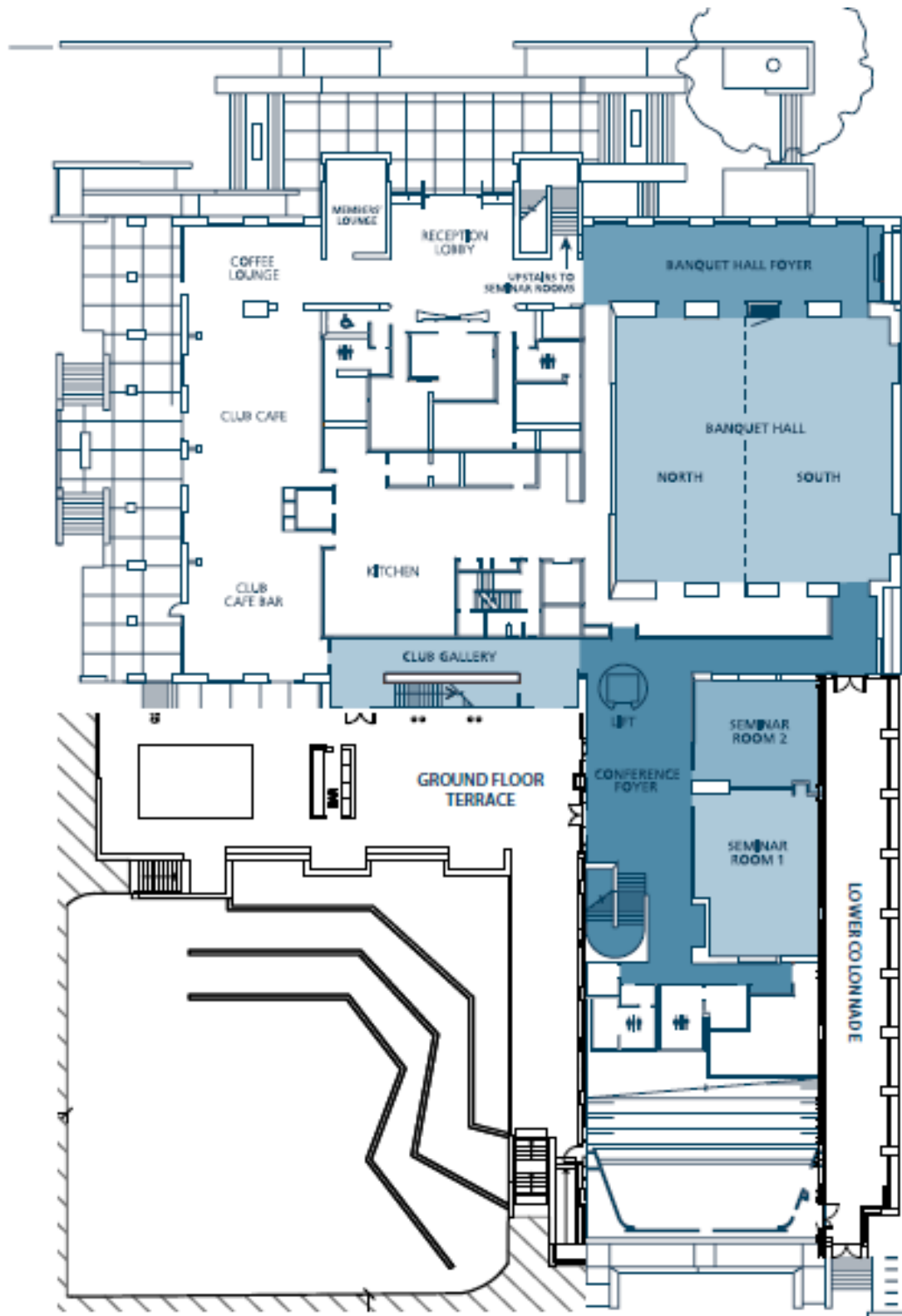
**Club Amenities** – all registered delegates have full UWA Club membership entitlements for the duration of the conference.

(<http://www.universityclubconferences.com.au/template.asp?CID=4>)

**Internet Access** – there is wireless internet technology in all rooms. Conference organisers can provide internet access credentials (complimentary) on request.

**Parking:** As the university is between teaching sessions the general public may park in student designated parking bays (yellow signed zones) for no charge – refer to campus map for parking zone locations.

## UWA Club – 1<sup>st</sup> Floor Plan





[http://www.uwa.edu.au/data/assets/pdf\\_file/0003/23367/campusmap.pdf](http://www.uwa.edu.au/data/assets/pdf_file/0003/23367/campusmap.pdf)



# Meeting Programme

	<b>Wednesday 10<sup>th</sup> July – UWA Club, UWA, Hackett Drive Entrance 1, Crawley</b>
17.30 – 19.30	<b>Early Registration and Mixer</b>

	<b>Thursday 11<sup>th</sup> July – UWA Club, UWA, Hackett Drive Entrance 1, Crawley</b>
8.00 AM	Registration Open/Refreshments
8.30	Introduction and Housekeeping, Dr Paul Greenwood
8.35	Welcome to Country and Conference Open, Prof Peter Davies (UWA PVC-Research)
	<b>SESSION 1 – Ecology: Chair - Dr Paul Greenwood</b>
8.45	<b>Plenary: Dr Andy Revill (CSIRO) - CSIA for understanding marine biogeochemical processes and ecological interactions</b>
9.30	Anais Pages (Student; S) - Abiotic sulfurisation of a modern stromatolite and the preservation of early-life
9.50	Andre Siebers (S) - Diurnal variation in dissolved carbon isotopes and ecosystem metabolism in pools of hydrologically variable dryland streams
10.10	Morning Tea
	<b>Session 2 - Ecological adaption/Climate Change: Chair - Dr Pauline Grierson</b>
10.35	<b>Keynote: Assoc Prof Paulo Vasconcelos (UQ) - Goechronology applied to Climate Change</b>
11.05	Alison Blyth - Unravelling the controls on carbon isotopes in speleothems – a multiproxy approach
11.25	Chris Gouramanis - High-resolution Holocene palaeoclimate using ostracod valve chemistry from Barker Swamp, Southern Western Australia
11.45	Jie Chang (S) - Application of stable isotopes from Australian chironomid (non-biting midge) head capsules as proxies for past climate change
12.05	POSTERS - INTRODUCTIONS
12.30	Lunch and Posters
	<b>Session 3 – Radio Isotopes: Chair - Dr Fred Jourdan</b>
13.25	<b>Plenary: Dr Quan Hua (ANSTO) - Radiocarbon Applications in Earth and Environmental Sciences</b>
14.10	Jonathan Sanderman - Are soil carbon decay constants truly constant? Insights from time series <sup>14</sup> C measurements
14.30	Sean Tomlinson - Using Radiolabelled <sup>86</sup> Rb Isotope to Measure Metabolism
14.50	Ian Cartwright - Multi-isotope perspectives on open-system calcite dissolution and implications for C-14 dating of deeper groundwater
15.10	Afternoon Tea
	<b>Session 4 - Radio Isotopes/Hydrology: Chair - Prof Ian Cartwright</b>
15.35	Axel Suckow - “Age of Groundwater” – a misleading and unnecessary term
15.55	Christopher Daughney - Groundwater age and transit time in the Lake Rotorua catchment, New Zealand
16.15	Douglas Ford - Analyses of saline water samples on a cavity ring-down spectroscopy instrument
16.35	Matt Fischer - A new continuum regression model and its application to climate and rainfall isotope relationships
16.55	Close to formal Proceedings
<b>18.00 – 21.00</b>	<b>Conference Dinner - JoJo’s Restaurant, Nedlands Bath Marina</b> (located on the jetty at the river end of Broadway, Nedlands; ~20 min walk from UWA)

	<b>Friday 12<sup>th</sup> July – UWA Club, UWA, Hackett Drive Entrance 1, Crawley</b>
8.00 AM	Registration Open/Refreshments
	<b>SESSION 5 - Ocean/Aquatic Systems : Chair – Dr Andy Revill</b>
8.30	<b>Plenary: Prof Malcolm McCulloch (UWA) - Resilience of Coral Calcification to Ocean Acidification: insights from boron isotopes</b>
9.10	Giri Kattel - Paleolimnological investigation of the use of stable isotopes of carbon and nitrogen in bulk sediment and Cladoceran zooplankton to reveal ecosystem changes in Kings Billabong, Northwest Victoria, Australia
9.30	Jens Zinke - Ningaloo Niño forcing of the Leeuwin Current (West Australia) since 1795
9.50	Debashish Mazumder - Stable isotope ( $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ) studies in aquatic ecosystems: responses to different conditions
10.10	Morning Tea
	<b>Session 6 - Trees, Litter and Soils: Chair – Dr Grzegorz Skrzypek</b>
10.35	Pauline Grierson - Australian dendrochronology and perspectives from isotopes of tree rings
10.55	Cemre Ustunkaya (S) - The application of carbon and nitrogen stable isotope analysis to plant macro remains in archaeological contexts
11.15	Courtney Creamer - Increased loss of soil-derived carbon in response to litter addition and temperature
11.35	Waqar Ahmad (S) - Use of stable carbon isotope for investigating inorganic carbon dynamics in a limed acidic soil
11.55	Crystal Maher (S) - Using sulfur isotope signatures to unravel the geochemistry of acid sulfate soil remediation using seawater
12.15	Lunch and Posters
	<b>Session 7 - Mass Extinctions/Palaeoclimates: Chair – Dr John Volkman</b>
13.10	<b>Plenary: Prof Kliti Grice (CUT) - Consistent changes in biomarkers (microbes and flora) and stable isotopes across the major extinction events of our planet</b>
13.50	Fred Jourdan - Mass extinctions due to climate shifts: volcanoes or asteroid impacts?
14.10	Svenja Tulipani (S) - A Pyrolysis-GC-IRMS approach for the analysis of methyltrimethyltridecylchromans (MTTCs): Investigation of origin and significance for palaeoenvironmental reconstructions
14.30	Pia Atahan - Late Quaternary environmental change at Lake McKenzie, southeast Queensland: evidence from microfossils, biomarkers and stable isotope analysis
14.50	Afternoon Tea
	<b>Session 8 - ANALYTICAL: Chair - Dr Alison Blyth</b>
15.15	<b>Keynote: Dr Colin Smith (Latrobe Uni) - LC-IRMS of Amino Acids and Archaeological Application</b>
15.45	Kate Dennis - Utilizing cavity ring-down spectroscopy for high-precision analysis of the triple oxygen isotopic composition of water and water vapour
16.05	Paul Gorjan - Rethinking EA-IRMS (elemental analyser – isotope ratio mass spectrometry)
16.25	Grzegorz Skrzypek - Normalization methods and standards selection in stable isotope analyses
16.45	Dr Grzegorz Skrzypek – Closing Comments/Awards (Best: Paper; Student Oral; Student Poster)
16.55	Close

## Poster presentations:

1. **Chris Brodie** - ITCZ and Asian monsoon variability from MIS 9 – MIS 2 from a south China perspective.
2. **Tegan Davies** - Response of microbial activity to long term nitrogen and phosphorus additions in arid mangroves is dependent on tidal position
3. **Juan Pablo D'Olive** - Variations in seawater pH from  $\delta^{11}\text{B}$  records of corals from the central GBR
4. **Mark Farrell** - The role of oligopeptides in terrestrial nitrogen cycling: An Australasian and global perspective
5. **Weiwei Fei** - The organic carbon isotope of lacustrine sediments of the upper Shahejie Formation in Huanghua Depression: a record of sedimentary environment and productivity of an ancient lake
6. **Lucy Georgiou** - Boron isotope systematics of *Porites Cylindrica* grown under natural pH regimes of Heron Island, GBR.
7. **Se Gong** - Challenge on carbon isotope analysis of trace level gases trapped in fluid inclusions.
8. **Paul Greenwood** - Compound specific  $\delta^{34}\text{S}$  analysis – Development and applications
9. **Caroline Jaraula** - Molecular marker and stable carbon isotope analyses of carbonaceous ambassador Uranium ores of Mulga Rock in Western Australia.
10. **Louise Kristensen** – The application of lead isotopes in tracing historic industrial lead emissions
11. **Debashish Mazumder** - Diet-tissue discrimination of  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  in a freshwater crustacean
12. **Alexandra Rouillard** - Unravelling sediment biogeochemistry of extreme hydroclimatic periods in the semi-arid Pilbara using stable isotopes and biomarkers.



## Biographies – Plenary and Keynote Speakers:



**Dr Andy Revill**  
(CSIRO Marine and  
Atmospheric Research)

**Dr Andy Revill** is a senior research scientist and team leader of the biogeochemical processes team. Having started life as an organic geochemist his research interests now lie in understanding the sources and fate of carbon and nitrogen in estuaries using a variety of lipid marker and stable isotope techniques, particularly the combination of both. He has been involved in projects around temperate, sub-tropical and tropical estuaries including the Huon (Tasmania), Coorong (SA), Fitzroy and Norman rivers (QLD) Darwin Harbour and the Daly river (NT) and the Ord (WA). He is currently leading two flagship projects - one about to start in the Kimberley to investigate the role of terrestrial material in coastal productivity and the other using compound specific stable isotopes to investigate changing trophic structure in south east Australian fisheries due to climate change.



**Assoc Prof Paulo  
Vasconcelos**  
(University of  
Queensland)

**Assoc Prof Paulo Vasconcelos'** major research interests focus on noble gas geochronology, low-temperature geochemistry, and landscape evolution. He is particularly interested in the development and application of novel geochronological methodologies to study weathering processes (Weathering Geochronology) and applying the results to unravel the paleoclimatic and geomorphological evolution of cratons. Paulo also works on the application of cosmogenic isotopes to quantify erosion rates on cratonic landscapes. Combining weathering geochronology and cosmogenic isotope erosion rates is also relevant to study the surficial history of Mars. Paulo is currently a member of the Mars Science Laboratory mission, and a member of the science team for the Mars 2020 mission. He is collaborating with colleagues at Caltech and JPL in the development of new approaches suitable for dating the Martian surface. Finally, Paulo also works on the application of high-resolution geochronology to date volcanic rocks as a way of determining the tectonic and landscape histories of continents and the geodynamics of magma generation in intra-continental settings.



**Dr Quan Hua**  
(ANSTO)

**Dr Quan Hua** is a Senior Research Scientist within the Institute for Environmental Research at the Australian Nuclear Science and Technology Organisation (ANSTO). He has over 15 years working experience in radiocarbon dating and its applications in Quaternary and climate change studies. His current research focuses on radiocarbon calibration, chronological reconstruction, and high resolution proxy records of climate series from corals, speleothems, tree rings and sediments. Dr Hua was a JSPS (Japanese Society for the Promotion of Science) Visiting Research Fellow at Center for Chronological Research, Nagoya University, Japan in 2009, and is a member of the AINSE (Australian Institute of Nuclear Science and Engineering) Archaeology and Geosciences Committee. He is the author of over 85 peer-reviewed scientific publications and 170 conference abstracts.



**Professor Malcolm McCulloch**  
(University of Western Australia)

**Winthrop Professor Malcolm McCulloch** is a coral reef expert at the School of Earth and Environment, The University of Western Australia. His research addresses important contemporary issues such as the impacts of climate change and direct human activities on coral reefs. He has developed innovative new indicators of how these processes have affected coral reefs over a range of timescales by utilising geochemical records preserved in the skeletons of corals. He has showed for example how boron isotopes preserved in corals act as a proxy for changes in seawater pH, with this now rapidly growing area of research providing the most reliable means for determining the rates of ocean acidification from increased anthropogenic CO<sub>2</sub> emissions. He has also developed other proxies to determine changes in ocean temperature, salinity and sediment/nutrient inputs into coral reefs, with important implications for the management of coastal catchments, the resilience of coral to climate change, as well as the capacity of the oceans to serve as a major sink for CO<sub>2</sub>. Professor McCulloch is an ARC Laureate Fellow at UWA and, until recently, a WA Premier's Research Fellow. He is leader of the UWA node of the ARC Centre of Excellence in Coral Reef Studies, a Fellow of the Royal Society and The Australian Academy of Sciences.



**Professor Kliti Grice**  
(Curtin University)

**Prof. Kliti Grice** holds an ARC Professorial DORA. She is a highly respected and internationally renowned organic geochemist who has demonstrated a passion for scientific research and education. Kliti obtained a PhD from the School of Chemistry, University of Bristol, UK on molecular fossils (biomarkers) and stable isotopes derived from Chlorobi (utilise toxic H<sub>2</sub>S in photosynthesis) in ancient deposits. She later worked with Prof. Sinninghe-Damsté at The Netherlands Institute of Sea Research on seminal food web and stable isotopic studies and the diagenetic sulfurisation of biolipids that have later proven important with her later research on mass extinction events, microbial geobiology and environmental sustainability. In 1998 she joined Curtin University where with university, government and other support she has established a world-class research centre (WA Organic and Isotope Geochemistry Centre; WA-OIGC) located in the new Chemistry and Resources Precinct at Curtin. Grice's research has focused on fundamental questions regarding the Earth's biosphere (past and present), and the sophisticated and integrated molecular and stable isotopic appraisal of organic sediments that she and her team practice has clarified our perceptions of many past Earth phenomena, with a special interest in the fundamental bases for the P-T mass extinction, more recently extended to the end-Triassic and end-Devonian events, all of which are associated with – and thus provide complimentary exploration information about – depositional conditions of rocks with petroleum generative potential. Grice et al. (Science, 2005) attribute these extinctions to biogeochemical processes in ancient seas in preference to a previously postulated asteroid impact. Kliti has supervised to completion 17 PhDs, 3 Masters, 26 Hons students, 7 Interns and 4 Outreach Students (WA program).



**Colin Smith**  
(La Trobe University)

**Dr. Colin Smith's** primary research area is biomolecular archaeology, and in particular investigating the preservation of biomolecules (proteins and DNA) in archaeological skeletal tissue and how this affects the information they contain. He studied in the UK and has also conducted research at the Museo Nacional de Ciencias Naturales (Madrid), in Uppsala and Stockholm Universities, Durham University and the Max Planck Institute for Evolutionary Anthropology (Leipzig). Previous research highlights include the development of the concept and models of 'Thermal Age' degradation of ancient DNA (with Professor Matthew Collins) as well as concepts of bone diagenesis and protein degradation (collagen and osteocalcin) in archaeological bone. His most recent research has focused on the application of stable isotope analysis to ancient proteins with a particular interest in analyzing them at the amino acid level. He currently leads the LC-IRMS facility at La Trobe University, where he is an ARC Future Fellow working on *Molecular Archaeology: Carbon isotope analysis of amino acids as a means to investigate diets, physiology, metabolism and palaeoenvironment.*





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**Abstracts**

**Oral Presentations**

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**Session 1**  
**Ecology**  
**Chair – Paul Greenwood**



## PLENARY

### COMPOUND SPECIFIC STABLE ISOTOPES AS A TOOL FOR UNDERSTANDING MARINE BIOGEOCHEMICAL PROCESSES AND ECOLOGICAL INTERACTIONS

Andrew T. REVILL<sup>1\*</sup>

*1. CSIRO Marine and Atmospheric Research, Hobart, TAS Australia*

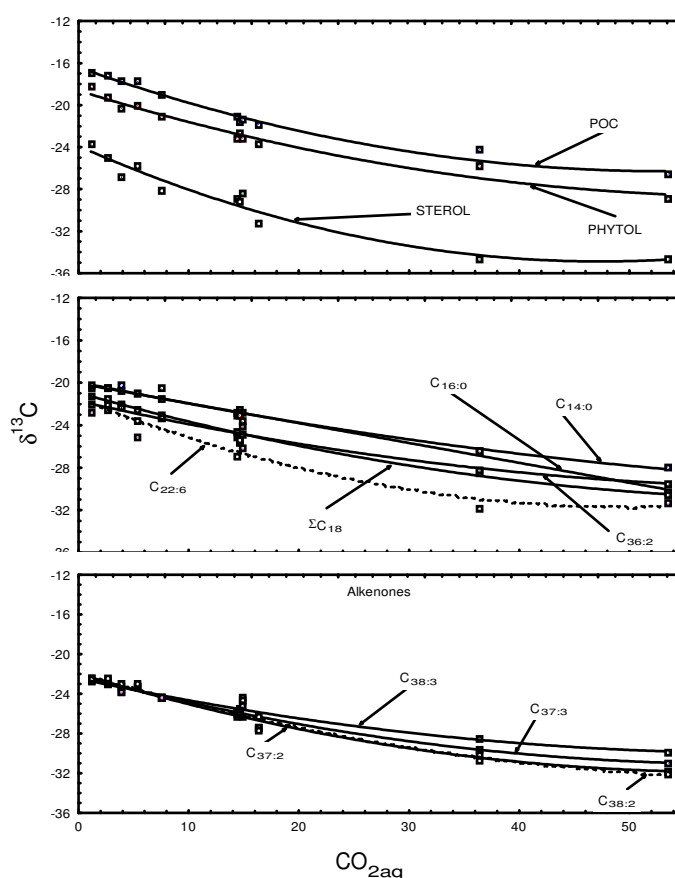
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Bulk stable isotopes have been used as a tool for investigating biogeochemical and ecological processes since the mid to late 1960s. In the late 1980s work by John Hayes and students at Indiana University developed the technique of compound specific stable isotopes. This opened up the possibility of combining the specificity of lipid markers with the discriminating power contained within stable isotopes but also spawned the realisation that we needed to better understand the processes controlling isotopic discrimination.

My own interest in this area started in the early 1990s during my post-doc work with John Volkman at CSIRO in Hobart when we were studying the Tasmanite oil shale and, working with Roger Summons at the then AGSO, used CSIA of alkanes and their apparently enriched  $\delta^{13}\text{C}$  values to elucidate the possibility that in this case, *Tasmanites* may have been a sea ice alga. However, our first real foray in to this area started in the late 1990s when we worked with Ulf Riebesell to investigate the effect of varying  $\text{CO}_2$  concentrations on the growth and isotopic fractionation in *Emiliana huxleyii*, including numerous lipid compounds (Fig.1). This showed that different compound classes were isotopically offset from the bulk signature, in proportion to the length of their biosynthetic pathways and while many varied in parallel to each other, some were obviously more metabolically active and did not vary quite so systematically.

This initiated a decade of interest in this area, and specifically how we could use this information to better elucidate biogeochemical and ecological pathways and in this talk I will use examples to show how we have progressed and tried to do this in a range of environments such as understanding algal ecology (Rowland et al., 2001), estuarine biogeochemistry (e.g. Cook et al., 2004; Oakes et al., 2005) and sources of eroded material to aquatic environments (Hancock and Revill 2013). Finally I will show how the latest advances have allowed us to measure stable nitrogen isotopes in individual amino acids and how we are using this to

investigate marine trophic ecology and the effects of climate change on marine biogeochemistry via long term archives in deep sea corals.



**Figure 1.** Variation of  $\delta^{13}\text{C}$  of POC and various lipids in *Emiliana huxleyi* grown under different  $\text{CO}_2$  concentrations. (From Riebesell et al., 2000)

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# ABIOTIC SULFURISATION OF A MODERN STROMATOLITE AND THE PRESERVATION OF EARLY-LIFE

Anais PAGES<sup>1\*</sup>, Kliti GRICE<sup>1</sup>, Ricardo JAHNERT<sup>2</sup>, Michael VACHER<sup>3</sup>, Roger E. SUMMONS<sup>4</sup>, Peter R. TEASDALE<sup>5</sup>, Dave T. WELSH<sup>5</sup>, Martin VAN KRANENDONK<sup>6</sup>, Paul GREENWOOD<sup>1, 7</sup>

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Stromatolites, fossil laminated sedimentary structures of biological origin, extend in the geological record to 3.5 Gyr and are recognised as the earliest trace of life on Earth (Walter et al., 1980; Hoffman, 2000; Allwood et al., 2006; Van Kranendonk et al., 2008) However, little is known about the early-life biogeochemical processes (Grotzinger and Knoll, 1999) and preservation pathways of these ancient stromatolites. Stromatolitic macrostructures, however, are recognised to present remarkable similarities with modern lithifying microbial mats (Grotzinger and Knoll, 1999). Consequently, modern microbial mats provide the opportunity to study complex and dynamic elemental cycles and preservation pathways of biosignatures. Modern highly laminated microbial mats have been reported in Shark Bay, Western Australia (Logan et al., 1970). Lipid analysis were performed on pustular and smooth mats from Hamelin Pool (Allen et al., 2010), however, preservation pathway of biolipids in modern stromatolites has never been investigated. Early diagenetic sulfurisation is a key process for the preservation of biolipids in the rock record (Sinninghe Damste and De Leeuw, 1990 and references therein). The formation of organic sulfur compounds (OSCs) requires the production of H<sub>2</sub>S by sulfate-reducing bacteria (SRB) and specific environmental conditions (Damste and de Leeuw, 1990). *In-situ* measurements were made of sulfide and iron(II) distributions (mm-resolution) across a modern layered smooth mat from Shark Bay. The two-dimensional distributions showed suitable conditions for the formation of OSCs, with an iron(II) concentration below 50 µM and a sulfide concentration up to 500 µM. For the first time, sulfur-bound aliphatic and aromatic compounds were discovered within a modern

stromatolite. Sulfur-bound and free carotenoids (e.g.: isorenieratane) from sulfur cycling organisms, *Chlorobi* and *Chromatiaceae*, were also identified. The discovery of C-S bound biomarkers implies strongly sulfidic and anoxic conditions in a contemporary microbial mat from Shark Bay. Through an increase of alkalinity, SRB also promote the precipitation of carbonates which favours mat lithification and formation of microbialites (Reid et al., 2000). The depleted  $\delta^{13}\text{C}$  of the bulk carbonate and the difference in  $^{13}\text{C}$  isotopic signature between free and carbonate-bound hydrocarbons corroborated biologically-induced carbonate precipitation.

The presence of reduced carotenoids from sulfur cycling organisms for the first time verified abiotic sulfurisation from  $\text{H}_2\text{S}$  provided by sulfate-reduction within a living stromatolite. In addition, SRB might have strongly contributed in mat lithification as demonstrated by  $^{13}\text{C}$  isotopic values. These results provide a compelling evidence for the initial preservation pathway for “living fossils” of early-life.

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# DIURNAL VARIATION IN $\delta^{18}\text{O}\text{-H}_2\text{O}$ , $\delta^{13}\text{C}\text{-DIC}$ , AND ECOSYSTEM METABOLISM IN SEMI-ARID STREAMS OF NORTHWEST AUSTRALIA

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Degassing of terrestrially-respired  $\text{CO}_2$  from streams and small rivers appears to be a significant component of watershed carbon budgets in small temperate streams. However, the significance of these processes in warm arid systems is largely unknown, particularly where surface water may be constrained to isolated pools in extensive drought periods. In this study, we examined diel patterns of  $\delta^{13}\text{C}\text{-DIC}$ ,  $\delta^{18}\text{O}\text{-H}_2\text{O}$ , and ecosystem metabolism in six pools of two dryland streams from the semi-arid Pilbara region of northwest Australia. We sought to understand the contribution of local hydrological variation to carbon cycling at the pool and catchment scales. All pools sampled were net heterotrophic, with GPP:R ratios ranging from 0.16-0.66. Across all pools,  $\delta^{13}\text{C}\text{-DIC}$  and DO concentrations increased during the day and decreased overnight. However, while DO maxima within pools were closely correlated with the time of maximum irradiance (from 12pm-2pm, depending on local shading patterns), pools were consistently most enriched in  $\delta^{13}\text{C}\text{-DIC}$  later in the afternoon (4pm). In addition, while diurnal variance in DO ranged widely over pools, from 0.7 to 7  $\text{mg L}^{-1}$ ,  $\delta^{13}\text{C}\text{-DIC}$  variance was consistently 0.7-0.9‰.  $\delta^{18}\text{O}\text{-H}_2\text{O}$  varied over the sampling period over a range of 0.4-0.5‰. Pools with suspected groundwater inputs had greater fluctuations over the time period, while those without showed a general trend of enrichment over time. None of the pools showed consistent diel cycles in  $\delta^{18}\text{O}\text{-H}_2\text{O}$ , and as such showed no correlation with  $\delta^{13}\text{C}\text{-DIC}$  or DO trends. These results suggest that photosynthesis and respiration are the most likely controls over DIC biogeochemistry in these pools, with little influence of short-term hydrological variation.



**Session 2**  
**Ecological Adaptation/Climate Change**  
**Chair – Pauline Grierson**



# KEYNOTE

## WEATHERING GEOCHRONOLOGY

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Geochronology applied to low-temperature chemical reactions in the weathering crust (weathering geochronology) provides information on changing environmental conditions through time (Vasconcelos, 1999). Proper weathering geochronology requires a combination of approaches traditionally applied in environmental and isotope geochemistry: detailed characterization of geochemical environments; high-resolution crystallography, crystal chemistry, and mineral physics of the phases to be dated; and high spatial resolution isotopic analysis. Weathering geochronology brings deep-time into environmental isotope studies. It contributes to determining what processes control the precipitation and dissolution of minerals in the surficial environment, when these processes were most active, and how and how fast these processes advanced. Knowing what, when, and how is necessary to determine the causal relationships controlling environmental processes shaping the Earth's surface.

Three geochronological tools have been refined for dating weathering processes: K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  (Vasconcelos, 1999), (U-Th)/He (coupled with  $^4\text{He}/^3\text{He}$ ) (Shuster et al., 2005; Vasconcelos et al., 2013), and U-series geochronology (Bernal et al., 2006). In addition, cosmogenic isotopic measurements on some of the phases suitable for weathering geochronology permits coupling the determination of weathering and exposure ages, further increasing our quantitative constraints on surficial processes (Shuster et al., 2012).

Some of these absolute dating techniques share some common features, such as high spatial resolution and the ability to identify and obviate the contribution of primary mineral contaminants (Vasconcelos, 1999; Vasconcelos et al., 2013). When applied in tandem, they can determine ages ranging from a few thousand years to the age of the solar system, enabling the study of environmental reactions for the entire history of the Earth and other terrestrial planets.

K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  requires the presence of K-bearing supergene minerals, and the most useful phases for weathering geochronology are hollandite-group Mn oxides  $[(\text{K},\text{Ba})_{1-2}(\text{Mn}^{3+},\text{Mn}^{4+})_{16}\cdot x\text{H}_2\text{O}]$  and alunite-group sulfates (alunite  $[\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6]$  and jarosite  $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ ). Supergene goethite and hematite are the most suitable phases for (U-

Th)/He geochronology because they are relatively common in weathering profiles and are He-retentive under most surficial conditions (Shuster et al., 2005). Hollandites, goethite, and hematite are also suitable for U-series dating, which provides information on chemical reactions modifying these minerals in the more recent past ( $< \sim 600$  ka), complementing data obtained by the other two methods.

The application of these geochronological approaches to Australian environments reveals a protracted and complex history of weathering and erosion. The oldest weathering profiles continuously exposed at the Earth's surface date as far back as the end of the Cretaceous, and these profiles show several periods of supergene mineral dissolution-reprecipitation. The downward propagation of weathering fronts through time is consistent with a history of progressive lowering of the groundwater table during aridification of the continent. The longevity of the weathering profiles also suggests very low erosion rates for Australia, consistent with rates measured by cosmogenic isotope analysis of coexisting phases.

Where more complete weathering records are preserved, particularly in the more recent past, a remarkable correlation exists between weathering reactions on the continent and warming episodes recorded in the oxygen isotope record of ocean floor sediments (Feng and Vasconcelos, 2007). This correlation suggests a strong climatic control on weathering profile evolution and links between the surficial evolution of continental landmasses and global climatic events.

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# UNRAVELLING THE CONTROLS ON CARBON ISOTOPES IN SPELEOTHEMS – A MULTIPROXY APPROACH

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Stable isotope records in speleothems are well established palaeoclimatic proxies, with oxygen isotopes in particular being used to create high resolution records of past climate. However, despite direct ecosystem links and climatic sensitivity, carbon isotopes have always been more problematic due to multiple controls on the signal. In particular, distinguishing between  $\delta^{13}\text{C}$  swings attributable to vegetation change, and those resulting from changes in soil conditions and microbial activity can be difficult.

Here we demonstrate how combining analysis of the  $\text{CO}_2$  derived signal in the calcite, with a novel analysis of the signal preserved in non-purgeable organic carbon (NPOC), can help better understand the dominant controls. In particular, we present a ground-breaking LC-IRMS analysis of the NPOC from a 2000 year old stalagmite from northwest Scotland, and compare it the calcite record and the  $\text{C}_{27}/\text{C}_{31}$  *n*-alkane biomarker record, previously linked in this sample to a landscape change from birch to peat dominated and an associated climatic decline. The results show clear correlations between the signals, with the NPOC and calcite  $\delta^{13}\text{C}$  responding in anti-phase. We suggest that this relationship results from increased soil saturation leading to reduced microbial activity, thus decreasing the relative amount of respired  $^{12}\text{C}$  in the  $\text{CO}_2$  pool (and so enriching the  $\delta^{13}\text{C}$  signal), and reducing the  $^{13}\text{C}$  enrichment of the residual organic matter. This relationship between the two signals may therefore have the potential to distinguish between substantial  $\delta^{13}\text{C}$  swings triggered by vegetation change (expected to vary in the same direction in both carbon pools), and those caused by climatic changes in soil conditions (where an anti-phase relationship would be expected). This highlights the importance and benefit of applying both organic and inorganic geochemical techniques to understanding palaeoenvironmental carbon isotope records.

# HIGH-RESOLUTION HOLOCENE PALAEOCLIMATE USING OSTRACOD VALVE CHEMISTRY FROM BARKER SWAMP, SOUTHERN WESTERN AUSTRALIA

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Compared with south-eastern Australia (SEA), very few, well-dated records of Holocene palaeoenvironmental change have been published from south-western Western Australia (SWA). Here we report on a 5.8 m continuous sedimentary sequence collected from Barker Swamp, Rottnest Island spanning the last 7.4 ka. Rottnest Island is formed primarily of aeolian calcarenite, and Barker Swamp is situated in the north-western portion of the island in an interdunal depression. The swamp is fed predominantly by precipitation, but a localised, fresh groundwater lens overlying infiltrated sea water contributes to the hydrology.

Geochronological control on the palaeoenvironmental record is constrained by 8 <sup>14</sup>C Accelerated Mass Spectrometry (AMS) dates performed on both ostracod valves (n=7) and plant fibres (n=1), and 15 quartz Optically Stimulated Luminescence (OSL) dates. Combined, these two dating techniques provide the highest resolution chronology of any Holocene sequence from SWA. However, a significant 2.2 ka offset in <sup>14</sup>C AMS dates of the carbonate material compared to the younger <sup>14</sup>C AMS dates obtained from plant fibres and the quartz OSL dates suggests a significant reservoir effect contributed by dissolving older carbonate from the surrounding calcarenite.

The coupled stable isotope ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ ) and trace metal (Mg/Ca and Sr/Ca) record analysed from ostracod valves recovered from the sedimentary sequence, and a salinity-based transfer function using the Modern Analogue Technique (MAT) plotted to the ostracods preserved in the Barker Swamp record, provide an unprecedented, high-resolution reconstruction of the aquatic conditions of Barker Swamp through time. The stable isotope data from the ostracod valves and the Mg/Ca<sub>water</sub> reconstructed from the ostracod valves record synchronous changes between from 7.4 to 1.4 ka reflecting changes in precipitation and evaporation (E/P) upon the swamp. The Barker Swamp record shows periods of higher

water levels in the swamp from 6.7 to 6.3, 5.6 to 4.5 and 2.3 to 1.4 ka indicative of decreased E/P. Low swamp levels, implying dry phases (increased E/P), occur between 7.4 to 6.7, 6.3 to 5.6, 4.2 to 2.3 and 1.4 ka to present. The latter part of the record (4.2 ka to present) records the development of the fresh groundwater lens that expands and contracts during wet and dry phases.

# APPLICATION OF STABLE ISOTOPES FROM AUSTRALIAN CHIRONOMID (NON-BITING MIDGE) HEAD CAPSULES AS PROXIES FOR PAST CLIMATE CHANGE

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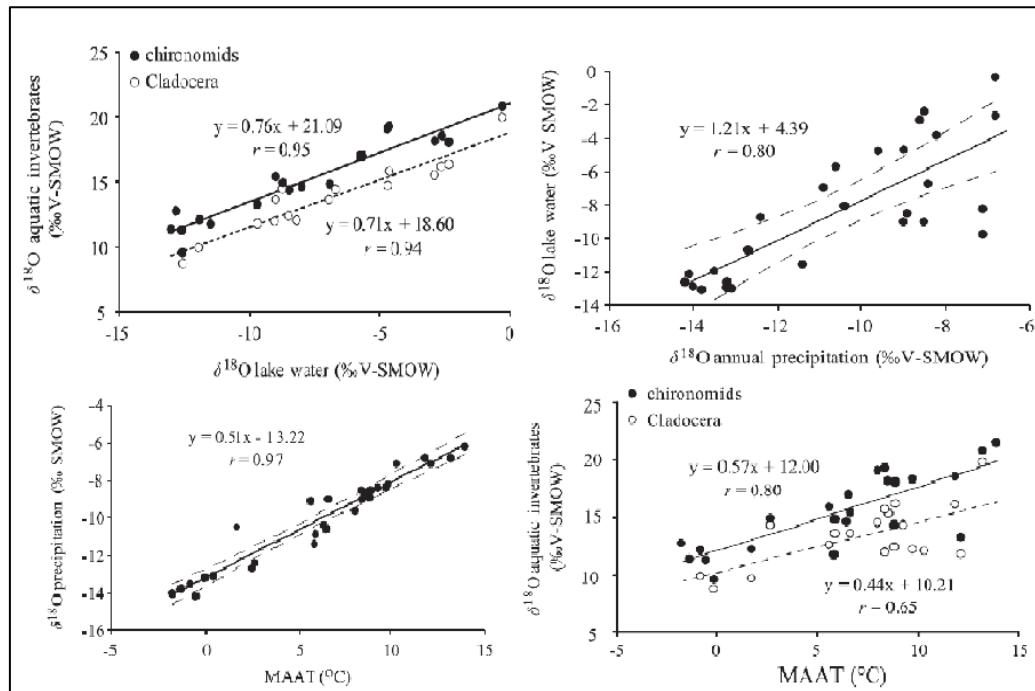
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Development of proxies that have the potential to provide long-term and reliable palaeoclimate records is a key to better reconstructing and understanding the past climate system. Ideally these proxies should be widely distributed and common in the environment. Chironomids (non-biting midges) occur in virtually all permanent and semi-permanent terrestrial water bodies. Growth of chironomids is strongly controlled by water temperature. Chironomids have a chitinous head capsule and studies (Wooller et al., 2004; Verbruggen et al., 2011) have shown that the fossilised chitinous heads of non-biting midge larvae act as a ‘time capsule’ that preserves the  $\delta^{18}\text{O}$  of the lake water in which they live. Wooller et al (2004) demonstrate a positive correlation between the mean annual air temperature above a lake and  $\delta^{18}\text{O}$  of the chironomids in the lake (Figure 1). Therefore, chironomids may be used as a proxy for modern and paleo-water temperature.

Fractionation due to temperature is one of the most important controls on lake water  $\delta^{18}\text{O}$  in southern Australia. Therefore,  $\delta^{18}\text{O}$  from fossilised chironomid heads will be used as a relatively new method for reconstructing past changes in temperature in Australia. The modern range of chironomid  $\delta^{18}\text{O}$  values will be developed based on 32 lake surface sediment sampled from South-eastern Australia (10 lakes from New South Wales, 15 from Victoria and 7 from Tasmania during the summers of 2012 and 2013). For these lakes, head capsules of single taxa will be picked to avoid complications from ‘vital effects’. These data will serve to establish the relationship of  $\delta^{18}\text{O}$  to modern lake temperatures.

To cross-check the validity of the  $\delta^{18}\text{O}$  relationship we are also developing a transfer function for the chironomids from these lakes. Transfer functions are standard techniques in paleolimnology and several exist for chironomids in the Australasian region (Woodward and Shulmeister, 2006; Rees et al., 2008). They are generally regarded as accurate to within 1°C and the results from the transfer function can cross-validate the stable isotope results and highlight where, if anywhere, the stable isotope signal is dominated by non-temperature fractionation effects.

Once verified, the stable isotope technique will be applied to chironomid head capsules extracted from lake sediment deposits in southern Australia that span the Last Glacial Maximum (LGM). The application of the stable isotope from chironomids will be the first use in the Southern Hemisphere. The combination of both a transfer function and stable oxygen isotope methods on chironomids to reconstruct past temperature from the same sites will be the first attempt worldwide. In this talk, I will focus on the chironomid stable isotope to air temperature relationship.



**Figure 1.** There is a well-known relationship between Mean Annual Air Temperature and  $\delta^{18}\text{O}$  of Precipitation, the  $\delta^{18}\text{O}$  of Precipitation and  $\delta^{18}\text{O}$  of Lake Waters are assumed to be directly related. Recent work (e.g. Wooler et al., 2004) has demonstrated a direct relationship between the  $\delta^{18}\text{O}$  of Lake Water and  $\delta^{18}\text{O}$  of Chironomid head capsules. Consequently the  $\delta^{18}\text{O}$  of Chironomid head capsules can be used to indirectly infer Mean Annual Air Temperature (Verbruggen et al., 2011, relationship derived based on 24 European lakes)

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**Session 3**  
**Radio Isotopes**  
**Chair – Fred Jourdan**





# PLENARY

## RADIOCARBON APPLICATIONS IN EARTH AND ENVIRONMENTAL SCIENCES

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Radiocarbon or  $^{14}\text{C}$  is one of the most important cosmogenic radionuclides for building reliable chronologies for various materials and archives for the study of environmental and climatic changes for the past 50 ka. Radiocarbon is also used as a powerful tracer of the carbon cycle and climatic systems. After a short discussion on recent advances in accelerator mass spectrometry (AMS)  $^{14}\text{C}$  analysis, this paper highlights several applications of radiocarbon in earth and environmental sciences that have been carried out at ANSTO.

The last 10 years saw a large shift in AMS instrumentation with more than 20 compact low energy AMS systems being installed worldwide (Synal and Walker, 2010). The terminal voltage of 3 MV used in the 1990s AMS systems for radiocarbon analysis was considerably reduced to 200-500 kV for these low energy systems without significant influence on the quality of  $^{14}\text{C}$  analysis. The size and cost of AMS systems were also reduced. In parallel, there were significant improvements in AMS radiocarbon target preparation with high efficiencies for the conversion of samples to graphite being achieved for microgram-sized samples. Samples containing as little as 10-20  $\mu\text{g}$  of carbon can now be reliably prepared and analysed by AMS (Hua et al., 2004; Smith et al., 2010). This has opened up opportunities for radiocarbon analysis of new materials such as single grains of specific skeletal components of carbonate sediments (eg, single foraminifera) and gas species ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ ) trapped in ice cores.

The radiocarbon method provides one of the most reliable and well-established means of dating the Holocene and Late Pleistocene (Hua, 2009). As the  $^{14}\text{C}$  concentration of the atmosphere has not been constant in the past, radiocarbon and calendar ages are not identical. The radiocarbon ages have therefore to be converted to the calendar ages using a calibration curve, which describes the atmospheric  $^{14}\text{C}$  concentration in the past measured in precisely and independently dated materials. New data sets of radiocarbon calibration, including IntCal13 (Reimer et al., in press) and SHCal13 (Hogg et al., in press) for the

Northern and Southern Hemisphere, respectively, will be available in June-July 2013. Updated calibration data for the last 60 years (the bomb period; Hua et al., in press) will also be available soon. A number of dating applications of radiocarbon will be discussed in this paper including: (a) reliable chronological reconstruction of reef island development using specific skeletal components of carbonate sediments, (b) investigation of occupation and demise at the medieval city of Angkor, Cambodia, (c) dating of recent Antarctic mosses to investigate biological effects of climate change, (d) chronological reconstruction for young speleothems, which could not reliably be dated by the standard Th/U method, etc.

Study of  $^{14}\text{C}$  in recent corals is valuable, not only to trace the evolution of the radiocarbon bomb spike after 1950 due to atmospheric nuclear detonations, but also to improve our knowledge in ocean circulation (Hua et al., 2005). Investigation of spatial and temporal variations in surface ocean  $^{14}\text{C}$  in the past using paired measurements of U/Th and  $^{14}\text{C}$  on corals also delivers crucial information about past climate variability and ocean circulation changes (Yu et al., 2010). Hua et al. (2009) reconstructed a floating chronology of Tasmanian Huon pine which filled in the gap of the absolute tree-ring chronologies in the Northern Hemisphere during the early Younger Dryas. By comparing the tree-ring  $\Delta^{14}\text{C}$  to marine  $\delta^{14}\text{C}$  and modelled  $\delta^{14}\text{C}$  based on ice-core  $^{10}\text{Be}$  fluxes, the authors concluded that changes in ocean circulation were mainly responsible for the onset of the Younger Dryas.

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# ARE SOIL CARBON DECAY CONSTANTS TRULY CONSTANT? INSIGHTS FROM TIME SERIES $^{14}\text{C}$ MEASUREMENTS

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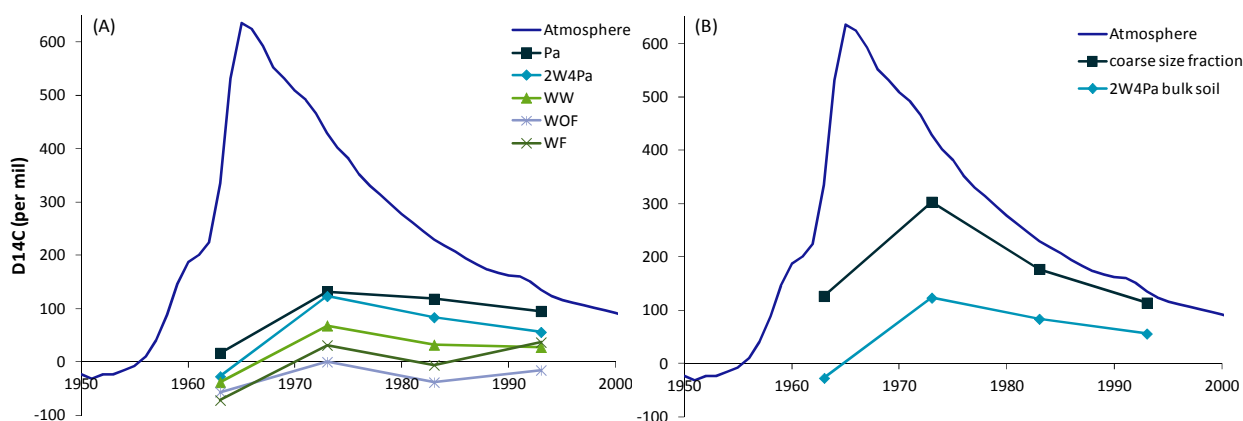
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Soil organic carbon can act as a large positive or negative feedback on the global carbon cycle. Our ability to predict these changes into the future rely completely on the quality of our models. Conceptual and numerical models of soil organic carbon currently hypothesize that the inherent decay rates of different carbon pools are invariant (e.g. Jenkinson 1990; Parton *et al.* 1987), particularly so to changes in agricultural practices. Here we have traced the spike in radiocarbon content due to atmospheric nuclear weapons testing through archived soils from the Permanent Rotation Trial at the Waite Agricultural Research Institute, South Australia, spanning the years 1963-1993 to provide a direct test of this critical hypothesis.

The Permanent Rotation Trial was established on a red Chromosol in 1925 with upgrades made to several treatments in 1948. Decadal soil samples were collected starting in 1963 at two depths, 0-10 and 10-22.5 cm, by compositing 20 soil cores taken along the length of each plot. We have chosen to analyze five trials representing a gradient in productivity: permanent pasture (Pa), wheat-pasture rotation (2W4Pa), continuous wheat (WW), wheat-oats-fallow rotation (WOF) and wheat-fallow (WF). Soil organic carbon concentrations in 1993 follow in this same order of productivity, decreasing from 2.46% in the Pa plot to 1.04% in the WF rotation (Grace *et al.* 1995). For each of the soil samples (40 in total), the radiocarbon activity in the bulk soil as well as size-fractionated samples was measured by accelerator mass spectrometry at ANU's Radiocarbon Dating Laboratory (Fallon *et al.* 2010).

Results indicate that uptake of the bomb-spike in atmospheric  $^{14}\text{C}$  into the soil was greatest in the trials with the greatest productivity (Fig. 1A). The coarse size fraction always had greater  $\delta^{14}\text{C}$  values than the bulks soil samples (Fig. 1B). In order to interpret these results in terms of soil organic carbon turnover rates, several different steady state and non-steady state models (i.e. Baisden *et al.* 2013) were used.



**Figure 1.** (A) Trends in  $\delta^{14}\text{C}$  for 0-10 cm bulk soil samples showing greater uptake of bomb-spike of  $^{14}\text{CO}_2$  with increasing productivity. (B)  $^{14}\text{C}$  was enriched in the coarse size fraction relative to the bulk sample. Atmospheric  $^{14}\text{CO}_2$  curve is given as reference.

Preliminary modelling results using only the bulk data suggest that the trials with pasture phases not only contain more carbon but, somewhat paradoxically, these soils also cycle carbon at a more rapid rate. If decay constants were prescribed in the modelling, then the fraction of carbon in the more actively cycling pools increased with increasing trial productivity/soil carbon stocks. If the allocation to each model pool was set based upon the carbon fractionation results, then the decay rate of the non-passive carbon pools increased with increasing trial productivity/soil carbon stocks. These initial findings, if substantiated, have significant ramifications for both soil carbon modelling and sustainable management of agricultural soils.

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# USING RADIOLABELLED $^{86}\text{Rb}$ ISOTOPE TO MEASURE METABOLISM

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The doubly-labelled water method (DLW) is widely used to measure field metabolic rate (FMR), but it has some limitations. Here, we validate an innovative technique for measuring FMR by comparing the turnover of isotopic rubidium ( $^{86}\text{Rb } k_b$ ) with DLW depletion and the rate of  $\text{CO}_2$  production ( $\dot{V}_{\text{co}_2}$ ) measured by flow-through respirometry for two dunnart species (Marsupialia: Dasyuridae), *Sminthopsis macroura* (17 g) and *S. ooldea* (10 g).

The rate of metabolism as assessed by  $\dot{V}_{\text{co}_2}$  (flow-through respirometry) and  $^{86}\text{Rb } k_b$  was significantly correlated for both species (*S. macroura*,  $r^2 = 0.81$ ,  $p = 1.19 \times 10^{-5}$ ; *S. ooldea*,  $r^2 = 0.63$ ,  $p = 3.84 \times 10^{-4}$ ), as was the correlation between  $\dot{V}_{\text{co}_2}$  from flow-through respirometry and DLW for *S. macroura* ( $r^2 = 0.43$ ,  $p = 0.039$ ) but not for *S. ooldea* ( $r^2 = 0.29$ ,  $p = 0.168$ ). There was no relationship between  $\dot{V}_{\text{co}_2}$  from DLW and  $^{86}\text{Rb } k_b$  for either species (*S. macroura*  $r^2 = 0.22$ ,  $p = 0.169$ ; *S. ooldea*  $r^2 = 0.21$ ,  $p = 0.253$ ). We conclude that  $^{86}\text{Rb } k_b$  provided useful estimates of metabolic rate for dunnarts.

Meta-analysis provided different linear relationships between  $\dot{V}_{\text{co}_2}$  and  $^{86}\text{Rb } k_b$  for endotherms and ectotherms, suggesting different proportionalities between metabolic rate and  $^{86}\text{Rb } k_b$  for different taxa. Understanding the mechanistic basis for this correlation might provide useful insights into the cause of these taxonomic differences in the proportionality. At present, it is essential that the relationship between metabolic rate and  $^{86}\text{Rb } k_b$  be validated for each taxon of interest.

The advantages of the  $^{86}\text{Rb}$  technique over DLW include lower equipment requirements and technical expertise, and the longer time span over which measurements can be made. The  $^{86}\text{Rb}$  method might be particularly useful for estimating FMR of groups for which the assumptions of the DLW technique are compromised (e.g. amphibians, diving species and fossorial species), and groups that are practically challenging for DLW studies (e.g. insects).

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# MULTI-ISOTOPE PERSPECTIVES ON OPEN-SYSTEM CALCITE DISSOLUTION AND IMPLICATIONS FOR C-14 DATING OF DEEPER GROUNDWATER

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Determining groundwater residence times is critical to our understanding of hydrogeological systems and to the sustainable management of groundwater resources. Because of its capacity to date groundwater that is up to 30,000 years old,  $^{14}\text{C}$  of dissolved inorganic carbon (DIC) is the most widely used radiogenic dating technique in regional aquifers. Closed-system dissolution of matrix calcite, methanogenesis, or mantle  $\text{CO}_2$  input adds  $^{14}\text{C}$ -free carbon that lowers the  $a^{14}\text{C}$  of DIC, potentially resulting in overestimation of groundwater ages. There are many studies that have used  $\delta^{13}\text{C}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios together with major ion geochemistry to correct  $^{14}\text{C}$  ages for these processes. Calcite dissolution, which is the most common of these processes, raises  $\delta^{13}\text{C}$  values and lowers  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios as  $a^{14}\text{C}$  decreases. However, open-system calcite dissolution during recharge is also potentially important. During open-system calcite dissolution in the unsaturated zone, DIC exchanges carbon with the relatively young reservoir of  $\text{CO}_2$  in the soil zone or regolith and hence maintains high  $a^{14}\text{C}$ .  $\delta^{13}\text{C}$  values of DIC increase because calcite dissolution raises pH, which increases the  $^{13}\text{C}$  fractionation between  $\text{CO}_2$  and DIC. Open-system calcite dissolution will also decrease  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in a similar manner to closed-system dissolution. While open-system calcite dissolution is tacitly recognised in many studies, there is commonly little attempt to assess its importance. This is probably due to  $^{14}\text{C}$  being commonly used to date deeper groundwater that is at some distance from its recharge area and hence removed from the site where open-system dissolution may have occurred. However, assigning all the changes in  $\delta^{13}\text{C}$  values and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios to closed-system calcite dissolution will overcorrect  $^{14}\text{C}$  ages.

This study uses  $^3\text{H}$  concentrations,  $^{14}\text{C}$  activities ( $a^{14}\text{C}$ ),  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, and  $\delta^{13}\text{C}$  values to constrain calcite dissolution in shallow groundwater from several catchments in southeast Australia. Taken in isolation, the  $\delta^{13}\text{C}$  values of DIC and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the groundwater imply that there has been significant calcite dissolution. However, the covariance of  $^3\text{H}$  concentrations and  $a^{14}\text{C}$  together with the calculated initial  $^{14}\text{C}$  activities imply that most of the groundwater cannot have dissolved more than 20% of  $^{14}\text{C}$ -free calcite

under closed-system conditions. Rather, calcite dissolution must have been partially an open-system process. Recognising that open-system calcite dissolution has occurred is important for dating deeper groundwater that is removed from its recharge area in southeast Australia and elsewhere.



**Session 4**  
**Radio Isotopes/Hydrology**  
**Chair – Ian Cartwright**



## **“AGE OF GROUNDWATER” – A MISLEADING AND UNNECESSARY TERM**

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Isotope hydrologists have determined “groundwater ages” for more than five decades. From this activity many publications evolved and more than a dozen tracers are in use today to assess processes in water on time scales of days to millions of years. In the early days of this scientific field there were discussions on the meaning of “dating” when applied to a system like water, which also led to the concepts of lumped parameter models. The discussion rose again recently, this time triggered by advances made using sophisticated computer models. These are now able to describe transport processes directly and attempt to model age itself.

Every human being has a very clear understanding of what age means: the time span elapsed since birth until the question. This understanding does not correspond to the answers isotope hydrology can give: the individual does not exist in water. This makes “age” a very misleading term causing severe misunderstandings between isotope hydrologists and their sample submitters and problem owners. A more detailed analysis demonstrates that “age” in itself is hardly ever a scientific target. Scientists studying fluid systems are interested in rates, fluxes and velocities, and all these quantities are related to time. But these quantities can be derived better with very easy conceptual models using the tracer concentrations and activities directly, without using the anthropocentric term “age”.

The talk demonstrates the contradictions of different age concepts with analytical examples and a new lumped parameter modelling code (“Lumpy”). A case study (Fischa, Austria) demonstrates what “success” in determining age actually means. In general, recharge rates can be derived from depth profiles of tracers, reaction rates can be derived from plots of contaminants versus tracers, velocities can be derived from tracer profiles along flow lines, dispersion can be derived from cross sections of tracer measurements, and flow rates can be derived from conceptual models. The term “age” may be useful during early discussion with project participants, but is not necessary for system understanding.

## **GROUNDWATER AGE AND TRANSIT TIME IN THE LAKE ROTORUA CATCHMENT, NEW ZEALAND**

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Lake Rotorua is a focus of culture and tourism in New Zealand. The lake's water quality has declined over the past 40 years, partly due to nutrient inputs that reach the lake via the groundwater system. Improved land use management within the catchment requires prediction of the spatial variations of groundwater transit time from land surface to the lake, and from this the prediction of current and future nutrient inflows to the lake. This study combines the two main methods currently available for determination of water age: numerical groundwater models and hydrological tracers. A steady-state catchment-scale finite element groundwater flow model is calibrated to match observed groundwater levels and stream base flows. The model is also calibrated to time-series measurements of tritium concentration in streams, springs and wells. Direct age simulations are then performed using the calibrated model. This allows determination of the distribution of water age and lifetime expectancy at each point in the model domain. Results show that travel time from the land surface through the aquifer system and into Lake Rotorua varies from a few years to more than 200 years, depending on location. Notable from a management perspective is that rainfall recharge to the aquifer system far from the lake can still reach the lake quickly where groundwater emerges into a river that then flows rapidly to the lake.

# ANALYSES OF SALINE WATER SAMPLES ON A CAVITY RING-DOWN SPECTROSCOPY INSTRUMENT

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The introduction of commercial instruments utilizing isotope ratio infrared spectroscopy for analysis of the stable hydrogen and oxygen isotope compositions in water has significantly reduced analytical costs. However, due to the principal physical limitation of this analytical method, these instruments are designed in particular for fresh waters and potentially an addition of other chemical compounds may compromise results. The influence of organic compounds was widely tested (e.g., West et al., 2010) and evaluation software developed. In contrast, the influence of water salinity and salt accumulation in vaporiser on the analytical uncertainty, are yet to be evaluated (Skrzypek and Ford, 2013), despite high demand for analyses of seawater and saline surface waters and groundwaters.

The stable isotope composition of saline water can be expressed on “concentration” or “activity” scale (e.g., Sofer and Gat 1972) depending on the method used and the purpose of study (e.g., Dutkiewicz et al., 2000). The values obtained on “activity scale” can be recalculated to the “concentration scale” based on concentration of particular salts (Horita, 1989) and analytical method (Lécuyer et al., 2009). In theory, the cavity ring down instruments (CDR) are providing results on “the concentration scale”, as the stable isotope composition is measured directly on obtained from sample water vapours. However, the evaporation process of water samples injected during analyses to vaporiser is occurring at low temperature (100 or 140°C), compared to distillation on traditional off-line vacuum systems (300 - 800°C). Therefore, potentially part of the water sample could be bound in the salt crystalline structure resulting in an isotope fractionation and consequently compromising results.

In this study, we aimed to confirm that the results obtained on CDR instruments are on “the concentration scale”. We assessed uncertainty rising from elevated salt concentrations (NaCl, KCl, MgCl<sub>2</sub> and CaCl<sub>2</sub>) analysed on a CDR instrument and the necessity of a correction. We prepared several saline solutions (TDS 0 to 339g/L) using water of known stable hydrogen and oxygen isotope composition. There was observed a very flat trend and  $\delta$ -values of water became more negative as salt concentrations increased. However, the range of observed change was ten-fold lower than expected for “activity” uncorrected results.

Furthermore, the variation in obtained uncorrected  $\delta$ -values (0.04‰ for  $\delta^{18}\text{O}$  and 0.4‰ for  $\delta^2\text{H}$ ) was much lower than analytical uncertainty reported by the manufacturer of the instrument (<0.10‰ for  $\delta^{18}\text{O}$  and <1.0‰ for  $\delta^2\text{H}$ ). CDR instruments can be successfully used for saline samples, in the range of studied concentrations, without a need of an additional correction if the vaporiser is frequently cleaned. The results are not compromised even if the total load of salt in the vaporiser reaches ~30 mg (equivalent of analyses of ~100 ocean water samples).

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# A NEW CONTINUUM REGRESSION MODEL AND ITS APPLICATION TO CLIMATE AND RAINFALL ISOTOPE RELATIONSHIPS

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Climate field reconstruction using networks of rainfall-isotope proxies is an example of a problem that requires the estimation of a model that aims to predict one field ( $Y$ ) using another field ( $X$ ). The general problem is to estimate a subspace of  $X$  that retains useful information for predicting  $Y$ . Methods to estimate such subspaces include principal components regression (PCR), partial least squares (PLS), redundancy analysis (RDA), and canonical correlation analysis (CCA), but these methods typically do not estimate the same subspace. One solution is to treat these different methods as end members of a continuous manifold of regression subspaces. By weighting the end member solutions in some way, we can search for the best regression subspace over the manifold.

In this study, a new continuum regression model is developed by extending an earlier method known as Principal Covariates Regression (PCovR). PCovR has two end members: PCR and RDA. Here, PCovR is extended by shrinking the covariance matrix of  $X$ . As a result, our new method regPCovR includes three end members (PCR, RDA and PLS) and is particularly suited to climate data, where the spatial dimension is larger than the temporal dimension, and where there are missing values in the response field ( $Y$ ). regPCovR includes both a weighting parameter and shrinkage parameter, which are estimated using cross-validation.

The benefits of regPCovR are illustrated using two examples. In the first example, the problem of predicting the southern Australian winter rainfall ( $P$ ) field from the regional winter sea level pressure (SLP) field is investigated. The best rank two regression subspace found by regPCovR explains over 50% of the variance in the rainfall field. This subspace thus estimates the relationship between SLP and  $P$  better than the end member subspaces. In the second example, PCovR is used to investigate the relationships between the winter SLP and  $P$  fields, and rainfall isotope ( $\delta^{18}\text{O}$ ) data from Australia and New Zealand. Two main patterns are identified, which explain about half the variance in the southern GNIP  $\delta^{18}\text{O}$  sites. Subspace projection is used to relate these patterns to various regional and Southern Hemisphere climate indices.

regPCovR will be useful for finding subspaces that better capture the relationships between climate and rainfall isotopes, which is a necessary step for quantitative palaeoclimatology.

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**Session 5**  
**Ocean/Aquatic Systems**  
**Chair – Andy Revill**



## PLENARY

### RESILIENCE OF CORAL CALCIFICATION TO OCEAN ACIDIFICATION: INSIGHTS FROM BORON ISOTOPES

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The process of bio-calcification is not only responsible for building the majestic coral reefs of the tropics, but is a key controller of the oceans carbonate chemistry and hence ultimately the CO<sub>2</sub> content of the biosphere upon which life depends. Understanding these processes is thus fundamental to quantifying the response of these key organisms to CO<sub>2</sub> driven global warming and ocean acidification. However, by its very nature, biologically controlled calcification occurs within a spatially restricted, physiologically controlled environment, whose connectivity to the external seawater environment is poorly known. Boron isotope systematics is an ideal tool to investigate these processes, as its speciation in seawater is strongly pH sensitive, and biocalcifiers specifically incorporate the isotopically distinctive borate species into their carbonate skeletons.

Using boron isotope systematics we show how biological up-regulation of the pH of the calcifying fluid, is a characteristic of both azooxanthellate and zooxanthellate bearing aragonitic corals. Scleractinian corals up-regulate pH at their site of calcification such that internal changes are approximately one-half of those in ambient seawater (Trotter et al., 2011). Although the absolute magnitude of the pH-buffering capacity is species-dependent, it nevertheless provides a mechanism to raise the saturation state of the calcifying medium, thereby increasing calcification rates at relatively little additional energy cost. This is especially evident in deep-sea scleractinian corals, where greater degrees of up-regulation of internal pH, has facilitated calcification at, or in some cases below, the aragonite saturation horizon. Models (McCulloch et al., 2012) combining biologically induced pH up-regulation with abiotic calcification, (IpHRAC) now make it possible to unravel the effects of increased temperature and reduced seawater saturation states upon calcification. Up-regulation of pH, is not however a ubiquitous among all calcifying organisms; those lacking this ability are likely to undergo severe declines in calcification as CO<sub>2</sub> levels increase. Quantifying the capacity of

calcifying organisms to up-regulate pH is thus central to understanding their resilience to CO<sub>2</sub> driven climate change and ocean acidification.

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# PALEOLIMNOLOGICAL INVESTIGATION OF THE USE OF STABLE ISOTOPES OF CARBON AND NITROGEN IN BULK SEDIMENT AND CLADOCERAN ZOOPLANKTON TO REVEAL ECOSYSTEM CHANGES IN KINGS BILLABONG, NORTHWEST VICTORIA, AUSTRALIA

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Northwest Victoria hosts a large number of shallow floodplain wetlands along the Murray River system. One of these, Kings Billabong, is known for its high conservation values. However, the naturally occurring flood pulses, which maintain ecological connectivity between river and wetlands, have been altered impacting the ecology of Kings Billabong. The human-induced river regulation in the Murray River following the arrival of Europeans, and increased farming activities around Mildura for irrigation, has switched Kings Billabong to a permanent water regime resulting in accelerated sedimentation rates and changed sources of carbon and, subsequently, altered ecological character. This study focuses on a 90 cm long sediment core taken from Kings Billabong in 2011, where the <sup>210</sup>Pb dating detected sediments at c. 60 cm depth to be c. 65 years old. Around this time (c. 1940-1945 AD), a systemic change occurred in the billabong. The enrichment of carbon substantially declined, while, in the meantime, nitrogen enrichment increased. Coincidentally, the subfossil cladoceran zooplankton assemblages revealed changes in the limnological conditions of the wetland ecosystem. Among the littoral species, the *Chydorus sphaericus* group, which prefers eutrophic water, became dominant. Since the early 2000s, the abundance of *Biapertura affinis*, a pioneer plant dwelling species, has declined. Before the assemblage of *B. affinis* began to decline, a large number of cladoceran ephippia were recorded in sediment samples indicating the elevated stress in the wetland. This study suggests that paleolimnological investigations, together with the use of stable isotopes of carbon and nitrogen in sediment samples, provides an opportunity to reveal the impacts of anthropogenic disturbances on the floodplain wetlands of the Murray River system across northwest Victoria, and potentially more widely across Australia.

## NINGALOO NIÑO FORCING OF THE LEEUWIN CURRENT (WEST AUSTRALIA) SINCE 1795

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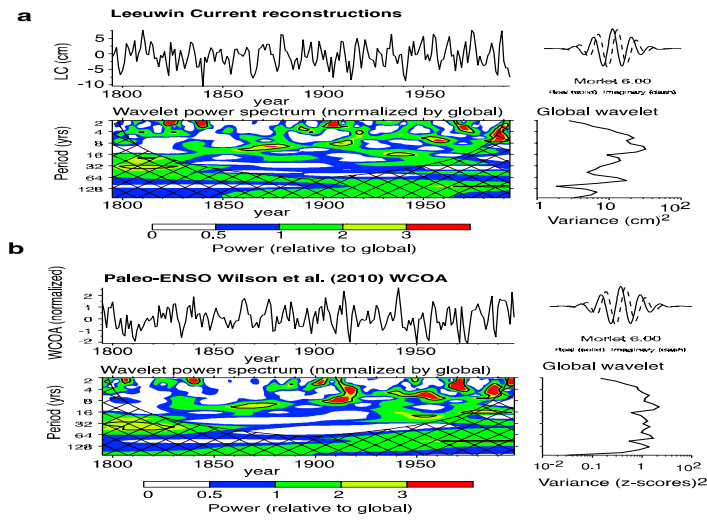
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The Leeuwin Current (LC), is a powerful poleward flowing eastern boundary current, offshore the western coastline of Australia in the south-eastern Indian Ocean (Feng et al., 2013). It transports heat from the Indonesia throughflow towards the southwestern tip of Australia shaping a unique marine environment with high biodiversity. Sea surface temperature (SST) within the LC offshore West Australia is recognized as a key region for Indo-Pacific climate teleconnections. Due to the lack of longer-term marine climate and environmental data from the south-eastern Indian Ocean the general response of southern Indian Ocean's to internal and remote climate forcing from the Pacific region is poorly understood.

Here, we use a linear combination of a well replicated coral proxy record ( $\delta^{18}\text{O}$ , Sr/Ca) of SST off western Australia in combination with a paleo-reconstruction of the El Niño-Southern Oscillation (ENSO) to hindcast the past variability of the LC. From this reconstruction we can conclude that interannual and decadal variations in LC strength are a natural component of the system over the past 215 years. These variations are clearly driven by past ENSO behaviour, with La Niña being associated with high sea-level anomalies and vice versa for El Niño events. We identify periods of major La Niña activity associated with a strong LC between 1800-1811 and after the 1860's and a quiescent period between 1820-1860. The late 20<sup>th</sup> century shows strong interannual variability with 1955 and 1999 being the strongest events on record. These extreme events are exacerbated by the strong increase in mean SST over the 20<sup>th</sup> century. Both, the 1955 and 1999 Ningaloo Niño events were aligned with an interdecadal peak in regional sea-level anomalies, emphasizing the importance of decadal-scale changes in driving LC variability and the amplitude of Ningaloo Niño's.



**Fig. 1:** The wavelet power spectrum of (a) Leeuwin Current (LC) sea-level anomaly hindcast for 1795 to 1993 and (b) paleo-ENSO index (WCOA) from Wilson et al. (2010) for the Nino3.4 index region in the central Pacific. The power has been scaled by the global wavelet spectrum (at right). The cross-hatched region is the cone of influence, where zero padding has reduced the variance. Black contour is the 10% significance level, using the global wavelet as the background spectrum. (c) The global wavelet power spectrum.

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## STABLE ISOTOPE ( $\delta^{13}\text{C}$ AND $\delta^{15}\text{N}$ ) STUDIES IN AQUATIC ECOSYSTEMS: RESPONSES TO DIFFERENT CONDITIONS

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Rivers and wetlands are complex ecosystems with numerous relationships between water, earth, air, plants and animals. The stable isotopes  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  were investigated in river and wetland ecosystems to evaluate food web structure complexity, with particular emphasis on their response to changing hydrological conditions. A study developed on the Shoalhaven River focused on assessing the differences in trophic conditions of fish populations found above and below Tallowa Dam. Some species displayed little variation in C or N signatures over the two years sampling period suggesting a preferential dietary niche, regardless of hydrological or density-dependent conditions. The variable diet sources between Australian bass revealed by source mixing calculation also indicated trophic discontinuity within these restricted environments.

We found variable trophic levels and sources for the same species of invertebrate and fish between habitats in wetlands show the effect of divergent ecological conditions and land-use practices. For example, in the Macquarie Marshes we found that an extended inter-flood interval caused the decline of riparian vegetation communities including river red gum signalling a shift from aquatic floodplain ecosystems to terrestrial ecosystems where grasses and chenopod shrubs dominate as an organic carbon source. Results provide insights into stable isotope use to better understand potential impacts of future climate variation on river and wetland systems.



**Session 6**  
**Trees, Litter and Soils**  
**Chair – Grzegorz Skrzypek**



## AUSTRALIAN DENDROCHRONOLOGY: NEW PERSPECTIVES FROM ISOTOPES OF TREE RINGS

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Proxy measures of climate from tree ring chronologies allow reconstruction of climate patterns back past the limit of instrumental records. Identifying new avenues for the development of accurate and climate-sensitive tree-ring chronologies is fundamental to understanding regional climate variability, particularly of rainfall. Understanding long-term changes in stomatal functioning also underpins assessment of the resilience of trees to changes in rainfall patterns and/or warmer temperatures. Although tree-ring-width chronologies have been widely used for temperature reconstructions, there are many sites around the world, including much of Australia, at which there is little evidence of a clear climate signal in the ring-width. Chronologies based instead on stable isotopes, particularly  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , may be more sensitive to climate patterns but interpretation is also predicated on knowledge of tree physiological responses. We use isotopic records developed from both leaves and wood to provide an integrated analysis of changes in growth and water use efficiency (WUE) of *Callitris*, a widespread native conifer. Relationships between rainfall, relative humidity and temperature with  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  of *Callitris columellaris* tree rings demonstrate that the Pilbara region of northwest Australia has become more humid and cooler since 1975 relative to the previous century. In contrast, a rainfall reconstruction for southwest Australia based on ring-widths of *C. columellaris* shows significant multi-decadal variability in rainfall over the last ~350 years, and reveals that the region has experienced extended periods of drought of many decades in the recent past. The *Callitris* chronology has now been coupled with a long-term historical North China rainfall proxy that has extended the rainfall reconstruction for SW of WA to around 700 years AD. The reconstruction shows that the southwest has been wetter over the last ~200 years than any other period in the last millennium. We are now developing new chronologies to assess cyclone frequencies and climate teleconnections with northern China and Antarctica.

# THE APPLICATION OF CARBON AND NITROGEN STABLE ISOTOPE ANALYSIS TO PLANT MACRO REMAINS IN ARCHAEOLOGICAL CONTEXTS

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Stable isotope techniques have been used in archaeological studies since late 20<sup>th</sup> century. However, the archaeological materials used for stable isotope analysis mostly originate from bones or soil layers. This study aims to understand if the Hittite Empire collapse was caused by agricultural stress due to climate changes. In doing so, direct evidence from anthropogenic remains such as: charred grains, seeds and wood charcoal have been used. The Hittite Empire is an important Bronze Age power in Central Anatolia region, modern Turkey. After c. 450 years of central power in Anatolia during Late Bronze Age period (c. 1200 BC) it came to an end (Bryce, 2002). Many neighbouring civilisations, in Mycenae (modern Greece), Levant and Mesopotamia region also declined in power or collapsed during the same period.

Many authorities state the reason behind the Late Bronze Age collapse as being climate change resulting in agricultural failure (Carpenter, 1966; Gorny, 1989). However, to date, there have been no studies that actually provide scientific evidence on climate change resulting in the agricultural failure of the Hittite state. This study aims to understand climate change and how climate change affected agricultural production. In order to do so, Nitrogen and Carbon stable isotope analyses have applied to plant macro remains from an archaeological site Kaman-Kalehoyuk, Turkey. Kaman-Kalehoyuk is a multi-occupation archaeological site starting from Early Bronze Age (3000 c. BC) and extending to the Ottoman period (c. 1500 AD) (Hongo, 1996). Continuous occupation of the site allows understanding of climate change and how agricultural stress contributes to management practices.

Application of Nitrogen stable isotopes analysis to plant macro remains is newly introduced to archaeobotany field in order to understand manuring practices in ancient agricultural societies (Bogaard *et al.* 2007). Carbon isotope analysis is applied to both wood charcoal and grains in order to understand water availability during the growth period of these plant materials (Farquhar *et al.* 1982). Carbon stable isotope analysis has also been used in order to understand ancient irrigation practices, if there are any. Nitrogen stable isotope analysis coupled with Carbon stable isotope analysis provides parallel data on how

agricultural management practices changed and how fluctuation in climate affected agricultural stress and yield diachronically.

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# INCREASED LOSS OF SOIL-DERIVED CARBON IN RESPONSE TO LITTER ADDITION AND TEMPERATURE

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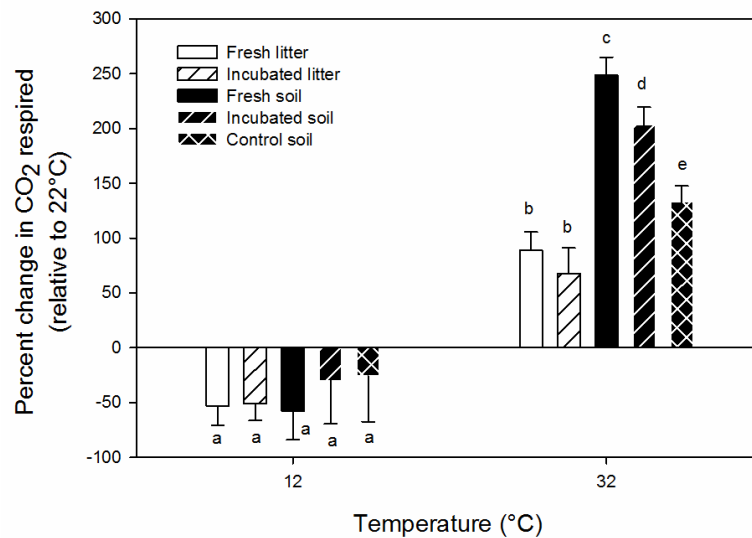
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Without substrate limitation, temperature sensitivity of soil organic matter (SOM) should depend inversely upon its quality, so lower quality material should degrade more slowly (Fierer et al., 2005; Davidson and Janssens, 2006). However, many contrasting results have been reported, in part due to our lack of understanding of the interacting influences of temperature sensitivity on substrate availability and microbial utilization of SOM (von Lützow and Kögel-Knabner, 2009; Allison et al., 2010; Conant et al., 2011).

The objective of this experiment was to determine how allocation of litter and soil-derived carbon (C) to various C pools is altered by temperature and substrate quality. Substrate quality will be represented as the difference between litter-derived (fresh and pre-incubated eucalyptus litter) and soil-derived organic matter. The <sup>13</sup>C and <sup>15</sup>N labelled litters were added to an Australian woodland soil and the soil/litter mixtures were incubated for 14 days at 22°C. The temperature of the soil/litter mixtures was then decreased to 12°C, increased to 32°C, or maintained at 22°C for another 14 days. The quantity and isotopic composition of microbial phospholipids and dissolved organic C was measured, along with the quantity of dissolved inorganic and organic nitrogen, at four destructive time points. The quantity and isotopic composition of respired CO<sub>2</sub> was measured throughout the incubation.

The mineralization of litter-derived and soil-derived C varied significantly in response to litter quality and temperature. Although the temperature sensitivities of the two litters were similar, soil-C was more temperature sensitive than litter-C (Fig 1). The temperature sensitivity of soil-C also increased with litter quality (control [no litter] < incubated litter < fresh litter) suggesting that decomposition of litter altered the availability or degradation of SOM. Microbial biomass was significantly higher in the litter treatments relative to the control across all sampling days, and enhanced production of extracellular enzymes by this larger microbial pool may partially explain the greater sensitivity of soil-derived C in the litter treatments relative to the control. Interestingly, we also observed negative priming of soil-C in the fresh litter treatment, and positive priming of soil-C in the incubated treatment relative to the control. This priming was responsive to temperature, where higher incubation temperatures resulted in greater release of soil-C relative to the control (at the same

temperature). The priming of soil-C was mirrored by trends in total dissolved N, which was highest in the incubated litter treatment and increased with temperature, suggesting that enhanced decomposition of SOM may result in greater N cycling, production, or destabilization from OM. These results help provide a more complete picture of the dynamic response of the microbial community to altered temperature and litter quality, information necessary to predict changes in soil C dynamics in response to climate change.



**Figure 1:** Percentage change in CO<sub>2</sub> respired at 12°C and 32°C relative to 22°C. Standard error is shown. Letters indicate significant differences ( $P \leq 0.05$ ) between temperature, C sources, and litter treatments.

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# USE OF STABLE CARBON ISOTOPE FOR INVESTIGATING INORGANIC CARBON DYNAMICS IN A LIMED ACIDIC SOIL

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Liming represents a common management practice for crop production on acidic soils. Agricultural lime ( $\text{CaCO}_3$  and  $(\text{CaMg}(\text{CO}_3)_2)$ ) either as lime sand or crushed limestone is usually applied to overcome soil acidity. In Australia, the use of agricultural lime has increased and approximately 2.5 Mt is applied annually to agricultural fields (Page et al., 2009). An increased mineralisation of soil organic carbon (SOC) after liming may particularly occur in acid soils because of an increase in microbial activity induced by the increase in pH with liming (Ahmad et al., 2013; Dumale Jr. et al., 2011). Carbonate dissolution (inorganic carbon, IC) from limed soils could also increase  $\text{CO}_2$  emission into the atmosphere (Ahmad et al., 2013; Bertrand et al., 2007; Biasi et al., 2008) and, there is a potential risk of overestimating the heterotrophic microbial activity in limed acidic soils by measuring the total  $\text{CO}_2$ -C fluxes without separating the IC and organic carbon (OC) derived fluxes (Biasi et al., 2008; Tamir et al., 2011). Further, liming may interact on the temperature sensitivity of  $\text{CO}_2$  produced by IC and OC in the soil.

We investigated the dynamics of IC and OC derived  $\text{CO}_2$  fluxes by analysing total and  $^{13}\text{C}$ - $\text{CO}_2$  emission under laboratory conditions using an acidic Red Kandosol. The soil contained 1.4 % OC, 72 % sand, 8% silt and 20 % clay. Analytical grade lime was thoroughly mixed into the soil at a rate ( $<1$  % w/w) to raise the pH above 6.0. The soil with and without lime addition were incubated at 20 and 40 °C for a period of 96 days. Alkali (NaOH) traps were used to capture  $\text{CO}_2$  emanating from IC and OC. Sub-samples from these traps were precipitated as  $\text{SrCO}_3$  and the  $\delta^{13}\text{C}$  analysis was performed using an isotope ratio mass spectrometer. The proportion of IC released from the lime amended soil (S + L) was successfully quantified using distinct  $\delta^{13}\text{C}$  values of lime ( $\delta^{13}\text{C}$  of  $-8.67\text{‰}$ ) and soil ( $-25.2\text{‰}$ ). Total IC derived  $\text{CO}_2$  constituted approximately 32% and 17% of the total C fluxes at 20° C and 40° C, respectively. During the 96-day incubation period, between 64% and 100% of the applied IC was released as  $\text{CO}_2$  from S + L at both incubation temperatures. Furthermore, an increase of 59% IC, 284 % soil derived C and 170% total C was found when



the incubation temperature was increased from 20 °C to 40 °C. However, the addition of lime decreased the temperature sensitivity of soil derived C compared to the non-amended soil. We conclude that the stable isotopes of C could yield very promising results for studying the dynamics of IC at higher rates of lime application.

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# USING SULFUR ISOTOPE SIGNATURES TO UNRAVEL THE GEOCHEMISTRY OF ACID SULFATE SOIL REMEDIATION USING SEAWATER

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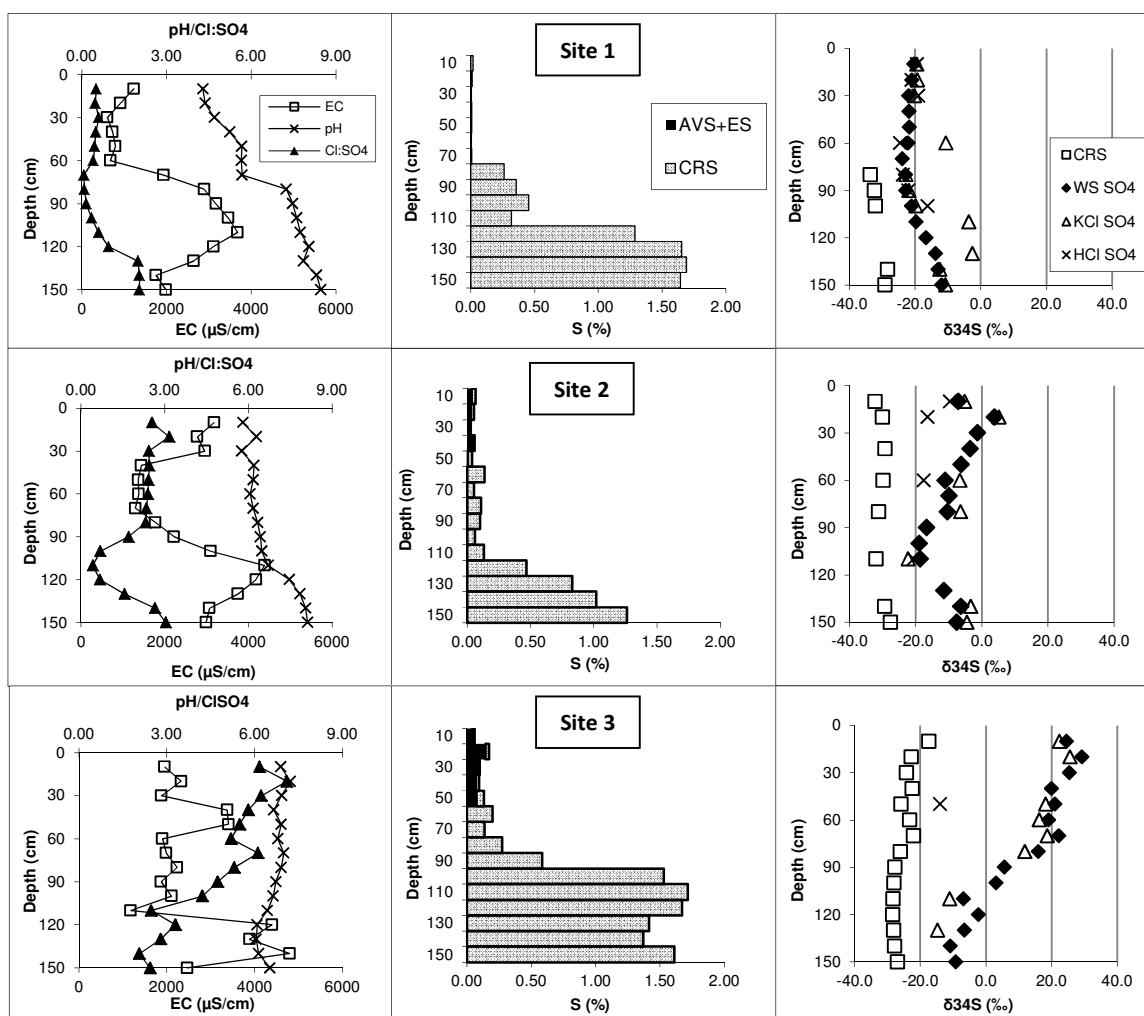
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The CRC CARE National Acid Sulfate Soil Demonstration Site is located at East Trinity, near Cairns in far north Queensland. In 2002 a remediation strategy that involved the use of lime assisted exchange of tidal waters was implemented to ameliorate the severe acidity caused by acid sulfate soils (ASS) (Powell and Martens 2005). This study aimed to use stable sulfur isotopes to examine the geochemistry during remediation.

Stable isotope signatures in the sulfide and SO<sub>4</sub> fractions were examined at three sites with different surface elevations. The sulfide fraction was represented using the chromium reducible sulfur method and included monosulfides, elemental sulfur and disulfide species. The SO<sub>4</sub> fractions included water soluble (WS), exchangeable (KCl) and acid soluble (HCl) SO<sub>4</sub>.

Results from the isotope studies and other geochemical studies are presented in Fig 1. Site 1 is at the highest elevation and did not receive tidal water exchange. Site 2 received intermittent tidal water and Site 3 was permanently inundated. Site 1 represents a typical acid sulfate soil in an unremediated state where oxidation of pyritic material in the upper surface layers has caused low pH and Cl:SO<sub>4</sub> ratios. Following remediation, Site 3 has higher pH and Cl:SO<sub>4</sub> ratios and contemporary sulfides have reformed at the surface. Site 2 is intermittent between Sites 1 and 3.

The WS and KCl SO<sub>4</sub> isotope signatures at Site 1 are negative throughout the profile and likely reflect SO<sub>4</sub> derived from the oxidation of isotopically negative sulfide (mainly pyrite). At Site 3 WS and KCl SO<sub>4</sub> isotope signatures reflect the reintroduction of tidal water and are similar to the isotope signature of seawater SO<sub>4</sub> (~+20‰). Site 2 represents a combination of both SO<sub>4</sub> sources: the oxidation of pyrite and SO<sub>4</sub> in seawater. The HCl SO<sub>4</sub> fraction is derived mainly from jarosite. The δ<sup>34</sup>S of this fraction is similar at all sites, regardless of remediation, suggesting this SO<sub>4</sub> fraction has considerable remnance.



**Figure 1.** EC, pH and Cl:SO<sub>4</sub> ratio (left), acid volatile sulfur (AVS) + elemental sulfur (ES), chromium reducible sulfur (CRS) (centre) and δ<sup>34</sup>S in the CRS, water soluble (WS), exchangeable (KCl) and acid soluble (HCl) SO<sub>4</sub> fractions (right) at Sites 1, 2 & 3.

Contemporary sulfide accumulation at Site 3 also reflect the varied soluble sulfate sources with δ<sup>34</sup>S signatures in the surficial sulfide accumulations being heavier than those of the relic sulfides at depth. The reformed sulfide had isotope signatures that indicated sulfate reduction from two sulfate sources: sulfate derived from the oxidation of relic pyrite as well as the heavier sulfate in the remediating tidal waters.

This study has shown that stable sulfur isotopes in various soil fractions can be used to help unravel the geochemistry of ASS undergoing hydrological changes be they the result of management practices such as remediation or by rising sea levels.

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**Session 7**  
**Mass Extinctions/Palaeoclimates**  
**Chair – John Volkman**



## PLENARY

### CONSISTENT CHANGES IN BIOMARKERS (MICROBES AND FLORA) AND STABLE ISOTOPES ACROSS SEVERAL MAJOR EXTINCTION EVENTS OF OUR PLANET

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The interaction of biological and geological processes has created the Earth and driven the evolution of its biodiversity from early life. Organisms have continually adapted to changing environments, the evolution of individual species has consequently impacted the chemical and physical properties of Earth. Life's signatures that reveal the evolution of biological forms and their geological consequences are not only restricted to visible remnants (e.g. fossils), but also can encompass biomarkers, isotopic signals and mineral associated fabrics. The changes in isotopic signals appear to be consistently similar for several major geological events of our planet. The 'mother' of all mass extinction events at the close of the Permian near to the Permian/Triassic Boundary (Grice et al., 2005) shows remarkably similar conditions to the series of events leading to the fourth largest extinction near to the Triassic/Jurassic boundary of the Phanerozoic (Jaraula et al., 2013). There is a consistent association with massive volcanism, synchronous isotopic perturbations in marine and atmosphere carbon reservoirs based on  $\delta^{13}\text{C}$  of plant waxes and marine sourced biomarkers. Chlorobi derived biomarkers and excursions in  $\delta^{34}\text{S}$  of pyrite confirm photic zone euxinia (and in several cases persistent photic zone euxinia) occurring at the onset of the marine collapse in both the end Permian and end the Triassic events. Further the isotopic changes are also strongly related to the collapse/ recycling of organic matter from the marine and terrestrial ecosystems (Nabbefeld et al., 2010).

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# MASS EXTINCTIONS DUE TO CLIMATE SHIFTS: VOLCANOES OR ASTEROID IMPACTS?

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The history of life on Earth is punctuated by large mass extinction events, with five large ones occurring in the Phanerozoic and several smaller ones occurring between them. Isotopic and elemental chemistry shows that the extinctions are somehow linked to drastic climate changes. However, the cause of these climate shifts is still debated. The most often advocated mechanisms include large volcanic eruptions and asteroid impact events.

The Cretaceous-Palaeogene (K-Pg) extinction event is well-documented, but controversy as to whether this was caused by an asteroid impact or the Deccan Traps has raged for many years (Shulte et al., 2010; Hofmann et al., 2000)], in particular because both events are demonstrably synchronous with the K-Pg boundary (Renne et al., 2013).

One important question is whether other significant extinction events were caused by impact, volcanism or the combination of both? To test these hypotheses, impacts and/or volcanic eruptions must be exactly synchronous with a mass extinction.

Quality-filtered radioisotopic age compilations based on U/Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  data show that whereas at least six large volcanic province – mass extinctions pairs have been recognized (including the newly added Kalkarindji – Middle Cambrian extinction pair at 510 Ma; Jourdan et al., submitted), only one asteroid – mass extinction pair has been demonstrated (Jourdan et al., 2012). A possible synchronicity between extinction and impact candidates can be tested using precise geochronology. For example, our  $^{40}\text{Ar}/^{39}\text{Ar}$  data on the Siljan Impact structure (Jourdan and Reimold, 2012) show that the impact occur several million years before the Frasnian-Famnenian boundary (~376 Ma). New data on Popigai and Chesapeake Bay (Langenhorst & Jourdan, unpublished) show that the two events are older than the mid-Eocene extinction. Some impact events (Rochechouart [Schmieder et al., 2010]; Araguainia [Tohver et al., 2012]) have ages that make them time-compatible with a major extinction levels, but their small sizes (20-40 km) rule out any possible link.

At the face value of the current radioisotopic age database, large outpouring of lava is a more recurrent kill factor in the evolution of life than large impacts. Although the exact mechanism is not yet understood, the likely factors responsible for climate shifts are due to

emission in the atmosphere of mantle gases (SO<sub>2</sub> and possibly CO<sub>2</sub>) dissolved in the magma, or gases (in particular CH<sub>4</sub> and SO<sub>2</sub>) generated by the interaction between magma and evaporite layers and/or oil-rich rocks.

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# **A PYROLYSIS-GC-IRMS APPROACH FOR THE ANALYSIS OF METHYLTRIMETHYLTRIDECYLCHROMANS (MTTCs): INVESTIGATION OF ORIGIN AND SIGNIFICANCE FOR PALAEOENVIRONMENTAL RECONSTRUCTIONS**

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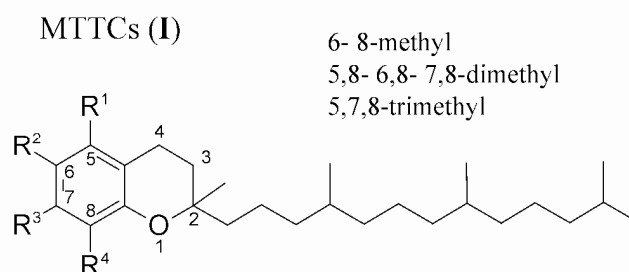
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Methyltrimethyltridecylchromans (MTTCs) are isoprenoid-substituted aromatic compounds (Figure 1) which have been widely detected in sediments and crude oils from various depositional settings. Although the “chroman ratio” between different isomers (5,7,8 trimethylMTTC/total MTTCs) is a frequently used palaeosalinity marker, it is still debated whether these compounds are directly biosynthesised by phytoplankton (e.g. Sinninghe-Damsté et al., 1993) or represent early diagenetic products from condensation reactions of chlorophyll-derived phytol with presumably higher plant-derived alkyl phenols (Li et al., 1995). A clarification of their source(s) would help to more accurately utilize chroman ratios to infer palaeosalinities (especially in a stratified water-column) and it may also broaden the field of MTTC applications in palaeoenvironmental reconstructions, particularly regarding a potential relation to terrigenous input or freshwater incursions.

Here we present an online pyrolysis-gas chromatography-isotope ratio mass spectrometry (PY-GC-irMS) method with the capacity to measure  $\delta^{13}\text{C}$  in fragments (trimethylphenol and pristenes) generated from 5,7,8-trimethyl-MTTC (Tulipani et al., 2013a). This analytical approach shows a great potential to further investigate the potential MTTC formation from condensation reactions of higher plant-derived alkylphenols with predominantly phytoplankton-derived phytol (typically the main source of chlorophyll in marine environments), since the different source organisms of the respective MTTC subunits will likely be reflected in their  $\delta^{13}\text{C}$  values.

We also identified MTTCs in Givetian/Frasnian sediments from the Canning Basin, Western Australia associated with Late Devonian extinction events, and introduced a novel

conceptual model using these biomarkers as indicators for freshwater incursions in the restricted marine palaeoenvironment (Tulipani et al., 2013b). This biomarker approach was based on the relation of chroman ratios and MTTC abundances to other molecular and stable isotopic indicators for water-column stratification, anoxia, salinity and photic zone euxinia (PZE), which indicated that the chroman ratio was strongly influenced by the persistence of water-column stratification and generally reflected low salinities in the overlying freshwater lens. Furthermore, the strong positive correlation of sedimentary abundances of MTTCs and perylene indicated a potential relation to terrigenous input. The similar  $\delta^{13}\text{C}$  values of pristane, phytane and MTTCs in these samples were also consistent with a MTTC-formation from the previously described condensation reactions.



**Figure 1.** Structures of methyltrimethyltridecylchromans (MTTCs) in geological samples

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**LATE QUATERNARY ENVIRONMENTAL CHANGE AT LAKE MCKENZIE,  
SOUTHEAST QUEENSLAND: EVIDENCE FROM MICROFOSSILS,  
BIOMARKERS AND STABLE ISOTOPE ANALYSIS**

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Unravelling links between climate change and vegetation response during the Quaternary is a research priority, and needed if the climate-environment interactions of modern systems are to be fully understood. Using a sediment core from Lake McKenzie, Fraser Island, we reconstruct changes in the lake ecosystem and surrounding vegetation over the last ca. 36.9 cal kyr BP. Evidence is drawn from multiple sources, including pollen, micro-charcoal, biomarker and stable isotope (C and N) analyses, and is used to improve understanding about the timing and spatial scale of past changes that have occurred locally and in the southeast Queensland region. The glacial period of the record, from ca. 36.9-18.3 cal kyr BP, is characterised by lower lake water levels and increased abundance of, or closer proximity to, plants of the aquatic and littoral zone. High abundance of biomarkers and microfossils of the colonial green alga *Botryococcus* occur at this time and include high variation in individual botryococcene  $\delta^{13}\text{C}$  values. A distinct period of dry or ephemeral conditions at the site is detected during deglaciation, causing a hiatus in the sedimentary record covering the time period from ca. 18.3-14.0 cal kyr BP. The recommencement of sediment accumulation around 14.0 cal kyr BP occurs with evidence of lower fire activity in the area and reduced abundance of terrestrial herbs in the surrounding sclerophyll vegetation. The Lake McKenzie record conforms to existing records from Fraser Island by containing evidence for a mid-Holocene dry period, spanning the time period from ca. 6.1-2.5 cal kyr BP.



**Session 8**  
**Analytical**  
**Chair – Alison Blyth**





## KEYNOTE

### LC-IRMS OF AMINO ACIDS AND ARCHAEOLOGICAL APPLICATION

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The acid insoluble fraction of sub fossil bone ('collagen') is the substrate of choice for routine isotopic ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) analysis for palaeodietary investigations in archaeology. If 'collagen' is poorly preserved or contaminated it may not be amenable for analysis and even when it is preserved in some environmental circumstances bulk collagen isotope data can be difficult to interpret.

Liquid chromatography isotope ratio mass spectrometry (LC-IRMS) is a technique capable of measuring stable carbon isotope ratios of single amino acids in protein hydrolysates (without derivatization). I will describe the technique and how we have been using it at La Trobe University to investigate amino acids in ancient proteins, preserved in archaeological bone, tooth and hair. These applications include; exploring the diet and subsistence economy of prehistoric Chileans at a fortnightly scale, the diet and health of historic famine victims in Europe and the quality of collagen preservation in contaminated ancient bone.

In addition, I will discuss the potential application of the technique to other less well characterized mineralized proteins in tissues such as corals, snail shell and eggshell and bulk carbon isotope analysis in stalagmites for palaeoenvironmental interpretation.

# UTILIZING CAVITY RING-DOWN SPECTROSCOPY FOR HIGH-PRECISION ANALYSIS OF THE TRIPLE OXYGEN ISOTOPIC COMPOSITION OF WATER AND WATER VAPOR

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High precision measurements of triple oxygen isotopes in water ( $^{18}\text{O}/^{16}\text{O}$  and  $^{17}\text{O}/^{16}\text{O}$ ) are expanding our understanding of the water cycle with applications to, among others, the present day (e.g., evapotranspiration studies) and the recent geologic past (e.g., fluctuations in humidity during glacial cycles). In particular,  $^{17}\text{O}$ -excess, which is sensitive to kinetic fractionation processes while being nearly invariant with temperature, is of particular interest.  $^{17}\text{O}$ -excess is defined as the anomaly in  $^{17}\text{O}$  from the Global Meteoric Water Line with a slope of 0.528. More specifically,  $^{17}\text{O}\text{-excess} = \ln(\delta^{17}\text{O}+1) - 0.528 \ln(\delta^{18}\text{O}+1)$  (Eq. 1).

For most applications, measurements of  $^{17}\text{O}$ -excess require a precision of  $\sim 5$  per meg (0.005 ‰). Such high precision has historically only been obtained by the conversion of small quantities ( $\sim 2 \mu\text{L}$ ) of  $\text{H}_2\text{O}$  to  $\text{O}_2$ , using reduction on  $\text{CoF}_3$  at  $370^\circ\text{C}$  (Luz and Barkan, 2005). The  $\text{O}_2$  gas is then analyzed by dual-inlet isotope ratio mass spectrometry (IRMS) for a period of 1 to 3 hours.

Cavity ring-down spectroscopy (CRDS) is commonly used for measurements of  $\delta^{18}\text{O}$  or  $\delta\text{D}$  in water, but extremely high precision measurements on small spectral peaks, such as  $\text{H}_2^{17}\text{O}$ , is challenging due to small signal to noise ratios, cross-talk between spectral peaks, and spectroscopic interferences. In general, CRDS provides several advantages over IRMS including streamlined sample handling, faster measurement speed, and the ability to measure ambient water vapor in the field (Crosson, 2008). However, the use of CRDS for  $^{17}\text{O}$ -excess poses unique challenges that are not addressed by any existing commercial instrument. While a  $\text{H}_2^{17}\text{O}$  absorption region is present in some commercial instruments today, the absorbance is small and influenced by the broad tail of the  $\text{H}_2^{16}\text{O}$  spectrum. The resulting precision is inadequate for distinguishing samples from the meteoric water line (Eq. 1).

Here, we describe a new CRDS system capable of high precision  $^{17}\text{O}$ -excess measurements. Key innovations include i) the use of two lasers that measure absorption in

two different near-IR regions, with rapid scanning and switching between the two, and ii) a new spectroscopic method in which the laser cavity resonance is more precisely determined, allowing for improved determination of molecular absorption frequencies. The system has been tested with commercially available sample introduction systems for liquids and vapor, and also a custom-built system that permits the continuous introduction of water vapor from liquid water vials at steady concentrations over a long time period (similar to Gkinis et al., 2011).

With 6 to 8 injections of liquid water (approximately one hour of analysis), we are able to demonstrate precision of better than 10 per meg. Likewise, for vapor measurements we obtain ~10 per meg precision after 20 minutes, and ~5 per meg precision after one hour. A preliminary calibration of a prototype instrument was completed using working laboratory standards previously calibrated with IRMS (Schoenemann et al., 2013). The results provide an accurate determination of VSMOW and GISP (0 per meg and 22 +/- 11 per meg, respectively), showing that both the precision and the accuracy of the new CDRS are competitive with IRMS methods. An additional benefit of the new instrument is improved precision of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (0.02 ‰ and 0.08 ‰, respectively).

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## RETHINKING EA-IRMS (ELEMENTAL ANALYSER – ISOTOPE RATIO MASS SPECTROMETRY)

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In 1983 two hybrid EA-IRMS systems were constructed, with a Japanese group using a quadrupole mass spectrometer with a modified carbon-nitrogen elemental analyser (Otsuki et al., 1983), and an English group reporting on interfacing an automatic Carlo Erba elemental analyser with an isotope ratio mass spectrometer (Preston and Owens, 1983). It is this last group that can be said to have invented the practice of "continuous flow-IRMS", which has led to the commissioning of upwards of 1,500 EA-IRMS systems worldwide. At present, 50 % of all new IRMS systems include an elemental analyser.

The Carlo Erba EA was made for elemental analysis of food, using wt% C as a proxy for carbohydrate content and wt % N as a proxy for protein content. The original focus of oceanographers was on the isotopic measurement of N, but the repurposed food analyser was quickly extended to analyse C and S (Pichlmayer and Blochberger, 1988). While the combustion EA provided a practical solution to isotopic analysis of reduced carbon and nitrogen in a wide variety of solid materials, the isotopic analysis of oxygen and hydrogen proved to be a more difficult challenge, one which occupied many groups over a 30 year period, most notably for the analysis of <sup>18</sup>O and D in cellulose. The keys to successful analysis were the use of glassy carbon at elevated temperatures (>1450 °C) and (for <sup>18</sup>O) the analysis of the CO rather than CO<sub>2</sub>. Analogous to the analysis of CO<sub>2</sub> and N<sub>2</sub> from a single combustion on the combustion EA, it is possible in continuous flow to analyze both CO and H<sub>2</sub> from a single carbon reduction. The key to accurate analysis is quantitative conversion from substrate to analytical species (in other words, yields of 100% are required, anything more or less than this is prone to error).

Automated isotopic analysis of more than one element in a sample has become a major theme in the rethinking of the EA-IRMS system. Fully automated analysis of sets of elements from a single analysis (CN, OH, CNS), or from ganged analyses (CNS-OH), presents a number of challenges, requiring extending the dynamic range. Sample weights can cover a range, from micrograms to milligrams. Concentrations of the elements of interest vary over several orders of magnitude, and the relative concentration of elements (e.g. C:N:S)

varies widely. One research direction that has been under investigation for a number of years is “nano-EA”, isotopic analysis of pollen grains, single organisms, which requires careful analysis of blanks with an eye towards elimination and correction; the identification of isobaric interferences. Current “no blank” design eliminates the atmospheric blank from the autosampler as well as eliminating the possibility of isotopic exchange or hydration of hygroscopic materials that are pending analysis in the autosampler. Approaches for dealing with the dynamic range from increasing the selection of reactor volumes, using the TCD signal to automatically select the dilution of the gases prior to mass spectrometry (“smart EA”), and extension of the computer-variable resistors to further enhance the dynamic range of the Faraday cups.

The discovery of widespread existence of non-mass dependent fractionation of S isotopes in nature has led to considerable interest in using EA-IRMS to analyze  $^{33}\text{S}$  and  $^{36}\text{S}$ , eliminating the need for conversion to  $\text{SF}_6$ . The modifications to the elemental analyser for this application are relatively modest, although great care must be taken to ensure that there are no isobaric interferences added (contaminants). The key to analysis of S is an extended collector array that allows static multicollection of all 8  $\text{SO}^+$  and  $\text{SO}^{2+}$  masses (48-49-50-52-64-65-66-68), which also detects  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{H}_2$ .

Tight helium supplies also pose a challenge to EA-IRMS. Because of the global shortfall in He supplies, leading not only to increase in price of analysis, but to rationing, we have investigated and implemented changes to He flow, to reactor design, to automated dilution, to autosampler flushing, which cumulatively can considerably reduce He usage by 30–40% over conventional practice without any loss of analytical function.

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## NORMALIZATION METHODS AND STANDARDS SELECTION IN STABLE ISOTOPE ANALYSES

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Significant inconsistencies between laboratories can result from use of different normalization methods and standards selection. The accuracy of various normalization methods has been compared by using both analytical laboratory data sets and Monte Carlo simulations (Skrzypek et al., 2010; Skrzypek and Sadler, 2011). Normalization methods using linear regression based on two or more certified reference standards have been identified as generating lower uncertainty than methods based on one standard or tank gas alone (Skrzypek, 2013). The multi-point normalization method produces a smaller induced uncertainty whenever the reference materials are bracketing the whole range of isotopic composition of unknown samples. However, even when normalization is based linear multi-point regression is used, the final normalization error still depends highly on the selection of reference materials (Skrzypek and Sadler, 2011). Furthermore, the uncertainties associated with the calibration of each of the reference materials influences the overall normalization uncertainty. We argue that the optimal selection of reference materials and an increase in the numbers of their replicates will significantly reduce the overall uncertainty in analysed samples. The uncertainty can be reduced by 50% if two different standards, bracketing the whole range of  $\delta$ -values of natural variability, are measured four times, or four standards are measured twice, with each batch of samples (Skrzypek, 2013).

It is crucially important that the same set of standards should always be employed in a stable isotope analysis across different laboratories. A world-wide unified protocol for normalization procedures, including a clearly defined optimal set of reference materials, would improve significantly the inter-laboratory comparison of results. A research paper presenting stable isotope results should clearly report the normalisation technique applied, what standards were used for normalization and the  $\delta$ -values that were obtained for those standards, to ensure that all published data can be recalculated if  $\delta$ -values of standards were to be updated.

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**Abstracts**

**Poster Presentations**

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## POSTER 1

### ITCZ AND ASIAN MONSOON VARIABILITY FROM MIS9 – MIS 2 FROM A SOUTH CHINA PERSPECTIVE.

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Here we report the first high-resolution, multi-proxy palaeoenvironmental reconstruction spanning MIS 9 – MIS 2 from palaeolake Tianyang, South China using bulk organic carbon isotopes ( $\delta^{13}\text{C}_{\text{OM}}$ ), total organic carbon (TOC), magnetic susceptibility, arboreal and non-arboreal pollen (AP/NAP) ratios, and lithology. This multi-proxy reconstruction shows strong glacial – interglacial (G–IG) variability. Glacial/stadial periods are generally cooler and drier, characterised by low TOC and  $\delta^{13}\text{C}_{\text{OM}}$  alongside coarser sediments and higher NAP over AP. Interglacial/interstadial periods are generally warmer and more humid, characterised by higher TOC and  $\delta^{13}\text{C}_{\text{OM}}$  alongside fine clay sediments and higher AP over NAP. The strong G–IG imprint on our proxies is associated with glacial forcing of the precipitation/evaporation balance (eccentricity), though evidence for precession driven insolation forcing, particularly during MIS 5, is apparent. A regional comparison of our record revealed a similar pattern of change in both South China and north Australia. We propose that this similarity results from a unique behaviour of ITCZ variability within the Australasian region that departs from the widely reported anti-phased inter-hemispheric differences resulting from insolation forcing. Our comparison implies a restricted movement of the convective activity associated with the ITCZ in Australasia, especially during glacial periods. This unique ITCZ movement can explain the differences in records dominated by precession (e.g. rainfall intensity) and eccentricity (effective moisture) forcing. Further investigation of this mechanism is required through modelling studies and development of high-resolution records from coastal regions near the ITCZ limits in Australasia.

## POSTER 2

### RESPONSE OF MICROBIAL ACTIVITY TO LONG TERM NITROGEN AND PHOSPHORUS ADDITIONS IN ARID MANGROVES IS DEPENDENT ON TIDAL POSITION

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Mangroves are considered one of the most efficient ecosystems in terms of carbon sequestration, despite growing in some of the most nutrient poor environments worldwide. However, coastal development, catchment modification and extreme weather events that transport nutrients from catchments to coasts may expose mangrove forests to higher nutrient levels. Nitrogen (N) and phosphorus (P) additions are known to increase aboveground productivity and modify N-cycling processes, although most studies worldwide have focussed on tropical ecosystems of high productivity. In the arid zone, pulses of nutrients resulting from cyclones may be particularly important for the maintenance of productivity. However, the influence of nutrient additions on microbial processing of carbon in sediments is unknown. Here, I assessed the responses of the sediment microbial community to long-term additions of N and P fertilisers. Study sites were focussed on contrasting *Avicennia marina* communities (shoreline and inland scrub), in the Exmouth Gulf of Western Australia. Shoreline mangrove communities were taller, denser and more productive, while scrub mangrove communities were smaller and relatively less productive. We measured soil organic matter, nutrient contents and  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  values of the sediment at three depth intervals (0-1cm, 1-4 cm, and 4-10 cm). Measurements were coupled with estimates of microbial biomass and enzyme activities in order to relate biogeochemistry to microbial activity. At the shoreline site, microbial N and P biomass were higher in the N fertilised sites at depths below 1cm. P additions at the shoreline site suppressed microbial P biomass and organic matter (%) in depths below 1cm. However, higher microbial P, lower activities of acid and alkaline phosphatases and more depleted  $\delta^{13}\text{C}$  suggest that, overall, microbial activity and respiration is enhanced in the top 1cm depth with P addition. Conversely, microbial biomass and activity at the inland scrub site responded more strongly to the N additions, but only in the top 1cm depth as indicated by the higher enzyme activity, more depleted  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ , higher

inorganic N and more organic matter (%). These results illustrate that microbial activity, and hence ability to process carbon, is enhanced by long-term fertilisation but is dependent on tidal position. These findings suggest that future studies of carbon sequestration potential of mangrove systems, especially in more arid regions, should consider interactions among limiting factors, especially of hydrologic regimes with organic matter dynamics.

## POSTER 3

### VARIATIONS IN SEAWATER pH FROM $\delta^{11}\text{B}$ RECORDS OF CORALS FROM THE CENTRAL GBR

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Ocean acidification poses a threat to the future of marine organisms, particularly those that deposit calcium carbonate structures, like reef forming corals. In order to properly assess the effects of ocean acidification it is first necessary to understand the variability of seawater pH in the natural environment and the factors controlling these changes. Unfortunately records of seawater pH are scarce and typically short. The  $\delta^{11}\text{B}$  signal stored in biogenic carbonate deposits offers the possibility to extend these records. Massive corals are an ideal archive being fast growing, long lived and sessile organisms, characteristics that make them ideal for environmental reconstructions. Here we present  $\delta^{11}\text{B}$  data at sub-annual and annual resolution from *Porites* corals of the central GBR representing two distinct environments the inner-shelf and the mid-shelf. The inner-shelf represent a more dynamic environment influenced by terrigenous material with a larger range in sea surface temperature and salinity variations compared to the more pristine environment of the mid-shelf area.

## POSTER 4

### THE ROLE OF OLIGOPEPTIDES IN TERRESTRIAL NITROGEN CYCLING: AN AUSTRALASIAN AND GLOBAL PERSPECTIVE

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Despite common assumptions that nutrients taken up by plants and microbes are in an inorganic form, dissolved organic nutrients also constitute a significant direct and indirect resource in many terrestrial and marine ecosystems (Jones et al., 2005; Gioseffi et al., 2012). They also represent one of the major nutrient loss pathways (e.g. stream water) although they are rarely included in ecosystem models. In recent years, interest has reignited in the field of dissolved organic nitrogen (DON) cycling in soils, with the focus mainly being on the role of amino acids as a direct source of N for both soil microbes and plants, and inter-species competition for this resource. Whilst in some low nutrient systems, amino acids may represent a significant proportion of the total dissolved nitrogen (TDN) pool, they are rarely the most abundant component. By comparison, proteinaceous and peptidic nitrogen has been shown to represent a larger proportion soil nitrogen, and this may provide a readily available source of N for soil microbes and plants after extracellular lysis by protease enzymes.

It has long been established from *in vitro* cultures that some mycorrhizal fungi are capable of direct, intact uptake of short-chain oligopeptides, however, the significance of this in the soil environment has only been explored recently (Farrell et al. 2013). We present evidence from a series of experiments that short-chain oligopeptides represent a readily-usable source of N for both microbes and plants (Hill et al., 2011), and that they also represent a larger pool of N than that of free amino acids.

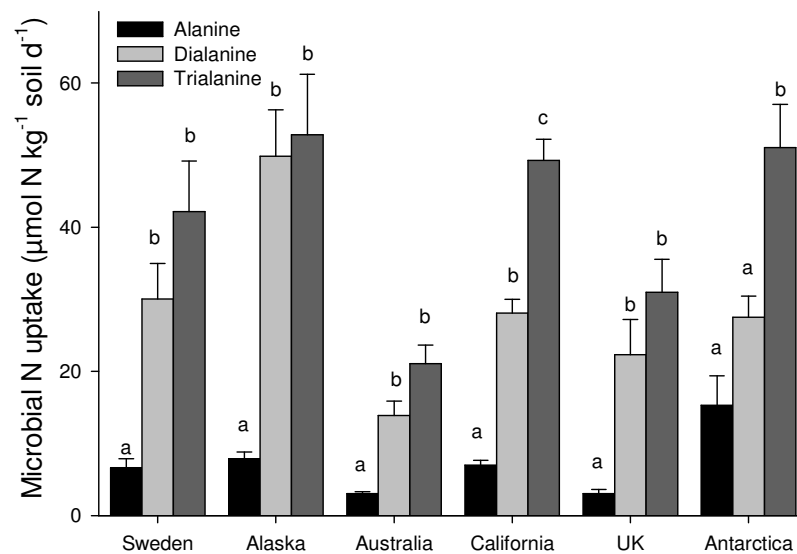


Figure 1. Soil microbial uptake of alanine (amino acid), dialanine and trialanine (peptides) in soils from across the globe (Farrell et al., 2013).

In this presentation, we bring together work demonstrating the importance of oligopeptides in natural and managed ecosystems from around the world, including more recent studies that are ongoing in Australia and New Zealand. Our results imply that DON represents an under-recognised pool of labile N in all ecosystems studied. As well as having fundamental implications for our understanding of resource partitioning between species, it may also contribute directly or indirectly to gaseous nitrogen emissions, and is often ignored or under represented when considering off-site nitrogen losses through leaching or run-off.

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## POSTER 5

### THE ORGANIC CARBON ISOTOPE OF LACUSTRINE SEDIMENTS OF THE UPPER SHAHEJIE FORMATION IN HUANGHUA DEPRESSION: A RECORD OF SEDIMENTARY ENVIRONMENT AND PRODUCTIVITY OF AN ANCIENT LAKE

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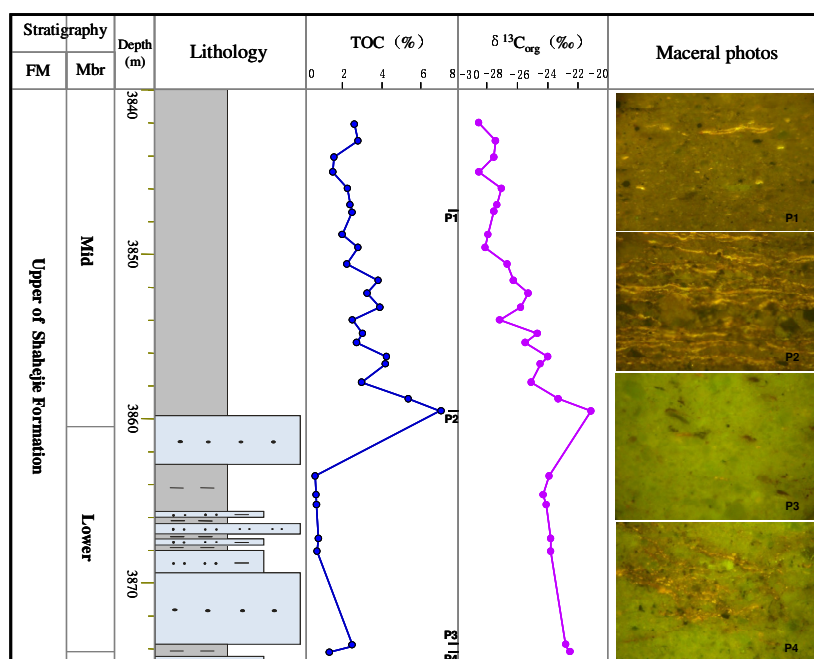
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Huanghua depression was one of the largest Paleogene rift lakes in Bohai Bay basin, eastern China. The lake had broad area and deep water in the period of development peak—Oligocene 36~38Ma B.C., when organic-rich mudstones of upper Shahejie Formation formed. Twenty eight distal lake facie samples of the upper Shahejie Formation from Well GS35 were analyzed for organic carbon isotope, TOC, hydrogen index and trace elements in order to investigate the controls of organic carbon accumulation in the lake. The results show that lacustrine mudstones in the middle member of the upper Shahejie Formation have a heavy organic carbon isotope (-28.6 ‰ to -21.1 ‰) and a intense fractionation which is more than 7‰. In addition, it shows a good positive correlation with the total organic carbon (TOC) (Figure 1).

Organic petrographic and organic geochemical analysis indicate that the biological inputs of the mudstone is dominated by algae and other aquatic organisms, and a low content of gammacerane prove the water is freshwater-brackish, so terrigenous organic matter and water salinity have little effect on its organic carbon isotope composition ( $\delta^{13}\text{C}_{\text{org}}$ ). It has well been documented that the climate in Bohai Bay basin was warm and humid during deposition of the upper Shahejie Formation, and the temperature did not change dramatically at that time (TaoZ et al., 2005). Ultimately, the heavy carbon isotope values of lacustrine organic matter may indicate the high productivity of ancient lakes.

The good correlation between total organic carbon (TOC) and organic carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ) as well as the widely existed organic-rich lamellae of the mudstone are the strong evidence for high paleoproductivity of the upper Shahejie Formation in Huanghua Depression during the deposition period.



**Figure 1.** Profiles of TOC,  $\delta^{13}\text{C}_{\text{org}}$  and maceral in the upper Shahejie Formation samples from Well GS35

(1) Organic-rich lamellae of the mudstone formed in anoxia and stable environment have been recognized as the best evidence of high paleoproductivity. The presence of organic-rich lamellae is the result of algae blooming and deposition in ancient lakes, as carbonate lamellae is the result of  $\text{CaCO}_3$  saturation precipitation with  $\text{CO}_2$  decreasing in surface water due to the algal blooming. Lamellar deposition pattern of the mudstone recorded the geological process of algae's blooming, death and burial.

(2) The carbon isotopic composition of organic matter can be a sensitive indicator of the relative significance of bioproductivity and redox conditions as the main factor controlling the formation of organic-rich sediments.  $\delta^{13}\text{C}_{\text{org}}$  shows a positive correlation with TOC when bioproductivity dominated, however, a negative correlation when redox conditions dominated (Harris et al., 2004). The study on biomarker shows pristane/phytane ratios nearly constant throughout the interval, suggesting the redox environments remained stable. The negative correlation between pristane/phytane ratios and TOC is not obvious, whereas  $\delta^{13}\text{C}_{\text{org}}$  shows a good positive correlation to TOC%, adjusted R is 0.89. Thus it can be seen that bioproductivity exerted a significant control on organic carbon accumulation in the upper of Shahejie Formation.

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## POSTER 6

### **BORON ISOTOPE SYSTEMATICS OF *PORITES CYLINDRICA* GROWN UNDER NATURAL pH REGIMES, HERON ISLAND, GBR**

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The boron pH-proxy is based on the preferential incorporation into marine carbonates of the isotopically distinct borate ion ( $\text{B}(\text{OH})_4^-$ ) relative to boric acid ( $\text{B}(\text{OH})_3$ ), with the relative proportions of the two species being strongly dependent on seawater pH. The use of the boron isotopes as a pH proxy in calcifying marine organisms has been of growing interest in recent years due to the increasing awareness of the effects of decreasing seawater pH or ocean acidification on the marine environment. Ocean acidification (Caldeira and Wickett, 2003) occurs through a chemical process as the oceans equilibrate with rising atmospheric  $\text{CO}_2$ , reducing the pH and hence the saturation state of the surface waters. Recent developments on boron systematics in corals (Trotter et al., 2011) have also provided insights into mechanisms controlling coral calcification, including the maintenance of calcification in reduced seawater pH, by regulating pH at the calcification site (pH up-regulation). Regulation of pH is an advantageous mechanism in corals since they live in dynamic environments where pH can vary daily by as much as one pH unit.

The natural variability and complexity in parameters such as ultraviolet light, pH and temperature, which occur on diurnal scales, are difficult to recreate in laboratory studies. The Coral Proto-Free Carbon Enrichment System (CP-FOCE) addresses these issues (Kline et al., 2012, Marker et al., 2010) by implementing *in situ* experiments maintaining natural diurnal variability in parameters such as light and temperature while manipulating carbonate parameters. A six month study using the CP-FOCE system at Heron Island (GBR) (Team led by Dr David Kline, Scripps Institute) maintained coral specimens (*Porites cylindrica*) at reduced pH (offset from that of the ambient water) following diurnal variability ENREF 5. These specimens are being analysed for boron at UWA's Advanced Geochemical Facility for Indian Ocean Research. This study explores the boron signals in these specimens at high resolution compared to detailed *in situ* data. The physiological mechanism of calcification (pH up-regulation) and the resilience of this species to ocean acidification is also explored by testing the recent IpHRAC model developed by McCulloch, et al. (2012).

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## POSTER 7

### CHALLENGE ON CARBON ISOTOPE ANALYSIS OF TRACE LEVEL GASES TRAPPED IN FLUID INCLUSIONS

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Fluid inclusions (FIs) are micro-scale capsules that trapped fluids (gas, oil, water or bitumen) during crystal growth or after crystallization (Roedder, E, 1984). FIs often formed sooner after the charge to oil and gas reservoirs, commonly occurring with two-phase inclusions where a liquid phase and a gas phase are present. Since FIs are so tiny and have to be observed under microscope, it is real challenge to analyse the stable isotope of such trace level gases trapped in the FIs. Carbon isotope analysis of FI gases is mainly limited by FI abundance and size. For samples with high abundances of FIs (rich samples), carbon isotope analysis of FI gases is relatively easier (Gong et al., 2008). Less than 1 g of samples could release sufficient amount of gases for carbon isotope analysis (Lüders et al., 2012). For samples with low abundance of FIs (lean samples), size does really matter for the amount of oil recovered from FIs (George et al., 2001). The same would apply to the gases released from FIs. This study aims to achieve analysing lean samples and also enable robust carbon isotope analysis of FI gases for various FI samples. The method adopts micro-trapping technology with on-line crushing which allows all the gases released from FIs to be trapped efficiently. The crusher can handle up to 10 g sample for very lean samples. In this study, GOI (the percentage of grains with oil inclusions) was used for assessing the abundance of FIs in the sample. Samples with different GOI values were tested to find out how lean the sample could be to achieve the carbon isotope analysis.

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## POSTER 8

### COMPOUND SPECIFIC $\delta^{34}\text{S}$ ANALYSIS – DEVELOPMENT AND APPLICATIONS

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The  $\delta^{34}\text{S}$  analysis of individual compounds was recently demonstrated following the interfacing of a gas chromatograph with a Neptune multi collector ICP-MS (Amrani et al., 2009). A second similar facility has now been set-up at the University of Western Australia for biogeochemical studies of the S-cycle, as well as to practically assist explorations for both oil and metal deposits. Naturally occurring S can span a range of oxidation states (-2 to +6) and  $\delta^{34}\text{S}$  analyses can reflect important biogeochemical processes – e.g. bacterial sulphate reduction can lead to  $\delta^{34}\text{S}$  fractionation of up to 50 ‰ depending on sulphate availability (Canfield and Teske, 1996).

Key aspects of this new analytical facility, including hardware (e.g., purpose built GC to ICP-MS interface) and analytical performance, as well as initial applications will be presented. For instance, the very high gas flows typically used to cool the ICP torch during ICP-MS operation have posed a significant challenge to the transfer of less volatile analytes from the GC. Optimisation of key GC and MS parameters and use of a purpose built GC to MS transfer line, however, have supported the detection of organic sulphur compounds (OSCs) as large as polymethyl- dibenzothiophenes (DBT) with sufficient temporal resolution for reliable  $\delta^{34}\text{S}$  measurement. To explore the enormous application potential of S compound specific isotope analysis (CSIA) we are in the process of measuring the  $\delta^{34}\text{S}$  values of OSCs in a range of oils and sediments:

- i. *Oil Analysis* - Bulk  $\delta^{34}\text{S}$  values of petroleum can vary over a wide range (-8 to 32 ‰; Faure and Mensing, 2005) and have proved very useful for oil-oil correlations (e.g. Gaffney et al., 1980). More powerful analyses can be anticipated from S-CSIA. Amrani et al. (2012) measured the  $\delta^{34}\text{S}$  value of OSCs in oils impacted by thermochemical sulphate production, and showed that the  $\delta^{34}\text{S}$  values of benzothiophene (BT) and DBT diverged on account of their different rates of production.



It was further suggested the extent of TSR might be implied from the difference in  $\delta^{34}\text{S}$  values of these two products (Amrani et al., 2012). To further investigate the potential of S-CSIA to assist the organic geochemical appraisal of oils we have analysed a suite of S-rich oils from various petroleum reservoirs and basins in China.

- ii. *Metal Deposits* -  $\delta^{34}\text{S}$  analysis of metal sulphides has been useful for investigations of ore deposits (e.g. Rye and Ohmoto, 1974).  $\delta^{34}\text{S}$  values might relate the OSCs present in relatively high abundances in some metal deposits to sulphides associated with the mineralising fluid. OSCs from the 'Here Your Chance' Pb-Zn-Ag deposit in NT have been isolated for  $\delta^{34}\text{S}$  measurement.
- iii. *Fluid Inclusions* – gaseous (e.g.,  $\text{H}_2\text{S}$ ) and liquid range OSCs have been detected in FI associated with petroliferous sediments and metal-deposits. Sulfur isotope signatures will complement measurements of their relative abundance and help establish hydrocarbon sources and important geological processes.
- iv. *Mass Extinction events and the S-cycle* - DBT is known to vary in concentration across mass extinction boundaries. The  $\delta^{34}\text{S}$  relationship of DBT and other OSCs may provide a valuable insight into the potential influence of the S-cycle on these phenomena.

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## POSTER 9

### MOLECULAR MARKER AND STABLE CARBON ISOTOPE ANALYSES OF CARBONACEOUS AMBASSADOR URANIUM ORES OF MULGA ROCK IN WESTERN AUSTRALIA

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Mulga Rock in Western Australia is a multi-element deposit containing uranium hosted by Eocene peats and lignites deposited in a paleochannel incised into Permian rocks of the Gunbarrel Basin and Precambrian rocks of the Yilgarn Craton and Albany-Fraser Orogen (Douglas et al, 2011). Uranium readily adsorbs onto minerals or phytoclasts to form organo-uranyl complexes to pre-concentrate uranium in this relatively young and seemingly amorphous uranium ore deposit. Molecular analyses were conducted to determine any association of uranium concentrations with organic matter (OM) composition.

Samples were collected from the mineralised Ambassador deposit containing low (<200 ppm) to high (>2000 ppm) uranium concentrations. The bulk rock C/N ratios of 82 to 153, Rock-Eval pyrolysis yields of 316 to 577 mg hydrocarbon/g TOC (Hydrogen Index, HI) and 70 to 102 mg CO<sub>2</sub>/g TOC (Oxygen Index, OI) are consistent with a terrigenous and predominantly vascular plant OM source deposited in complex shallow system ranging from lacustrine to deltaic, swampy wetland and even shallow lake settings as proposed by Douglas et al (2011).

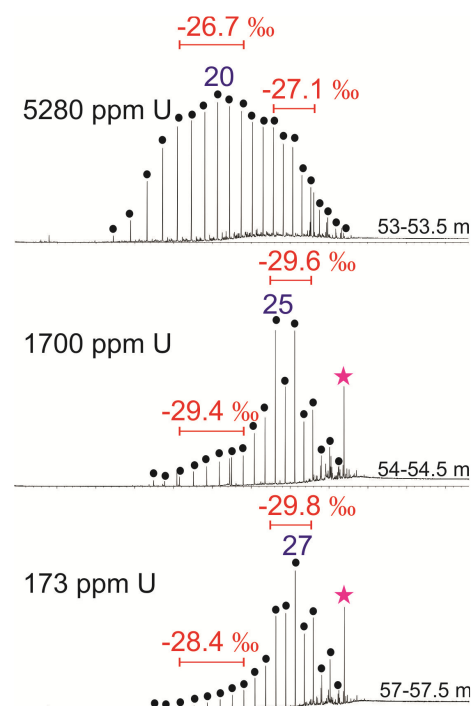
Bitumens were separated into saturated, aromatic, ketone, free fatty acid and alcohol components. The molecular profiles appear to vary with uranium concentration. In samples with relatively low uranium concentrations, long-chain *n*-alkanes alcohol and fatty acid distributions (C<sub>27</sub> to C<sub>31</sub>) dominate with an odd/even preference (Carbon Preference Index, CPI=1.5), interpreted to be derived from epicuticular plant waxes. Average  $\delta^{13}\text{C}$  of -27 to -29 ‰ for long-chain *n*-alkanes is consistent with a predominant C3 plant source, which use the Calvin Cycle. Samples with relatively higher uranium concentrations contain mostly intermediate-length *n*-alkanes, ketones, alcohols, and fatty acids (C<sub>20</sub> to C<sub>24</sub>) with no preferential distribution (CPI~1) (Fig. 1). Intermediate length *n*-alkanes have modest carbon

isotope enrichment compared to long-chain *n*-alkanes. These shorter-chain hydrocabons are likely alteration products.

The diversity and relative abundance of ketones in highly mineralised Mulga Rock peats and lignites are not consistent with aerobic and diagenetic degradation of terrigenous OM in oxic environments. Moreover, molecular changes cannot be associated with thermal breakdown due to the low maturity of the deposits. It is possible that the association of high uranium concentrations and potential radiolysis resulted in the [1] oxidation of alcohol functional groups into aldehydes and ketones (Nakashima et al., 1984) and [2] breakdown of highly aliphatic macromolecules (i.e. spores, pollen, cuticles, algal cycts). These phytoclasts are considered to be recalcitrant as they evolved to withstand chemical and physical degradation as well as ultra-violet light radiation. Petrographic analyses by Douglas et al (2011) show that spores, pollen and wood fragments are preferentially enriched in uranium. Their molecular compositions are feasible sources of short- to intermediate-length *n*-alkanes that dominate the mineralised peats and lignites. Further molecular, petrographic and stable isotope analyses are underway to study the physical and chemical traps of uranium in this organic-rich deposit.

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**Figure 1.** Total ion chromatograms of Ambassador deposits. Dots indicate *n*-alkanes with the most abundant carbon number labelled in blue. Average  $\delta^{13}\text{C}$  (‰) for range of *n*-alkanes are delineated in red.  $\text{C}_{31}$  homohopanes are indicated with a pink star.

## POSTER 10

### THE APPLICATION OF LEAD ISOTOPES IN TRACING HISTORIC INDUSTRIAL LEAD EMISSIONS

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Analysis and assessment of past industrial lead emissions into the Australian environment is challenging without having any atmospheric samples to utilise. The nature of winemaking, with yearly harvests and bottling, allows for the sensitive and accurate capture of past atmospheric conditions. By applying the environmental fingerprinting tool of lead isotopes to Australian wine, it is anticipated that historical lead emissions can be measured and traced. This was shown to be successful in the Bordeaux wine region, France, where the lead isotopic composition of wine followed the atmospheric lead isotopic pattern. The rise and fall of leaded petrol and lead mining activity in South Australia have altered atmospheric lead levels over time. However, little data is available to assess past lead industrial activity.

The lead isotopic fingerprint of single vineyard wines in two wine regions in South Australia dating back to the 1960s were determined and measured against the lead isotopic signature of the vineyard soils for baseline comparison. This will allow for the determination of contributing sources of lead in wine, whether they are industrial pollution or natural from soil. The lead concentration in the wine samples also shows a similar trend to the limited available lead in air data for Adelaide. Strontium isotopes have been analysed concurrently as a control and to assist in determining wine provenance.

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## POSTER 11

### DIET-TISSUE DISCRIMINATION OF $\delta^{13}\text{C}$ AND $\delta^{15}\text{N}$ IN A FRESHWATER CRUSTACEAN

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Knowledge and understanding of discrimination factors ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) for carbon-13 ( $\delta^{13}\text{C}$ ) and nitrogen-15 ( $\delta^{15}\text{N}$ ) are important when using stable isotopes for trophodynamic studies. We performed a controlled laboratory diet-switch experiment to examine diet–tissue discrimination factors for muscle, carapace and stomach tissues of freshwater crustacean, *Cherax destructor*. A range of diets of differing  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  isotopic values were fed to *C. destructor* until equilibrium. For the various tissue types,  $\delta^{15}\text{N}$  discrimination was highest in muscle, followed by carapace then stomach, whilst  $\delta^{13}\text{C}$  was highest in carapace followed by stomach, then muscle. The resulting diet–muscle discrimination factors were similar to, but varied from the 1‰ for  $\delta^{13}\text{C}$  and 3.4‰ for  $\delta^{15}\text{N}$  values that are often used for diet-muscle discrimination. The results highlight variation among differing diet types, and consumer tissue types as applied to stable carbon and nitrogen isotopes in the food-web studies.

## POSTER 12

### UNRAVELLING SEDIMENT BIOGEOCHEMISTRY OF EXTREME HYDROCLIMATIC PERIODS IN THE SEMI-ARID PILBARA USING STABLE ISOTOPES AND BIOMARKERS

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Lacustrine sediments can preserve records of multiple proxies that illuminate the processes and conditions under which the sediments have formed. An integrated multiproxy approach, including the development of isotopic profiles, has been useful in many places around the world for elucidating the history of biogeochemical cycling and for understanding the range of paleoenvironmental conditions associated with sediment transport and deposition. However, the sediments and paleoenvironments of the northwest region of Australia remain undescribed. Retrieval of well-preserved sediment archives in the Pilbara in particular is challenging due to the temporary and dynamic nature of hydrological systems and complex interactions between surface and ground waters. In addition, paleorecord interpretability is limited by a lack of detailed knowledge of pool and catchment functioning. Here, we used bulk and organic C and N elemental and stable isotopes profiles of cores obtained from the largest wetland in the northwest of Western Australia, the Fortescue Marsh, to investigate past biogeochemical processes of this extreme environment. We also developed sediment proxies based on particle size analysis, elemental profiles obtained through ITRAX and biomarker characterization. Our results show the overall C (<2%) and N (<0.2%) content in the sedimentary sequence to be extremely low. Collectively, our results provide evidence of cycles of altered redox conditions with hydroclimatic variation, evaporative sequences and differing origins of C in permanent pools over the last 1000 years or so. This study is a critical first step in extending climatic and environmental records for northwest Australia.

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