

Climate Change: The Karst Record
7th International Conference

KR7 “Down Under”



Melbourne, Australia
29th September – 3rd October 2014

Scientific Programme and Abstracts

Climate Change – The Karst Record (KR7 “Down Under”)

The University of Melbourne
29th Sept – 3rd October 2014

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With thanks to the following University staff and students for their contributions towards the organising and running of the conference:

Bella Ansell, Andrea Columbu, Bronwyn Dixon,
Helen Green, Kerry Grieser, Janet Hergt, John Pederick, and Safana Sellman

MONDAY 29 September 2014

9:00 - 9:15

Welcome and opening address

Morning session (CHAIR: Paul Williams)

Records of orbital-scale palaeoclimate

9:15 - 9:45	Derek Ford (invited)	A review of speleothem studies at McMaster University, 1966 - 2000 CE	pg.79
9:45 - 10:00	Petra Bajo	Radiometric confirmation of obliquity and precessional pacing of terminations during the Middle Pleistocene Transition	pg.29
10:00 - 10:15	Nick Scropton	Stalagmite survival: natural attrition and cyclical growth patterns of stalagmites in southwest Sulawesi over the past 530,000 years	pg.146
10:15 - 10:30	David P Matthey	Speleothem archives of Gibraltar Caves: their record of environment and regional climate over multiple ice-age cycles	pg.121

MORNING TEA 10:30 - 11:00

Pre-lunch session (CHAIR: Dave Matthey)

Records of orbital-scale palaeoclimate

11:00 - 11:15	Alena Kimbrough	The glacial-interglacial monsoon in Sulawesi	pg.102
11:15 - 11:30	Xinggong Kong	The 100-kyr cycle in speleothem carbon isotope	pg.107
11:30 - 11:45	Sophie Verheyden	The end of the Last Interglacial as registered in speleothems from caves in Belgium	pg.163
11:45 - 12:00	Ming Tan	A preliminary study on glacial termination-II in Northern China	pg.155
12:00 - 12:15	Paul Williams	A review of New Zealand palaeoclimate from the Last Interglacial to the global Last Glacial Maximum	pg.176
12:15 - 12:30	Kerstin Braun	Terrestrial paleoclimate of Southern South Africa and the influence of Southern Hemisphere climate forcing	pg.44

LUNCH 12:30 - 13:30

Post-lunch session (CHAIR: Mira Bar Matthews)

Monsoon records	13:30 - 14:00	Claire Krause (invited)	New insights on tropical vegetation productivity and atmospheric methane over the last 40,000 years from speleothems in Sulawesi, Indonesia	pg.108
	14:00 - 14:15	Prof Pingzhong Zhang	Climate variation in the Asian monsoon fringe over the past 60 ka	pg.187
	14:15 - 14:30	Yongjin Wang	Seasonal- to decadal-scale monsoon variability over the last two centuries derived from Chinese cave records	pg.167
	14:30 - 14:45	Marianne Brett	A 3000-year-long annually resolved record of precipitation on the Shillong Plateau, NE India: evidence for drought and flood events and implications for regional monsoon intensity	pg.46
	14:45 - 15:00	Xianfeng Wang	Hydroclimate change in the Amazon lowlands: a tale of two cave records	pg.166

AFTERNOON TEA 15:00 - 15:30

Afternoon session (CHAIR: Dominique Genty)

Millennial-scale palaeoclimate records	15:30 - 15:45	Mira Bar-Matthews	Dansgaard-Oeschger (D-O) and Heinrich (H) events and their connection to the last Great Expansion Out of Africa at ~60-50 ka	pg.34
	15:45 - 16:00	Wuhui Duan	The D/O events 16-14 during the Last Glacial period in North China: stalagmite isotope record	pg.74
	16:00 - 16:15	Dirk Hoffmann	A Gibraltar speleothem record for the Last Glacial period and implications for climate stability in the western Mediterranean	pg.97
	16:15 - 16:30	Denis Schölz	Reconstruction of precipitation variability in the Caribbean during the Last Glacial (80 - 7 ka BP)	pg.144

Late Glacial - Holocene palaeoclimate records	16:30 - 16:45	Pete Akers	A 48,000 year record of climate change in west-central Argentina from stalagmites in Caverna de las Brujas, Mendoza Province	pg.20
	16:45 - 17:00	Izabela Walczak	The onset of Mediterranean climate constrained using computed tomography-derived density variations in an Iberian stalagmite	pg.165

17:00 - 19:00: Poster session 1 – Skeats laboratory, McCoy Building (School of Earth Sciences)

Emily Peckover	Mid-Late Holocene climate and environmental change in southwest Anatolia from speleothem stable isotopes, trace elements and carbon layers	pg.133
Lewis Adler	A comparison of oxygen isotope records from radiocarbon dated groundwater and U-Th dated flowstone	pg.17
Veronica Chiarini	Holocene climate variability of the peri-Adriatic area through the study of carbonate speleothems	pg.50
Gyrögy Czuppon	Changes in temperature and precipitation seasonality during the 8.2 ky event in Central Europe as recorded by combined H-C-O isotope compositions in speleothem calcite and inclusion-hosted water	pg.61
Jiaoyang Ruan	Synchronous mid-Holocene climate deterioration events in east and west Mediterranean	pg.141
Zhenqiu Zhang	A 700-yr speleothem record of annual bands and geochemical proxies in the mid Holocene from Qintian Cave, central China	pg.189

Kyoung-nam Jo	Quasi-cyclic dry events in northeast asia since the mid Holocene	pg.101
India Ansell	New insights into the effect of the bipolar seesaw on the mid-latitudes of the Southern Hemisphere during the Last Glacial period	pg.24
Chris Hendy	Isotopic excursions in New Zealand speleothems coincide with abrupt retreats of New Zealand glaciers from their maxima	pg.96
Gabriella Koltai	Preliminary results of Late Glacial to Holocene climate variations recorded by calcite-aragonite speleothems in an inner alpine dry valley (Vinschgau, northern Italy)	pg.104
Miguel Bartolomè	Speleothem records from northeastern Iberia since the Younger Dryas: identifying synchronies and asynchronies with northern European latitudes	pg.36
Romina Belli	Sources and sinks of Strontium and Magnesium in two Late Glacial stalagmites reconstructed from a multi proxy approach	pg.38
Hongying Yang	Hydrologic variability during the Younger Dryas and Holocene based on speleothems from Laos	pg.181
Ellen Corrick	An investigation of millennial-scale climate events in an Italian speleothem: a pilot study covering the Last Glacial period	pg.57
Chen Shitao	A high-resolution East Asian monsoon record around 2.8ka B.P. from Mt.Shennonjia, central China	pg.149

Jiangying Wu	Decadal-scale variability of East Asian monsoon during LGM revealed by an annually-laminated stalagmite from Hulu Cave	pg.179
Yumiko Watanabe	Paleoclimate study based on high time resolution analyses of stalagmite from Java island, Indonesia	pg.174
Xiaoyan Zhu	Century-scale monsoon climate fluctuations from a middle Holocene stalagmite record in Yunnan, China	pg.190
Stacy Carolin	Mulu mystery: investigating consistent U-234 depletion in tropical northern Borneo stalagmites	pg.48
Dominique Genty	Evidence of a correlation between stable isotopes and wet/dry episodes controlled by the monsoon and Sun activity in a 3-ka-old stalagmite from South-Central India	pg.85
Julie B. Retrum	A high-resolution stalagmite paleoclimate record from northern Venezuela: a record of Caribbean climate change	pg.136
Weihong Zhang	A detailed East Asian monsoon history surrounding the Mystery Interval derived from three Chinese speleothem records	pg.188
Dr Peter Rowe	An abrupt drying event in southern Turkey early in the Last Interglacial recorded by speleothem stable isotope and trace element data	pg.175
Mirona Chirienco	Paleoclimate and speleogenesis : a conceptual model from Donnehue's Cave, midwestern USA	pg.52
Zhang Maoheng	Millennial and orbital changes of Asian Monsoon inferred from Chinese stalagmite data	pg.186

Stef Vansteenberge	A Belgian speleothem from the Last Interglacial: insights in the onset of glacial conditions in northern Europe	pg.162
Gabriella Koltai	First results of a central European flowstone recording climate changes during MIS 5 and 6	pg.105
Judit Torner	Western Mediterranean ocean-atmosphere evolution along the Last Interglacial ending	pg.156
Maša Surić	Speleothem records of climate variability from OIS 5 to the late Holocene from the Croatian littoral (Manita peć Cave)	pg.152
Andrea Columbu	Deciphering intra-decadal climate variations in the Central Mediterranean area during the Last Interglacial using speleothems	pg.55
Andrea Columbu	Local response to global warm pulses over the last 250,000 years: the case of Central Italian gypsum karst	pg.53
David P Matthey	ENSO periodicity recorded in an annually resolved speleothem record from Voli Voli Cave, Fiji	pg.122
Clement Bourdin	Transferring rare earth elements into speleothems : a comparison between natural and experimental conditions	pg.41
Yuan Shufang	Tropical hydroclimate change during the last deglaciation: A statistics study on speleothem oxygen isotopic records	pg.185
Helen Green	A new late Pleistocene to Holocene palaeoclimate record for South East Australia	pg.86

TUESDAY 30 September 2014

Morning session (CHAIR: Maša Surić)

Late Glacial - Holocene palaeoclimate records	9:00 - 9:30	Michael Griffiths (invited)	Tropical Pacific modulation of global climate variability over the past millennium	pg.91
	9:30 - 9:45	Jasper Wassenburg	Major reorganization of the North Atlantic Oscillation during the Early Holocene deglaciation	pg.170
	9:45 - 10:00	Jiaoyang Ruan	A 14-kyr record of climate and environment variability in the southwest of France – a multiproxy approach on a stalagmite from Villars Cave	pg.139
	10:00 - 10:15	Jennifer Wurtzel	Holocene climate variability recorded in an aragonite-calcite speleothem from Sumatra, Indonesia	pg.180
	10:15 - 10:30	Helen Green	The influence of the Austral westerlies recorded in new Late Pleistocene stalagmites from South Africa	pg.87

MORNING TEA 10:30 - 11:00

Pre-lunch session (CHAIR: Dirk Hoffmann)

General & Modelling	11:00 - 11:15	Armstrong Osborne	The deep karst record	pg.131
	11:15 - 11:30	Robyn Pickering	New U-Pb ages for the Hominin site of Drimolen, South Africa: a regional pattern of contemporary flowstone formation	pg.135
	11:30 - 11:45	Jan-Hendrik May	Assessing chronologies for dryland speleothems in the northeastern Flinders Ranges	pg.70
	11:45 - 12:00	Matej Lipar	Aeolianite, calcrete, and pinnacle karst in Southwestern Australia, as indicators of middle to late pleistocene palaeoclimates	pg.112
	12:00 - 12:15	Matt Fischer	Predictable components in global speleothem ¹⁸ O	pg.77

12:15 - 12:30	Alexander Baker	Modelling the stable oxygen isotope composition of precipitation at the northerly limit of the East Asian Summer Monsoon region	pg.33
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LUNCH 12:30 - 13:30

Post-lunch session (CHAIR: Pauline Treble)

Novel techniques and proxies	13:30 - 14:00	Adam Hartland (invited)	A new era of quantitative palaeohydrology from speleothem trace elements?	pg.94
	14:00 - 14:15	Chaoyong Hu	Spurious thermoluminescence in speleothem: implication for paleoclimate	pg.98
	14:15 - 14:30	Robert Andrew Jamieson	Volcanic ashfall events in a speleothem identified using principal component analysis of an exceptionally high resolution trace element dataset	pg.99
	14:30 - 14:45	Silvia Frisia	Sulphur concentration in cave dripwater and speleothems: an overview of its significance as proxy of environmental processes and climate forcing	pg.81
	14:45 - 15:00	Meighan Boyd	ITRAX XRF and colour intensity analysis on modern and mid-Holocene Greek speleothems	pg.43

AFTERNOON TEA 15:00 - 15:30

Afternoon session (CHAIR: Ian Fairchild)

Novel techniques and proxies	15:30 - 16:00	Hubert Vonhof (invited)	Isotope analysis of fluid inclusion water in speleothems	pg.164
	16:00 - 16:15	Stephane Affolter	Water isotope measurement of speleothem fluid inclusions from Switzerland and Borneo using cavity ring-down spectroscopy	pg.19
	16:15 - 16:30	Alan Matthews	Fluid inclusion stable isotopes and clumped isotopes study of eastern Mediterranean caves during glacial – interglacial transitions	pg.123

16:30 - 16:45	Kale Sniderman	Fossil pollen records of U-Pb dated speleothems: New insights into vegetation and climate history	pg.150
16:45 - 17:00	Marine Quiers	Environmental changes in mountain environments during Holocene. A record from organic proxies in stalagmites	pg.116

17:00 - 19:00: Poster session 2 – Skeats laboratory, McCoy Building (School of Earth Sciences)

Juncal Cruz Martinez	Evaluation of laser-induced breakdown spectroscopy (LIBS) for obtaining trace element time-series in speleothems	pg.59
Attila Demèny	Mediterranean influence in the Carpathian Basin (Central Europe) at the beginning of the last interglacial reflected by combined H and O isotope compositions of inclusion-hosted water in stalagmites	pg.64
Ke Lin	High-precision U/Th dating by MC-ICP-MS and its applications on carbonate samples	pg.111
Jasper A. Wassenburg	Speleothem aragonite partition coefficients for Mg, Sr, Ba and U assessed from calcite-aragonite transitions	pg.172
Attila Demèny	Cave-hosted travertine deposit as a potential subject for paleoclimate studies (Béke Cave, NE Hungary)	pg.66
Stacy Carolin	Iranian stalagmites: A proxy for past climate change in the desert?	pg.49
Isabelle Couchoud	Seeking cyclonic activity records in speleothems from Central Pacific: preliminary sample screening	pg.58

Marine Quiers	Interest of using organic matter fluorescence as an environmental proxy in stalagmite studies.	pg.118
Jon Woodhead	The U-Pb in speleothem chronometer: current progress and future prospects	pg.178
Weijun Luo	Oxygen isotopes and hydrogeochemical characteristics of cave drip waters in Liangfeng Cave, Guizhou, SW China	pg.114
Veronica Chiarini	Stable oxygen isotope composition of rainfall in Italy	pg.51
Tim Atkinson	Pipe and sponge: seasonal ventilation of caves from the point of view of ground air circulation in the rock around them	pg.25
Maša Surić	Assessment of the hydrological behaviour in cave environments at varying altitudes on the eastern Adriatic coast (Croatia)	pg.153
David Domínguez-Villar	Modern calibration of a speleothem oxygen isotope record analyzed by SIMS in Postojna Cave (Slovenia)	pg.69
Harriet Ridley	High-resolution monitoring of a tropical cave system reveals dynamic ventilation and hydrologic resilience to seismic activity	pg.137
Maximilian Hansen	Processes affecting stable isotope fractionation during formation of stalagmites: investigation with laboratory experiments	pg.92
Gyrögy Czuppon	Hydrogen and oxygen isotopic variation of cave drip waters: implications for recent climate and paleoclimate signal in stalagmite	pg.62

Ian Fairchild	Testing the contribution of aerosol deposition to pigmented flowstones, Yarrangobilly Caves, NSW, Australia	pg.72
Pilar Aliaga	High-resolution variability of REE in stalagmites: linking stalagmite REE with farmed calcite experiments	pg.22
Hongying Yang	Tropical Indo-Pacific modern and paleo-hydrology : comparison of paleoclimate modeling and speleothem data	pg.183
Fahu Chen	The affecting factors of precipitation $\delta^{18}\text{O}$ variation in westerlies-dominated northwestern China and the significance for understanding stalagmite $\delta^{18}\text{O}$ records	pg.133
Inaki Vadillo	When crystals become dust: speleothem degradation processes in Praileaitz I Cave (northern Spain)	pg.158
Heather Stoll	Interpreting climatic signals from stalagmite trace element and isotopic records using simple geochemical models and growth rate constraints	pg.151
Rachel Bertram	Quantifying the large terrestrial "ground air" carbon reservoir on geological timescales	pg.40
Safana Sellman	A reconstruction of Pliocene climate using speleothems from the Nullarbor Plain, southwest Australia	pg.148
Maria Belen Munoz-Garcia	Palaeoenvironmental implications of monetite layers in ancient speleothems	pg.129
Robyn Pickering	Monkeys of the Caribbean: new U-series ages constrain the antiquity and longevity of Dominican primate <i>Antillothrix bernensis</i>	pg.134

Valentina Vanghi	Coralloid speleothems associated with Neanderthal skeleton in Altamura cave (Southern Italy): environmental constraints and paleoclimate significance	pg.160
Anna Meckler	Comparison of temperature proxies in tropical stalagmites	pg.125
Michael Griffiths	Hydrologic influence on the radiocarbon variability in an Indonesian speleothem during the Younger Dryas	pg.89
Petra Bajo	The "outlier problem" in speleothem geochronology - high-resolution dating of a Holocene stalagmite	pg.31

WEDNESDAY 1 October 2014

Mid conference field trip

THURSDAY 2 October 2014

Morning Session (CHAIR: Robyn Pickering)

Monitoring	9:00 - 9:15	Chris Waring	Two-year, high-resolution speleothem growth, CO ₂ , cave ventilation and methane depletion record responding to season and weather	pg.168
	9:15 - 9:30	Simon Mischel	Potential and limitations for reconstructing the North Atlantic Oscillation from speleothem oxygen isotope values: a case study from the Herbstlabyrinth, central Germany	pg.127
	9:30 - 9:45	Dominique Genty	Rainfall - cave dripping water $\delta^{18}\text{O}$ relationships on long-monitored stations: examples of Villars, Chauvet and Orgnac sites, south France	pg.83
	9:45 - 10:00	Pauline Treble	Eight-years of cave monitoring at Golgotha Cave, SW Australia: implications for speleothem paleoclimate records	pg.157
	10:00 - 10:15	Carol Tadros	Tracking the climate signal in stalagmite dripwaters from Harrie Wood Caves, SE Australia	pg.154
	10:15 - 10:30	Monika Markowska	Using karst unsaturated zone hydrology to inform speleothem choice for high-resolution Holocene palaeoclimate reconstructions	pg.120

MORNING TEA 10:30 - 11:00

Pre-lunch session (CHAIR: Andy Baker)

Monitoring	11:00 - 11:15	David Domínguez-Villar	Is global warming affecting cave temperatures? Importance for speleothem paleoclimate records	pg.67
	11:15 - 11:30	Tim Atkinson	Ground air flow around caves in Gibraltar – an important and dynamic control on cave air CO ₂ and the isotopic composition of speleothems	pg.27

11:30 - 11:45	Kristina Krklec	Quantification of the impact of moisture source regions on the oxygen isotope composition of precipitation: case study from Eagle Cave, central Spain	pg.109
11:45 - 12:00	Dana Riechelmann	Physicochemical characteristics of drip sites: influence on crystal morphology of recent cave calcite precipitates	pg.138
12:00 - 12:15	Helen Rutledge	Artificial infiltrations informing interpretation of trace element records in speleothems	pg.143
12:15 - 12:30	Ian Fairchild	Soil Carbon Export characterized using Novel Tracers (SCENT): a programme of research linking soil behaviour and speleothem archives	pg.75

LUNCH 12:30 - 13:30

13:30 - 14:00 BUSINESS MEETING

Afternoon - Conference workshops

	Organiser	Theme
From 14:00	Andy Baker John	Isotope forward modelling
From 14:00	Hellstrom and Robyn Pickering	Dating sample strategies
From 14:00	Bence Paul	Laser Ablation ICP-MS/Iolite
From 14:00	Silvia Frisia	Speleothem petrography

NB: further information will be provided regarding maximum numbers, registration processes and venues. All workshops are free of charge.

CONFERENCE DINNER 19:00 to late

A COMPARISON OF OXYGEN ISOTOPE RECORDS FROM RADIOCARBON DATED GROUNDWATER AND U-TH DATED FLOWSTONE

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Introduction

Groundwater $\delta^{18}\text{O}$ records have the potential to provide an important long-term record of Australia's past climate, but many uncertainties exist when using groundwater archives and they are therefore considered low-resolution records. In contrast, speleothems are much higher-resolution records that can be used to obtain terrestrial paleoclimate records, specifically they are used for climate reconstruction from their oxygen and carbon isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$). In this study we compare measured $\delta^{18}\text{O}$ values from both groundwater and speleothem records for the first time from the South West of Western Australia (SW WA).

Methods

We used a compilation of 282 groundwater samples from the Perth Basin, SW WA, to determine regional groundwater isotopic composition. Groundwater samples were analysed for $\delta^{18}\text{O}$ by IRMS and dated using radiocarbon ($^{14}\text{C}_{\text{DIC}}$) by AMS. A MAT253 IRMS in conjunction with a Kiel IV carbonate device was used to obtain $\delta^{18}\text{O}$ at high temporal resolution from a flowstone deposited from Easter Cave, in the same region. Flowstone ESF1 formed part of a massive flowstone block which was not active when sampled. The flowstone was dated using U-Th methods.

Results

Groundwater $\delta^{18}\text{O}_w$ was $-4.62 \pm 0.42\text{‰}$ (n=282) for samples dated between 0 and 40,000 years before present. Over the Holocene period, groundwater $\delta^{18}\text{O}_w$ was $-4.50 \pm 0.41\text{‰}$ (n=120). The speleothem U-Th dates covered the latter time period, with rapid flowstone deposition in the early to mid Holocene. Over the whole of the Holocene, flowstone $\delta^{18}\text{O}_c$ was $-3.50 \pm 0.51\text{‰}$ (n=719) and $\delta^{13}\text{C}$ was $-9.77 \pm 1.23\text{‰}$. Groundwater $\delta^{18}\text{O}_w$ was converted to a calcite equivalent, using the mean annual modern cave temperature of 16.7°C . At this temperature, mean predicted calcite $\delta^{18}\text{O}_c$ was -5.23‰ , and applying a $\pm 2^\circ\text{C}$ temperature range, predicts calcite $\delta^{18}\text{O}_c$ between -4.76‰ and -5.70‰ .

For the Holocene, predicted $\delta^{18}\text{O}_c$ (-4.76 to -5.70‰) is generally lighter than that observed flowstone $\delta^{18}\text{O}_c$ ($-3.50 \pm 0.51\text{‰}$). Only for short time periods, around 7.7ka and 9.7ka, does the observed $\delta^{18}\text{O}_c$ fall within the range of $\delta^{18}\text{O}_c$ predicted from groundwater $\delta^{18}\text{O}_w$. A comparison of flowstone $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}$ shows a strong correlation ($r=0.71$) with a gradient of 3.3, indicative of disequilibrium deposition.

Conclusions

This is the first such comparison of groundwater and speleothem-derived water isotopes in a drought affected region. We demonstrate that using both groundwater and speleothem-derived measurements of $\delta^{18}\text{O}$ is a useful method for identifying disequilibrium processes in speleothem deposition. In our case study, disequilibria was further confirmed through conventional comparison of the correlation between $\delta^{13}\text{C}$ vs $\delta^{18}\text{O}$ in the flowstone sample. Our approach helps in the use of speleothem archives to understand groundwater recharge processes in a drought affected region.

WATER ISOTOPE MEASUREMENT OF SPELEOTHEM FLUID INCLUSIONS FROM SWITZERLAND AND BORNEO USING CAVITY RING-DOWN SPECTROSCOPY

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Fluid inclusions represent natural repositories of cave drip water and they are often present in speleothems. The oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) isotopic composition of the water trapped in speleothem fluid inclusions are used as proxies for paleotemperature or for investigating changes in the moisture source and strength.

We have developed a new method based on laser absorption spectroscopy to measure speleothem fluid inclusions [1]. This method uses a Picarro L1102-i instrument where the measuring principle is based on the wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology that has the main advantage of allowing simultaneous measurement of δD and $\delta^{18}\text{O}$ isotopes on a same sample. The extraction line is simple and consists of basically three units: (i) a water background generator; (ii) a syringe injection unit to allow injections of standard water and (iii) a simple home-made crushing device. We can summarise the measurement procedure as follows: prior to crushing, the speleothem sample is placed into a copper tube, fixed to the line previously heated at 140°C and flushed with a nitrogen and standard water mixture. Thereafter, the speleothem sample is crushed using a simple hydraulic crushing device and the released water from fluid inclusions is transferred by a nitrogen gas stream to the analyser. This method avoids any water treatment prior to their isotopic determination such as the pyrolysis when combining gas chromatography and IRMS and it also avoids the step of water freezing treatment. Reproducibility of standard water measurements is typically better than 0.4 ‰ for $\delta^{18}\text{O}$ and 1.5 ‰ for δD for an extended range between respectively at least -27 to 0 ‰ and -210 to 0 ‰. The reproducibility for real stalagmite samples is in the same range.

With this new method, we successfully established new δD and $\delta^{18}\text{O}$ isotopic records of stalagmites from Borneo and Switzerland. In northern Borneo (tropical West Pacific), a stalagmite from Whiterock cave covering almost two glacial-interglacial cycles from MIS 12 to early MIS 9 (460-330 ka) was analysed [2], as well as two modern samples. For Switzerland, we measured two stalagmites from Milandre cave covering the Bølling-Allerød, Younger Dryas cold phase and the Holocene, as well as a modern sample. Our results show a good correlation with $\delta^{18}\text{O}$ isotopic composition of the calcite and allow the reconstruction of paleotemperatures.

References: [1] S. Affolter et al. (2014), *Clim. Past Discuss.*, 10, 429-67, [2] Meckler et al. (2012) *Science* 336, 1301-1304.

A 48,000 YEAR RECORD OF CLIMATE CHANGE IN WEST-CENTRAL ARGENTINA FROM STALAGMITES IN CAVERNA DE LAS BRUJAS, MENDOZA PROVINCE

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Past climate changes in the rain shadow region immediately east of the Andes Mountains of west-central Argentina are very poorly known. More detailed climate data are needed to understand what conditions were like when humans first occupied the area and how variations in climate affected these early peoples. We report here on a study of three stalagmites from Caverna de las Brujas (35.80°S, 69.82°W, 1800 m asl), south of Malargüe, in Mendoza Province. Precipitation is approximately 300 mm per year, although interannual variation can be large. Precipitation is somewhat bimodal, with winter precipitation originating from westerlies-driven Pacific moisture spilling over the Andes and summer precipitation largely derived from convective storms fuelled by Atlantic and Amazon moisture. Oxygen isotope ratios of precipitation in the region typically range from -1 to -10‰ vs. VSMOW, although extreme low values of -20‰ have been recorded. Monthly $\delta^{18}\text{O}$ increases by ~5‰ from a minimum in austral winter to a maximum in austral summer. This increase may be partially explained by the increase in air and cloud temperature during summer months, as well as a change in moisture source during summer to the heavier Atlantic-sourced moisture. No clear correlation with rainfall amount is apparent in modern records. Precipitation $\delta^{18}\text{O}$ is likely quite locally variable in this topographically diverse region; however, a lack of long-term precipitation records and coverage limits the current understanding of regional $\delta^{18}\text{O}$ controls and variability.

The stalagmites are small, consist of massive calcite, grew relatively slowly, and are light brown in color suggesting humic acids in fluid inclusions. Stalagmite BRU1 is 67 mm high and 7 U-Th ages indicate deposition from ca. 38-15 ka. Stalagmite BRU2 is 153 mm high and 9 U-Th ages show two phases of deposition from ca. 47-39 ka and from 27-17 ka that were separated by a depositional hiatus. The third deposit, BRU-N, is a stalagmite complex 130 mm high, with four distinct growth axes that were each dated and sampled individually. An older core dating to 23-18 ka (2 ages) is overlain by three younger stalagmites each horizontally offset from one another; the oldest dating to 13-7.3 ka (9 ages), the second to 7.3-3.9 ka (7 ages), and the youngest dating from 3.6 ka to recent times (6 ages). Thus, the two simple stalagmites and the

complex third stalagmite have provided paleoclimate proxy data for the last ca. 48 ka. Significantly, deposition of BRU1 and BRU2, and the older section of BRU-N, ceased after ca. 18-15 ka, possibly due to drier conditions in and above the cave. Samples were micro-milled from the three stalagmites for oxygen and carbon stable isotope analysis. Samples from BRU1 (n=70) and BRU2 (n=169) were drilled at a 1.0 mm interval, while samples from the four growth axes in BRU-N (n=349) were drilled at 0.5 mm intervals. Values for $\delta^{18}\text{O}$ ranged from -11 to -6.5‰ vs. VPDB, while $\delta^{13}\text{C}$ ranged from -7 to +3‰ vs. VPDB. Highest values of both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ are found during the Last Glacial Maximum (LGM). Digital transects of natural light reflectance and ultraviolet-stimulated luminescence along the growth axes of the three stalagmites as well as petrographic analysis of thin sections also provided information on past climate conditions near the cave.

Higher values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the Las Brujas stalagmites are generally interpreted as indicating drier climatic conditions, the first reflecting the kinetic effects of evaporation on soil and cave waters (higher values with increased evaporation) and the second the level of CO_2 in the soil (higher values with decreased CO_2). Other possible controls on stable isotope variability, such as moisture source, ocean isotopic composition, and temperature changes are also being considered. Variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in the Las Brujas stalagmites over the last ca. 48 ka appear to correlate with variations in the $\delta^{18}\text{O}$ of ice in the NGRIP core; warmer conditions over the Greenland Ice Sheet broadly match drier conditions at Las Brujas. The high $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values during the LGM suggest very cold, dry, and windy conditions that may explain the existence of extensive contemporary dune fields, such as that north of San Rafael. The time of the Bolling-Allerod (B-A) warm period in the northern hemisphere appears to have been very dry at Las Brujas, coinciding with the Antarctic Cold Reversal (ACR) seen in Antarctic ice cores. Just prior to the onset of the B-A, all three Las Brujas Cave stalagmites stopped growing, and only Stalagmite BRU-N resumed growth afterwards, beginning around 13 ka BP and continuing to the present.

Stalagmite BRU-N has provided the most detailed record of Holocene climate change for any part of Argentina so far. The data show a change to much wetter conditions around 5 ka BP correlating in timing with an increase in Antarctic sea ice and major changes in climate at sites around the world. The BRU-N Holocene isotope record shows that the early and late Holocene were relatively wet in the Mendoza area but that there was a lengthy mid-Holocene dry period that lasted from ca. 8.0-3.7 ka BP with peaks in dryness at 6.5 and 4.5 ka that were separated by a short wet interval at ca. 4.7 ka. This long, dry interval in the stalagmite record correlates with a period of low archaeological visibility in the area that lasted from 6-4 ka; it is likely that people moved out of the area because of the much drier conditions.

The Caverna de las Brujas stalagmite climate records presented here are the first detailed and high-resolution climate records for the last 48 ka for Argentina and as such are extremely important in our understanding of South American and Southern Hemisphere climate changes. Ongoing research on additional speleothems from both Las Brujas and other Argentine sites will continue to advance our knowledge of the region's paleoclimate.

HIGH-RESOLUTION VARIABILITY OF REE IN STALAGMITES; LINKING STALAGMITE REE WITH FARMED CALCITE EXPERIMENTS

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Rare earth element (REE) signals are a frontier area in speleothem science and in this work a holistic approach including drip calibration and farmed calcite collection was undertaken to understand the time variation in speleothems.

The calibration was carried out between January 2007 and May 2011 at Las Karmidas in east-central Mexico. Las Karmidas is a shallow erosion cave hosted within a rhyolitic tuff (Xaltipan igmmimbrite), but with classical karstic decoration, esteeming from calcite saturated waters from the dissolution of limestone-clasts (from a breccia over the tuff) and a river -that runs above and through the cave- with upstream-dissolved limestone.

There the monitoring encompassed, for relative humidity, T and CO₂ in the air, alkalinity (mainly in pooled water), pH and trace elements (Ca, Mg, Sr, P, Si and REE) in percolating water and REE in farmed calcite. Followed by the collection of the two previously calibrated stalagmites.

The results show that REE in drip water and calcite present changes in concentration and fractionation, however such variations are not synchronous. Moreover, REE patterns in drip water are not reproduced in calcite, implying a particular controlling mechanism for REE transport and incorporation into calcite.

The hydrochemical speciation -based on thermodynamical complexation constants- suggest that in drip water, within the observed range of pH (7.7-8.6), alkalinity (140-400 mg/L), Si (26-31 mg/L), P (11-128 µg/L) and humic acids (<15 mg/L); it is the REEH₃SiO₄²⁺ and REE(CO₃)₂⁻ complexes that transport and incorporate the LREE and HREE respectively. Humic acid and hydroxide complexes are always below 1% in these conditions, whereas REECO₃⁺ and REEPO₄ are variably important, but are dependent on the precise water chemistry.

Another issue however is that organic matter (OM) could also be transporting the REE as colloids and, at higher P concentrations, phosphates could play a more significant role. Hence, we performed a fluorescent OM (350-390 nmEX/ 420-470nmEm) full scan of both stalagmites by stitching together individual frames taken on a Leica DMRE microscope equipped with a single band pass green fluorescence dichroic filter set. Later we obtained the Fluorescent OM time series by acquiring the “green-scale” register using Weber *et al.* (2010) automated laminae recognition and counting tool. This provided the record of fluorescent OM and allowed us to seek for correlations with trace elements.

Finally, two stalagmites that grew underneath the monitored drip sites were analysed by LACIPMS for Mg, Sr, Ba, U, REE, Ca and P, but also elements known to be associated to OM (Y, Fe and Pb) and humic substances (Cu, Ni, Zn and Co); as well as Mn for its highly reactive surface.

The calibration denotes that during the wet season, the signal in the stalagmite would be characterized by low REE concentrations and low LREE/HREE ratios, whereas an increase in water flux –such as that provided by Hurricane Dean in 2007- results in similar LREE/HREE fractionation, but higher REE concentrations. In contrast, dry conditions also results in REE enrichment but with higher LREE/HREE ratios; revealing that the drier the circumstances are, the larger the LREE/HREE fractionation seems to be (e.g. dry season vs +ENSO). Hence, REE concentration and fractionation variations in calcite are strongly dependant on both, water chemistry and availability.

NEW INSIGHTS INTO THE EFFECT OF THE BIPOLAR SEESAW ON THE MID-LATITUDES OF THE SOUTHERN HEMISPHERE DURING THE LAST GLACIAL PERIOD

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Throughout the last several million years, Earth's climate has undergone regular fluctuations between glacial and interglacial periods. Previous studies show that Antarctic climate experienced broad co-variance with the North Atlantic climate during the last glacial period (~115ka to ~12 ka). However, shorter-duration (millennial) climate events in the two hemispheres did not vary synchronously. This phenomenon, transmitted via the 'the bipolar seesaw' of ocean circulation, has been interpreted as resulting from changes in the northward movement of heat by the Atlantic Ocean. Most palaeoclimate research covering this period is strongly biased towards Northern Hemisphere and sub-equatorial sites. Thus, little is known about the possible teleconnections during abrupt climate changes in the southern subtropics and middle latitudes. Evidence shows that timing of climate events from the North Atlantic to the southern equatorial tropics during the last glacial period principally coincide with that detailed in the Greenland ice-core record. There is, however, a lack of long, continuous, high-resolution palaeoclimate archives from mid-southern latitudes. A more comprehensive record is necessary to provide insight into the geographic extent of North Atlantic influence, and thus define the mechanisms driving the bipolar seesaw.

This project will assemble a palaeoclimate time-series spanning the last glacial period from a speleothem collected from Nettlebed Cave in NW Nelson, New Zealand. Measurements of climate-sensitive geochemical properties ('climate proxies') in the speleothem (stable oxygen and carbon isotopes, trace elements and radiometric dating) will resolve the presence, nature and timing of climate fluctuations. Together with existing data from nearby Hollywood Cave (Whittaker et al. 2011), this record will help determine the extent to which the 'northern response' penetrated the southern mid-latitudes or whether the climate of the region was more in sync with that of Antarctica.

PIPE AND SPONGE: SEASONAL VENTILATION OF CAVES FROM THE POINT OF VIEW OF GROUND AIR CIRCULATION IN THE ROCK AROUND THEM

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The concepts of conduit and diffuse flow of water in limestone aquifers are familiar to karst hydrologists. The same concepts can be applied to air movement in the unsaturated zone, as air is a fluid capable of movement through a porous medium under a gradient of potential energy. Within a defined region of unsaturated rock with homogeneous permeability to an incompressible gas, the steady-state pattern of diffuse flow depends solely on the values of potential energy per unit weight of gas (a.k.a. *potential*, or *head*) at the boundary of the region. If either the values themselves or their local normal gradients are specified for the whole boundary, then the internal flow lines can be found by obtaining a solution of Laplace's equation appropriate to these boundary conditions. Many analytical solutions of Laplace's equation are known for specific geometries, but for practical problems it is often easier to use a numerical technique known as the Boundary Integral Equation Method (BIEM) to obtain values of potential for points within the region of interest and to find the gradients of these to obtain a graphical representation of flow lines.

For ground air movement in an unsaturated aquifer with no caves, the region of interest is bounded by the ground surface and underground by the water table. The driving force for movement is the difference in density between ground air and external air. This is primarily due to differences in temperature, though the contents of water vapour and CO₂ also affect density. Because of the large amount of heat stored in bedrock, underground air is essentially isothermal with a temperature close to the mean annual temperature on the surface. It can therefore be regarded as possessing constant density, as the effects of pressure on density can be neglected for height differences of a few hundred metres. If we now consider a region with topography – e.g. a hill rising from a flat plain – then at a point on the hillside at height h above the plain the atmosphere exerts a pressure on the ground surface of $P_o - \rho_e gh$ where ρ_e denotes the density of external air and g is gravitational acceleration. However, for an *underground* point adjacent to the surface at the same level the density is ρ_g and therefore the pressure potential per unit weight of ground air on the boundary is $-\rho_e h/\rho_g$ relative to atmospheric pressure at the level of the plain. The elevation potential for unit weight of ground air at the same point is h , so the total energy per unit weight of ground air (or hydraulic head) is $h(\rho_g - \rho_e)/\rho_g$. Clearly the hydraulic head at the boundary of the region of interest changes with altitude at a rate that depends on the relative difference in density between external air and ground air. This drives the steady-state motion of the ground air. As the external air will generally be colder and denser than ground air in winter, the hydraulic head decreases with altitude and the ground air flow within the hill will be upwards. Cold, relatively dense external air will enter the ground through the lower part of the hillsides, rapidly acquiring heat from the bedrock and reaching the normal temperature and density of ground air as it does so. It will then flow within the

bedrock along rising paths, and will exit again through the surface in the upper parts of the hillsides. This flux will depend on the density contrast and the permeability, but the precise pattern of flow paths will also depend on the shapes of the boundaries, i.e. the height and shape of the hill and the shape of the water table. In principle, this type of flow is universal in permeable topography, the flow direction reversing if the density contrast reverses in sign, as would occur in summer in the extra-tropical latitudes. Thus, ground air exchanges with atmospheric air on a seasonal basis in these latitudes. Within the tropics, however, the daily temperature range may be larger than the seasonal range. A steady-state model has severe limitations under such circumstances, as the flows will be transient, but nevertheless predicts that in the tropics the direction of flow would tend to reverse diurnally. Diurnal reversals can also be expected in extra-tropical regions during periods in autumn and spring.

Though very simple, this model can be adapted to take account of the presence of caves. Compared with the gas permeability of fractured bedrock, caves have almost infinite permeability for flows along their length. They are like zero-resistance pipes embedded in a somewhat permeable sponge. The walls of the cave can be treated as an internal boundary to the region of interest. The air in single entrance caves can therefore be treated as having a hydraulic head equal to the head on the hillside at their entrance elevation. Caves with two entrances at different levels will have classical chimney-effect winds along their length, and to a first approximation the head at intermediate points along the passage length can be linearly interpolated between the entrance values. (We note that this does not constitute a proper coupling between the diffuse and conduit flows of air, but maintain that it is a useful approximation for insights into the effect of the cave on ground air flows. We note also that other causes of air flow in caves are not represented at all in this approach.)

We have examined the effect of a cave using the BIEM method for a variety of simple 2-D geometries, allowing us to deduce the season in which the cave acts as an outward-flowing discharge conduit for ground air. As ground air is enriched in CO₂, this should be the season in which the CO₂ levels of cave air are highest. In contrast, if the cave acts as a conduit by which external air enters the diffuse flow, it will have low CO₂ levels. The relevance of this for palaeoclimatology is that speleothem $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ will be raised by the rapid degassing that occurs when cave air CO₂ is low, whereas $\delta^{18}\text{O}$ should be nearer to isotopic equilibrium with drip water when CO₂ is high and degassing is slower.

Single entrance caves beneath flat, horizontal plateaux experience little density-driven air movement because of the lack of topographic relief in the surface. Caves entered at the bottoms of dolines have highest CO₂ in summer, lowest in winter. The same applies to caves with single entrances in valley floors or in the lower parts of hillsides. Caves with single entrances in the upper parts of hillsides, or on hilltops, or on culminations of knolls on otherwise extensive plateaux, should have higher CO₂ in winter. Those with entrances close to the mid-height of the local topography (for example, half way up the side slope of a gorge incised into a level plateau) may experience relatively little seasonal contrast in CO₂, because they will act as outlets for ground air flowing from below in winter, and from above in summer.

Caves with multiple entrances are generally well-ventilated by virtue of the chimney-effect winds that flow along them, so will tend to have low CO₂ levels. These will be augmented in summer by the entry of high-CO₂ ground air if both entrances lie below the average elevation of the local topography, and in winter if both lie in the upper half of the topography.

GROUND AIR FLOW AROUND CAVES IN GIBRALTAR – AN IMPORTANT AND DYNAMIC CONTROL ON CAVE AIR CO₂ AND THE ISOTOPIC COMPOSITION OF SPELEOTHEMS

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Speleothems provide coded geochemical records of climatic and other events on the surface, modified by the karst system in which the cave is embedded and by conditions within the cave itself. Decoding a record in terms of useful climatic insights requires the fullest possible understanding of the local karst system as a whole and its specific influence on the chemistry of speleothem calcite. Most cave monitoring has concentrated on gas and water chemistry in the two locations that are easiest to reach, namely the cave itself and the soil. The zone of unsaturated bedrock that links them has received much less attention, and in the case of air and trace gases there has been a tendency to regard the cave space as somewhat isolated from the ground air in the bedrock. This paper examines the physical exchanges that occur between cave air and ground air, and uses the example of the Rock of Gibraltar to demonstrate that the seasonal regime of cave air CO₂ is determined by ground air flow in the surrounding bedrock in combination with CO₂ production in the unsaturated zone. The topology of the cave and the shape of overlying topography both exert a profound influence, as they determine the boundary conditions for ground air flow. Simple 2-D mathematical models based on Laplace's Equation provide insight into this, and suggest that the man-made tunnels in Gibraltar have a strong influence on cave ventilation.

It was long ago inferred from karst water chemistry that CO₂ levels in ground air are in places consistently higher than those in soil air, and this was later confirmed by direct measurements of ground air CO₂ in boreholes. CO₂ ranges up to 1.5 % by volume in Gibraltar boreholes, well in excess of the maximum observed in soil air during ten years' monitoring and comparable with values in boreholes near Cueva de Nerja, Spain. Some drip waters are in equilibrium with even higher levels of PCO₂. Atkinson (1977, *J. Hydrol.*) and Wood (1984, *Water Resources Res.*) suggested that elevated CO₂ in ground air is due to decomposition of organic matter transported into the unsaturated zone. Our observations of water, soil and cave air chemistry, including isotopic chemistry, are consistent with this. Thus one can regard high CO₂ levels as a 'tracer property' of ground air in the unsaturated bedrock in Gibraltar.

We have monitored CO₂ in cave air in two caves within the 440 m high Rock of Gibraltar. New St Michael's is a 200 m long, horizontal tunnel at ca.275 m altitude with a single entrance. CO₂ levels are high in winter when air flows out from the entrance, and low in summer when air flow is inwards. Measured air discharges are ~10 L.s⁻¹ in winter, and roughly correlate with the difference between the external temperature and the constant value of 17.9 °C inside the cave. In spring and autumn, when diurnal changes in outside temperature cause this difference to reverse in sign,

the direction of air flow also reverses diurnally and cave air CO₂ levels fluctuate as low-CO₂ air from outside is alternately drawn in and mixed with high-CO₂ air, and then expelled again. This expulsion is accompanied by rapid rises in CO₂, implying that high-CO₂ ground air must flow into the cave from fissures and fractures in the bedrock. In effect, the cave acts as an ultra-permeable conduit, through which ground air can exchange with outside air and vice versa. Rough calculation suggests that the semi-diurnal fluxes are ~0.1 of the cave volume, and that the half-yearly flux is ~20 times the cave volume, but only ~0.4 of the volume of ground air contained in the parts of the Rock associated with New St Michael's Cave .

The density of ground air depends on its CO₂ content and virtual temperature (i.e. the temperature of dry air with the same density), and is greater than that of external air in summer, less in winter. The large reservoir of heat stored in the soil and solid bedrock buffers the temperature of underground air almost as soon as it enters the ground, while water buffers its humidity. In a hill made of permeable rock the density contrast will cause a flow of air underground. In winter outside air will flow into the ground in the lower parts of the hillsides, rise upwards underground, and exit through the upper parts of the slopes. In summer the flow will reverse. This seasonally reversing movement of air does not require the presence of caves. However, if they are present they will act as conduits through which ground air is discharged, or external air can enter the bedrock.

To gain insight into the flow pattern of ground air in the Rock of Gibraltar and its influence on CO₂ in New St Michael's Cave, we employed a 2-D mathematical model representing a cross-section through the Rock. The results confirmed the concept of a ground air circulation through the whole Rock, rising upwards in winter, descending in summer. The modelled flow lines around a cave representing New St Michael's showed that ground air both entered and left the cave through its walls, producing a net imbalance in flux that is the modelled equivalent of airflow through the entrance. The model cave exported ground air in winter and imported external air in summer, in agreement with observations. Including the artificial Fosse Way tunnel in the model drastically altered the flow pattern and increased the net flux in the cave six-fold, suggesting that tunnels have caused large increases in external ventilation and increased the seasonal contrast in CO₂ levels in cave air.

The concept of a whole-Rock circulation has a corollary in that low-altitude caves are predicted to have a seasonal ventilation regime in anti-phase to high-level caves like New St Michael's. We extended our monitoring to the Ragged Staff system, which ranges in altitude from zero to 75 m and has a pattern of draughts that indicates unequivocally that the cave has two unknown natural entrances in addition to the artificial entrance made when tunnelling intersected it. The vigorous chimney-effect draught in this cave reaches ~100 L.s⁻¹ and the cave air has CO₂ levels much lower than in New St Michael's. Nevertheless there is a clear seasonal cycle which, as predicted, has lowest CO₂ in winter and slightly higher values in summer, indicating an influx of ground air.

The observations in Gibraltar confirm the importance of ground air exchange in regulating the CO₂ levels of caves. In an accompanying poster, we use the same modelling principles to predict the seasonal regime of CO₂ in cave air for a variety of caves classified by their geometry in relation to the shape of the overlying ground. This is important for palaeoclimatology, because degassing rates of drip waters and the resulting isotopic values of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in calcite are strongly influenced by the difference between PCO₂ of the solution and PCO₂ of the cave air.

A SPELEOTHEM RECORD OF SOUTH EUROPEAN CLIMATE DURING THE MIDDLE PLEISTOCENE TRANSITION

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The Middle Pleistocene Transition (MPT) represents the single biggest perturbation in the global climate and environmental system during the Quaternary period. It is characterised by the shift from 40-kyr to quasi-100-kyr glacial-interglacial cycles which apparently occurred without any change in orbital forcing. Despite being studied for more than thirty years, particularly by the oceanography community, our understanding of climate conditions during this time period is limited. One of the major obstacles to answering the questions about the duration, character and causes of the shift from the 40-kyr to 100-kyr world partially stems from the fact that there is no robust chronology during this time period.

Here we present the first U-Pb radiometrically dated speleothem record of two full glacial-interglacial cycles and three glacial terminations during the MPT, which highlight that speleothems of this age have great palaeoclimate potential beyond the limits of U-Th dating.

The samples were collected from Corchia cave in Italy. Their chronologies are based on high-resolution U-Pb dating. The record has been replicated in three stalagmites datable by U-Pb method and one subaqueous core, which together add robustness to the palaeoclimate interpretation and improve the previously published age-depth model for this period (Bajo et al, 2012).

The Corchia $\delta^{18}\text{O}$ time series were matched to SST record from the North Atlantic following the approach of Drysdale et al. (2009) and in this way our radiometric chronology is transposed to the marine benthic $\delta^{18}\text{O}$. The benthic records on the Corchia chronology are then compared to the orbital configuration of the time. This has enabled us for the first time to test orbital hypotheses of glacial-interglacial variability at this time period without tuning to the astronomical time scale.

The results support the ~40-kyr glacial-interglacial frequency linked to changes in obliquity. Furthermore, our time series reveals that precession also played an important role with each Termination occurring when summer insolation in either the Northern or Southern Hemisphere was high. This rules out the importance of an

exclusively Northern Hemisphere summer insolation maximum in triggering the timing of these terminations, consistent with the model proposed by Huybers (2011).

Additionally, high-frequency climate oscillations are superimposed on glacial-interglacial variability in Corchia $\delta^{18}\text{O}$ time series. These are possibly related to millennial-scale climate events recorded in marine cores from the North Atlantic, as well as to two sapropel events recorded in the Mediterranean during the MIS25, all linked to precession modulation of insolation.

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THE “OUTLIER PROBLEM” IN SPELEOTHEM GEOCHRONOLOGY- HIGH RESOLUTION DATING OF A HOLOCENE STALAGMITE

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Age outliers beyond that which can be explained by measured analytical uncertainty are a feature of many U-Th studies. Anecdotally from discussion with workers from other labs, they are often underreported in published datasets. Their existence and treatment has gained formal attention recently in discussion of age-depth modelling (e.g. Scholz et al, 2012).

Here we present high-resolution U-Th dating results for a Holocene stalagmite (CC26) from Corchia Cave in Italy. Forty-seven samples extracted along the central growth axis were first chemically prepared for analysis, and then typically split into two or three sub-samples prior to mass spectrometric analysis following Hellstrom (2003). The resulting 122 sub-samples were in each case measured at least one week apart from each other to capture any long-term variability of the mass spectrometric technique.

The replicate measurements of individual chemically processed samples were in very good agreement with respect to their measured analytical uncertainties, ruling out a mass spectrometric origin for any age outliers observed in the dataset. Nonetheless, five of the 47 samples showed an offset from neighbouring samples amounting from 3 to 40 per cent. One extreme sample was more than four times older than its expected age of 3.95 ka.

Sample pieces leftover from these five analyses were then chemically re-processed for repeat measurements. In all five cases, the repeat analyses were now consistent with those of neighbouring samples, in line with the overall pattern of low growth-rate variability throughout the Holocene for this speleothem.

We reject the possibility of an analytical origin for the observed outliers in that the quality of measurement replication eliminates any chance of flaws in the mass spectrometric procedure. The possibility of sample contamination during calcite sampling or chemical separation procedures over multiple sample batches can be rejected both procedurally and purely on a mass balance approach. Instead we believe that in this speleothem, macrocrystalline calcite crystals may in reality contain microstructural defects (Frisia et al., 2000) which allowed for significant, and in one case extreme, uranium loss.

Where outliers are discovered in speleothem age-depth models it is often assumed that analytical misadventure is likely responsible, but we would argue that the speleothems themselves might not have behaved as perfectly closed systems as is commonly thought.

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MODELLING THE STABLE OXYGEN ISOTOPE COMPOSITION OF PRECIPITATION AT THE NORTHERLY LIMIT OF THE EAST ASIAN SUMMER MONSOON REGION

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The East Asian Summer Monsoon (EASM) generates intense seasonal rainfall in eastern and southern China, impacting the world's most populous region. Accurate prediction of future rainfall variability necessitates reliable palaeomonsoon reconstructions from proxy data. Absolute-dated stalagmite $\delta^{18}\text{O}$ records from Chinese cave sites have been interpreted as direct records of past rainfall or EASM intensity fluctuations, but recent research suggests precipitation $\delta^{18}\text{O}$ instead integrates multiple hydroclimatic processes, including upstream depletion during atmospheric moisture transport from tropical oceanic sources, rather than a local precipitation signal. We used a quantitative Lagrangian tool, based on atmospheric trajectories, to detect the sources of modern precipitation at Wanxiang Cave, a site near to the northerly EASM limit, and modelled $\delta^{18}\text{O}$ evolution along the diagnosed three-dimensional moisture transport pathways. Our results show that Wanxiang rainfall originates in the northern Indian Ocean and undergoes intense summer recycling. The isotopic compositions of 37 rainfall events sampled at Wanxiang were modelled using European Centre for Medium-Range Weather Forecasting analysis data (e.g., sea surface temperature, specific humidity, and pressure), achieving a reasonable correspondence between observed and modelled summer precipitation $\delta^{18}\text{O}$. Modelled values overestimate the observed isotopic depletion during winter months for the sampled events, which is likely related to the influence of the Westerlies at this northerly site. Nevertheless, our results firmly suggest that such an approach can be used to isolate the precipitation amount signal from other factors affecting precipitation $\delta^{18}\text{O}$ in this region.

DANSGAARD-OESCHGER (D-O) AND HEINRICH (H) EVENTS AND THEIR CONNECTION TO THE LAST GREAT EXPANSION OUT OF AFRICA AT ~60-50 KA

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The Late-Middle Palaeolithic period in the Levant is characterized by intensive human activity activity of both Neanderthals and Anatomically Modern Humans (AMH'S), as evident from cave sites in Mount Carmel and the Galilee region in northern Israel. Early modern human fossils discovered in Skhul and Qafzeh caves were dated to ~110-100 ka. Neanderthal fossils found in Tabun, Kebara and Amud caves (Israel), Dederiyeh Cave (Syria), were dated to 112-47 ka.

One of the most remarkable events in human evolution occurred at the end of the Middle Palaeolithic between 60,000 and 40,000 years ago where by modern humans of African origin expanded across Eurasia, replacing all other forms of hominines. The timing of this later expansion is largely based on genetic rate of mutation data and from cultural changes noticed in several dated (¹⁴C) sites found in Africa, Europe and the Levant.

The question posed in this study is whether speleothems data in association with other climatic proxies (marine and pollen records) from the Eastern Mediterranean and the Sahara Desert, can furnish us with a more accurate time for this exodus? And whether this late migration was triggered by improved climatic conditions?

The Eastern Mediterranean semi-arid region was hospitable for humans and animals during both glacial and interglacial periods. Yet, migrating populations from Africa faced the challenge of first crossing the large Saharo-Arabian Desert. Growth periods of speleothems during the last 250 ka from Arabia and Northern Sahara and their isotopic composition point to periods of increased rainfall that coincide with intensification of the African/Arabian monsoon system and increased precipitation from Mid-latitude cyclones. During these episodes the Saharo-Arabia desert belt was reduced in size, mainly during peak interglacials: at ~230-220; 190-200; 130-120, 108-98, 87-84 ka, and in the early Holocene. These humid periods are also evident in the deep sea organic-carbon rich sapropel layers of the Eastern Mediterranean Sea.

Can the very rapid human population expansion outside Africa during last glacial period at ~ 60-40 ka be considered as the “glacial analogue” to the wet interglacial periods? The most pronounced $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ oscillations in the speleothem records from the Eastern Mediterranean occurred between the H6 and H5 events, at ~60 - 50 ka, during D-O events 16 to 13. The sharpest transition to almost interglacial wet conditions occurred during D-O interstadial 14 from ~56 ka to 51 ka, coinciding with high 65°N insolation and followed by a gradual change to full arid glacial conditions at ~50-48 ka. Similarly, the $\delta^{18}\text{O}$ record of the planktonic foraminifera *G. ruber* from

the Eastern Mediterranean Sea follow the D-O cycles, and pollen records show that the typical vegetation of dry and cold periods consisting of low tree cover and the dominance of steppe vegetation was replaced by vegetation typical of more humid conditions, with a peak between 56 to 54 ka. At high altitudes in the southern extension of the Levantine Alpine karst range (Mizpe Shalgim Cave, Mt. Hermon; 2224 m a.s.l.) marked episodes of speleothems growth occurred during most of D-O interstadial 14 due to warming. Thus, there is remarkably strong body of evidence for a milder and wetter favourable climate during the 60-50 ka period.

In an attempt to strengthen the connection between the amenable climate period and modern human migration, we have carried out new speleothems studies at Manot Cave. The site is located in the Western Galilee region of northern Israel (33.03°N/35.19°E). Manot is a relict karst cave within the Cenomanian limestone host rock, and is rich in speleothems, lithic assemblages and animal bones pointing to its occupation by modern humans. Part of the lithic assemblages were sealed by flowstone layers, or covered by carbonate crust. Dating these carbonate crusts and flowstones using U-Th methods requires correction due to the high concentrations of detrital material. Several correction methods were applied: using the isochron method; comparing to a non-corrected age (low detritus) from the same laminae, and by wiggle-matching of the stable isotopic profile of Manot speleothems with dated speleothems from nearby sites. Similar correction factors were found using all three methods, enabling us to directly date the archaeological artifacts to cover the time period between ~55 and 30 ka. The earlier ages overlap with the later and most significant phase of modern human expansion out of Africa, at a time when the most favorable climatic conditions existed during D-O interstadial 14.

Speleothem records from northeastern Iberia since the Younger Dryas: identifying synchronies and asynchronies with northern European latitudes

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Speleothems from NE Iberia allow exploring the environmental response on land to rapid climate events since last deglaciation and appear as the most suitable terrestrial archive to explore the timing of some of the events. To characterize the higher-frequency climate variability at a regional scale, speleothems can provide the necessary chronological accuracy and high sampling resolution. Studied caves are selected in a latitudinal (42 – 40°N) and altitudinal (2000 – 800 m asl) transect from the Pyrenees to the Iberian Range where speleothem formation mostly occurs during the Holocene although data from Greenland Stadial 1 (GS-1) are also documented.

Terrestrial response to the GS-1 cooling appears to be delayed by several decades in northern Europe but the environmental consequences on land and their timing are still under discussion. Here, we present a sub-decadal stalagmite record from the Pyrenees that reveals a remarkable temperature correlation with Greenland ice cores demonstrating the southern influence of North Atlantic cooling and the rapid response on land. Two phases in the hydrological regime are observed from isotopic composition indicating a bipartite character of the Younger Dryas signal in NE Iberia and suggesting a lag of about 300 years from southern to northern Europe in the response to sea-ice retreat at mid-YD transition (Bartolomé *et al.*, in preparation).

At the onset of the Holocene there is a spectacular increase in the number of stalagmites growing in the studied caves. Interpretation of $\delta^{18}\text{O}$ values in terms of temperature variability is not straightforward at the latitude of the Iberian Peninsula but is supported by monitoring surveys in the studied caves (Moreno *et al.*, 2014) and correlation of isotopic records from recent speleothems with instrumental data. Thus, in spite the range of variation of $\delta^{18}\text{O}$ records is low (about 2‰) it is still associated to temperature variability, although changes in the source of precipitation (Atlantic vs Mediterranean) or the influence of fresh-water outbursts in North Atlantic can not be totally neglected (Moreno *et al.*, in preparation). $\delta^{13}\text{C}$ profiles, together with Mg/Ca or Ba/Ca ratios that are usually good indicators of aridity, point to an increase in humidity during the Early Holocene (11.6-8.2 ka BP), followed by a decrease of water availability afterwards. This general pattern is interrupted by several shorter episodes characterized by more negative isotopic values ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) in synchrony with European high lake level phases, interpreted as cold but probably wetter periods with denser vegetation cover and soil development over the caves (Pérez-Mejías, 2013).

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SOURCES AND SINKS OF STRONTIUM AND MAGNESIUM IN TWO LATE GLACIAL STALAGMITES RECONSTRUCTED FROM A MULTI PROXY APPROACH.

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Strontium (Sr) and magnesium (Mg) are commonly used to obtain palaeohydrological information from speleothems. The dissolution of carbonates in soil and bedrock is commonly assumed to be the major sources for these cations, and, for a given Me/Ca ratio, their incorporation into the carbonates is believed to depend on growth kinetics (for Sr) and temperature (for Mg). However, allogenic sources of Sr and Mg to the soil are likely to contribute to drip water chemistry when airborne dust is deposited above the cave, or anthropic activities alter the soil structure. In addition, the incorporation of Sr and Mg in cave carbonates is complicated by interactions between the solution and the crystal surface or organic compounds and crystal surfaces. For example, discrepancies between actual Sr concentration in speleothems and the theoretical concentration as calculated from the partitioning coefficient suggests that Sr may even be accommodated in “extra lattice” sites. Similarly, it has been suggested that increases in Mg concentration in some speleothems may be associated with particulates carried by drip waters during heavy infiltration events.

Here we propose a multi-proxy approach to interpret Sr and Mg concentration variability in two coeval stalagmites (SV1 and SV7) that have grown at low rates (average 15 $\mu\text{m}/\text{year}$) under different flow regimes at Grotta Savi, NE Italy. The SV1 record ranges from 15.3 ± 1.6 to 9.4 ± 0.2 ka, and entirely overlaps the tuned chronology (13.0-10.8 ka) of the growth phase of the second stalagmite, SV7 (Belli et al., 2013). In addition to major and trace elements (Mg, Sr and Th), petrography, lamina counting and stable isotope data ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$), we used radiogenic Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) variations to reconstruct the sources of Sr and its mechanisms of incorporation. The Sr incorporation in the SV stalagmites appears to be controlled by three processes: growth rate, the carrier of Sr in soil above the cave, and hydrological variability.

Hydrology, particularly flow regime, has a strong control on Mg input, with Mg derived from dissolution of carbonate host-rock under low-to-moderate flow regimes and influenced by incongruent carbonate dissolution, and Mg partially associated with particulate matter during high-flow regimes. After removing the interference of growth rate and sources (Sr) and particulate transport (Mg), it is possible to combine Sr and Mg time series in a robust independent palaeohydrological proxy.

This multi-proxy approach on two stalagmites from the same cave allows recognition of the contribution of the hydrological component to the proxy signal. Consequently, it allows for more robust interpretation of discrepancies between the Mg-Sr and $\delta^{18}\text{O}$ variations in speleothem time series in terms of non-hydrological influences on the $\delta^{18}\text{O}$ signal, such as changes in air mass provenance.

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QUANTIFYING THE LARGE TERRESTRIAL “GROUND AIR” CARBON RESERVOIR ON GEOLOGICAL TIMESCALES

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Concentrations of carbon dioxide (CO₂) in the unsaturated zone are over 150 times greater than atmospheric levels, implying generation of CO₂ within this zone. CO₂ measured in soil air and epikarst air does not fully quantify the exceptionally high values recorded in subterranean environments, such as those taken from cave air and in deep boreholes. Air permeating the whole of the unsaturated zone, “ground air”, accounts for this discrepancy. It is contained within the unsaturated zone pore spaces, cracks and fractures and is characterised by high concentrations of CO₂.

Glacial to interglacial transitions are characterised by rapid rises in atmospheric carbon dioxide concentrations, but no clear source for this carbon exists. Consideration of ground air as a CO₂ store has important implications for understanding climate change on geological timescales. Variations in global mean sea level (GMSL) modulate the unsaturated zone volume and therefore allow this reservoir to act as either a sink or a source of carbon.

To quantify this carbon store on geological timescales, the global depth to water table, bedrock porosity, total land area and the CO₂ concentration of ground air are considered. To investigate the CO₂ concentrations in ground air, laboratory experiments evaluated the maximum production of CO₂ under varying quantities of organic material. Estimates suggest ground air CO₂ concentrations of 2-7%. Quantities of organic material between 2.5% and 10% in the unsaturated zone are sufficient to account for these high CO₂ concentrations. The influence of sea level variations on ground air concentrations are supported by both field experiments of the unsaturated zone at beach environments and a high-resolution cave air *p*CO₂ record from a Caribbean cave site.

The current global ground air store is estimated to contain 3.9 – 53.8 Petagram of Carbon (PgC). Since the Last Glacial Maximum (LGM), up to 86.2 PgC transferred from ground air due to rising sea levels inundating the land and causing CO₂ outgassing from this reservoir. This rise alone accounts for up to 41% of the increase in atmospheric CO₂ concentrations recorded in ice cores between the LGM and pre-industrial levels. Ground air in the unsaturated zone is a non-negligible store of carbon; consideration of it in climate models is therefore imperative.

TRANSFERRING RARE EARTH ELEMENTS INTO SPELEOTHEMS : A COMPARISON BETWEEN NATURAL AND EXPERIMENTAL CONDITIONS

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REE (Y and the 14 lanthanides) are a family of elements with similar properties, with a decreasing atomic radius from light (LREE) to heavy rare earth (HREE). They are present in trace to ultra-trace amounts in speleothems (ppb to ppm) and despite their usual valence is +3 (except Ce et Eu) they have a ionic radius close to Ca^{2+} and can be substituted for Ca in the calcite lattice (Elzinga et al., 2002).

REE content in speleothems has recently begun to be used as an environmental proxy (Bourdin et al., 2011; Zhou et al., 2008). REE can potentially be used to indicate the past contributions of soil weathering versus bedrock weathering that vary following climatic changes (Zhou et al., 2008). The assumption behind this is that the fractionation between REE during dissolution, transport and incorporation is negligible. Most of these factors likely to control the REE concentration in speleothems are poorly known. Among them, the mode of transport and the incorporation of rare earth elements into calcite are not as straightforward as for some divalent cations present in the dissolved phase. Direct and indirect methods showed that, in the few investigated sites, REE were mostly present in the particular or large colloidal phase (Borsato et al., 2007; Zhou et al., 2012; Hartland et al., 2012). The transport of particles being sensitive to flushes happening during the wet season, the final concentration of REE in speleothems is thus likely to be dependent on the intensity of these hydrological events. Furthermore, the particle-REE binding is competing with the REE-calcite binding so the incorporation of REE into calcite should depend on the lability of the particle-REE complex.

Here is investigated the fate of REE in an experimental calcite precipitation setup and in a cave in Western Europe where the overlying soil is poorly developed, allowing the bedrock to be the main source of the REE in the cave waters and subsequently in the secondary calcite deposits. This site is characterized by the low REE/Ca ratio in unfiltered cave waters, showing that at least 90% to more than 99% of all REE are scavenged or precipitated upstream from speleothems. Comparing seepage water and modern deposit compositions allows calculating apparent partition coefficients (D_{REE}). All D_{REE} are much higher than 1, around 100 except for D_{Ce} which is in the 10-30 range. On the contrary, experimental D_{REE} measured from calcite grown from the dissolution of the cave bedrock are all lower and around 10. This points to the role of REE speciation in their incorporation in calcite. In experimental conditions where REE are likely to be mainly present in water as carbonate complexes all REE are similarly incorporated in calcite. On the other hand, REE were all partitioned more efficiently in the cave environment, except Ce whose

precipitation is certainly slowed down by its binding with particles. The role of organic matter in REE speciation is thus suspected to be a major control in REE partitioning into calcite. Furthermore, no significant fractionation between heavy and light REE was observed whether in cave or experimental environments, contrary to what had been found previously in seawater (Zhong and Mucci, 1995).

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ITRAX XRF AND COLOUR INTENSITY ANALYSIS ON MODERN AND MID-HOLOCENE GREEK SPELEOTHEMS

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Speleothems from Alepotrypa Cave, southern Greece, have been analysed using ITRAX XRF analysis and scanning colour intensity methods to evaluate the possibilities of combining established non-destructive techniques from dendrochronology with traditional speleothem stable isotope analysis and lamina counting. Analysis has been conducted on a modern stalagmite taken from a set of concrete stairs within the cave and a dense calcite stalagmite which has been dated using uranium series technique to between 5.4-1.5ka B.P. This site is of particular interest as Alepotrypa Cave is the location of an extensive Neolithic age habitation which lasted until ~5.2ka when an earthquake collapsed the cave, trapping the inhabitants inside. Work on speleothems from the cave seeks to provide past climate information to archaeologists, which may contribute to the interpretation of the human societal record from the region.

TERRESTRIAL PALEOCLIMATE OF SOUTHERN SOUTH AFRICA AND THE INFLUENCE OF SOUTHERN HEMISPHERE CLIMATE FORCING

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Southern South African climate is determined by strong variations in the amount and seasonal distribution of rainfall, due to its location at the intersection of sub-tropical and temperate climatic regions. During summer, tropical easterly trade winds bring rainfall from the Agulhas Current region to the east coast, whereas in winter temperate westerlies bring frequent rainfall to the south west. The central south coast receives rainfall throughout the year from both systems. Differences in the temperature and isotopic composition of the surface water in the source regions causes a seasonal variation of the rainfall oxygen isotopic composition ($\delta^{18}\text{O}_r$) in Mossel Bay on the south coast by about 4 ‰ between ~ -1 ‰ in February and ~ -5 ‰ in May. Changes in the contribution from the different source regions and rainfall seasonality on millennial to glacial-interglacial timescales therefore, may be recorded in the $\delta^{18}\text{O}$ of speleothem carbonate ($\delta^{18}\text{O}_c$). Due to the rainfall seasonality, there is also a strong difference in the temperature during the main growth season of vegetation which leads to the dominance of C3 vegetation in the winter rainfall region, whereas C4 grasses are more common in the summer rainfall region. In the intermediate rainfall region, both vegetation types occur in patches or alternate between seasons. Changes in the vegetation type may be recorded in the $\delta^{13}\text{C}$ of speleothems.

Composite $\delta^{18}\text{O}_c$, and $\delta^{13}\text{C}$ of speleothems from Pinnacle Point, near Mossel Bay in the intermediate rainfall region, and from Robertson Cave in the inland winter rainfall region were compared to each other and to other proxy records representative of temperature changes, variations in the $\delta^{18}\text{O}$ of sea water ($\delta^{18}\text{O}_{sw}$), runoff from the summer rainfall region and northern hemisphere millennial scale climate variations. The record, from Pinnacle Point covers the time interval between 508 and 41 ka with several hiatuses. $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}$ variations correlate to variations in Antarctic temperature and $\delta^{18}\text{O}_{sw}$ in MIS 13-12 and MIS 8-7, whereas during MIS 5-3 they are anti-correlated. The river runoff from the summer rainfall region is also correlated with $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}$ in MIS 7 and MIS 5-3, indicating that changes in the amount of rainfall in the summer rainfall region were also expressed on the central south coast.

The $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}$ record of Robertson Cave speleothems covers the interval between 535 and 203 ka and shows overall lower variability in $\delta^{18}\text{O}_c$ of ~ 2.6 ‰ and in $\delta^{13}\text{C}$ ~ 2.3 ‰. The low variability of the $\delta^{18}\text{O}_c$ and $\delta^{13}\text{C}$ variations at Robertson Cave support a climatic stability compared to other, coastal cave sites which show higher amplitude of changes, e.g.: at Pinnacle Point $\delta^{18}\text{O}_c$ values vary by ~ 3.5 ‰ and $\delta^{13}\text{C}$ by ~ 8.1 ‰. Although the variations in Robertson cave speleothems are small the $\delta^{18}\text{O}_c$ values are negatively correlated with changes of $\delta^{18}\text{O}_{sw}$ on glacial-interglacial

timescales indicating that variations on these timescales are caused by temperature variations rather than changes in rainfall seasonality. $\delta^{13}\text{C}$ values below -8 ‰ indicate that the vegetation remained constant with C3 vegetation during glacial and interglacial intervals, which was essential for the evolution of the highly diverse plant communities of the Cape Floral Region.

$\delta^{18}\text{O}$ values of paleo-cave water ($\delta^{18}\text{O}_{\text{cw}}$) were calculated for Pinnacle Point and Robertson Cave using the temperature dependent fractionation of oxygen between cave water and speleothems (Tremaine et al. 2011). The temperatures used are based on various proxy methods representative of sea surface temperatures (SST) in different ocean water masses south of South Africa as well as relative temperature changes in Antarctica. The calculated changes of $\delta^{18}\text{O}_{\text{cw}}$ relative to the average interglacial value, $\delta^{18}\text{O}_{\text{cw-rel}}$, is similar independent of the SST record used for the calculations. The local cave water $\delta^{18}\text{O}$, $\delta^{18}\text{O}_{\text{cw-local}}$, was calculated after correcting temperature records for the difference between the present-day temperature at the cave and the sediment core site/Antarctica. At Robertson Cave, values of $\delta^{18}\text{O}_{\text{cw-rel}}$ above the interglacial average occur only during peak interglacials, whereas during glacials, values usually are below the interglacial average. The $\delta^{18}\text{O}_{\text{cw-local}}$ values based on SST records representative of cold water masses in the South Atlantic show similar glacial-interglacial variations as the $\delta^{18}\text{O}_{\text{cw-rel}}$, thus supporting the strong influence of winter rainfall at the site. The low and constant values of $\delta^{13}\text{C}$ also support the dominance of winter rainfall and climatic stability at this cave site. At Pinnacle Point, variations of $\delta^{18}\text{O}_{\text{cw-rel}}$ above and below the interglacial average are most likely due to changes in the sources of rainfall and seasonality. Calculations of $\delta^{18}\text{O}_{\text{cw-local}}$ using SST records representing the warm waters of the Agulhas Current show a similar pattern to the $\delta^{18}\text{O}_{\text{cw-rel}}$ and thus support the strong influence of the Agulhas Current on the coastal climate. The strong variations in rainfall seasonality at Pinnacle Point are reflected in the strong changes of $\delta^{13}\text{C}$ related to changes in the abundances of C3 and C4 vegetation.

Tremaine, D. M., Froelich, P. N. and Wang, Y. (2011). *Speleothem calcite farmed in situ: Modern calibration of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ paleoclimate proxies in a continuously-monitored natural cave system*. *Geochimica et Cosmochimica Acta* **75**: 4929 - 4950.

A 3000 YEAR-LONG ANNUALLY RESOLVED RECORD OF PRECIPITATION ON THE SHILLONG PLATEAU, NE INDIA: EVIDENCE FOR DROUGHT AND FLOOD EVENTS AND IMPLICATIONS FOR REGIONAL MONSOON INTENSITY

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Monsoon behaviour is linked to atmospheric circulation between the equatorial oceans and higher latitudes by teleconnections that are not well understood back in time. Whilst millennial-scale records reveal first order relationships between monsoon intensity, solar forcing and orbital dynamics, far less is known about decadal-scale behaviour that impacts more directly on the lives of those living in monsoon regions. Oxygen and carbon stable isotope ratios in stalagmites are widely used to construct climate proxy records, and high resolution, annually resolved speleothem proxy records provide a very detailed record of water balance in the karst environment that, with knowledge of the local cave processes obtained through monitoring, can be linked to the local intensity of precipitation during the monsoon.

Here we report an annually resolved reconstruction of precipitation dynamics in a 600 mm long speleothem (UMS10) from Krem Umsynrang cave, near Jowai on the Shillong Plateau, NE India. The local climate has a limited 10°C range in temperature and strongly seasonal rainfall with intense monsoon rain falling between June and September. The cave environment was monitored since 2006 and these data are augmented with daily rainfall data from Shillong providing a detailed record of the isotopic evolution of the summer monsoon rains.

UMS10 was taken from the upper level of the cave, which is characterised by a small seasonal variation in temperature and year round relatively low pCO₂. We anticipate that cave ventilation remains high throughout the year, hence water balance is expected to be the dominant driver of degassing and calcite precipitation. UMS10 exhibits intervals of regularly paired laminations of ca. 300 µm thickness, consisting of alternating transparent (dark) and pale macroporous calcite. The regularity of these pairs, coupled with the strong climatic seasonality, suggests that these are annual layers reflecting changing drip-rates and hence local effective precipitation. We also observe 'dark bands' formed of dense clear calcite where the annual laminations are absent. These may represent periods of slower growth during severe drought.

A preliminary age model has been constructed using both 10 U-Th dates and laminae counting. UMS10 spans over 3000 years, with modern growth at the tip and the base dated at 3.012±0.030 ka with no evidence of major hiatuses. An additional set of samples are processed to further constrain the ages of the dark bands. Carbon and oxygen isotopes have been analysed at 1 mm resolution along the growth axis; selected traverses across regular laminated fabrics and dark bands have been

micromilled for analysis of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ at 0.1 mm resolution, accompanied by trace element analysis by laser ablation. The oxygen isotope record shows detailed inter- and intra-decadal variability but no long-term trend across the 3000-year record. At seasonal resolution the paired laminae show regular cycles in $\delta^{13}\text{C}$ interpreted as seasonal changes in degassing rates. These changes are driven by high drip rate during the wet season (summer) leading to lower $\delta^{13}\text{C}$ values, and greater degassing during low drip rates resulting in elevated $\delta^{13}\text{C}$ values in the stalagmite calcite. Strontium data corroborate this interpretation, as elevated strontium is present in the pale calcite part on each paired laminae.

The record also preserves sharp jumps representing higher or lower than normal $\delta^{18}\text{O}$ as single points at the 1mm scale, representing 3-5 year periods of growth. These are repeatable and often concurrent with changes in calcite fabric and may be consistent with more extreme periods (wetter and drier) in monsoon intensity. Preliminary high resolution isotope profiles across dark bands show that seasonal cyclicity weakens or disappears entirely and the interval is characterised by rising $\delta^{13}\text{C}$. It falls to the baseline value as normal annually laminated growth resumes. This is consistent with longer period of reduced effective infiltration related to weakening of the monsoon.

Daily rainfall data from Shillong confirms the systematic change in $\delta^{18}\text{O}$ through the course of the monsoon, whereby precipitation becomes isotopically lighter towards the end of the season (Breitenbach et al. 2012). Back trajectory and multivariate analysis of these data will allow identification of the changing source regions of monsoon rainfall evolving through the season and an improved climate-transfer function to interpret the UMS10 record. The 3000 year, annually resolved record from Krem Umsynrang, allied with cave monitoring and rain event isotope data provide a unique new yardstick for constraining the timing and duration of monsoon weakening and links to ENSO and the IOD.

MULU MYSTERY: INVESTIGATING CONSISTENT U-234 DEPLETION IN TROPICAL NORTHERN BORNEO STALAGMITES

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The depleted or near-secular equilibrium $^{234}\text{U}/^{238}\text{U}$ activity ratios measured in every stalagmite sample collected from tropical northern Borneo caves (4°N, 115°E) is a puzzling observation. Uranium disequilibrium in karst waters may be caused by two different mechanisms, either (i) alpha recoil of ^{234}U directly into solution, or (ii) preferential leaching of ^{234}U from crystal lattice sites disrupted by alpha decay. Both mechanisms input additional ^{234}U into the karst waters, increasing their ratios and leaving a depleted weathered limestone. However, Gunung Mulu National Park host rock samples are enriched in ^{234}U , while stalagmite $^{234}\text{U}/^{238}\text{U}$ activity ratios range from 0.35 to 1.04. This observation leads to the “Mulu limestone conundrum” of apparent enriched overlying bedrock and depleted stalagmite-forming waters.

The missing U-234 in stalagmites requires specific weathering scenarios. Our proposed theory is a karst system composed of mixed previously weathered limestone (depleted) and secondary precipitated calcite (enriched), in which the collected stalagmites form from dripwaters in contact with the weathered limestone and not the secondary calcite precipitate. We construct a simple numerical model that incorporates uranium isotopes and magnesium and strontium concentrations, elements related to prior calcite precipitation, to investigate uranium isotope transport through a karst system with varying residence times. We measure a suite of trace elements in bedrock, dripwaters, and stalagmites to help understand the degree that prior precipitation affects U-series activity ratios. We also measure U-isotopes in water exiting the cave in underground rivers and streams and samples collected downriver from the Mulu limestone to resolve the complete karst hydrological system.

IRANIAN STALAGMITES: A PROXY FOR PAST CLIMATE CHANGE IN THE DESERT?

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Important developments in human society in the arid climate of Iran may be related to substantial regional climate variability, though past hydrologic and temperature change in Iran is poorly constrained. Iran is situated today at the transition between diverse climate systems, with the arid Arabian desert to the south and the humid eastern Mediterranean to the west. Robust paleoclimate records could provide insight into any past variability in the regional extent and influence of these climate systems. A sediment record from Lake Zaribar in western Iran uses stable analysis of calcareous sediments with pollen and microfossil analyses to propose changes in seasonality and climate from the last glacial maximum through the Holocene (1). Other studies from eastern Iran use evidence of past alluvial fan abandonment, river terracing, and lake deposition to investigate environmental changes during the Holocene (eg. 2). The existing climate records are sparse, and lack the resolution and chronological control to constrain past hydrologic or temperature variations. Decorated caves span a large portion of the arid and semi-arid regions of Iran, however, providing an opportunity to investigate speleothems as a potential Iranian climate recorder.

Here we present our preliminary analysis of the speleothem samples collected from eight caves in the mountains and hills of northern Iran crossing ~1000km (34°N to 36°N, 48°E to 59°E). Two caves are located less than 50 km north of the Teheran GNIP Station (Global Network of Isotopes in Precipitation), which has collected and analyzed rainwater samples from 1961-1976, 1979-1981, 1985-1987, and 2000-2004. U-series analyses show top/bottom stalagmite ages range from 40 kybp to 377 kybp, and we have recently collected samples that likely formed during the Holocene. Stable isotope and trace metal analysis will be performed on the best candidate samples. If applicable, water isotope-enabled models may be used to interpret oxygen isotope variability.

1. Stevens et al., *Holocene* **11**, 747 (2001).
2. Walker, R.T. and Fattahi, M., *QSR* **30**, 1256 (2011).

HOLOCENE CLIMATE VARIABILITY OF THE PERIADRIATIC AREA THROUGH THE STUDY OF CARBONATE SPELEOTHEMS

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Situated at the border between subtropical African atmospheric circulation and continental European circulation, the Mediterranean area is particularly sensitive to climate changes. Considering the concentration of population settled in this area it is of great importance to understand how different regions can respond to changes in present-day climate conditions. The study of past climate variability at a regional scale can give important information about future climate evolution in these regions.

Although the Holocene climate variability of the Mediterranean area has been intensively investigated, very few studies have focused on the Periadriatic region, especially those using speleothems as source of palaeoenvironmental information. In fact, considering the eastern side of the Italian peninsula and the Adriatic side of the Balkan region, only stalagmites from Grotta Savi (Friuli Venezia Giulia; Frisia et al. 2005; Belli et al. 2013) and submerged speleothems of the Croatian coast (Surić et al. 2005) have been investigated for Holocene climate reconstruction. In addition, several studies from lake sediments have been carried out in Apulia, Macedonia, Albania and Montenegro which cover the Holocene only partially.

The aim of this PhD project is to investigate Holocene climate fluctuations at a regional scale through the study of speleothems coming from various caves of the Periadriatic region. Particular attention will be paid to the analysis of contrasting patterns registered in Northern and Southern regions of the Adriatic area.

The team working in this project involves experts in karst, paleoclimatology and limnology from the Universities of Bologna, of Savoie and of Melbourne. We are collecting speleothems from caves in Apulia, Emilia Romagna, Slovenia and Bosnia for radiometric dating and isotopic, mineralogical and geochemical analyses. The time constrained proxy-records obtained will be compared with records coming from other paleoclimatic archives, in particular lake sediments, in order to improve the precision and the understanding of local/regional climate fluctuations over the Holocene on the Adriatic area.

STABLE OXYGEN ISOTOPE COMPOSITION OF RAINFALL IN ITALY

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Longinelli and Selmo (2003) investigated the stable oxygen isotope composition of rainfall throughout Italy over ten years ago. They carried out a monthly cumulative sampling in several Italian locations in order to identify the possible presence of a gradient in the isotopic composition of precipitation. They highlighted the local influence of morphology on the isotopic composition rather than latitude.

Considering the importance of a detailed knowledge of present-day stable isotope composition of rainfall for paleoclimatic reconstructions, on the base of the study of Longinello and Selmo (2003), we are developing a project on the stable oxygen isotope composition of rainfall in Italy. A rainwater sampling campaign started in January 2014 and will go on till the beginning of 2015 (with possible extension) in order to sample rainfall during the hydrological year. On the contrary to the work of Longinelli and Selmo, we are focusing our attention on single rainfall events which are being sampled thanks to collaborators coming from 14 Italian regions covering almost all the Italian peninsula and main islands.

Rainwater is sampled using plastic bottles pre-filled with a vaseline oil layer to prevent evaporation and left in the field only during precipitation. The water samples are collected in 4 ml glass vials using a syringe paying attention not to leave air bubbles inside. The vials are stored at cold temperatures before spectroscopic analysis planned at the university of Melbourne, Department of Resource Management and Geography.

The aim of this project is to give a better picture of the stable oxygen isotope composition of rainfall in Italy and to identify any pattern related to the precipitation origin of single events. Special attention will be given to the possible isotopic composition differences of rainfalls of the same atmospheric perturbation sampled in different locations, as well as seasonal and intra-seasonal variations in the same location. The data set obtained may be used to compare stable oxygen isotope data related to the atmospheric circulation in the past, in particular data coming from speleothem records. The calibration of the cave site, including modern meteorological patterns, is in fact essential for an appropriate interpretation of paleoclimate data considering the local sensitiveness of each karst system. The results will improve the understanding on the impact of single rainfall events on the isotopic composition of precipitation, supporting existing and future researches based in Italian carbonate and gypsum karst systems.

PALEOCLIMATE AND SPELEOGENESIS : A CONCEPTUAL MODEL FROM DONNEHUE'S CAVE, MIDWESTERN USA

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A major obstacle in the overall understanding of continental climatic fluctuations in the Midwestern USA is the scarcity of the well-dated paleoclimate records. In this investigation we provide additional data from the Midwestern USA and put forth a conceptual model of the development of a cave in an area proximal to past glacial margins.

We focus on Donnehue's Cave, which is located in Midwestern USA in the state of Indiana, within a few kilometers of both the Illinois and Wisconsin glacial maxima. Its location is optimal for paleoclimate studies---most surface records from this area have been either bulldozed by the advancing glaciers or otherwise disturbed by the melt waters during the interglacial periods. The cave has two levels: a lower passage and an upper passage. Using U-Th dating of 12 speleothems from the two levels and OSL dating of one sediment sample, we formulate a conceptual model of cave formation extending to 400,000 years before present (BP).

We dated speleothems (11 stalagmites and 1 flowstone) by MC-ICP-MS using the U-series (²³⁴U/²³⁰Th) technique that covers a time span of several hundred to ca. 500,000 yrs BP. We collected all the speleothems from poorly ventilated areas of the two levels of the cave. We find that the ages of the speleothems from the lower passage (ca. 55,800 to 440 yrs BP) are significantly younger than those from the upper passage (ca. 400,000 to 91,800 yrs BP). One sample of sediment (DC 35), collected from the lower passage and dated by OSL, is 140,000 +/- 9,490 yrs BP.

The Donnehue's speleothem ages indicate that the temperatures inside the cave have been above freezing even during the glacial episodes, allowing speleothem precipitation in between ca. 400,000 to 91,800 yrs BP in the upper passage of the cave. Based on ages determined for the sediment sample (DC 35) and for the speleothems from the upper and the lower passage, we formulate a conceptual model for Donnehue's Cave development. The salient features of this model are: 1) the upper passage formed first and its minimum age, as inferred by the oldest stalagmite age, is ca. 400,000 yrs BP; 2) the initiation of the second passage followed several hundreds of thousands of years later, with a minimum age of 140,000 yrs BP constrained by sample DC 35; this age correlates with the end of Illinois glacial episode, suggesting a strong influence of the glacial melt waters on the cave development.

LOCAL RESPONSE TO GLOBAL WARM PULSES OVER THE LAST 250,000 YEARS: THE CASE OF CENTRAL ITALIAN GYPSUM KARST

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The paleoclimate significance of gypsum karst is still poorly explored in comparison with limestone karst, mainly because of the worldwide less extent of gypsum bedrock. However, the central Italian Spipola-Acquafredda (12 km tunnels) and Monte Tondo (11 km tunnels) karst systems, among the world's largest epigenic gypsum caves, give the possibility to fill this gap in literature.

Two striking features characterize these systems:

1) the paucity of carbonate speleothems; 2) the age/growth periods of the speleothems.

In fact stalactites/stalagmites are very rare, while flowstones cover sporadically subhorizontal to subvertical surfaces. The lack of decoration could derive from primary unfavourable conditions for the deposition of speleothems or secondary erosion-breakdown related to the highly dynamic gypsum environment. On the other hand the age of 6 generations of flowstones sampled in the area of study fit with relative warm peaks over the last 240,000 years. Furthermore, the growth is not extended in time but lasted for a few thousand years, stopping in correspondence with relatively cold periods. These speleothems correlate with the MIS 7 and MIS 5e peaks, Greenland Interstadials 24, 22 and 20 and Holocene, also in accordance with sapropel events S5, S3 and S1 and precursory sapropel events S4 and S3.

The relative scarce number of speleothems vs the limited duration of precisely constrained warm periods raise the question if the deposition of carbonate speleothems in Mediterranean gypsum karst directly responded to regional upper Quaternary climate oscillations. In the central Italian peninsula the sensitiveness of the speleothemic production to global climate oscillation is demonstrated by the absence of carbonate deposition during cold periods, in an area where ice-sheets were absent during the last two glacial peaks. Even very short cold pulsations hampered the formation of speleothems during the DO cycles, meaning that the karst system reaction was synchronized to external climate forcing. The formation of the speleothems seems regulated by a strong climatic threshold, with the deposition of CaCO₃ triggered only during relative warm/wet stages.

The vegetation probably played an important role in this process, causing the production of the right amount of CO₂ in the soil, and so in the percolating water, necessary for the deposition of these carbonate speleothems. In this perspective reduction in vegetation amount or soil activity would have taken place during warm/cold climate variation, in time spans of a few hundreds of years. Furthermore

the characteristics of rainfall have been important too, considering that the speleothems grew during extraordinary wet periods that also allowed the deposition of sapropel layers in the Mediterranean basin.

At the moment there are not enough data to propose a more detailed explanation on carbonate speleothem deposition in gypsum caves and speleogenesis in the study area, but an ongoing exploration of the cave systems is aimed to find new flowstone samples in order to obtain further reliable ages. The validation of this model will give the opportunity to anchor the Mediterranean climate pulsation to the global well constrained climate chronology, giving new emphasis on the study of gypsum karst that still remains poorly understood in comparison to limestone karst.

DECIPHERING INTRA-DECADAL CLIMATE VARIATIONS IN THE CENTRAL MEDITERRANEAN AREA DURING THE LAST INTERGLACIAL USING SPELEOTHEMS

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Some aspects of the climate of the last Interglacial (LIG) still appear poorly understood, such as the short-scale Rainfall vs Temperature variability. The North Atlantic Oscillation (NAO) is the main atmospheric pressure system controlling the intensity and direction of westerly winds, and distribution of moisture and heat across the Mediterranean area. NAO has different cycles of variation, from 2 to 130 years. Identifying the intra-decadal climate variation during the LIG in the central Mediterranean and evaluating the presence of NAO-like fluctuations are among the main aims of my PhD study.

Speleothems offer a great opportunity to investigate the hydrogeological conditions of the karst environment from which they derive. Oxygen and Carbon stable isotopes, trace elements and fluid inclusions, coupled with the mineralogical variation of the carbonate layers, are in fact very sensitive to the chemical/physical characteristics of cave seepage water. Furthermore, U-series decay dating allows a considerable high accuracy and precision at least for the last 500,000 years.

A ~65 cm thick flowstone (RTf) was sampled in the Re Tiberio gypsum karst system (Emilia Romagna, North Italy). 5000±250 well preserved layers form this speleothem, showing a promising attitude for high temporal-spatial resolution analysis. Thirteen preliminary U-Th dating precisely constrain RTf to the peak of MIS5e, displaying a growth history from 131,102±1,872 to 125,169±1,229 ky BP, probably indicating the annual origin of carbonate bands.

Spectrometric analyses for stable isotopes reveal that $\delta^{18}\text{O}$ varies from -5.42‰ to -7.52‰ and $\delta^{13}\text{C}$ from -5.76‰ to -11.15‰ referring to VPDB international standard. Despite the moderate shift in the absolute value, as expected considering the general stability of the LIG, the stable isotopes curve demonstrates a remarkable high frequency variation in the order of $\pm 0.6\text{‰}$. Ten laminae, chosen for Hendy test, show the calcite was deposited under equilibrium condition, even if this method is still controversial.

Trace elements first results report a positive correlation of Sr-Ba and Cu-Zn-P-Y, and inverse correlation of Sr/Ba-Mg. High Sr (2000-5000 ppm) and P (100-300 ppm) contents derive from the evaporative gypsum context. Higher peaks in Sr and Ba and relative lower Mg peaks seems to coincide with thicker-darker layers, demonstrating the relation between these elements and the hydrological flow during RTf formation. Analysis for fluid inclusions will establish the isotopic link between the original seepage water and $\delta^{18}\text{O}_{\text{c}}$, determining to which extent the paleo-rainfall isotopic signal has been transferred to the calcite layers.

The ongoing monitoring of the cave site will allow to understand the actual influence of NAO seasonal variation in rainfall and cave seepage water. The expected goal is to find out to which extent rainfall and cave water isotopic composition is controlled by rainfall amount. For this reason rainfall water is being collected for each precipitation event while cave infiltration water is sampled seasonally; the sampling campaign will operate for at least two hydrologic years.

The 1st year PhD preliminary results are proposed in this session.

An investigation of millennial-scale climate events in an Italian speleothem: a pilot study covering the last glacial period

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A coherent explanation for the absolute timing and underlying cause of millennial-scale climate fluctuations remains elusive. One major obstacle to resolving the mechanisms of these fluctuations is the difficulty in providing a single record of the changes that is anchored in radiometric time. Speleothems (secondary cave deposits) are ideally suited to overcome this obstacle as they preserve long, continuous records, contain multiple climate sensitive properties and can be accurately and precisely dated.

A 23-cm-long core collected from a subaqueous calcite mound in Corchia Cave, NW Italy, provides a ~continuous climatic record extending back almost 1 million years. Corchia cave is ideally suited to the study of millennial-scale climate events due to the synchrony of regional climate with that of the North Atlantic. This subaqueous speleothem thus presents an unprecedented opportunity to yield a precisely constrained record of millennial-scale climate fluctuations over the last 1 million years.

This pilot research investigates whether this subaqueous speleothem actually records evidence of millennial-scale climate events by focusing on the section representing the last glacial period. Stable oxygen isotope and trace element microanalyses have been performed to produce a palaeoclimate reconstruction. Microanalyses are essential given the extremely slow growth rate of this speleothem. High-resolution uranium-thorium dating (Drysdale et al. 2012) has been undertaken to provide age constraints. The resulting time series will be compared to the Greenland ice-core record to determine if the Corchia Cave speleothem preserves evidence of the same millennial-scale climate fluctuations that are recorded in Greenland ice. If this is the case, it should pave the way for assembling a unique, 1-million-year record of millennial-scale climate change.

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SEEKING CYCLONIC ACTIVITY RECORDS IN SPELEOTHEMS FROM CENTRAL PACIFIC : PRELIMINARY SAMPLE SCREENING

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The western half of the Tropical Pacific is the hot spot of cyclogenesis on Earth, with an average of 10 cyclones impacting the SW Pacific region per year. During El Niño years, cyclone activity migrates eastwards and affects the islands and populations of the central Pacific. To evaluate the spatial and temporal evolution of this hazard in the context of global climate change, it is necessary to improve our knowledge about its natural variations over longer time-scales and at high resolution.

Speleothems can register, under given hydrological and geomorphological conditions, cyclonic events as abrupt variations of their oxygen isotope ratios or as mud layers. Focusing on the Australes archipelago, a frequently hit region of southern Polynesia, this exploratory project aims at: 1) identifying speleothems capable of recording cyclones; and 2) reconstructing a chronicle of cyclonic activity over the past few millennia.

We found caves hosting speleothems on the uplifted atoll of Rurutu. The island is located in the eastern part of the South Pacific Convergence Zone (SPCZ), the activity and position of which are essentially controlled by ENSO (annual scale) and by the IPO (longer time scales). Maximal cyclone occurrence is during El Niño periods.

To evaluate the capacity of the sampled speleothems to register cyclones hitting the island, we are studying the response of the karst hydrological system to meteorological variations, and the physico-chemical conditions of calcite precipitation. We will then identify among the sampled speleothems the most suitable specimens for detailed study according to their growth period and rate.

We present here the results of this preliminary work aiming at a better understanding of the signals recorded by the speleothems and at selecting the appropriate archives for reconstructing past climate and extreme rainfall events in this area of the central Pacific.

EVALUATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR OBTAINING TRACE ELEMENT TIME-SERIES IN SPELEOTHEMS.

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The reconstruction of paleoclimate series from speleothems commonly involves large amounts of geochemical analyses performed from tiny samples. So the task requires of analytical techniques capable of achieving a good balance between: 1) the volume of material analysed (and hence the spatial scale of analysis), 2) the precision and accuracy of the results, and 3) the speed and cost of the analytical process. Unfortunately, when working with speleothem trace elements, that balance is not always conveniently reached.

In the task of looking for new techniques for trace element analyses in speleothems, the potential of Laser-Induced Breakdown Spectroscopy (LIBS) has been investigated. Despite its potential and advantages, (low cost, non-destructive, rapid analysis, essentially no sample preparation...) LIBS has been only sporadically used in speleothems (e.g., Vadillo et al. 1998, Ma et al. 2010, Galbacs et al, 2011, Forte et al., 2012) with promising but still very preliminary results. The technique provides semi-quantitative elemental measurements with micrometric spatial resolution. Main advantage is direct sampling by laser ablation under atmospheric pressure and in situ analysis of the plasma. The analytical technique is performed by laser beam focusing over a sample. The great amount of energy deposited in a small area (microns) is able to vaporize, atomize and ionize the sample producing a high-temperature plasma. The spectral analysis of such plasma gives complete information about the atomic composition of the sample in the spot area.

This work presents an evaluation of the performance of LIBS as analyser to construct accurate trace element time-series based in speleothems. For this a series of tests performed on polished sections of a stalagmite were made. The chosen stalagmite, retrieved from Kaite Cave (Northern Spain), consists of calcite and shows a well-defined micrometric annual lamination.

The steps followed to perform the evaluation refer to two aspects: adaptation of the appropriate sample strategy for the analysis and characterization of precision of the technique in terms of repeatability under controlled and stable working conditions (fixed plasma temperature and laser pulse length). The selected elemental ratios for the study were Mg/Ca and Sr/Ca, which are among the most frequently used ones for paleohydrological/paleoclimate studies.

To choose the adequate sampling method a series of measurements were made on the polished section of the stalagmite in order to check the homogeneity of the sample in terms of uniformity of results along a single (annual) growth layer. The test was based in twelve analyses that revealed a remarkably lateral continuity in both Mg/Ca and Sr/Ca intensity ratios. After the measurements, the laser induced damage was determined by optical microscopy to assess both the spatial distribution of the spots along the growth layer and their morphology and diameter. The spot area shows an ellipsoidal shape crater around 300µm of average diameter, lower than the thickness of the growth layer (average 450 µm wide).

The analytical repeatability was assessed by measuring Mg/Ca and Sr/Ca intensity ratios of 140 single points along two transects separated 3mm, parallel to the growth axis of the stalagmite, showing a good match between both transect. The average pulse length was 4ns and the stability of the signal was assessed from repetitive measurements on the same spot area (20 laser shots at each sample position). The plasma temperature was monitored by the ratio of emission intensities of two lines of calcium: Ca (I) at 430.77 nm and Ca (II) at 318.13 nm (ICa430.77/ICa318.13), showing that the plasma temperature is kept nearly constant throughout the experiment LIBS, minimizing the effect matrix and providing more accurate results.

Results support LIBS as a suitable system for trace elements analysis on speleothems. Main advantages of the technique are: relatively low operational costs and less maintenance and man-power compared to other techniques. The technique demonstrates good precision and is able of simultaneous detection of several species.

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CHANGES IN TEMPERATURE AND PRECIPITATION SEASONALITY DURING THE 8.2 KY EVENT IN CENTRAL EUROPE AS RECORDED BY COMBINED H-C-O ISOTOPE COMPOSITIONS IN SPELEOTHEM CALCITE AND INCLUSION-HOSTED WATER

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Within the Holocene several short term climate anomalies have been recognised, among which the 8.2 ky event was the most pronounced. Here we present new isotopic data of calcite and inclusion hosted water of stalagmite from Béke Cave (NE Hungary, Carpathian Basin) that covers the time interval from 10500 to 4500 yr BP. The oxygen isotopic composition of the stalagmite calcite recorded the 8.2 ky event by elevated $\delta^{18}\text{O}$ values between 8000 and 8400 yr BP, while the carbon isotopic compositions do not show significant changes during this period.

Beside the C and O isotope compositions of the speleothem calcite, hydrogen and oxygen isotopic compositions of the inclusion hosted water of the studied stalagmite have been determined by using vacuum crushing and cavity ring-down spectroscopy. The relatively high water content allowed us to achieve ~5 mm sampling (and hence ~ 50 year age) resolution. Both hydrogen and oxygen isotopic compositions of inclusion hosted water show positive excursions around 8.2 kyr where the host calcite yielded elevated oxygen isotope compositions.

The observed positive anomalies in O isotopic compositions in both the host calcite and its fluid inclusion content is in contrast to other western European speleothems which recorded this cooling event by marked decreasing of $\delta^{18}\text{O}$ values of the calcite. The different response to this event in the Carpathian Basin might be caused by 1) decrease of the amount of winter precipitation and summer temperature resulting relatively more infiltration of summer precipitation leading to enhanced annual isotopic composition; 2) increased influence of air masses originated Mediterranean delivering precipitation with enhanced $\delta^{18}\text{O}$ values (i.e. relative decrease of Atlantic air masses that is characterised by lower $\delta^{18}\text{O}$).

Relatively drier and cooler conditions have been inferred from other paleoclimate archives in Europe for the 8.2 ky event. The dataset presented in this paper would be in agreement with these observations if the relative amount of winter precipitation decreased along with temperature drop resulting in lower evaporation rate during the warm seasons. This would increase the relative contribution of warm season precipitation – and hence elevated δD and $\delta^{18}\text{O}$ values – in the dripwater from which the stalagmite was formed. This model would be consistent with the constancy of carbon isotope composition indicating that soil activity was not affected significantly.

HYDROGEN AND OXYGEN ISOTOPIC VARIATION OF CAVE DRIP WATERS: IMPLICATIONS FOR RECENT CLIMATE AND PALECLIMATE SIGNAL IN STALAGMITE

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In order to better understand the temporal and spatial variation of stable isotope compositions in karst waters and their implications for interpreting the potential paleohydrological signal preserved in speleothems at the sites we have investigated the stable isotope compositions of drip waters within Csodabogyós cave, Keszthely Mt., Western Hungary. Within the cave five dripping sites (1.Oltár, 2.Baldachin, 3.Lián-terem, 4.Bársony-terem, 5.G-járat) in the depths of 15 to 40m were monitored from 2011. Based on the hydrogen and oxygen isotope compositions of drip water in these five sites two groups can be identified (1-group: $\delta D \approx -68$ to 64‰ and $\delta^{18}O \approx -10.0$ to -9.3‰ ; 2-group: $\delta D \approx -72$ to 69‰ and $\delta^{18}O \approx -10.6$ to -9.9‰) indicating the complexity of the infiltration process within the studied karst-system. Both groups show almost no variation of stable isotope composition during the year (i.e. no seasonal variation) despite ~ 8 - 10‰ seasonal amplitude for $\delta^{18}O$ in atmospheric precipitation at the site that was estimated by two independent methods: 1) geospatial model (Kohán and Kern 2012), using the data from the surrounding stations; 2) based on the T- $\delta^{18}O$ scaling in the precipitation obtained in Croatia (Vreca et al., 2006). Furthermore, no obvious relationship was found between the volumes of seepage water at the sites and amount of the precipitation in the area. This suggests a significant karstic reservoir above the dripping sites buffering/filtering the short-term effect of precipitation events. This is in line with the observed lack of seasonal variability of the water isotope signal in drip water. The stable oxygen isotope ranges of both groups are lower than the expected amount weighted mean value, therefore the infiltrated water seem to be skewed towards winter season. The tendency toward winter dominance is slightly more pronounced in the 2-group. Deuterium excess values for both groups ($d=10$ - 12‰ , see Dansgaard, 1964) are slightly but systematically higher than the global value suggesting influence from Mediterranean region which is generally characterized by elevated d-excess (e.g. $d=11$ - 16‰ Croatia and Slovenia, Vreca et al., 2006). In addition, stable isotope compositions of modern calcite formation have also been determined to evaluate equilibrium fractionation and select appropriate sites for paleoclimate research.

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MEDITERRANEAN INFLUENCE IN THE CARPATHIAN BASIN (CENTRAL EUROPE) AT THE BEGINNING OF THE LAST INTERGLACIAL REFLECTED BY COMBINED H AND O ISOTOPE COMPOSITIONS OF INCLUSION-HOSTED WATER IN STALAGMITES

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Inclusion-hosted water may provide direct information on the isotopic composition of the dripwater from which cave deposits formed. The water content of stalagmites is generally in the thousand ppm range that makes the stable isotope analyses of the H₂O possible by different techniques. In the last decades stable H isotope analyses were usually conducted by mass spectrometric measurements, O isotope compositions were seldom determined due to the rather tedious and sophisticated methods required. Laser-based spectroscopic analyses of water δD and $\delta^{18}\text{O}$ values, however, became routine in the last decade and the number of applications on fluid inclusion-hosted H₂O measurements is growing nowadays. We have developed a technique to analyse δD and $\delta^{18}\text{O}$ values in inclusion-hosted waters using a Los Gatos Ltd. laser spectrometer (LWIA-24d) and a preparation line (Czuppon et al., 2014). The method applied here is slightly modified after Czuppon et al. (2014) to conduct vacuum crushing in helium flow to reduce the possibility of H₂O-CaCO₃ oxygen isotope exchange during the extraction. The accuracies of δD and $\delta^{18}\text{O}$ data were tested by analysing recently forming stalagmites where dripwater compositions are known and calcite samples whose isotopic compositions had been determined by independent mass spectrometric measurements.

The technique was applied to study inclusion water compositions in a double stalagmite that covers a large part of the period of the last interglacial. The stalagmite actually comprises two columns that grow beside each other and show strikingly similar internal textures. U/Th age dating revealed that the stalagmite formation started at about 127.4 ky BP and ended at about 110.1 ky BP with a hiatus. The studied stalagmite section is about 23.5 cm long and were dated by 7 U/Th age dates, all in stratigraphic order. An age-depth model was established using the StalAge program (Scholz and Hoffman, 2011). The stalagmite columns were correlated using textural characteristics and analysed for C and O isotope compositions of the calcite as well as H and O isotope compositions of inclusion-hosted water. The isotope data are supplemented with trace element compositions determined using laser-ablation ICP-MS.

At the beginning of the stalagmite formation the infiltrating groundwater flushed the karstic water reservoir and dissolved the material that precipitated on the walls of cracks during the dry glacial period preceding the last interglacial. This flushing and dissolution process is reflected by the high trace element concentrations

at the beginning and subsequent decrease. The calcite C and O isotope compositions decrease and increase, respectively, with time, indicating development of warm and humid climate at about 120 ky, then drying and warming at about 116-118 ky, and a strong cooling after 116 ky. This scheme is similar to the climate evolution suggested by other records. H and O isotope compositions of inclusion-hosted water, however, indicate additional effects. The 120 ky climate optimum and the cooling at 116 ky is clearly reflected by both records, but between 127 and 124 ky – when the calcite $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show fluctuations – both a δDw and $\delta^{18}\text{Ow}$ values show strong negative excursions. The negative shifts can be well correlated with Mediterranean records that indicated enhanced rainfall influence that is not observed in western European records. These data may point to the change in meteorological circulation regime during the last interglacial with stronger Mediterranean influence in the early part and a domination of Atlantic moisture transport to the Carpathian Basin in the middle to the late period.

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CAVE-HOSTED TRAVERTINE DEPOSIT AS A POTENTIAL SUBJECT FOR PALEOCLIMATE STUDIES (BÉKE CAVE, NE-HUNGARY)

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Travertine deposits are frequent in the caves of the Aggtelek Karst (together with the Slovak Karst is on the World Heritage list). The travertines are formed as dams and terraces in underground creeks as well as massive deposits at cave springs. Both types were studied whether they can be used for paleoclimate investigations. The white travertine deposits formed at underground springs seemed to be clean enough to continue the investigations. Beside the disadvantage of higher risk of detrital Th contamination, the advantage of these deposits is that they can be analysed along several sections and can be drilled at several locations to get a better insight of carbonate formation processes and to have the possibility of re-sampling if needed. One travertine deposit of the Béke Cave was studied in detail whose results will be presented here. Stable C and O isotope compositions and trace element concentrations were measured along several transects on the surface of the travertine in order to determine if the carbonate show signs of kinetic fractionation. Two drill cores were taken at two different parts of the deposit. Trace element and isotope compositions suggest that these parts of the travertine deposit were precipitated from waters originating from different pathways. The core showing negligible kinetic fractionation was studied in detail. The ~40 cm long core was dated by U-Th dating and lamina counting. Four U-Th dates were used for estimating the deposition age interval (recent to 4 ky BP). Lamina counting was possible in ~30 cm, yielding 4576 laminae in 281.7 mm. Optical microscopic analyses revealed that the macroscopically well visible laminae are actually rhythmically deposited detrital layers that – together with the U-Th age estimation – may be related to the 11 years solar cycling. Microscopic texture types (columnar calcite in water clear layers, straight or wavy laminae, or dendritic calcite) show a good correspondence with lamina thickness. Lamina thickness is also related to $\delta^{13}\text{C}$ values with more negative $\delta^{13}\text{C}$ data in sections with reduced lamina thickness. This relationship points to variations in carbonate saturation in the water that may depend on rainfall amount. Comparing the C and O isotope composition records of the core with independent stalagmite records from the region, strikingly good correspondences are revealed that suggests that the selected travertine drill core data may potentially be useful as a paleoclimate proxy record with the advantage of ample material that is easily accessible and can be re-sampled if needed.

IS GLOBAL WARMING AFFECTING CAVE TEMPERATURES? IMPORTANCE FOR SPELEOTHEM PALEOCLIMATE RECORDS

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It is generally accepted that, in most cases, deep sectors of caves have a relatively stable temperature similar to the mean annual temperature outside the cave. Therefore, if there is a link between both, surface and cave atmosphere temperatures, thermal changes at the surface should be recorded underground. However, the processes and response times of the heat transfer are still poorly understood. The period of global warming experienced during the last decades represent an ideal scenario to evaluate the sensitivity of caves to external temperature and the delay in the transfer of the thermal signal.

Here we present a 5 year temperature monitoring study of a case study, Postojna Cave, located in Slovenia. This study includes the characterization of the main controls affecting the cave temperature variability in the studied hall and their quantification. A thermal model is implemented for the studied site, where the signal of external atmosphere temperature is transferred underground and the reliability of the model validated with the measured data.

The study site was selected for its ideal conditions to evaluate the transfer of external temperature underground. The region has experienced an atmosphere temperature increase of >1.5 °C since the onset of the 1980s and the vegetation cover over the cave has been maintained for >50 years, not affecting the coupling between atmosphere and ground temperatures. Additionally, the studied cave chamber has a limited advection dynamic allowing the conduction of heat from the ground temperature above the study site to be transferred to the cave by conduction, dominating the low-frequency cave atmosphere temperature.

The atmosphere of the studied gallery presents advection processes caused by air density and pressure changes, which provides high frequency and seasonal perturbations. At the depth of the studied gallery (37 m), the drip waters are in equilibrium with the cave bedrock and do not affect cave atmosphere temperature variability. With a limited advection, the changes in temperature seem to be controlled by cave walls temperature. We implemented a thermal conduction model

for this chamber that transfers the surface atmosphere temperature of the last decades from the surface to the cave. The results show that the global warming is already being recorded in this particular chamber, although with a delay of 20-25 years. The delay of the thermal signal for a particular depth depends on the duration of the period, and therefore, thermal anomalies with shorter periods have a faster response time in the cave. However, due to the attenuation of the thermal amplitude, periods <5 years are not recorded with a precision of 0.001 °C.

In those caves having their atmosphere temperature dominated by thermal conduction (most of caves' deep sectors lacking running streams, fast infiltration drainage or very dynamic air advection), the depth of the cave is a critical parameter to determine whether a cave has already recorded the onset of global warming.

As temperature affects most of the proxies studied in speleothems, the understood of cave temperature responses to surface atmosphere temperature changes becomes of critical importance since can introduce a significant noise to the interpretation of our proxies or become one of the main controls of the variability of some proxies. The substantial delay between any major thermal change over the cave and its record underground in speleothems is potentially significant for long-term thermal changes. This delay would depend mostly on the depth of the cave, and may introduce a bias in the identification of very precise onset or demise of events recorded in high resolved chronologies. Finally, the changes in cave temperature of one hall in relation to the rest of the cave might be responsible for drastic ventilation dynamics being responsible of changes in growth rate, seasonal deposition and even the occurrence of hiatuses in speleothem records.

Given the importance of cave temperature dynamic to understand the detail processes affecting speleothem records, we recommend when presenting a speleothem record, to provide as much information as possible regarding the thermal dynamic of the cave, and specially, to report at least a rough estimation of the depth of the cave, a parameter of critical importance that is frequently omitted from cave environment characterization when reporting speleothem records.

MODERN CALIBRATION OF A SPELEOTHEM OXYGEN ISOTOPE RECORD ANALYZED BY SIMS IN POSTOJNA CAVE (SLOVENIA)

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The interpretation of proxy records from speleothems is generally based on numerous assumptions. The calibration of the recent portion of the speleothem records with instrumental records of climate or other environmental variables minimizes these assumptions and refines their proxy interpretations. Here we present the calibration of the oxygen isotope record of a stalagmite top from Postojna Cave (Slovenia). The top 500 micrometers of the stalagmite PO2 were analyzed by SIMS (Secondary ion mass spectrometry). We provided a continuous $\delta^{18}\text{O}$ record with a spatial resolution of 14 micrometers. To evaluate the analytical reliability, the record was triplicated. Confocal and ultraviolet microscope imaging were used to characterize the speleothem banding and to locate the analytical spots within the bands. The monitoring of the cave hall microclimate where PO2 was collected and its drip water isotope values together with its drip rate have been also studied in order to understand the nature of the banding.

We found an outstanding similarity between the recorded oxygen isotope speleothem signal and the weighed mean annual record of oxygen isotopes in precipitation at the nearby IAEA station of Ljubljana. The speleothem is able to capture the same amplitude as the mean annual weighed isotope values of precipitation, suggesting that the residence time is close to one year. Although the speleothem is laminated, we do not find a significant intra-annual seasonality in the speleothem record. This is in agreement with the drip water oxygen isotope monitoring study carried out in this site. Thus, the drip water isotope record shows an inter-annual variability with no clear seasonality. This lack of seasonal pattern in the calcite isotope record is recorded not just during the calibrated period, but also in lower sectors of the speleothem, with slightly different laminated patterns and growth rates.

The high resolution study of the oxygen isotope signal at the top of PO2 stalagmite demonstrates that the isotope signal of this speleothem is a reliable record of the oxygen isotope composition of precipitation in the region, and that cave processes do not modify the variability of the averaged oxygen isotope composition in precipitation. Finally, we can conclude that due to the residence time of the water at the aquifer, the speleothem signal does not represent a seasonally biased record of oxygen isotope values in precipitation.

ASSESSING CHRONOLOGIES FOR DRYLAND SPELEOTHEMS IN THE NORTHEASTERN FLINDERS RANGES

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Late Quaternary palaeo-climates and environments of Central Australia are mostly constrained from the interpretation of geomorphic archives such as lake sediments, beach ridges, dunes, and fluvial or alluvial deposits. This is a consequence of the scarcity of high-resolution proxy records in this region. While these approaches provide valuable hints on the longer-term and landscape-scale impact of past climatic changes on Central Australian landscapes, their use as direct and quantified measures for the type and magnitude of precipitation changes is not straightforward. To improve our understanding of the complex interactions between climate, environment and geomorphic processes in drylands, additional archives for the detection of precipitation changes are required.

In this context, recent studies in the arid to semi-arid northern Flinders Ranges suggest that dryland speleothems are frequent features in small caves and rockshelters, and may have significant potential for recording intervals of increased regional-scale humidity (Gliganic et al., 2014; Quigley et al., 2010). Quigley et al. (2010) placed the onset of aridity in the Flinders Ranges at 5 ka. However, this was based on the youngest age of a single speleothem, which may reflect local climatic conditions. More recently, Gliganic et al. (2014) suggested that wetter conditions were still prevalent until ~2 ka. However, here too this was based on one speleothem, raising questions on the spatial significance of these results.

Here we present a systematic attempt of establishing chronologies for a range of selected cave and pedogenic carbonates from Mt. Chambers Gorge in the northeastern Flinders Ranges, using laser-ablation U/Th dating. We have collected and analysed four flowstones, one stalactite, one travertine and three pedogenic carbonates. Samples were cut and polished, before analysis by laser ablation multi-collector ICP-MS at the Research School of Earth Sciences, Australian National University followed methods detailed in (Eggins et al., 2005). Only one out of the three pedogenic carbonates yielded a U-Th age, as the others showed ($^{230}\text{Th}/^{234}\text{U}$) activity ratios >1.

Results suggest several periods of carbonate growth: 110-140, 32, 27, 22, 17, 12 and 3-4 ka. While the absence of carbonate growth record for Marine Isotope Stages 3, 4 and 5a-c may be the result of a sampling or preservation bias, the lack of dates in the early to mid Holocene is striking. This confirms that wet conditions could have been sustained until 2-3 ka. Our broader sampling strategy shows that laser-ablation U/Th dating of carbonates can provide robust constraints on regional palaeo-climatic conditions.

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TESTING THE CONTRIBUTION OF AEROSOL DEPOSITION TO PIGMENTED FLOWSTONES, YARRANGOBILLY CAVES, NSW, AUSTRALIA

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Flowstone offers the potential to develop long-term palaeoenvironmental analyses, but this is typically limited by highly variable growth rates. Aerosol contributions to speleothem chemistry are expected to be maximized during times of slow growth (Dredge et al., 2013) and hence flowstone offers opportunities to examine the aerosol record. In dryland environments, fire incidence is of considerable environmental interest. Here we test the hypothesis that blackened growth layers in flowstones and on modern surfaces at Yarrangobilly Caves relate to smoke or charcoal deposition. The caves are in an upland area of New South Wales (800 m altitude) with a mean annual temperature around 12 °C and rainfall around 1000 mm. Vegetation is of a sclerophyll type and soils are thin (<30 cm) and loamy to clay-rich, and organic-poor in composition, resting on Silurian limestones. Both Jersey Cave and Harrie Wood cave contain blackened modern horizontal surfaces and the former cave manager Andy Spate reports smoke entering the caves during a forest fire in 1985. Flowstone samples from Jersey cave were dated by U-series and trace element chemistry determined by laser ablation. Aerosol collections were made in both Jersey and Harrie Wood caves using surrogate surfaces for aerosol deposition and studied for their organic and inorganic chemistry and by scanning electron microscopy as were with flowstone residues. Some preliminary biochemical analyses were made in the modern caves.

U-Th dating established confirmed that flowstone growth was slow and intermittent. Sample JD1 grew 10 cm during the last 120 ka with a pronounced hiatus between 47 and 88 ka and faster growth of pale calcite between 88 and 92 ka. Black pigmentation is not restricted to narrow surfaces, but characterizes both hiatuses and cm-scale zones of growth. Some intervening zones of slow growth have red pigmentation. Samples JD2 grew at intervals between 400 and 45 ka to a total of 7 cm. There were insufficient dates to identify specific hiatuses, but a broad zone of black calcite characterizes the interval from 244 to <100 ka. and red calcite between 244 and 290 ka and beyond about 400 ka.

Significant spatial variation was apparent in inorganic components of aerosol collections, but less so for organic components. In the black calcite a smaller range of organic compounds with lower molecular weight are incorporated at concentrations higher by a factor of 2-3 relative to white calcite. Dilute acid residues from flowstone appear primarily to be aluminosilicates with only one carbon-rich grain observed in

electron microscopy. Trace element covariations were examined using principal components analysis and different patterns were observed with growth stage, although Fe was consistently highly loaded on the first principal component whereas Sr and Mg were consistently in the second component. P showed variable enrichment in black calcite (JD1) or red calcite (JD2), and Fe (with Th and Ce) in red calcite, and Mn in red calcite and intermittently in black calcite. Abrupt changes in trace element abundances are likely to reflect hiatuses in deposition and hiatus zones already known to exist from U-series chronology are seen to be enriched in various trace elements.

Polyaromatic hydrocarbon (PAH) aerosol supply in the modern environment, in the absence of fires at the time of monitoring, is orders of magnitude greater than that required to result in levels observed in both white and black flowstone concentrations. Modern PAH emission from anthropogenic activity will likely cause much higher atmospheric levels than historically. However, this suggests that forest fire PAH supply is not required to produce the PAH concentrations in black calcite. The absence of identifiable charcoal fragments in speleothem residues confirms that black coloration is not caused by soot. A relative enrichment of low molecular weight organic components may indicate fractionation during transport in dripwater. Aerosol deposition of elements such as Sr, Mg, Al, P and Zn, although spatially variable, is well in excess of that required to account for speleothem deposition at low mean growth rates (1.7 mm/year for YD1) and hence, given that significant supply would also be expected from water during growth phases, element incorporation is highly inefficient. Currently oxygen isotope analysis is being carried out to help test the posited links between relative climatic humidity and the growth patterns of the speleothems.

Increased levels of palaeofire proxies in black calcite are predominantly attributed to reduced retention/increased incorporation due to climatic, soil and environmental processes and variable growth rates. Growth of red calcite is likely to occur during periods of oxygenated soils rich in Fe-oxide, with coloration simply being a representation of elemental transport from the overlying soils. Elevated P may mark vegetative die-back events and correlate with the transition to drier more oxic soils with Fe and Mn transport through organic complexing. PCA analysis results presents an association between colloiddally derived elements and coloration. Additionally, greater supply of bacteria in infiltrating waters may be occurring during periods of increased solution colloidal supply resulting in oxide bioaccumulation processes and coloration.

The modern blackened surfaces remain unexplained by inorganic processes and fire inputs and an alternative bacterial origin can be posited. Denaturing gradient gel electrophoresis analysis of swabs in the cave has identified Actinomycetes on blackened surfaces, and specifically by light microscopy *Hypomicrobium* spp., a bacterial strain found to produce iron and manganese oxides producing coloured deposits on cave surfaces in Guadalupe Caves. Hence coloured calcite could be produced both by diffuse incorporation of soil-derived colloids during relatively wet periods or relatively dry periods when more sharply defined element enrichments develop at hiatuses, with enhancements by bacterial fixation.

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THE D/O EVENTS 16-14 DURING THE LAST GLACIAL PERIOD IN NORTH CHINA: STALAGMITE ISOTOPE RECORD

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Although the loess and stalagmite in China can record the millennial-scale climate oscillations (D/O events) during the last glacial period, there are still some significant differences between them in the sub-millennial-scale variabilities of D/O events 16-14. That may be caused by the variances of the resolution or age error among the records, therefore, the regional uniqueness or differences in response to climate change cannot be excluded. Here we present a stalagmite isotope profile (XL-1) from Xinglong Cave (40°29'N, 117°29'E, 591m a.s.l.) in North China, constrained by high precision ²³⁰Th dates, registering a detailed history of the climate change in North China from 56.8 to 50.8 ka BP. The $\delta^{18}\text{O}$ profile exhibits remarkable similarity to the records from Hulu and Wulu caves in South China, and the $\delta^{18}\text{O}$ -depletion events between records matches each other very well within their dating errors, which corresponds to the Dansgaard-Oeschger interstadials recorded in the Greenland ice cores (Greenland Interstadials, GIS) 16-14. For details, GIS 15 in our record is clearly marked by the same 'double spike' pattern (GIS 15a and 15b) observed in all the Greenland ice core records, some cave records (Wulu and alpine Klee gruben Cave records) and even loess grain size record (Gulang) in Northwest China. The trough between the doublets appears similar to Greenland ice cores, alpine Klee gruben cave and Gulang loess records but more intense than Wulu cave record. In summary, the timings and structures of the GIS 16-14 recorded in our profile are more similar to Greenland ice core than other cave records in South China, which offers an evidence for the hypothesis that the millennial and sub-millennial climate oscillations during Last glacial period may originate from North Atlantic and the signals are transmitted from high latitude to low latitude. Additionally, our records compares well to the time scale of NGRIP (GICC05) record with absolute age differences of less than 200 years from 56.8 to 50.8ka BP, suggesting high accuracy of both event durations and absolute age estimates of NGRIP (GICC05).

SOIL CARBON EXPORT CHARACTERIZED USING NOVEL TRACERS (SCENT): A PROGRAMME OF RESEARCH LINKING SOIL BEHAVIOUR AND SPELEOTHEM ARCHIVES

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Recent work (e.g. Hartland et al. 2012, 2014) has focused on the role of natural organic matter as an agent of transport of transition elements and other trace species present in cave dripwaters and speleothems. As a result attention is focusing on the role of speleothem chemistry as an archive of past delivery of organic matter and hydrological conditions. At the same time, a different community of researchers has been concerned about increasing levels of (nominally) dissolved organic carbon (DOC) in temperate rivers in recent decades and whether this water quality issue arises from temperature rise, recovery from formerly acidification of catchments, or some other cause. We are now funded by the UK's Natural Environment Research Council for a 3-year project led by one of us (RB) to combine these two research agendas in order to identify the main cause of increased levels of DOC.

We are adopting a combination of experimental and observational approaches, using soils and speleothems from four distinct locations with different environmental histories during the last 200 years. Heshang Cave in central China is in a region that is currently receiving acid atmospheric precipitation, whereas Yok Balum cave in Belize has never done so. Tartair Cave in NW Scotland only ever had a weak acidification signal, whereas Browns Folly Mine in SW England has made a recovery from a distinct phase of acid sulphate input. All these sites except Yok Balum have experienced warming in recent decades. Previous experimental studies by RB (Bartlett et al., 2005, 2009 and unpublished; Bottrell et al., 2009) show that microbial responses to sulphate addition can buffer acidity and might further complicate the soil DOC response to acid loadings under waterlogging conditions (Bartlett et al 2009 Bottrell et al 2005 Bartlett et al 2005 + Bartlett et al unpublished data). Tartair's peaty soils are most prone to waterlogging and hence potential reducing conditions, whereas Heshang and Yok Balum appear to be freely draining. The $\delta^{34}\text{S}$ record at Browns Folly Mine implies little role for waterlogging there. Thus there is a clear rationale to connect the soil biogeochemical processes with the speleothem records.

The main work package is to implement a series of laboratory mesocosm soil column experiments leaching the soils, with a basal neutralizing layer of carbonate rock, under different conditions of water chemistry and temperature. These experiments will be closely monitored for a variety of inorganic and organic determinands and will run over a year. We will explicitly test for the role of trace metals as proxies for organic matter transport and trace metal ratios as potential indicators of the variable proportion of functional groups on organic moieties released, which in turn may be controlled by environmental variables and soil biogeochemistry.

The results will be compared with multidecadal-scale data on organic carbon content of streams from the UK and laser-ablation ICPMS data on trace metals from speleothems in the study site combined with fluorescence characteristics. The speleothem data will be particularly valuable in enabling us to test the “recovery from acidification” hypothesis for the increase in riverine organic carbon because the acidification is mainly a product of what has been termed the “great acceleration” of anthropogenic activity since World War II and the speleothems will trace back to an earlier pre- or low-industrial era.

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PREDICTABLE COMPONENTS IN GLOBAL SPELEOTHEM $\delta^{18}\text{O}$

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Predictable components are the components of a climate field that are in some way predictable, that is past and present values of a component time series are correlated. This is different from principal components analysis (PCA) which selects components by their variance not predictability, so the leading principal components may be more noise than signal. Predictable Components Analysis seems a more natural way to examine the dynamical components of climate fields because we expect dynamical systems, such as the ice-ocean-atmosphere system, to have some predictability, rather than to be unpredictable. There are several different ways to measure predictability, which lead to five different methods of extracting predictable components, including: Optimal Persistence Analysis (OPA), Slow Feature Analysis (SFA), Principal Trend Analysis (PTA), Average Predictability Time Decomposition (APTD) and Forecastable Components Analysis (ForeCA). These methods produce sets of components which are ordered by their predictability not variance. Further, some of these methods can be used not only to investigate the predictability within a field, but also to explore the predictability between fields, such as between the northern hemisphere field and the southern hemisphere field.

From the global speleothem $\delta^{18}\text{O}$ dataset (Shah et al., 2013) plus some additional records, 23 records, each spanning much of the period 22-0 kyr BP, were selected for analysis. Application of the five methods above to this global dataset shows that the oxygen-isotope signal in speleothems consists of three main dynamical components. The first two components are a monotonic trend, and a low-frequency oscillation with a periodicity of $\sim 21,000$ years. The methods ForeCA and PTA cleanly separate these two components from higher-frequency signals. The monotonic trend has a globally negative pattern, and is related to the isotopic depletion of the oceans due to glacial melt. The low-frequency oscillation has a spatially asymmetric pattern, and is related to the effect of precession on the summer monsoons. The global third predictable component is a higher-frequency signal which ramps up during Heinrich Stadial 1, and falls thereafter. Generalized APTD is used to investigate what components of southern hemisphere speleothem $\delta^{18}\text{O}$ records are predictable with northern hemisphere records. The third southern hemisphere predictable component is unlike the global third predictable component, suggesting a dynamical difference in the way that northern and southern hemisphere speleothem responded to millennial-scale variation during the deglacial period. Predictable components analysis is a useful tool for improving the interpretation of paleo-isotope records, and for model-data comparisons.

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A REVIEW OF SPELEOTHEM STUDIES AT McMASTER UNIVERSITY, 1966-2000 CE.

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U series and other dating. In 1962 Rosholt and Antal published findings suggesting that young carbonates could not be dated reliably by U series methods because of post-depositional leaching of ²³⁴U. In 1965 Cherdyntsev ('the father of U series dating'), Kazachevsky and Kuzmina reported that they obtained reliable results from young travertines and speleothems. As a geomorphologist who had recently completed a PhD on cave genesis, Ford appreciated the significance of being able to date speleothems to ≤ 350 ky, far beyond the range of the problematic ¹⁴C method. In 1966 Henry Schwarcz (isotope geochemist) agreed on a joint investigation to establish whether U series methods were indeed applicable. Peter Thompson (PhD 1973) was recruited as a first student to do the dirty work. The standard method, ²³⁰Th/²³⁴U dating by alpha particle counting, was labour intensive, slow and tedious. $U \geq 0.1$ ppm was the lower limit for analysis; up to 100 gm of calcite might be needed for one age, giving very low spatial resolution in many samples. Nevertheless, by 1970 we had enough successful results, primarily from West Virginian caves, to demonstrate statistically that Cherdyntsev was correct for the majority of specimens with sufficient U: one particular stalagmite yielded eight reliable ages in correct stratigraphic order, for example. The first application to a geomorphic problem – rate of entrenchment of antecedent river canyons in the Northwest Territories of Canada - appeared in 1972. Russell Harmon's PhD studies (1975) extended our investigations to Mammoth Cave (Kentucky), the Canadian Rockies and drowned caves in Bermuda and the Bahamas. In 1977 a first set of age histograms that distinguished periods of speleothem growth and hiatus in cold or arid regions was published. Mel Gascoyne (PhD 1979) then did pioneer work in the Yorkshire and Mendip caves in UK, but was frustrated by too low U in a major study in Jamaica. Alf Latham (PhD 1981) undertook systematic studies of the magnetism in speleothems, showing that they carried natural remanent (NRM) signals with chemically precipitated (CRM - hematite) and detrital (DRM - magnetite) components. With this, our dating range could be expanded to <780 ky and the interval, 780-1,200 ky, bracketed by ²³⁴U: ²³⁸U equilibria. A first 'hard data' estimate of the age of the mean topographic relief in the Canadian Rockies (~1500 m) was published in 1981.

Dr Alan Dickin tried TIMS Th:U dating of sample speleothems at McMaster in 1982/3 but failed to get clean results. Larry Edwards (Caltech) succeeded with corals in 1986 and we adapted his techniques to obtain the first ages for speleothems in 1988 (Joyce Lundberg, PhD 1990). Increasingly we were being requested to date archaeological sites and Henry was largely lured away into this field.

Moorbath et al. obtained the first Pb:U ages on carbonates in 1987. In the succeeding decade

we tried with speleothems of probable pre-Quaternary age from the Rockies, Alps, Northwest Territories, Yukon, even elevated spring travertines from the Ebro Valley,

Spain. Uniformity of ^{204}Pb : ^{206}Pb in the samples thwarted us until success (92 ± 7 Ma) with subaqueous calcites from the first phase of karst activity in the Guadalupe Mountains, New Mexico (2000).

Stable isotopes and other environmental measures. Investigation of the O and C isotope paleo-environmental potential of speleothems proceeded in tandem with the explorations of dating, beginning with a mass spec designed and built at McMaster. It and subsequent VG commercial machines during the 1970s required about one gram or more of calcite for an analysis, allowing only low resolution; and there were no autocarb options ! Hendy and Wilson, (New Zealand -1969) proposed a criterion to establish whether O isotopes were deposited in equilibrium with ambient conditions in a cave, which we adopted. J-C Duplessy and his students (France) also published early O isotope curves along stalagmite growth axes, but neither of these groups had good dating control. Our work did have such control: the first speleothem O isotope records of climate cycles in North America between MIS 1 and 9 were published in 1974 and 1976.

Drip waters sampled across the continent were found to adhere closely to the Craig-Dansgaard line, warranting the first fluid inclusion studies to determine α_{c-w} (Schwarcz et al.1976). In very wet Vancouver Island, Gascoyne et al.(1981) combined modern drip water partition findings with a stalagmite O record to track a mean temperature decline from 6° to 0° C between 60 and 28 ka BP when deposition ceased. Modern drip-speleothem partition coefficients of Mg and Sr were also investigated there but showed no seasonal variation. Chas Yonge (PhD 1985) undertook fundamental lab studies of paleo-water retention in speleothems, and collected drips along a N-S transect from northern New York to Texas over a hydrologic year to further illuminate the reliability of D/H readout from fluid inclusions.

Yavor Shopov (Bulgaria; pioneer of speleothem calcite luminescence studies in the 1980s) joined the McMaster group as a visiting scientist in 1991 to instigate our final series of new explorations in the lab and field. The principle sources of luminescence were determined and many periodic features ranging from individual seasons to 10^4 years discovered (van Beynen, PhD 2000).

As we have often emphasized, calcite stalactites and stalagmites are ‘trees of stone’ which, even more than those of wood, can conserve records of a wide range of environmental conditions and changes. It is very satisfying to see new generations of enthusiasts taking up a research field that has given us much intellectual adventure.

SULPHUR CONCENTRATION IN CAVE DRIPWATER AND SPELEOTHEMS: AN OVERVIEW OF ITS SIGNIFICANCE AS PROXY OF ENVIRONMENTAL PROCESSES AND CLIMATE FORCING

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Sulphur concentration in speleothems have been investigated as proxy of volcanic eruptions, regional atmospheric sulphur pollution and biogeochemical cycling through vegetation and soil (Badertscher et al., 2014; Frisia et al., 2005, 2008; Wynn et al., 2008, 2010, 2013). Sulphate concentration in cave dripwater depends on several factors including: (i) the input from the atmosphere, (ii) the soil/bedrock composition, (iii) the biomediation through the vegetation and the soil, (iv) the homogenization, storage and mixing occurring in the aquifer (Wynn et al., 2013).

Soil and aquifer characteristics as well as biogeochemical cycling of sulphur through vegetation and soils may influence S fractionation and delay the response time to atmospheric S load in cave dripwaters and, eventually, speleothems (Wynn et al., 2010, 2013; Badertscher et al., 2014). Systematic studies on sulphur in karst are urgently needed to provide better understanding on the palaeoclimate/environmental significance of S variability in speleothems.

In this study we provide the first long-term record of sulphate concentration of cave dripwater in the Italian Alps compared with time-series of karst spring-waters from the same region. Both records display a decreasing trend which is related to decreasing sulphur dioxide emissions in Europe, although all responses differ because of site-specific effects. Fast flow drip *st1* in Grotta di Ernesto, located in the narrow Valsugana valley, which is strongly affected by S-anthropogenic emissions, exhibits a sharp decreasing trend of $-322 \mu\text{g L}^{-1}\text{yr}^{-1}$ in the past 20 years. By contrast, karst springs in the Brenta Dolomites, show a decreasing of just $-19 \mu\text{g L}^{-1}\text{yr}^{-1}$, which suggests a minor influence of S-anthropogenic.

A 'memory effect' inherited from mixing with stored sulphate in the soil and aquifer is well documented for Grotta di Ernesto drips, where SO_4 is systematically higher in slow-drips (due to a greater proportion of a long residence-time, high sulphate concentration component) and lower in fast drips. As a result, in ER78 stalagmite, which is fed by a slow drip rate site, the S peak is offset by ~ 20 years with respect to the peak in sulphur dioxide emissions in Europe (Frisia et al., 2005, 2008; Wynn et al., 2010, 2013).

The most recent analyses of karst spring waters and cave dripwater reveal a reduced component of S-anthropogenic emissions to the total sulphate. However, the presence of fluids with high S concentration still stored in the porous and less transmissive parts of the aquifer, enhance the S content in long residence time waters. For this reason, SO_4/Ca vs. Mg/Ca ratios can potentially be utilized to recognise rock water interaction, as well as prior calcite precipitation.

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Rainfall - cave dripping waters $\delta^{18}\text{O}$ relationships on long monitored stations Examples of Villars, Chauvet and Orgnac sites, south France

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The long (i.e. > 15 years for the longest) isotopic monitoring of cave dripping water revealed a very stable behaviour in most dripping stations of Villars, Chauvet and Orgnac caves, south France. We used local rainfall ($\delta^{18}\text{O}$ and quantity), monitored over same periods, as the input signal in the karst system over these caves. We found out that in order to explain the observed isotopic values of the cave waters and their stability over years, it is necessary to consider a mixing, in a reservoir, of the rainfall (weighted $\delta^{18}\text{O}$ of all months of the year or without August, the driest month) during several months to several years, even for shallow depths (i.e. 10-50m). The common idea that the cave dripping $\delta^{18}\text{O}$ can be assimilated to the mean annual weighted rainfall $\delta^{18}\text{O}$ is not true in all of our studied sites. Such a 12 month averaging still displays too large $\delta^{18}\text{O}$ variations (i.e. > 1-2 ‰) while the dripping stations $\delta^{18}\text{O}$ maximum changes are, in most cases, less than 0.2 ‰ over a > 10 years long period, with a standard deviation of 0.05 ‰. On the Villars cave (4 monitored dripping stations), in the 2 upper gallery stations, at about 10 m deep, the observed dripping $\delta^{18}\text{O}$ value is attained (with a recharge during all months of the years) after ~28 months, and a relative stability (i.e. $1\sigma \sim 0.3\%$ regularly decreasing) after ~43 months. In the lower gallery, about 30m deep, the observed dripping value is reached much later, at about 140 months. If we consider that during the hottest month of the year, in August, no rainfall contributed to the recharge, then the upper gallery $\delta^{18}\text{O}$ value is never reached during the stable period, but stays too low by 0.2 – 0.3‰. For similar input conditions, the lower gallery $\delta^{18}\text{O}$ dripping stations (2) values of Villars cave are reached after ~32 months of rainfall integration. The reservoir feeding stalagmites is likely fed by slow and fast flow components and our isotopic modelling approach gives an apparent residence time of the dripping water which is surprisingly long. Tritium-Helium3 dating and tritium measurements made at the same places in Villars cave from 2009 to 2012, even if their interpretation is not straightforward, are consistent with the above results: Tritium-Helium3 ages are < 3years for both galleries. The ratio of tritium concentration between upper #10A and lower galleries indicates an apparent age difference between 200 and 300 days.

Another interesting results is the small, but significant $\delta^{18}\text{O}$ difference (0.2 ‰), observed between the dripping $\delta^{18}\text{O}$ of the upper (-6.17‰, two stations, 12 years average) and lower (-6.38‰, two stations, 12 years average) galleries of the Villars cave. No certain explanation is given but lower $\delta^{18}\text{O}$ values in the lower galleries might be due to winter season overflows during infiltration and/or to older rain water with a different isotopic composition that reaches the lower galleries after years.

Despite its deeper position (50m/surface), the Chauvet cave stations isotopic composition is reached much earlier than in Villars cave and at 6 months of rainfall integration, dripping isotopic value of is reached. On the Orgnac cave, where 4 dripping stations are monitored since 2010, the deepest dripping station, about 100m deep, displays quite stable values ($<0.15\text{‰}$) whose mean value is reached after 53 month of rainfall averaging. Other less deep stations, at 55, 45 and 35m/surface, show more variability ($<1\text{‰}$). Finally, water monitored from a nearby well drilling, has a similar $\delta^{18}\text{O}$ composition to the other dripping stations and display close variability (i.e. $<0.7\text{‰}$).

Parallel to average residence times of the dripping water, this set of isotopic data also permits to draw conclusions on rainfall/local temperature relationships, position of dripping waters on LMWL and comparison with mesoscale climate model REMOiso whose numerical simulations well reproduce sub-annual $\delta^{18}\text{O}$ variations.

Evidence of a correlation between stable isotopes and wet/dry episodes controlled by the monsoon and Sun activity in a 3ka old stalagmite from South-Central India

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The stable isotopic record of a 38 cm long stalagmite from Munagamanu Cave, South Central India (15°N, 77°E) associated with well-marked calcite-aragonite changes, reveals changes linked to humidity that are strongly correlated with total solar insolation (TSI) for the last 3 ka. After calcite/aragonite corrections, the isotopic signatures exhibit high fluctuations, about 2 ‰ in d¹⁸O and ~6‰ in d¹³C over this period. Strong correlations between d¹³C and d¹⁸O along the growth axis and along single growth laminae indicate deposition out of isotopic equilibrium. This is confirmed by the discrepancy between temperature calculated from modern calcite d¹⁸O and modern dripping water d¹⁸O (~22°C) and actual cave temperature (~30°C). Sampling of local rainfall and dripping cave waters permits to characterize the LMWL and shows that the Munagamanu dripping water composition falls on this line (dD = 7.8*d¹⁸O + 9.4). Growth age model, constructed with annual laminae for the most recent part (<160years) and with 10 MC-ICPMS U-Th ages, show a growth hiatus between 0.6 and 1.2 ka BP. The fastest growth rates occurred between 3.2 ka and 2.5 ka and between 0.6 ka to present day. The most recent part of the record (last 600 years) shows similarities with other Indian speleothem records, but, more strikingly, with TSI and sunspot number time series where solar minima of Wolf, Spörer, Maunder and Dalton are visible on the d¹³C stalagmite profile. Annual to sub-annual isotopic sampling obtained thanks to micro-drilling on parts of the sample displays a decadal variability.

A NEW LATE PLEISTOCENE TO HOLOCENE PALAEOCLIMATE RECORD FOR SOUTH EAST AUSTRALIA

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Despite being one of the Southern Hemisphere's largest landmasses, Australia displays a limited pool of palaeoclimatic information and the production of a new, robust record providing an insight into the response and timing of key climatic events is paramount to generating a more comprehensive characterisation and improved understanding of palaeoclimate in this region.

The amenability of speleothem to radiometric dating, allowing the establishment of robust and reliable chronologies to which their multi-proxy records can be anchored means speleothem provide a clear opportunity to explore and expand palaeoclimatic knowledge at sites across the globe.

Here, state of the art technology is used to exploit relatively recent advances in U-series dating to construct reliable and detailed records of south east Australia's response to palaeoclimatic fluctuations over the last 50 kyr using speleothem samples collected from cave sites from across the states of Victoria and New South Wales. 28 speleothem samples have been analysed in terms of both their coincident growth intervals and stable isotope variation to provide records with palaeoclimatic implications at a range of time scales. The production of a chronological template of speleothem growth intervals has enabled the assessment of south east Australia's response to some of the key local and global millennial scale climatic events of the last glacial to interglacial transition and detailed stable isotope analysis of selected samples have been interpreted with the aid of a thorough cave monitoring programme, identifying increased variability in the region's climate during the late Holocene. The palaeoclimatic records developed represent a significant step forward in Southern Hemispheric palaeoclimatology, offering valuable new data for both palaeoclimatologists exploring south east Australia's past climate and those investigating climatic fluctuations at a hemispheric to global scale. The high resolution and robust chronology of the records produced means that they provide a benchmark to which future records might be anchored.

THE INFLUENCE OF THE AUSTRAL WESTERLIES RECORDED IN NEW LATE PLEISTOCENE STALAGMITES FROM SOUTH AFRICA

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South Africa represents one of the Southern Hemisphere's key climatic zones for palaeoclimatic research, situated at the interface of tropical, sub-tropical, and temperate climate systems, as well as the Indian, Atlantic and Southern oceans. Influenced by both ocean and atmospheric systems of hemispheric to global influence, southern Africa is well positioned to reflect Southern Hemispheric circulation changes and consequently for the study of large scale environmental change over glacial-interglacial cycles. However, the generally semi to hyper arid climates experienced in South Africa are not conducive to the preservation of a range of palaeoecological proxy data sources and resultantly the region is characterized by limited well dated, high resolution records of climate change.

However, speleothems can serve to remedy this flaw, protected from degradation by the unfavourable conditions, their growth intervals alone provide crucial information regarding environmental conditions over extended time intervals. Here we present securely dated, multi-proxy palaeoclimate data from three stalagmite samples representing the different precipitation zones characterising contemporary South African climate. Namely, Sudwala Cave in the Lowveld, Wonder Cave in the Highveld and Cango Cave in the winter rainfall zone. Uranium-series dating was used to anchor high resolution stable isotope, trace element and petrographic variations to robust chronologies for speleothem encompassing varying portions of the late Pleistocene.

The collection of stalagmite samples, provide evidence for an antiphased relationship identified in the growth intervals of samples from both the summer and winter rainfall zones, dominated by the ITCZ and austral westerly systems respectively. Stalagmite CC1 collected at Cango Cave, situated in the climatically sensitive year-round precipitation zone and host to stalagmite V3; a rare, relatively continuous record of temperature and a cornerstone of South African palaeoclimatology (Talma and Vogel, 1992), provides a particularly important record. CC1 displays a coeval growth interval to V3 and consequently the high resolution proxy data and age control serve to both improve and readdress this key archive and to demonstrate a mid-late Holocene poleward retreat of the austral westerlies potentially related to increasing temperatures and the onset of the modern climate regime. This data supports numerous climate models predicting a poleward migration of the austral westerlies in response to anthropogenic warming and the potential aridity surrounding this shift renders it an important present issue in terms of public water provisions, farming and fire frequency. Further, this study highlights the importance of petrographic analysis in speleothem samples utilised for palaeoclimate research. Laser-Raman spectroscopy techniques are used alongside petrographic analysis to identify fluctuations between the two CaCO₃ polymorphs and provide an important opportunity to highlight the potential impact of aragonite to calcite

transformation on the palaeoclimatic signal inherited by both the petrographic and geochemical data.

This study serves to focus the attention of the speleothem community on this under sampled yet crucial region for palaeoclimatic information fundamental to assessing the correlation of deglacial and Holocene climate change in relation to both other Southern Hemispheric landmasses and the rest of the globe, ultimately enabling an improved understanding of the processes forcing global climate change.

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HYDROLOGIC INFLUENCE ON THE RADIOCARBON VARIABILITY IN AN INDONESIAN SPELEOTHEM DURING THE YOUNGER DRYAS

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Constraining the temporal variations in the radioactively dead carbon [i.e. dead carbon fraction (DCF)] that is incorporated into a speleothem is critical to reliable ¹⁴C_{spel} chronologies, and has important implications to radiocarbon calibration. Whilst some recent studies have highlighted the potential utility of speleothems to extend/improve the radiocarbon calibration curve (e.g. Hoffman et al., 2010; Southon et al., 2012), others have shown some potential complications associated with such an undertaking, because in certain settings the DCF (which is derived from the soil and bedrock) is sensitive to cave recharge and hence did not remain constant through time (e.g. Griffiths et al., 2012; Noronha et al., 2014). To further assess the potential hydrological control on speleothem radiocarbon variability, we constructed a new high-resolution DCF record from an Indonesian speleothem that encompasses a previously documented pluvial event in Flores, Indonesia—namely the Younger Dryas (YD) (Griffiths et al., 2009). Twenty ¹⁴C analyses, anchored to a U-Th age model constructed from ~60 U-Th dates, were conducted on pieces of calcite extracted at ~5-mm increments along a ~100-mm section of stalagmite LR06-B1. To better characterize the paleoclimate, high-resolution stable-isotope ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) and trace-element (Mg/Ca, Sr/Ca) measurements were also conducted along the same section of stalagmite.

Broad comparison of the DCF record with the hydrologically-controlled proxy data suggests that the sudden increase in rainfall at the onset of the YD was matched by an increase in the DCF, which remained at this level until the abrupt termination of the YD ~1,000 years later. Closer inspection reveals that the decadal-scale shifts in Flores hydroclimate were also characterized by DCF anomalies. In line with a previous interpretation of DCF variability for the same specimen, but during the late Holocene (Griffiths et al., 2012), we interpret the DCF during the YD to have been primarily controlled by limestone dissolution associated with changes in open- versus closed-system conditions, rather than other potential factors such as kinetic fractionation and/or variations in the age-spectrum of soil organic matter above the cave. It then follows that more abundant monsoon rainfall in Flores during the YD resulted in the soil-karst system being in a more closed state, which inhibited carbon isotope exchange between the karst-water dissolved inorganic carbon and soil-gas CO₂, and ultimately led to a greater contribution of dead-carbon from the bedrock. This finding

lies in stark contrast to, for example, the dead carbon behavior in speleothem records from the Asian monsoon region (e.g. Southon et al., 2012), which shows little to no variation in DCF through the YD climate anomaly.

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TROPICAL PACIFIC MODULATION OF GLOBAL CLIMATE VARIABILITY OVER THE PAST MILLENNIUM

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The El Niño-Southern Oscillation (ENSO) and Interdecadal Pacific Oscillation (IPO) dominate hydroclimate variability in the tropical Pacific. Observations and climate model simulations highlight the key role of the Pacific Walker circulation (WC), a component of ENSO/IPO, in shaping recent trends in global temperatures. However, the extent of the tropical Pacific's influence in modulating regional hydroclimates and global temperatures over multicentury timescales is still poorly known. Here, we present a 2,000-year, high-resolution stalagmite $\delta^{18}\text{O}$ record for Flores, Indonesia, which documents changes in deep convective rainfall in the western ascending limb of the WC. The composite record, based on two absolutely dated stalagmites, reveals significant reductions in Australian-Indonesian monsoon rainfall at ~250-600 C.E. and ~950-1300 C.E., and a stronger monsoon at ~1350-1600 C.E. These variations are in phase with marine paleorecords for the western equatorial Pacific, but antiphased with hydroclimate records for the central and eastern equatorial Pacific. The zonal pattern of climate change across the tropical Indo-Pacific region supports recent ENSO reconstructions showing a weaker WC during the Medieval Climate Anomaly (MCA, ~950-1250 C.E.) and a stronger WC during the Little Ice Age (LIA, ~1350-1850 C.E.). However, our paleodata-model comparisons show that the full amplitude of century-scale climate variability is not well reflected in climate model simulations. Critically, the intervals of strong divergence correspond with the MCA and LIA, suggesting that century-scale variations in the WC could have served to amplify the global climate response. Our findings highlight the inference from recent decades that natural variations in the WC can amplify or suppress radiative forced shifts in global temperatures.

PROCESSES AFFECTING STABLE ISOTOPE FRACTIONATION DURING FORMATION OF STALAGMITES: INVESTIGATION WITH LABORATORY EXPERIMENTS

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The most widely applied climate proxies in speleothems are stable carbon and oxygen isotopes ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$). These can be measured at high temporal resolution, and in combination with precise U-series dating, they provide continuous, long-term climate records from all parts of the world. However, the interpretation of speleothem stable isotope signals in terms of past temperatures and/or precipitation variability is difficult because both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values depend on a complex interplay of various processes occurring in the atmosphere, the soil, and karst above and inside the cave. This has rendered quantitative reconstruction of temperature and precipitation impossible so far.

Here we present laboratory experiments aiming to understand the basic physical and chemical processes affecting the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values during precipitation of calcium carbonate on the surface of a stalagmite and to verify recently published modeling studies (Dreybrodt, 2008; Scholz et al., 2009; Dreybrodt and Scholz, 2011). Our experiments extend previous studies (i.e. Henderson and Day, 2011; Polag et al., 2010; Wiedner et al., 2008) and are closer to the conditions in natural caves.

In a first experiment, we determine the time constants for isotope exchange between the dissolved inorganic carbon (DIC) in a thin film of water and the CO_2 of the cave atmosphere. We establish a thin film of a NaHCO_3 -solution ($\delta^{13}\text{C} = -5.6\text{‰}$) with variable concentration and expose it to different pCO_2 ($\delta^{13}\text{C} = -45.6\text{‰}$). After different exposure times, the DIC in the solution is instantaneously precipitated as SrCO_3 for isotopic analysis. We find progressively more negative $\delta^{13}\text{C}$ values with increasing exposure time, finally approaching an equilibrium value. The temporal evolution can be fitted by an exponential decay, with the time constant for isotope exchange, τ_{ex} . τ_{ex} depends on the concentration of NaHCO_3 , the film thickness, temperature and atmospheric pCO_2 . The film thickness in our experiments ranges from 0.05-0.1 cm. For these values, τ_{ex} is in the range of 10-20 min. This shows that isotope exchange will only affect the $\delta^{13}\text{C}$ values of the DIC in case of very long precipitation times, τ_{pr} . We further present first modeling efforts in order to estimate the exchange time, which indicate that $\tau_{\text{ex}} = T * (\text{HCO}_3^-) / (\text{K}_\text{H} * \text{pCO}_2)$, where T is a time constant, and K_H is Henry's constant. For extremely thin water films, $T = 1/k$, where k is the rate constant for the reaction $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$. T is only weakly dependent on the film thickness, and increases to about $T = 2/k$ for film thicknesses up to 0.1 cm.

In a second experiment, a thin film of a CaCO_3 - CO_2 - H_2O -solution supersaturated with respect to calcite flows down an inclined calcium carbonate plate. Drip water is

sampled after different distances of fluid flow and, thus, different residence times on the plate. Subsequently, pH, electrical conductivity and the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ value of the DIC are determined. All parameters influencing the stable isotope values, such as pCO_2 , temperature and relative humidity are controlled during the experiments. The conductivity of the solution is linearly related to the DIC and calcium concentration. We observe an exponential decay of conductivity with τ_{pr} . For a film thickness of 0.01 cm, at $T = 20^\circ\text{C}$ and a 5 mmol/l CaCO_3 -solution, τ_{pr} is ca. 500 s. Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values show a linear increase along the flow path due to progressive precipitation of CaCO_3 and degassing of CO_2 . Our experiments aim to test (i) whether calcite precipitation occurs under conditions of isotope equilibrium and (ii) to determine the fractionation factors in dependence of the experimental parameters.

In a third experiment, a chemically identically $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ -solution flows down an inclined sandblasted borosilicate glass plate, and calcite is precipitated. This allows determination of the fractionation factors between the DIC and the precipitated CaCO_3 .

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A NEW ERA OF QUANTITATIVE PALAEOHYDROLOGY FROM SPELEOTHEM TRACE ELEMENTS?

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Over the past two decades numerous workers have studied the fluorescent natural organic matter (NOM) present in cave dripwaters and speleothems. Since NOM may be a semi-conservative tracer of flow, several early studies explored its utility as a direct recorder of hydrology in karst dripwaters. Subsequent research has demonstrated that the controls on NOM transmission are complex and depend to a large degree on the coupling of the soil-aquifer system. More recently, attention has turned to the complexes formed between NOM and trace metals in dripwaters. This work has shown that NOM in dripwaters is dominated by nominally-dissolved compounds which reside at the boundary between the colloidal and dissolved (i.e. with dimensions of a few nanometres). New information from hyperalkaline speleothems demonstrates that NOM-metal complexes are generally not captured in stoichiometric unity. In other words, transition metals carried by these complexes are able to dissociate and preferentially partition into calcite. When the lability (exchangeability) of the complexes is considered, transition metals are found to have similar apparent partition coefficients. This finding is consistent with data from experimental studies showing strong and long-lasting complexes form between Cu, Ni, Zn, Pb and calcite, rather than with un-dissociated (*ternary*) complexes. Therefore, the trace metals may provide the best measure of the original transmission of NOM in dripwaters.

Elemental data in numerous speleothems indicates that the transmission of natural organic matter (NOM) and complexed trace metals can occur in the dripwaters of even the deepest caves, such as Obir Cave in the Austrian Alps, although liable to attenuation on karst aquifer walls. We are now in the position to assign variations in transition metal concentration in speleothems to changes in the interaction between NOM-metal complexes and the speleothem growth surface. What then do variations in transition metals in speleothem mean? The behaviour of these complexes at the calcite-water interface is currently a major unknown, preventing their unambiguous interpretation as palaeoclimatic proxies.

In this study we used an in-situ gel-based sampler to measure the dissociation kinetics of NOM-metal complexes in dripwaters from Heshang Cave, China. The data acquired demonstrate that the first-row transition metals are kinetically hindered compared to the alkaline earth metals, reflecting their slow dissociation from NOM-metal complexes. This is consistent with the known properties of humic-metal

complexes studied in laboratory experiments. Since the mass of dissociated metal increases as a function of time, we suggest that at slow drip-rates ($< 15 \text{ drips min}^{-1}$) the transition metals which preferentially-partition into calcite speleothems (e.g. Cu) are more efficiently delivered as free ions to the speleothem surface. Hence trace element content of calcite may inversely encode drip discharge behaviour. We explore the possible implications of this phenomenon for interpreting speleothem trace elements and point to the next, necessary steps, for the development and implementation of this proxy.

Isotopic excursions in New Zealand Speleothems coincide with abrupt retreats of New Zealand glaciers from their maxima

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Coincident negative excursions in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in two New Zealand stalagmites (HW5-03 from Hollywood Cave in the West Coast of the South Island and RK5-03 from Ruakuri Cave, Waitomo in the North Island) have previously been linked to the Heinrich Excursion H1 on the basis of $^{230}\text{Th}/^{234}\text{U}$ dating. Now it has been shown from exposure age dating that at this time major glaciers on the eastern side of the Southern Alps underwent abrupt recession. It is suggested by both lines of evidence that the Inter Tropical Convergence (ITC) shifted southward during H1 resulting in much increased precipitation over at least western New Zealand. Although such evidence of rapid glacial recession is difficult to obtain from earlier glacial advances as the land surfaces on which they might have been found were reoccupied by subsequent glacial advances, similar isotopic excursions occurred in the New Zealand speleothems during earlier Heinrich Events. It is likely that earlier Heinrich Events may also have resulted in abrupt glacial recessions in New Zealand.

A GIBRALTAR SPELEOTHEM RECORD FOR THE LAST GLACIAL PERIOD AND IMPLICATIONS FOR CLIMATE STABILITY IN THE WESTERN MEDITERRANEAN

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The western Mediterranean occupies a critical boundary position between polar and subtropical air masses and its climate is influenced by the Mediterranean Sea and the Atlantic Ocean. It is therefore a key region for climate research and the understanding of the interplay of different climate zones. Gibraltar is situated in a critical position at the western end of this region between the Mediterranean and the Atlantic. We present a new speleothem record from Ragged Staff Cave, Gibraltar, for the last glacial period. The record is derived from three speleothems, one flowstone drill core (Gib 10-d) and two stalagmites (Gib 10-e and Gib 10-f), collected in the 'Silent Pool' section of Ragged Staff Cave. The two stalagmites were submerged at the time of collection and recovered from depth of -4m and -8m below current water level. The water level in Silent Pool is depending on the sea level and thus formation of the two stalagmites took place at times with lower sea levels. The outside of the stalagmites show some corrosion features. However, the inside of both specimen largely consists of pristine calcite. Gib 10-f has a second layer with corrosion features inside the specimen indicating another previous time of submergence. The drill core consists of dense pristine calcite.

Chronology for the two stalagmites so far is based on initial low spatial resolution U-Th dating results. The stalagmite Gib 10-e formed between 106 ± 0.6 ka and 39 ± 0.2 ka. Gib 10-f has a basal age of 164 ± 1.4 ka and a top age of 60 ± 0.6 ka. The timing of the corrosion feature within the specimen is constrained by bracketing ages of 156 ± 1.6 ka and 97 ± 0.7 ka, indicating submergence during MIS 5 before 97 ka. The age model for Gib 10-d is based on 15 U-Th ages along the 28 cm long drill core. The basal age of the flowstone is 102 ± 0.8 ka and it has a top age of 32 ± 0.2 ka. We identify two hiatuses, the first between 89 ± 0.6 ka and 70 ± 0.4 ka and the second between 43 ± 0.4 and 37 ± 0.2 ka. We present the stable isotope records for the last glacial period derived from the three specimens. Overall, isotope records replicate well where we find overlap and age control is well constrained. The Gibraltar $\delta^{18}\text{O}$ record shows oscillations which closely resemble D-O cycles. Our record is very similar to NGRIP $\delta^{18}\text{O}$ where we have good dating and high resolution records. We find D-O cycles strongly imprinted on our calcite record indicating that warming in the polar region coincides with Gibraltar calcite oscillating to lower $\delta^{18}\text{O}$ values. We find a rapid initial response in calcite $\delta^{18}\text{O}$ to interstadial excursions but dynamics of the return to stadial conditions appear more complex. We will discuss implications of our isotope record for climate stability in the Western Mediterranean in context with our understanding of the cave system based on monitoring results and compare results to other climate archive proxy data from the region.

SPURIOUS THERMOLUMINESCENCE IN SPELEOTHEM: IMPLICATION FOR PALEOCLIMATE

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Spurious thermoluminescence (TL) is an intrinsic non-dose-dependent emission, which is common in natural calcite deposits, such as speleothems. Previous studies explain the spurious TL as triboluminescence due to grinding, charge transfer from deeper traps due to light exposure and chemiluminescence produced by surface oxidation during TL readout. Spurious TL has been widely investigated in order to avoid interference in the dating of calcite, but less so for the purpose of paleoclimatic reconstruction. In this study we first investigated the thermoluminescence of calcite in two absolute-dated speleothems (HS2 and HS4) from Heshang cave, Qingjiang valley, China, and interpret the spurious TL as an indicator of East Asian Monsoon. We heated the calcite powder (~200 mesh) from 50 to 400°C at a heating rate of 5°C/s in an air atmosphere to measure the natural thermoluminescence intensity of the speleothems. It is observed that speleothems produce the typical natural TL of calcite with a glow peak at ~370°C. TL signal can be reduced or even eliminated by using a CO₂ atmosphere during TL readout, which suggests that spurious TL originated from the chemiluminescence by oxidation of the native organic matter in the speleothems. TL in both speleothems was weaker in calcite formed during the last deglaciation, stronger in the early Holocene and weaker again during the late Holocene. TL variation was correlated with the speleothem $\delta^{18}\text{O}$ signal during the last 20ka, implying the spurious TL can be related to the intensity of the East Asian monsoon. Our interpretation is that while the East Asian summer monsoon prevails, the warm and humid climate results in strong greater production of organic matter in the soil, which contributes to abundant organic matter (mainly organic acids) in the dripwater, and thus in the speleothem. Therefore, the spurious thermoluminescence in these speleothems is a new proxy for the monsoon. The correlation of TL to the organic matter concentration and composition should be investigated in the future.

VOLCANIC ASHFALL EVENTS IN A SPELEOTHEM IDENTIFIED USING PRINCIPAL COMPONENT ANALYSIS OF AN EXCEPTIONALLY HIGH RESOLUTION TRACE ELEMENT DATASET

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Large multivariate trace element datasets produced by LA-ICP-MS speleothem analysis can pose difficulties for interpretation in a palaeoclimatic context. Processes acting on various timescales and magnitudes affect trace element concentrations, and deconvolving the most important controls is often complex. Principal Component Analysis (PCA) is a multivariate statistical technique often used to analyse large, complex datasets (e.g., ice core elemental records¹) that identifies the modes of variation within a dataset which best explain the overall variability. Here PCA is applied to an exceptionally high resolution (10 μ m vertical resolution) multivariate trace element record produced by LA-ICP-MS² from a modern (1979-2001) Belizean stalagmite ATM-7 with excellent age control^{3,4}.

Principal Component 1 (PC1) is defined by a weak correlation between multiple elements, and is interpreted as reflecting non-carbonate material incorporated within the speleothem. Elevated PC1 scores in ATM-7 occur in rainy seasons following regional volcanic eruptions which produced ash clouds extending over the cave site, as demonstrated by satellite aerosol records and trajectory modelling. Previous trace element analysis of stalagmite used Empirical Orthogonal Function analysis to identify a volcanic signal corresponding to the El Chichón eruption of 1982, here we demonstrate that with higher resolution measurements additional ash deposition events can be identified⁵. NASA remote sensing data from the Total Ozone Mapping Spectrometer⁶ and HYSPLIT trajectory modelling⁷ are used to confirm that the spikes in PC1 correspond only to eruptions which produce detectable ash clouds above the cave site. Spikes in PC1 are not synchronous with volcanic ash deposition but instead occur at the beginning of the wet season (as inferred from magnesium concentrations). We interpret this pattern as a seasonal flushing event that transports ash supplied elements through the epikarst and incorporates them within the speleothem.

Our results show that PCA is a valuable tool for distinguishing among significant controls on the trace element geochemistry of ATM-7, simplifying exploration of our large laser ablation dataset. This technique should be applicable to other sites where volcanic ashfall has occurred, potentially adding tephrochronology to the stalagmite dating toolkit or, conversely, identifying previously unknown or uncertainly dated eruptions.

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QUASI-CYCLIC DRY EVENTS IN NORTHEAST ASIA SINCE THE MID-HOLOCENE

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Orbital timescale East Asian monsoonal intensity throughout the Holocene shows a first order decreasing trend in the subtropical southeastern Asian sector. This long-term trend is also extended to a variety of paleoclimate records from various regions of the globe. But, the shorter-term paleoclimatic episodes such as millennial-timescale events are in a much debate for their regional presences and periodities. Here we report a stalagmite $\delta^{18}\text{O}$ record from Baek-ryong Cave in the central Korean Peninsula that shows the changes in East Asian monsoon intensity since the last 5,000 years.

The general pattern of stalagmite $\delta^{18}\text{O}$ record can be divided into 3 orders changes. Most long-term variation in the $\delta^{18}\text{O}$ record is orbital scale increasing upward trend with about 0.8 ‰ differences. Middle-term variation is most apparent and about 1,000 years-scale quasi-cyclic variations with about 0.6~1.0 ‰ changes, and short-term variations are few decades-scale fluctuations with about 0.20 ‰ changes.

The middle-term cyclic variations are very obvious based on the separation from the range of standard deviation. The variations also display a similarity with most of Chinese stalagmite $\delta^{18}\text{O}$ records in their overall trends and prominent millennial-scale cold/dry events since mid-Holocene. These results support that the $\delta^{18}\text{O}$ record was controlled mainly by the changes in East Asian monsoon intensity possibly with minor contribution of atmospheric temperature effect. We interpreted that these millennial-scale variations in East Asian monsoon have been affected by changes in solar forcing and North Atlantic overturning circulations. Also, we suggest that 1,000 years quasi-cyclic dry events were at least regional to hemispheric episodes since the mid-Holocene.

THE GLACIAL-INTERGLACIAL MONSOON IN SULAWESI

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The Indo-Pacific Warm Pool (IPWP) is a primary source of heat and moisture to the global atmosphere and is a key player in tropical and global climate variability. There is mounting evidence that atmospheric convection and oceanic processes in the tropics can modulate global climate on orbital and suborbital timescales (Clement et al., 2001; Chiang, 2009; DiNezio et al., 2011). Although glacial-interglacial cycles represent some of the largest and most rapid natural climate changes over the last 800,000 years, our understanding of tropical atmospheric convection throughout these climatic transitions is limited.

Tropical speleothem $\delta^{18}\text{O}$ has proven to be a remarkable hydrological proxy that enables the tracking of changes in atmospheric convection and associated rainfall patterns over long timescales. Over the last decade, speleothem research has significantly enhanced our understanding of global monsoon systems and variability in tropical hydrology. Most speleothem research has concentrated on understanding monsoon variability in the Northern Hemisphere, and few of these records extend beyond the penultimate glacial termination (~140 kyr BP; kyr BP, thousand years before AD 1950). Much less is known about the climate history of the Southern Hemisphere tropics and the Australian-Indonesian Summer Monsoon (AISM) in particular over multiple glacial-interglacial cycles.

We present the first speleothem $\delta^{18}\text{O}$ record for southwest Sulawesi, located at 5°S, 119°E in the IPWP, spanning the period ~250-170 kyr BP.. The development of this record involves a multi-proxy approach ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$, Mg/Ca, Sr/Ca) to provide insight into the mechanisms controlling AISM variability throughout Termination III and IIIa at ~248 and ~220 kyr BP respectively. Preliminary results suggest that the near-equatorial sector of the AISM has orbital-scale variability associated with glacial-interglacial conditions and possibly precessional insolation forcing. The most prominent decreases in the Sulawesi $\delta^{18}\text{O}$ record correlate with rapid rises in sea level during TIII and TIIIa. The ~2-3‰ decreases in $\delta^{18}\text{O}$ at these times are much larger

than the accompanying ice-volume-related changes in seawater $\delta^{18}\text{O}$ and its corresponding influence on rainfall $\delta^{18}\text{O}$. Therefore, the lighter speleothem $\delta^{18}\text{O}$ values indicate that summer monsoon rainfall increased rapidly through TIII and TIIIa. Measurements of speleothem $\delta^{13}\text{C}$, together with initial Mg/Ca results, support a rapid increase in rainfall at TIIIa.

The speleothem $\delta^{18}\text{O}$ record for southwest Sulawesi indicates that AISM rainfall may be responding to the combined influences of regional hypsometry and tropical temperature gradients. With further development, this new record, together with other palaeomonsoon records, will help unravel the ocean-atmosphere dynamics influencing tropical monsoon intensity during times when Earth's climate was warming rapidly.

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PRELIMINARY RESULTS OF LATE GLACIAL TO HOLOCENE CLIMATE VARIATIONS RECORDED BY CALCITE-ARAGONITE SPELEOTHEMS IN AN INNERALPINE DRY VALLEY (VINSCHGAU, NORTHERN ITALY)

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The Vinschgau is an inneralpine valley in the Southern Alps (Ötztal Alps). The area is characterized by anomalously low precipitation today, but local climate archives (e.g. debris-flow fans, speleothems) suggest that the Holocene and the Late Glacial were characterised by periods of a distinctly more humid climate.

The region is built up by metamorphic rocks characterised by a high degree of tectonic deformation. Speleothems occur along the South-facing slope of this valley, although carbonate rocks are very rare and karst features are not known in this area. These speleothems formed as a result of a water-rock interaction combined with evaporation (Spötl et al. 2002). Springs are commonly supersaturated with respect to calcite and minor tufa occurrences are known there as well. The exceptionally high U content (up to 1000 ppm) of the speleothems reflects the non-carbonate lithology of the fractured aquifer.

Inactive calcite-aragonite flowstones were analysed by various petrographic methods in order to identify characteristic fabrics and evidence of mineralogical alteration (replacement of aragonite by calcite). In addition to stable carbon and oxygen isotope measurements, high-resolution U-series dating was performed with the aim of gaining a deeper understanding of changes in the local climate of this region which cannot be obtained from other archives. Preliminary data show that flowstone deposition occurred intermittently between ca. 14.1±0.1 ka and 0.4±0.01 ka BP and ongoing work is focussing on pinpointing the precise timing of growth intervals which are regarded as a first-order proxy of humid conditions in this area.

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FIRST RESULTS OF A CENTRAL EUROPEAN FLOWSTONE RECORDING CLIMATE CHANGES DURING MIS 5 AND 6

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A flowstone from Abaliget Cave (Mecsek Mts, southern Hungary) provides a new palaeoclimate record for the Carpathian Basin including some of the interesting warm and cold phases from Middle and Upper Pleistocene. Three drill cores were taken from a speleothem located in a chamber 500 m behind the entrance of the cave, with the purpose of reconstructing past climate changes for Central Europe.

Cave air temperature and relative humidity were monitored for a year and drip water samples were collected regularly in order to study present-day conditions. The air temperature of the cave chamber fluctuated between 11.5 to 12.0°C, showing slightly higher values than the mean annual temperature of the area (10.5°C) while relative humidity remained above 97%. The $\delta^{18}\text{O}$ and δD values of the drip water varied from -9.5 to -9.1‰ and from -65.9 to -63.0‰, respectively, consistent with the local meteoric water line.

Providing the master curve for our study, the top 19 cm of the first flowstone core (ABA 1) was analysed for its stable carbon and oxygen isotope composition at 0.3 mm intervals. In order to replicate the record, the top 19 and 7.5 cm of the second (ABA 2) and the third (ABA 3) drill cores were analysed at the same resolution. U/Th measurements were performed on these younger, laminated parts of ABA 1, ABA 2 and ABA 3 drill cores, respectively. The resulting ages range from 109.3±0.63 to 160.2±1.3 ka BP and from 123.2±3.4 to 159.4±1.7 ka BP for ABA 1 and ABA 3, respectively, covering Marine Isotope Stages (MIS) 5d, 5e and most of 6. Although the U-series dating of the ABA 2 drill core yielded similar ages, some of the dates are not in strict stratigraphic order.

$\delta^{18}\text{O}$ of the three drill cores shows consistent changes and major shifts at the MIS 5e/5d and 6/5e boundaries. Changes in $\delta^{13}\text{C}$ lag those recorded by $\delta^{18}\text{O}$. The large increase in $\delta^{18}\text{O}$ values (e.g. 3.4‰ in ABA 1) at the onset of MIS 5e suggests a major change not only in temperature but also in the $\delta^{18}\text{O}$ value of precipitation. During

MIS 6 (130 to 149 ka BP) the $\delta^{18}\text{O}$ values remained relatively high. A similar pattern was recorded by deep-sea sediments for MIS 6 (de Abreu et al. 2003).

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THE 100KYR-CYCLE IN SPELEOTHEM CARBON ISOTOPE

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The 100kyr cycle was identified in a wide range of paleorecords from ice cores, marine and lake sediments, and Chinese loess deposits. However, Chinese speleothem $\delta^{18}\text{O}$ records are dominated by the 20kyr cycle, which is proposed to tie to the intensity of Eastern Asian Summer Monsoon (EASM). The lack of the 100kyr cycle in speleothem $\delta^{18}\text{O}$ records fuels the debate whether the EASM is forced by insolation or ice volume. Here we established a high resolution of stalagmite $\delta^{13}\text{C}$ cover the last four glaciation from the high altitude mountain, Shengnongjia, central China. The most feature of $\delta^{13}\text{C}$ record is the 100-kyr ice volume cycle that is differ from the 20-kyr precessional insolation cycle recorded by the same stalagmite $\delta^{18}\text{O}$. During the last four terminations, we find that the $\delta^{13}\text{C}$ lead $\delta^{18}\text{O}$ about 6-7kyr. We propose a forcing mechanism on Asian monsoon that the monsoon precipitation was following the precessional insolation as recorded by $\delta^{18}\text{O}$, but the continental air temperature was paced by 100kyr cyclicity related to the ice volume and sea surface temperature (SST) as recorded by $\delta^{13}\text{C}$.

New insights on tropical vegetation productivity and atmospheric methane over the last 40,000 years from speleothems in Sulawesi, Indonesia

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Speleothem $\delta^{13}\text{C}$ remains an underutilized proxy since a number of factors can contribute to the $\delta^{13}\text{C}$ signal, including climate change, karst processes, vegetation productivity and soil temperature. In this study, we combine speleothem $\delta^{13}\text{C}$ data with model experiments to better understand the relationship between speleothem $\delta^{13}\text{C}$ variability, tropical vegetation productivity, and glacial-interglacial changes in atmospheric methane.

Our speleothem record from southwest Sulawesi, Indonesia spans the last 40,000 years and serves as a proxy for tropical vegetation and soil productivity. Changes in soil CO_2 and temperature during the last glacial-interglacial cycle appear to be the key driver of speleothem $\delta^{13}\text{C}$ variability in southwest Sulawesi. Other proxy records from the region, and trace element analysis of the Sulawesi speleothem, support this interpretation.

These results are compared with simulations provided by the Sheffield Dynamic Global Vegetation Model (SDGVM) forced with snapshot climate simulations covering the last glacial-interglacial cycle using the HadCM3 coupled ocean-atmosphere global circulation model. Temporal changes in soil respiration in the model experiments are in good agreement with trends in the speleothem $\delta^{13}\text{C}$ time series for Sulawesi, supporting our interpretation of $\delta^{13}\text{C}$ as a proxy for vegetation productivity. A strong relationship between soil respiration and methane emissions within the SDGVM suggests that tropical vegetation plays a key role in determining the atmospheric methane budget. The relationship between speleothem $\delta^{13}\text{C}$, tropical vegetation and atmospheric methane is particularly strong during the last glacial when methane production in high-latitude boreal wetlands was suppressed.

The Sulawesi speleothem $\delta^{13}\text{C}$ record and SDGVM model results provide new insights into the role of tropical vegetation in driving the global atmospheric methane budget over the last 40,000 years. In the tower karst terrane of southwest Sulawesi, speleothem $\delta^{13}\text{C}$ acts as a proxy for tropical vegetation productivity, thus providing, for the first time, a direct proxy for tropical methane contributions to the last glacial atmospheric methane budget.

QUANTIFICATION OF THE IMPACT OF MOISTURE SOURCE REGIONS ON THE OXYGEN ISOTOPE COMPOSITION OF PRECIPITATION: CASE STUDY FROM EAGLE CAVE, CENTRAL SPAIN

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The ratio of oxygen isotopes 18-O and 16-O is among the most used proxies in reputed archives of past climate such as ice and ocean cores or speleothems. Its variability in continental records depends to a great extent on the variability of the isotope composition of the precipitation. The variables affecting the oxygen isotope ratios in precipitation are relatively well known and include several controls or effects, some of them having a direct empirical link to climate, like the temperature or the amount of precipitation. Although often difficult to compute, there are other controls also affecting the stable isotope variability like changes in seasonality, the ice volume effect or the modification of the moisture sources.

The moisture source is an important component of the hydrological cycle that controls, in part, the isotope composition of precipitation. Thus, moisture sources affect the recharge water variability over caves where paleoclimate studies based on oxygen isotope records are studied. Although moisture sources have been proved to be important controls of isotope variability in records like polar ice cores, their study in the continental mid and low latitudes is still scarce. Despite the importance of constraining the source of moisture variability to improve the interpretation of oxygen stable isotope paleorecords, these studies are scarce due to the complexity of the traditionally used general circulation models that enables the computation of oxygen isotopes.

Here, we present 5-days reconstruction of air mass history for the days with precipitation at Eagle Cave (central Spain). Together with the calculation of the moisture uptake locations along the back trajectories, we identify the moisture sources of precipitation for this site from the years 2009 to 2011. During this 3-year period, around 30% of the precipitation at Eagle Cave was originated from moisture recycled within the Iberian Peninsula (IP), with the Proximal Atlantic being also a main source region of moisture, whereas the Mediterranean Sea and the Distal Atlantic have large variability during the studied period and other source regions are minor precipitation contributors. The comparison of monthly oxygen isotope composition of precipitation at Eagle Cave with the monthly percentage of precipitation originated in source regions shows a significant negative correlation for the IP region. Thus, the moisture recycling process in the IP region explains 12% of the variability of the monthly oxygen isotope composition of precipitation (p-value <0.1). However, when temperature, amount of precipitation and all source regions are considered, 74% of

the variability of the monthly oxygen isotope composition of precipitation is explained (p-value <0.05). Therefore, although for Eagle Cave amount of precipitation and temperature are main contributors of the precipitation oxygen isotope variability ($r^2=0.54$; p-value <0.001), the moisture uptake distribution among source regions is a substantial control and should be considered when interpreting oxygen isotope speleothem records from this cave.

This research highlights the importance of moisture sources in controlling the oxygen isotope composition of precipitation in mid-latitudes, and the need of the quantification of this effect in order to improve the interpretation of oxygen isotope paleorecords that depend on the isotope composition of precipitation.

High-precision U/Th dating by MC-ICP-MS and its applications on carbonate samples

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We have set up U/Th dating techniques on a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS, a Thermo Scientific Neptune Plus) at the Earth Observatory of Singapore, accompanying with an ultra-clean geochemistry laboratory for actinide element separation and purification. When the instrument is equipped with a large interface pump (OnTool Booster pump), Jet sample cone, and X-skimmer cone, and coupled with a CETAC Aridus II desolvating nebulizer system and a PFA ESI-50 nebulizer, we routinely obtain an ionization efficiency of ~4%. Using the SEM peak-jumping method, we can achieve a precision of $\pm 1-2\%$ (2σ) for abundance determination of ~20 fg ^{234}U or ^{230}Th .

To test the robustness and accuracy of our measurements, we first refined the chemistry processes to reduce procedural blanks, and the chemistry blanks for ^{238}U , ^{232}Th and ^{230}Th can be routinely measured as 0.0005 ± 0.0005 pmol, 0.0005 ± 0.0005 pmol, and 0.0001 ± 0.0001 fmol, respectively. In addition to run the NBL-112A uranium standard solution on the instrument ($\delta^{234}\text{U} \sim -38.5 \pm 1.0\%$ in a year-long reproducibility), we further tested our chemistry and instrument methods using two carbonate samples with known ages. For a stalagmite sample collected in 2003 A.D. and with a fresh top, we obtained a U/Th age of 1996.8 ± 0.8 A.D. on a subsample about 4-6 bands below its top. For a secular equilibrium flowstone sample, we obtained values of $\delta^{234}\text{U}$ and ($^{230}\text{Th}/^{238}\text{U}$)-activity as $1.5 \pm 1.5\%$ and 1.0002 ± 0.0032 , respectively. The U/Th dating methods have also been successfully applied to a variety of carbonate samples, including speleothems, corals and travertines.

AEOLIANITE, CALCRETE, AND PINNACLE KARST IN SOUTHWESTERN AUSTRALIA, AS INDICATORS OF MIDDLE TO LATE PLEISTOCENE PALAEOCLIMATES

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Pleistocene aeolianites with calcreted and karstified surfaces are well exposed on the Swan Coastal Plain in southwest Western Australia. Field mapping, thin section examination, U/Th and OSL dates, and mineralogical, chemical and isotopic analysis identified the timing and palaeoenvironments of the sand deposition, calcrete formation, and karstification, providing an important insight into Pleistocene palaeoclimates in this region. Five periods of aeolianite deposition have been defined: MIS ≥ 13 , MIS 11, MIS 9, MIS 7 and MIS 5, reflecting interglacial highstands accompanied by strong, predominantly southerly to southwesterly winds. Dating and oxygen isotope analyses of the calcrete layers overlying the aeolianites indicate deposition during the arid to semi-arid climate of each glacial period under lower mean temperatures ($\Delta T = 2.55^\circ - 5.45^\circ$) than today's mean temperature of 18.85°C . Different types of calcretes were deposited at different times, suggesting that the climate during glacial periods was not identical for each cycle, although the constant trend of aridity during these periods still remains. Dry climate during glacial periods is additionally indicated by the deposition of the quartz sand in MIS 3 (the Cooles Sand). Pinnacle karst was formed on the (palaeo)surface of two aeolianite members deposited in MIS 7 and 11, indicating a wet climate, probably wetter than present.

THE AFFECTING FACTORS OF PRECIPITATION $\Delta^{18}\text{O}$ VARIATION IN WESTERLIES-DOMINATED NORTHWESTERN CHINA AND THE SIGNIFICANCE FOR UNDERSTANDING STALAGMITE $\Delta^{18}\text{O}$ RECORDS

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Abstract: The high-resolution and absolutely dated stalagmite $\delta^{18}\text{O}$ records from the East Asian summer monsoon (EASM) region demonstrated a detailed EASM change during the Holocene. The variation of $\delta^{18}\text{O}$ records from this region are attributed to Northern Hemispheric summer insolation. However, the recently published Kesang Cave stalagmite $\delta^{18}\text{O}$ record from Xinjiang in northwestern China, where the westerlies dominated the climate variabilities and experienced an out-of-phase moisture history with that from the EASM region during the Holocene, underwent a similar variation. Thus, here we propose to utilize the correlation between modern precipitation $\delta^{18}\text{O}$ and temperature, rainfall to explore the paleoenvironmental significance of stalagmite $\delta^{18}\text{O}$ change in westerlies-dominated China. According to the data from Global Network of Isotopes in Precipitation (GNIP), three sites (Urumqi, Hotan, Tashkent) all show prominent positive correlation between monthly weighted average precipitation $\delta^{18}\text{O}$ variation and monthly averaged temperature variation ($p < 0.01$, at 99% confidence) on seasonal scale. However, the annual weighted average precipitation $\delta^{18}\text{O}$ and annual averaged temperature in Urumqi denote a negative correlation, which was supported by the correlation of precipitation $\delta^{18}\text{O}$ variation inferred from ice cores in middle-eastern Tien Shan Mountain and instrumented regional temperature change during past 40-50 years. In addition, we found that the water vapor mainly come from distant Atlantic and Arctic Ocean during warm years while the precipitation $\delta^{18}\text{O}$ values were much negative, and the water vapor originated from Mediterranean, Caspian sea and Aral sea increased during cold years and the precipitation $\delta^{18}\text{O}$ values become very positive, and all of which were controlled by the location of westerly jet. Therefore, we conclude that the long-term precipitation $\delta^{18}\text{O}$ change was affected by the water vapor sources and paths which were connected with the location of westerly jet. Furthermore, our results suggest that the stalagmite $\delta^{18}\text{O}$ variation on orbital scale are also more likely determined by the westerlies in northwestern China.

Key words: stalagmite $\delta^{18}\text{O}$, precipitation $\delta^{18}\text{O}$, water vapor sources, westerlies, northwestern China

OXYGEN ISOTOPES AND HYDROGEOCHEMICAL CHARACTERISTICS OF CAVE DRIP WATERS IN LIANGFENG CAVE, GUIZHOU, SW CHINA

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Oxygen isotope ($\delta^{18}\text{O}$) is one of the most commonly used palaeoclimate proxies, and monitoring their modern evolutionary processes is very significant for palaeoclimate reconstruction. In this study, cave drip water samples are daily collected from two drip sites in Liangfeng Cave, Guizhou Province, SW China, between June 2008 and June 2010. The stable hydrogen and oxygen isotopes of these samples and the contemporary precipitation samples are measured. The relationships between the isotopes and the local air temperature, precipitation and relative humidity are analysed. The results show that the hydrogen and oxygen isotopic compositions of precipitation have obvious seasonal variations in the study area: lower in the rainy season and higher in the dry season. The local meteoric water line (LMWL) is $\delta\text{D} = 8.64 \delta^{18}\text{O} + 17.44$. Precipitation is the only source of cave drip water, and its oxygen isotope signals are reflected in the two drip waters (SD: slower drip rate and previously called 1#, and FD: faster drip rate and previously called 5#). However, the amplitude of the drip water oxygen isotope variation is much smaller than that of the precipitation, i.e., homogenization occurs to some extent. However, there are significantly different responses to precipitation between the two drip sites. The response time of SD to precipitation is much longer than that of FD. The amplitude of oxygen isotope variation in SD, where the isotopic data deviate from the LMWL to a higher degree, is much smaller than that in FD, suggesting that it results from greater evaporation intensity caused by the lower drip rate in the SD. A comparison of these isotopic differences with previous researches (Luo et al., 2013; Yang et al., 2012; Zhu, 2011) in the same cave indicates that the isotopic differences between the two drip waters result from different flow paths. The oxygen isotope signal in cave drip water perhaps mainly reflects summer monsoon information in the study area. The speleothems fed by drip waters (e.g. FD) with shorter response time to precipitation may be more suitable for high-resolution palaeoclimate research. Moreover, the *d*-excess from speleothem fluid inclusion has the potential to be used as an indicator of relative humidity of local air.

On the other hand, by monitoring the amount of rainfall, air temperature and relative humidity, and cave air temperature and relative humidity, as well as drip rate, water temperature, pH value, electric conductivity and HCO_3^- concentration of cave drip water from April 2011 to April 2013, and monthly collecting rain and drip water from three drip sites (SD, FD and 6#) for hydrogen and oxygen isotopes, respectively. The results show that the amount weighted average $\delta^{18}\text{O}$ value of rainfall is -8.3‰ in the first hydrological year (2011 to 2012), lighter than that in the second hydrological year (2012 to 2013) which is -5.9‰, indicating that the near source, Pacific Ocean, offers a larger portion of water vapour to precipitation in the second hydrological year

than that in the first hydrological year. Arithmetical average $\delta^{18}\text{O}$ values of the SD, FD and 6# are similar to those of multi-year weighted average for precipitation. After hydrological and hydrochemical analysis of drip water, it reveals that the FD flows fast, and then followed by the SD and 6#; meanwhile, strong mixing new water with old water in epikarst exists. In spite of this, the seasonal differences of $\delta^{18}\text{O}$ value from three drip sites show that rainfall signals in the current year still reflect in drip waters. The small precipitation in the dry season is hard to be infiltrated into cave and cause low $\delta^{18}\text{O}$ values of the SD, while the inner cave evaporation leads to heavy $\delta^{18}\text{O}$ values of 6# in the dry seasons. Owing to calcite deposited on the dry seasons, the mean $\delta^{18}\text{O}$ values of dry seasons during the two years are different each other. This indicates that drip water inherits signals of rainfall and the corresponding speleothems can be used for paleoclimatic studies. However, it's requisite to choose speleothems precipitated under the faster drip sits (similar to that mentioned in the above paragraph) and to monitor relative air humidity for avoiding evaporation inside the cave.

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ENVIRONMENTAL CHANGES IN MOUNTAIN ENVIRONMENTS DURING HOLOCENE. A RECORD FROM ORGANIC PROXIES IN STALAGMITES.

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Stalagmites are well established as accurate archives for paleoclimate and paleoenvironmental records, with inorganic proxies being widely used. Organic proxies are a growing field, providing access to information stored in a separate carbon pool, and relating to microbial activity, vegetation cover, and temperature. However, the key factors controlling these proxies are not yet well defined.

$\delta^{13}\text{C}$ analysis of speleothem calcite (effectively the dissolved CO_2 pool) is a routinely used technique, but the controls are not as well defined as for $\delta^{18}\text{O}$, with the proxy record potentially affected by vegetation change, soil conditions or microbial activity. Parallel measurement of $\delta^{13}\text{C}$ of the preserved organic matter has been suggested as a method of resolving this signal, with an inverse relationship between the two records previously being suggested as a proxy for microbial control. However, this technique is in its infancy in speleothems, and requires testing in a greater range of contexts.

This study uses a multi-proxy approach, combining $\delta^{13}\text{C}$ analysis of calcite and the preserved organic matter, with a highly novel laser fluorescence technique to investigate climatic and land-use driven environmental variations during the Holocene period. Four stalagmites were sampled in the same room of the Garde-Cavale karst system (1300m a.s.l.), in the Bauges massif, in the northern Prealps. These samples cover the last 12 ka. $\delta^{13}\text{C}$ analysis of soluble acid bulk organic matter was performed via LC-IRMS at La Trobe University and the University of Orléans. $\delta^{13}\text{C}$ of the calcite was performed at University of Melbourne, Australia. Organic matter fluorescence was measured at the University of Savoie, France. This fluorescence technique provides a high resolution record (100 μm step along the growth axis), and is a non-destructive method. The three proxies show different trends during the Holocene period, although major environmental events are marked by changes in all records. Further work is needed to establish whether the differences in the proxy records are due to differing environmental controls, or whether there are methodological factors affecting the record. In particular, the organic $\delta^{13}\text{C}$ proxy is currently under further investigation to test for sensitivity to fluctuations in

instrumental parameters and matrix effects. However, in the long term, this multi-proxy approach, combining organic and inorganic techniques has great promise in resolving our understanding of environmental variations.

INTEREST OF USING ORGANIC MATTER FLUORESCENCE AS AN ENVIRONMENTAL PROXY IN STALAGMITE STUDIES.

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Fluorescence in stalagmites is a non-destructive method to reconstruct paleoenvironmental evolutions using quality and quantity variations of organic matter. Stalagmites are today well established as accurate archives for paleoclimate and paleoenvironmental records. Fluorescence of organic material was widely used, mainly via the studies of speleothems luminescence banding. Those results were especially used to obtain chronologic information and as a climate proxy. However, only few studies use the fluorescence as an environmental proxy. But organic matter fluorescence technic presents the advantages to be rapid method to measure quality and quantity variations of organic matter in order to evaluate environmental and climatic evolutions.

We present here fluorescence measurements on 3 stalagmites spanning the Holocene period. These results can be interpreted in terms of quantity and quality variations of organic matter. Indeed, fluorescence emission wavelength is related to the type of organic matter. Modifications of the molecule structure, induced by the nature of organic material or humification processes occurring in soils, entail a change in emission wavelength. Emission wavelength variations or peak ratios between the different fluorophores can be used for that purpose. These evolutions are closely linked to environmental changes as soil or vegetation changes impact directly the type and the humification processes of organic matter.

Secondly, for a steady quality, fluorescence intensity is related to the amount of organic matter trapped in calcite. An increase of organic matter content leads to an increase of the fluorescence signal intensity. This can be caused by an increase of rainfall amount, an increase of organic matter production or by erosion processes. This last process generally leads to a change in both quantity and quality. Organic matter is exported in higher amount and provided by various soil layers. So fluorescence intensity can provide information on relative quantity variations of organic matter joining the system under climatic or anthropic influence. However, those variations remain semi-quantitative. To avoid this problem and obtain a quantitative flux of organic carbon from soils, we developed a method using soil fluorescence to estimate organic carbon concentration of stalagmites. Thus, intensity variations can be transformed in quantitative variations of organic carbon concentration exported from soils.

Finally, hypothesis on climate and environmental factors influencing the proxies variations can be improved by the comparison of fluorescence organic matter with other organic proxies and with the $\delta^{13}\text{C}$ record. So, the fluorescence signal is an interesting tool providing different information on both climate and environmental changes. The method is non-destructive, rapid, and with a high resolution and makes fluorescence a really interesting complementary proxy to organic and inorganic proxies.

USING KARST UNSATURATED ZONE HYDROLOGY TO INFORM SPELEOTHEM CHOICE FOR HIGH RESOLUTION HOLOCENE PALAEOCLIMATE RECONSTRUCTIONS

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Groundwater mixing and storage residence times may alter the composition of speleothem-forming drip waters. Identifying and constraining non-climatic controls, such as these karst hydrological processes (eg. soil moisture storage and evaporation) in the unsaturated zone, is highly informative for reconstructing palaeoclimate signals in speleothems. Cave monitoring allows us to identify the most suitable speleothems prior to collection for high-resolution (i.e. annual) reconstruction of past climatic and hydrologic variability, at least over the last 1-2 ka where decadal variation may be of interest.

High-frequency, spatially-dense drip discharge monitoring was conducted over 15 months to characterise unsaturated zone flow at Harrie Wood Cave, in the Snowy Mountains, Yarrangobilly (SE Australia). The cave was formed in the Late Silurian Yarrangobilly Limestone, a fractured rock associated with no primary porosity due to past diagenesis. Response times between soil moisture saturation and cave discharge showed a moderate relationship ($r^2 = 0.52$), whilst weak relationships were found between depth and maximum, mean and median discharge overall. Principal Component Analysis (PCA) and Agglomerative Hierarchical Clustering (AHC) were used to classify similar drip regimes, revealing five unique drip types. Non-linear discharge behaviour was observed, suggesting secondary porosity and thus a combination of matrix and fracture flow is significant in controlling unsaturated zone flow at this site. Using the PCA and AHC derived drip types, three speleothems fed by different hydrological regimes were chosen for palaeoclimate reconstruction and the preliminary data will be presented here. This study highlights the heterogeneous nature of hydrological flow in karst and the need to understand unsaturated zone hydrology at the individual drip discharge level, prior to any speleothem study for high-resolution palaeoclimate reconstruction.

SPELEOTHEM ARCHIVES OF GIBRALTAR CAVES: THEIR RECORD OF ENVIRONMENT AND REGIONAL CLIMATE OVER MULTIPLE ICE AGE CYCLES

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The Rock of Gibraltar contains many solution caves which initially formed near sea level and now span elevations to over 300m as a result of slow uplift over time. In the modern climate, Gibraltar holds an important position near the southern limit of the tracks taken by the depressions that deliver rainfall to Europe from the North Atlantic sector of the atmosphere. Monitoring in St. Michaels and Ragged Staff caves has been carried out since 2004 by monthly sampling and deployment of logging instruments which reveals that speleothem growth is most strongly influenced by seasonally reversing cave ventilation that permeates the entire rock. The results provide unprecedented insight into how cave environments respond to seasonal change, variations in sea level and neotectonic uplift and the ways that regional climate is recorded as chemical proxies in an evolving cave environment.

A preliminary 500ka merged record was obtained as an average of the mean isotopic composition of 1ka time slices for 12 records with age models. Replication is excellent, even between caves with different local environments and seasonal capture bias. The Gibraltar record is characterised by elevated $\delta^{18}\text{O}$ during glacial maxima, associated with higher $\delta^{13}\text{C}$ caused by greater degassing or lower soil pCO_2 by weakened vegetation activity during cool arid glacials. This pattern is repeated across 5 glacial cycles and, where we have good age models and high resolution, the Gibraltar record records a clear imprint of SST and atmospheric reorganization associated with Holocene ice rafting events and D-O cycles during MIS 3-5. The Gibraltar record is strikingly similar to the Greenland ice record but the $\delta^{18}\text{O}$ range is notably more subdued and less extreme than other comparably long speleothem records dominated by stronger insolation forcing such as Soreq and China.

We present an overview of the results of comprehensive cave monitoring, climate-proxy calibrations and a new proxy record of precipitation, sea level and environmental change over the past 500ka constructed from twenty-four dated speleothems. Records vary in length and are often punctuated as a consequence of water balance and submergence during high sea level stands. Calcite deposition spans most of the stadials, but growth slows towards glacial maxima. Records also tend to be absent from interstadials (early Holocene and MIS 7, 9, 11). Absence of growth suggests increasingly negative water balance during the cool dry glacial maxima, but also during interstadials, perhaps in response to a shift in Mediterranean climate towards drier winters, offsetting lower summer temperatures and consequently lower ET. Some records provide constraints on local uplift rates as they are punctuated by submergence during high sea level stands, recorded in stalagmites that are now up to 60 m asl as a result of neotectonic activity.

ENSO PERIODICITY RECORDED IN AN ANNUALLY RESOLVED SPELEOTHEM RECORD FROM VOLI VOLI CAVE, FIJI

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The modern tropical Fiji climate is characterised by seasonal rainfall controlled by the position of the South Pacific Convergence Zone, which is closest to the islands during the wet summer season and weakens when migrating north during the drier winter season. Annual rainfall is strongly modulated on decadal timescales by ENSO with higher rainfall associated with La Nina events with dry spells sometimes leading to drought conditions during El Nino events. A laminated speleothem from Voli Voli cave Fiji spans a 1500 year interval across the transition from the Medieval Warm Period into the Little Ice Age. Around 1200-1300 AD the speleothem fabric changes from finely laminated calcite with thin clay layers, to white well laminated calcite. The older record is characterised by elevated $\delta^{13}\text{C}$ values followed by a rapid decrease in $\delta^{13}\text{C}$ that coincides with the onset of clean calcite deposition. $\delta^{18}\text{O}$ values define a simpler trend that monotonically decreases by $\approx 1\%$ across the entire record but micromilling of the younger laminated calcite at 100 micron resolution reveals unusually smooth oscillations in $\delta^{18}\text{O}$ that span groups of laminae.

A key question is whether the laminae or the isotope cycles can be shown to be annual features and to understand relationships between local cave processes and seasonal weather patterns, a program of cave monitoring has been undertaken since 2009. Voli Voli cave is a descending passage that terminates near a fissured cliff facing the SE trade winds; these are more persistent during the winter and weaken during the summer and cave monitoring shows that high cave air CO_2 levels decline near the cave termination as a result of weak incoming ventilation by atmosphere driven by wind strength or chimney ventilation. The high resolution $\delta^{13}\text{C}$ record shows regularly spaced peaks that are also correlated with fabric and cycles in P and Sr. These are interpreted as annual markers driven by rainfall and seasonal ventilation so the smooth $\delta^{18}\text{O}$ cycles have a wavelength of 3-7 years ie a similar frequency to modern ENSO. The cycles have an amplitude of 2-3‰ which would be equivalent to an amount-effect related change in annual precipitation of around 50%. Although La Nina years tend to be wetter, there is a large interannual variation in rainfall so mixing and storage would be required to account for smoothness of the $\delta^{18}\text{O}$ cycles. Sea surface temperature and salinity, modulated by changes in the position of the warm pool may also play a role in modulating the local precipitation isotope record and work is in progress to understand this through a study of local rain event isotope data. The Voli Voli record provides new evidence of an underlying climatic change around 1300 AD and the clay layers are associated with micro hiatuses suggesting periods of drought which are much more frequent prior to the 1300 AD transition which is known to have had a widespread impact on societies in the Pacific Basin resulting in increased conflict, shifts in settlements and changes in subsistence strategies.

FLUID INCLUSION STABLE ISOTOPES AND CLUMPED ISOTOPES STUDY OF EASTERN MEDITERRANEAN CAVES DURING GLACIAL – INTERGLACIAL TRANSITIONS

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Clumped isotopes thermometry is a unique tool for paleotemperature determination using the mass 47 anomaly (Δ_{47}), but its application to speleothems is complicated by the occurrence of kinetic isotope effects (KIE) that accompany CO_2 degassing during carbonate precipitation. This study uses a new empirical calibration of the modern-day Soreq Cave stalagmites that accounts for kinetic isotope effects in both Δ_{47} and the calcite-water oxygen isotope fractionation ($1000 \ln^{18}\alpha$)¹. Δ_{47} temperatures allow the calculation of cave water $\delta^{18}\text{O}_w$ using the calcite-water $1000 \ln^{18}\alpha$ relationship. New techniques for the direct measurement of δD_w and $\delta^{18}\text{O}_w$ in fluid inclusions² (FI) allow measured $\delta^{18}\text{O}_w$ values to be compared and correlated with those calculated from Δ_{47} temperatures and $\delta^{18}\text{O}_{cc}$. In this study, we examine the temperature-hydrological history of the Eastern Mediterranean Soreq Cave and alpine karst Mizpe Shlagim (MS) cave³ (2224m a.s.l.), during the transitions from the Last Glacial Maximum to the Late Holocene period (T1 warming) and from the termination of the penultimate glacial period to MIS 5e interglacial (TII warming).

Soreq Cave Δ_{47} data show temperature minima (*ca* 12°C) at the Last Glacial Maximum (LGM) and the penultimate glacial maximum. Both minima were followed by sharp temperature rises into the Holocene (*ca* 20-25°C) and stage 5e interglacial (18-20°C, apart for a brief cold period at ~130 ka), respectively. The T1 warming shows temperature rise and fall during the Bølling-Allerød and Younger Dryas, but at the onset of the Holocene temperatures became more uniform (~20-22°C) with maximum values (25°C) recorded during the Sapropel S1 event. Higher resolution, centennial-scale, Δ_{47} studies of the late Holocene speleothems also show uniform temperatures of *ca* 22°C. Similar to T1, sharp temperature oscillations are observed in the TII warming. Δ_{47} thermometry of the MS Cave speleothems confirms that temperatures rose well above freezing during interglacial periods and brief warming events during the glacial.

Good compatibility is found between the measured FI $\delta^{18}\text{O}_w$ values and those calculated from the combined $\delta^{18}\text{O}_{cc}$ - Δ_{47} data. Calculated and measured water $\delta^{18}\text{O}_w$ values show a marked shift from ^{18}O -enriched values of ~-2.5‰ at the LGM and ~-3.0‰ at the penultimate glacial maximum, to ^{18}O -depleted values at the peak interglacial stages, corresponding to Sapropel S1 (~-5.5‰) and Sapropel S5 (~-6‰), respectively. These $\geq 3\%$ downward $\delta^{18}\text{O}_w$ shifts reflect a number of effects: the change in sea surface water $\delta^{18}\text{O}_w$ resulting from glacial melting; massive input of fresh water into the Eastern Mediterranean Sea during sapropels; and an interglacial ‘amount’ effect in which $\delta^{18}\text{O}_w$ of rainfall is inversely correlated with rainfall amount⁴. Paleo-hydrological relationships (Meteoric Water Line) determined using FI

δD_w and $\delta^{18}O_w$ values suggest that LGM and penultimate glacial maximum had d-excess values (~5-10‰) closer to those of the present day global system, whereas the Holocene and Stage 5e interglacials shows higher d-excess values (~20-30‰), as characteristic of present-day Eastern Mediterranean rainfall. Although d-excess depends on both temperature and relative humidity⁵, the glacial-interglacial temperature changes are not sufficient to account for this d-excess shift and there must have been a lower relative humidity gradient above the sea surface during the glacial. This shift in d-excess may reflect either a local reduction in Eastern Mediterranean relative humidity gradient above the sea during the glacial periods, or a major southward shift in the Mediterranean storm tracks in the glacial periods relative to today.

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COMPARISON OF TEMPERATURE PROXIES IN TROPICAL STALAGMITES

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Several new tools to reconstruct past temperatures with stalagmites have recently emerged, which we have compared for the first time using stalagmites from Northern Borneo (4.1°N, 114.9°E). Temperatures were inferred from 1) the partitioning of oxygen isotopes between fluid inclusion water and calcite [1], 2) the density of fluid inclusion water determined by liquid-vapor homogenization [2], 3) noble gas concentrations in fluid inclusions [3], and 4) the carbonate isotopologue (or ‘clumped isotope’) composition of the calcite [4]. The temperature sensitivity of two of the proxies, fluid inclusion $\delta^{18}\text{O}$ and clumped isotopes, is currently debated. The results of this study contribute also to these ongoing debates. We furthermore compare two different methods for measuring the isotopic composition of fluid inclusion water [1, 5].

Stalagmite WR5 used for this study covers two glacial-interglacial cycles, from Marine Isotope Stage 12 to the beginning of Marine Isotope Stage 9 (460-330 ka). The sample has previously been used to infer past changes in precipitation [6]. In addition to this old stalagmite we analyzed two recent samples in order to compare proxy data to measured cave temperatures. Within error, all methods yielded consistent temperature estimates in agreement with the modern cave temperature. We used the equation of Tremaine et al. [7] for calculating temperatures from fluid inclusion $\delta^{18}\text{O}$ and a new clumped isotope calibration obtained at ETH, based on synthetic calcites [8]. The results from WR5 suggest 4-5 °C temperature difference between the glacials and interglacials contained in our record, which is similar to the amplitude of reconstructed regional sea surface temperature records [9, 10] when considering sealevel-driven glacial-interglacial changes in cave elevation.

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POTENTIAL AND LIMITATIONS FOR RECONSTRUCTING THE NORTH ATLANTIC OSCILLATION FROM SPELEOTHEM OXYGEN ISOTOPE VALUES. A CASE STUDY FROM THE HERBSTLABYRINTH, CENTRAL GERMANY

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The North Atlantic Oscillation (NAO; Hurrell, 1995) is an expression of the variability of the westerlies over Europe and the Atlantic area, with the most dominant impact during winter months (DJFM). Baldini et al. (2008) showed that the two GNIP stations Koblenz and Wasserkuppe/Rhön (central Germany) exhibit the highest positive correlations of all 43 GNIP stations in Germany between the $\delta^{18}\text{O}$ of precipitation and the NAO (0.68 and 0.8, respectively). Both stations also show a high correlation between temperature and the NAO of 0.51 and 0.64, respectively. Therefore, Baldini et al. (2008) concluded that climate archives from this area should have great potential for NAO reconstruction.

The Herbstlabyrinth-Adventhöhle cave system (HL) is located in central Germany, in between the two GNIP stations. In order to evaluate the potential of $\delta^{18}\text{O}$ signals recorded in speleothems from this cave for NAO reconstruction, a cave monitoring program has been set up in 2010. In addition to several geochemical and physical parameters, the $\delta^{18}\text{O}$ values of local precipitation and of drip water collected at various drip sites inside the cave are measured on a monthly basis. Furthermore, drip rates and the amount of precipitation at the cave site are recorded.

Using the results from our monitoring program and an extended climate data set from Frankfurt am Main, we calculated the infiltration at the cave site for the last 143 years. We use this value as a weighting factor for the $\delta^{18}\text{O}$ values of precipitation, as proposed by Wackerbarth et al. (2010). Using their model, we calculated the $\delta^{18}\text{O}$ value of the cave drip water for the last 143 years.

We found a significant correlation of $r=0.31$ between the modelled $\delta^{18}\text{O}$ values of the drip water and the NAO. This low correlation coefficient is surprising, because the majority of recharge at the HL occurs during winter months and the NAO is a winter phenomenon reflected in the $\delta^{18}\text{O}$ values of precipitation. The most likely explanation for this unexpectedly low correlation is the contribution of strong precipitation events during summer months, such as thunder storms, to the drip water reservoir. A reconstruction of the NAO from speleothem $\delta^{18}\text{O}$ values, thus, appears challenging, even for this cave site located in a sensitive area.

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PALAEOENVIRONMENTAL IMPLICATIONS OF MONETITE LAYERS IN ANCIENT SPELEOTHEMS

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Phosphates are the third largest group of cave minerals after carbonates and sulfates. Among them, brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) is one of the most common, formed under acidic and damp conditions. It easily loses the water molecules converting to monetite (CaHPO_4). These minerals are usually found as crusts, nodules, powdery or earthy masses derived from accumulations of bat guano. When the accumulation is large enough, the phosphates can even have economical interest and have been exploited in many caves.

In the afotic galleries of the Atapuerca Karst System (northern Spain) some phosphate aggregates are found in the form of very fine growth layers of monetite inside Holocene stalagmites. They are usually associated to a dark-black layer in which some amorphous organic matter still remains. In other cases, it can be only observed as an earthy and porous yellow-orange layer inside the stalagmite (Fig. 1a and b), which is always problematic when trying to obtain a date by U-Th means.

The SEM allows a better recognition even though the monetite layers very often retain some humidity (maybe inside the pores or even as part of the crystal lattice of the non-dehydrated brushite mineral), and therefore the SEM images can be sometimes of poor quality (Fig. 1c). The phosphates usually appear as masses or aggregates (Fig. 2a and b) or as alveolar coatings in the pores formed in previously corroded calcite (Fig. 2c).

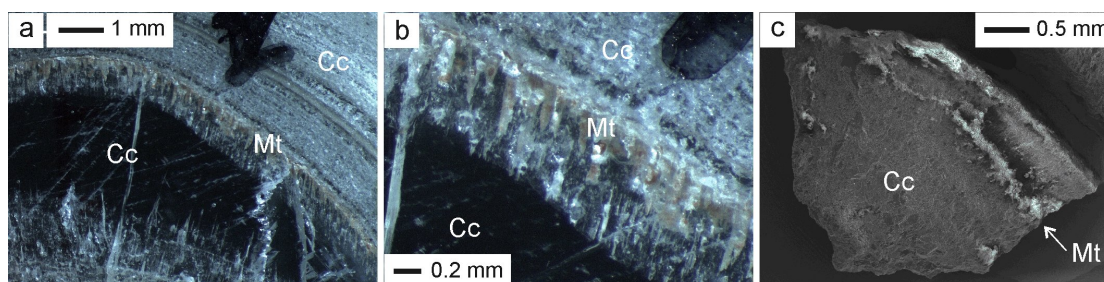


Figure 1. a-b) Microphotographs of a monetite (Mt) layer inside a calcite (Cc) stalagmite. The images were taken with true color light reflecting on a thin section located on a black background. c) SEM image of a monetite (Mt) layer in a freshly fractured sample of a calcitic (Cc) stalagmite. The monetite layers always display different amounts of humidity and appear as bright aggregates.

The monetite layers very often present some organic features that range from varying amounts of amorphous organic matter (Fig. 3a) to different kinds of microorganisms (Fig. 3b and c). The study of this range allows to propose a model for the formation of these layers, the environmental conditions present during its deposition and the possible time interval related with each kind of layer.

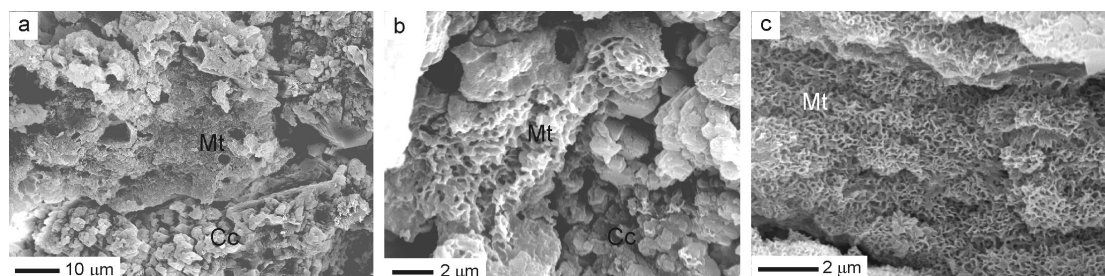


Figure 2. SEM images of monetite (Mt) masses inside a calcite (Cc) stalagmite. a) The monetite constitutes an almost amorphous aggregate associated to microcrystalline calcite. b) The monetite appears as irregular patches with alveolar habit. c) The alveolar monetite coats the whole surface of the pores, maybe replacing some extracellular polymeric substances.

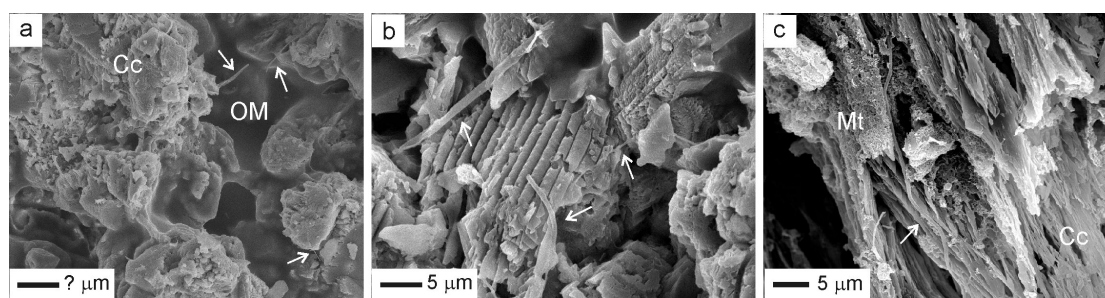


Figure 3. SEM images of some of the most typical organic features associated to the monetite (Mt) layers. The arrows point to filaments of organic origin. a) Amorphous organic matter (OM) coating a corrosion pore in calcite (Cc). b) Association of different microorganisms and organic structures in a monetite layer. c) Reticulated filaments that appear as a monospecific community associated to alveolar monetite and corroded calcite.

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THE DEEP KARST RECORD

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In addition to the record in speleothems, caves contain a deeper record of the past environment preserved in clastic sediments, relict sediments and palaeokarst deposits intersected by the caves. In Australia and perhaps surprisingly also in parts of Europe the most common example of this is the well known “red earth and bones”, aeolian silt frequently containing Pleistocene megafauna that in some caves is tens of metres deep.

If we go further back in time, climatic changes during the Pliocene can be observed in the Phosphate Mine beds at Wellington Caves where a turbidite sequence is interbedded with mud-crack horizons and at some levels with speleothem growth.

What we currently know about the cave record in eastern Australia has an enormous break between the Pliocene and the Permian. In Slovenia, however Zupan Hajna *et al.* (2008), using a combination of palaeomagnetic dating and rodent biostratigraphy, have reported cave sediments with an age range from 1.5 to 35 Ma.

The ultimate find, Late Cretaceous dinosaurs and crocodiles together, is reported from palaeokarst deposits intersected by motorway construction at Kozina in southern Slovenia (Debeljak *et al.*, 2002)

Filled caves containing Late Triassic and Early Jurassic reptilian and mammalian faunas occur in the Mendip Hills in the UK (Ford, 1989). In Poland, Early Triassic reptile and frog fossils occur in palaeokarst deposits exposed by quarrying at Czatkowice quarry (Borusk-Białynicka *et al.*, 1999.)

While that lack of Mesozoic sediments in caves close to the margin of the Sydney Basin (Jenolan, Colong, Wombeyan and Bungonia) is not surprising the apparent lack of Mesozoic sediments or palaeokarst deposits in caves far away from the Sydney Basin is a puzzle. This lack of Mesozoic cave sediments may be due to a lack of dating attempts on cave sediments than to a real absence. Another explanation emerges from new research in Brazil, only more research will tell.

It was long thought that caves close to the margin of the Sydney Basin would contain relict Permian sediments of intersect Permian palaeokarst. K-Ar dating by Osborne *et al.* (2006) at Jenolan strongly suggests that much of the material previously thought to be Permian is more likely Carboniferous in age. Supposed Permian, but undated palaeokarst deposits occur also at Bungonia Caves in NSW and at Exit Cave in Tasmania (Osborne, 1995).

Mass flow deposits at Jenolan dated by Osborne *et al.* (2006) as Late Carboniferous probably represent the onset of the Permo-Carboniferous glaciation. Caymanites (marine carbonate turbidite palaeokarst) are clearly older than dated Carboniferous clays at Jenolan and appear to represent a marine transgression that is only preserved in the cave record. This dating is very controversial and attempts are now being made to directly date this material.

Middle Devonian volcanoclastic palaeokarst is well developed at Wombeyan Caves, where Bindook Porphyry Complex material has filled surface karst features and fills extend underground, intersected by “modern caves” (Osborne, 1993). Late Devonian palaeokarst has long been suspected at Wellington Caves, dating work in progress has indicated that it is there, and that Carboniferous deposits may also be there.

The deep karst record has complex stratigraphy, includes strange rocks and is difficult to read and conclusively date. It already tells us about Pleistocene aridity, tropical Late Cretaceous southern Europe, Permo-Carboniferous glaciation in Australia, an unknown marine transgression and Devonian volcanism. We have hardly read the first page of the deep karst record in Australia. Many surprises await future readers of our underground stone book.

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Mid-Late Holocene climate and environmental change in southwest Anatolia from speleothem stable isotopes, trace elements and carbon layers

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A 490 mm-long stalagmite from Sirtlanini Cave, southwest Turkey, has provided a stable isotope record from ~6.7 ka to 2006 A.D.. The $\delta^{18}\text{O}$ record shows no long-term trend but exhibits frequent oscillations of $>1\text{‰}$, particularly between 6 ka and 3 ka, and an overall amplitude of 3‰. $\delta^{13}\text{C}$ values trend towards more negative values through the mid-late Holocene and superimposed on this trajectory are several abrupt excursions of $>2\text{‰}$ to both more positive and negative values. The highest values occur around 6 ka, which is interpreted as a relatively dry phase, and the lowest at ~1 ka. There is no correlation between the carbon and oxygen data. The cave site lies at an altitude of 830 metres and is 100 km northwest of Lake Golhisar which has yielded a low resolution Holocene isotopic record (Eastwood et al. 2007). Work in progress is aiming to elucidate the climatic connections between the two records. The cave also lies 120 km northwest of the archaeological site of Caltılar Höyük (Momigliano et al., 2011), one of the early urban settlements in the region. The Caltılar Archaeological Project's primary research is focussed on human settlement in the Neolithic to Iron Age period (7th to 1st millennia BC) and the role that the environment played in determining settlement choice and culture and the effects of intensive upland settlement on deforestation and the environment. Deciphering the climatic and environmental factors that have influenced our speleothem record will contribute towards this goal. Of particular interest are six grey layers within the stalagmite, usually a few mm thick but exceptionally ≤ 10 mm. They contain charcoal, detrital quartz, clay and organics and relatively high abundances of Fe and Zn, the latter associated with the $>100\text{nm}$ colloidal fractions of soil organics (Hartland et al., 2012). It is likely that these layers precipitated during periods of higher infiltration. They are associated with positive $\delta^{13}\text{C}$ excursions and may result from natural or anthropogenic burning on the surface above the cave. Estimated ages for these events are ~6.5 ka, ~6.3 ka, ~6.1 ka, ~4.5 ka, ~3.0 ka and ~2.2 ka based on a preliminary age model. The largest positive $\delta^{18}\text{O}$ excursion in the record occurs at ~3.4 ka according to the age model, just prior to the regional Late Bronze Age collapse. Laminations, which may be annual, occur between ~1.4 ka and 0.6 ka, and will be the subject of future study.

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**MONKEYS OF THE CARIBBEAN:
NEW U-SERIES AGES CONSTRAIN THE ANTIQUITY AND LONGEVITY OF
DOMINICAN PRIMATE *ANTILLOTHRIX BERNENSIS***

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Since the days of Darwin, the endemic monkeys of the New World have been considered a classic subject of biogeography. Cenozoic exposures yielding terrestrial vertebrates from the Caribbean are rare, with fewer than two dozen samples of fossil mammal species, representing three orders, that have been dated by chronometric techniques. Given that the vast majority of West Indian fossil mammals have been collected in dry caves and sinkholes, generally without stratigraphic context and only rarely in connection with datable material, researchers have struggled to formulate robust models of colonization, inter- and intra- island biogeography, mammalian longevity in this hazard-prone environment, and a temporal context pertinent to extinction, the levels of which are extraordinarily high in this region.

Here we describe a subfossil primate tibia recovered by scuba divers from a flooded Dominican Republic cave, which has also produced cranial and dental remains identified firmly as the primate *Antillothrix bernensis*. Importantly, this primate species represents one of just two exclusive to Hispaniola. This specimen was encased in cave carbonate (speleothem) when recovered. U-Th dating of this host cave carbonate returns ages consistently at the 500 ka upper limit of the technique. However, U-Pb, capable of resolving ages of greater antiquity, is more robust in this context, returning a secure age of 1.3 ± 0.11 Ma. This date is the oldest chronometric age recorded for a Hispaniolan mammal. For West Indies primates, it is surpassed only by an isolated Miocene talus; a taxonomically difficult specimen, originating from Cuba.

Crucially, this study demonstrates the utility of U-series chronometry as a tool in the Caribbean where, for vertebrates, datable fossiliferous rocks and terrestrial sedimentary deposits are rare. *Antillothrix* is part of the pitheciid clade of New World monkeys and although its origins are obscure, like its manner and time of arrival in the Greater Antilles, the dentition bears particular resemblances to early Middle Miocene primates from Patagonia. The data presented here suggest this species endured the continuous climatic perturbations of much of the Pleistocene for at least 1 million years on this hazard prone island, relatively unchanged, as a frugivorous climbing quadruped. It hints at an interesting link between the history of monkeys in the Caribbean and the preponderance of taxonomic and morphological stasis indicated by various mainland fossil primates from Colombia and Argentina.

NEW U-Pb AGES FOR THE HOMININ SITE OF DRIMOLEN, SOUTH AFRICA: A REGIONAL PATTERN OF CONTEMPORARY FLOWSTONE FORMATION

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U-Pb dating of speleothems, stalagmites and flowstones, has recently reached a level of maturity where it can be applied both precisely and routinely. The early human (hominin) bearing cave sites of South Africa have benefited greatly from this innovation, as these sites were previously undated, with a widely held belief that they were undateable. In all major cave sites, within the area known as ‘The Cradle of Humankind’, the fossil bearing sediments occur sandwiched between flowstone layers. These flowstone can be U-Pb dated and in an ideal case, ages for flowstones above and below fossil bearing horizons can be used to infer an age for the interbedded fossils.

The site of Drimolen is famous for the remarkably complete *Parathropus robustus* skulls recovered from the main fossil bearing deposits. The age range of this highly specialised hominin is of particular interest and has always been poorly defined in South Africa, limiting comparisons with equivalent material from East Africa. As with the other sites within the Cradle, there are a number of well preserved flowstone layers in association with the sediments at Drimolen. Three of these layers are now U-Pb dated, with ages ranging from 2.6 – 1.8 Ma.

The uncertainty surrounding the initial ²³⁴U values sometimes leads to necessarily large errors on the U-Pb ages, which in turn means that the ages estimates for the fossils are as broad, in the worst cases up to 500 ka. The palaeomagnetic resonance of both the flowstones and sediments can be very useful in these situations, as the pattern of reversed and normal signals can be used to narrow down the time window defined by the U-Pb ages. This combined approach has been employed with great success at the sites of Sterkfontein and Malapa, and now at Drimolen, providing new ages ranges for the hominins.

These new ages contribute to the growing data set of U-Pb dated flowstones from the Cradle, where over the last nine years, five cave sites and close to twenty flowstones have been successfully dated. It is now possible to begin to look for regional patterns within these data – it is reasonable to suppose that as flowstones need specific climatic conditions to form (a positive water balance within the cave) that multiple caves across this 10x15km area would record flowstones of the same age. Periods of contemporary flowstone development are observed at ~2.6, 2.2, 2.0 and 1.8 Ma, hinting at some large scale climatic conditions forcing changes in the caves.

A HIGH-RESOLUTION STALAGMITE PALEOCLIMATE RECORD FROM NORTHERN VENEZUELA: A RECORD OF CARIBBEAN CLIMATE CHANGE

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The dearth of studies and data in the tropics hinders our understanding of atmospheric and oceanic interactions between the low latitudes and the rest of the globe. To understand better the interactions, specifically between the Caribbean and the North Atlantic, three stalagmites were collected from Cueva Zarraga in the Falcón Mountains of northwestern Venezuela and analyzed to determine local paleoclimatic history. Stalagmites ages were determined by U/Th disequilibrium and show a nearly complete Holocene record and a late Pleistocene record from ~19 – 65 ka. Fluorescent banding was identified in both Holocene and late Pleistocene portions of a stalagmite using confocal laser fluorescent microscopy. Some banding counts are consistent with U/Th dates and likely represent annual bands. Both the carbon and oxygen isotope records preserve quasi-millennial oscillations and show a major depletion shift from the last glacial period into the Holocene, suggesting warmer and wetter conditions during the Holocene. The preservation of quasi-millennial oscillations and of high frequency multi-decadal changes by the $\delta^{13}\text{C}$ indicates that the soil-vegetation-stalagmite system is acting as an amplifier of the climatic signal produced by climatic events and changes. A prominent $\delta^{18}\text{O}$ enrichment event is recorded in all the stalagmites that correspond to the 8200 cal yr BP event. The 8.2 ka event is represented by a double peak with duration of ~ 180 years. Other short-term $\delta^{18}\text{O}$ enrichment events likely correspond to Bond and Heinrich events. The late Holocene record, like other Caribbean records, indicates that the climate system diverges from insolation and may represent an atmospheric rearrangement that resulted in ENSO increase instability or in reduced seasonal movement of the Inter-Tropical Convergence Zone (ITCZ). Today, Cueva Zarraga is at the northern extent of the ITCZ and has two rainy seasons. The $\delta^{18}\text{O}$ enrichment events during the Holocene suggest drier conditions southern displacement of the ITCZ, also suggested by Brazilian speleothem records that show trends that anti-correlate with Cueva Zarraga. The Cariaco Basin and Cueva Zarraga records show similar trends. The close proximity of Cueva Zarraga to Cariaco Basin may allow for a high resolution tropical terrestrial and oceanic climatic response comparison.

High resolution monitoring of a tropical cave system reveals dynamic ventilation and hydrologic resilience to seismic activity

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The nature of cave ventilation is of interest to cavers, speleologists and palaeoclimatologists working with stalagmites. Because cave ventilation systematics may change over the growth span of a stalagmite, understanding what factors affect them is critical for determining events that may have potentially affected climate proxies contained within the carbonate. Similarly, understanding how the hydrology of the drip feeding a stalagmite evolves through time and responds to surface climate is key to building robust records of palaeoclimate. Here we present data from an extensive, ongoing monitoring effort at Yok Balum Cave, Belize, initiated in 2011, that characterises high resolution ventilation and hydrology dynamics at this site. Seven characteristically diverse drip regimes were studied to facilitate the selection of speleothem samples which display good hydrological connectivity with the surface. Clear seasonal ventilation regimes exist, driven by thermally induced inside-outside air density differences. The winter regime is dominated by air inflow and lower karstic drawdown into the cave and a limited diurnal signal, while summer is dominated by air outflow, high karstic CO₂ drawdown and drip water degassing and a strong diurnal signal. Active monitoring during a large (M7.4) earthquake in November 2012 provides a unique opportunity to assess the response of cave atmosphere and hydrology to substantial seismic activity. Cave atmosphere and hydrology is found to be highly resilient to seismic activity, with no observable disturbance occurring around the earthquake, despite there being considerable evidence of physical disruption in the cave. Monitoring included a complete cross-section of different drip hydrologies, and no drip type was affected by the earthquake. This suggests that stalagmite-derived palaeoclimate records are not affected by seismic activity, except in extreme cases where the stalagmite or conjugate stalactite are damaged or reoriented.

PHYSICO-CHEMICAL CHARACTERISTICS OF DRIP SITES: INFLUENCE ON CRYSTAL MORPHOLOGY OF RECENT CAVE CALCITE PRECIPITATES

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Crystal fabrics of speleothems are increasingly used as a palaeoclimate proxy. However, the parameters that control speleothem petrography, in particular calcite crystal morphology are still poorly understood. In order to understand these processes and their products, calcite precipitation experiments of recent carbonate crystals were performed on watch glasses and glass plates in seven caves in Germany, Morocco and Romania. Three caves were selected in Germany (Bunker, Zoolithen and Kleine Teufels Cave) and Morocco (Grotte Bab Maфраque, Grotte Prison de Chien, and Grotte de Piste), and one cave in Romania (Cloșani Cave).

Drip waters were analysed for their fluid Mg/Ca molar ratio with ICP-OES (Heidelberg). Corresponding watch glass precipitates were analysed with respect to their calcite crystal morphology via SEM (Bochum) and the Mg/Ca molar ratio of calcite with ICP-OES (Bochum). In addition, growth rate of watch glass precipitates were determined.

Six different types of calcite crystal morphology were observed on the watch glasses. On most watch glasses two morphology types occurred with one type being dominant. Only a few watch glasses were characterised by a single type, whereas even less watch glasses were characterised by three types. The main process leading to a change in calcite crystal morphology is the amount of Mg²⁺ incorporated into the calcite crystal lattice, which is related to the drip water Mg/Ca ratio. Four distinct changes are observed with increasing Mg²⁺ incorporation: (i) development of new forms (steeper rhombohedra and base pinacoid) at the edges and corners of the crystal seed, whereas the newly formed rhombohedra and base pinacoid are stepped (rough faces), (ii) crystal habit tend to elongate along [001] due to slower growth of faces with high Mg²⁺ densities (rough faces), (iii) reconstitution of crystal faces with low Mg²⁺ densities (smooth faces), and (iv) occurrence of calcite crystals with bended faces and edges due to very high Mg²⁺ (Mg/Ca ratios of 0.009 to 0.051) incorporation. Growth rates and possibly also organic compounds, however, may also affect the morphology of calcite crystals.

Based on the data shown here, the relation of Mg²⁺ incorporation and the resulting changes in calcite crystal morphologies are now better understood. Further work should aim at linking the calcite crystal morphology of watch glass precipitates with calcite crystal fabrics in speleothems in order to exploit the petrographic archive of speleothem deposits.

A 14-KYR RECORD OF CLIMATE AND ENVIRONMENT VARIABILITY IN THE SOUTHWEST OF FRANCE – MULTIPROXY APPROACH ON A STALAGMITE FROM VILLARS CAVE

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We present a decadal resolution record of climate and environment variability in SW-France since 14-kyr ago based on $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and elemental analyses of a stalagmite (Vil30) from Villars Cave. The chronology was constrained by 18 MC-ICPMS U/Th dates with uncertainties ranging from decades to at most 137-yr. We tested the reliability of Vil30 isotopic record by comparing it to three overlapping stalagmites. The significant correlations between the records demonstrate that Vil30 records are preserving a high climatic signal to local noise ratio.

Vil30 time series show the following events on its 14-kyr long growth period:

- 1) The Bölling-Alleröd: a strong decrease in both Mg/Ca (from 14 to 8mmol/mol) and $\delta^{13}\text{C}$ (from -5 to -8.8‰) and a slow increase in ice volume-adjusted $\delta^{18}\text{O}$;
- 2) The Younger Dryas: an increase in Mg/Ca and $\delta^{13}\text{C}$ and a delayed $\delta^{18}\text{O}$ decrease;
- 3) The Holocene optimum: relatively higher values in all proxies (from 6.9 to 9.8-kyr) compared to the mid-to-late Holocene;
- 4) 8.2-kyr BP event: certainly the most striking feature of our record, an abrupt $\delta^{18}\text{O}$ decrease of ca. -0.7‰ followed by a gradual recovery and a gradual Mg/Ca decrease of ca. 40%;
- 5) 4.2-kyr BP event: a synchronized increase in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$;
- 6) 1-kyr BP: the sharpest increase in all proxies.

Our climatic interpretations of Vil30 proxy records are reinforced by more than a decade of monitoring study on local/cave environments, infiltration hydrology, and by isotopic and geochemical analyses on rain/drip waters and modern deposits (Genty 2008; Bourdin 2012; Genty 2014). Villars dripwater Mg/Ca variability was controlled by the prior calcite precipitation (PCP) (Bourdin 2012) and thus can reflect the hydrologic balance (Fairchild 2012). The PCP control on Mg/Ca variability is further supported by the observation of a significant correlation between Mg/Ca and $\delta^{13}\text{C}$ profiles. Thus, we interpret Vil30 Mg/Ca as an indicator of effective precipitation - with higher Mg/Ca values corresponding to drier conditions and *vice versa*. Villars dripwater $\delta^{18}\text{O}$ variability represents a mean weighted $\delta^{18}\text{O}$, over several years, of precipitation ($\delta^{18}\text{Op}$) falling above the cave. $\delta^{18}\text{Op}$ is controlled by the temperature at which the precipitation form at mid-latitude European sites (Dansgaard 1964) and is influenced by $\delta^{18}\text{O}$ of Atlantic surface water on longer timescales. A correlation at 90% confidence between $\delta^{18}\text{Op}$ and temperature (0.56‰/°C) was observed at Villars site on inter-annual timescales (Genty 2014), thus, one can expect a net temperature-dependent of stalagmite calcite $\delta^{18}\text{O}$ ($\delta^{18}\text{Oc}$) of 0.35‰/°C after removing the offset effect of cave temperature on $\delta^{18}\text{Oc}$ (-0.21‰/°C) at equilibrium deposition associated with stalagmite formation. Although $d\delta^{18}\text{Op}/dT$ relationship displays generally a low

correlation coefficient and might vary over time, we tentatively interpret the ice volume-adjusted Vil30 $\delta^{18}\text{O}$ as a proxy of temperature, presuming that the observed relationship persisted and the stalagmite precipitated at (or at close to) equilibrium over last 14-kyr. Villars stalagmite $\delta^{13}\text{C}$ significantly responds to changes in soil and vegetation activity, especially since 85% - 90% of stalagmite carbon comes from soil biogenic CO_2 (Genty 1999). Vil30 $\delta^{13}\text{C}$ closely correlates to Mg/Ca ($r = 0.68$) and $\delta^{18}\text{O}$ ($r = 0.69$) variability which demonstrates that both precipitation and temperature are key factors influencing soil and vegetation developments, or to a lesser extent indicates an additional common control on these proxies via kinetic processes.

According to above hypotheses, main features of climate and environment history in SW-France during the last 14-kyr can be drawn:

- 1) A wetting trend and slightly warmer during the Bölling-Alleröd;
- 2) A drying and cooling trend during the Younger Dryas;
- 3) An extremely wet and cold 8.2-kyr event;
- 4) A drier and warmer early Holocene vs. a wetter and cooler mid-to-late Holocene;
- 5) A drought between 4.5 and 3.8-kyr;
- 6) A fire-associated forest clearance event at c. 1-kyr.

More than presenting a lot of similarities to other contemporary proxy records from western Europe, the Alps and circum-Mediterranean region, our reconstructed climate records in SW-France can be viewed as one of the most continuous and detailed records for the last 14-kyr. For instance, the 8.2-kyr event, marked by sharp decreases in Mg/Ca and $\delta^{18}\text{O}$ which reflect an extremely wet and cold condition is, to our knowledge, among the best reconstructions for these regions.

The ice volume-adjusted Vil30 $\delta^{18}\text{O}$ profile generally follows the insolation curve, which demonstrates an external forcing on local temperatures. However, this synchronicity was interrupted around 4-kyr BP indicating an additional driving by the ocean-atmosphere circulation which likely reflects a regional re-organization during that time (McDermott 2011). Finally, changes in temperature and precipitation on millennial or longer timescales are coupled, however their relationship changes from Late-Glacial to the Holocene. During the Late-Glacial period, when the insolation increases, a warmer period corresponds to a wetting trend and *vice versa*; during the Holocene, when insolation decreases, a warmer period is associated with a period of dryness and *vice versa*.

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SYNCHRONOUS MID-HOLOCENE CLIMATE DETERIORATION EVENTS IN EAST AND WEST MEDITERRANEAN

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Projections of future climate change in the circum-Mediterranean region suffer much uncertainty, partly due to the large regional climate variability and the complexity of the climatic forcings. Previous studies suggested an east-west climate division in the Mediterranean region during the Holocene (Roberts 2011); while recently a synthesis work proposed a north-south Holocene paleohydrological contrast in west and central Mediterranean (Magny 2013). However, well-dated long-term terrestrial paleoclimate records are rare in the southern part of west Mediterranean and to this day no such record can be found in northern Algeria. Moreover, recent archaeological work in N-Algeria revealed that cultural changes (Kherbouche 2014) and mammal extinctions (Faith 2014) occurred during the mid-Holocene. Thus, paleoclimate records in this area are of great interest to test these hypotheses and possibly link ancient civilizations to past climate changes.

Here we present absolutely-dated decadal resolution climate records for the mid and the late Holocene (6034-3185yr BP and the last 650yr BP) based on the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ analyses of three stalagmites from Gueldaman GLD1 Cave (36°26'N, 4°34'E, 507 m asl), northern Algeria. The chronology was well constrained by 21 U/Th dates, with uncertainties commonly of decades. Isotopic profiles of two contemporary stalagmites show similar variations, which demonstrate a high climatic signal to local noise ratio.

GLD1 Cave is an archaeological site where the Neolithic anthropogenic deposits were identified and dated mainly at 6000 yr BP (Kherbouche 2014). It is located on the southeast slope of Gueldaman mountain, ca. 60 km southern inland from the Mediterranean sea. In this area, hot-summer Mediterranean climate prevails with an annual mean temperature of ca. 17.2 °C and a total precipitation of ca. 516 mm. The cave is well ventilated *via* a ca. 12 m-diameter entrance and is extended nearly horizontally from c. 80 m to the end.

GLD1 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles show large amplitude; $\delta^{13}\text{C}$ varies from -0.57 to -11.93‰, while $\delta^{18}\text{O}$ varies from -0.63 to -7.82‰. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ profiles of all stalagmites significantly correlate with each other ($r = 0.87 - 0.93$). Both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values analysed in a single growth layer clearly increase from the apex to the edge. Additionally, isotopic profiles from a smaller stalagmite, that assumed to grow under a slower-dripping site, show more positive values and larger amplitudes than those from the bigger stalagmite that assumed to grow under a faster-dripping site. All these evidences point to a kinetic control on GLD1 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variability. Given that the temperature remained almost constant since mid-Holocene (Martrat 2004), we thus interpret GLD1 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records as a qualitative indicator of past

precipitation through modulation of the kinetic processes during CO₂ degassing and evaporation in/above the cave; more positive $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values correspond to drier climates permitting stronger kinetic effects and *vice versa*.

GLD1 isotopic records reveal four dry periods: 5700-5500yr BP, 5300-5000yr BP, 4500-3800yr BP, and 412-145yr BP. Within dating uncertainties, the timings of these three mid-Holocene dry periods at GLD1 are synchronous with the dry events recorded in speleothems from Italy (Drysdale 2006), southwest-France (see abstract by Ruan et al.) and Israel (Bar-Matthews 2011). Those results are arguing against neither a south-north nor an east-west climate contract in the Mediterranean on centennial-event timescales during mid-Holocene. The climate deterioration at 4500-3800yr BP is harsher than these at 5700-5500yr BP and 5300-5000yr BP in west Mediterranean, while the opposite scenery occurs in east Mediterranean.

Direct comparisons between climate records and archaeological units are not possible due to limited ¹⁴C analyses on charcoal samples at the moment; upcoming dates will provide a mean to link cultural evolutions to past climate changes.

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ARTIFICIAL INFILTRATIONS INFORMING INTERPRETATION OF TRACE ELEMENT RECORDS IN SPELEOTHEMS

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A series of repeated artificial irrigation experiments were conducted at Wellington Caves, NSW, Australia in different seasons and simulating different amounts of rainfall. The conclusions from these irrigations have informed the interpretation of trace element records in stalagmites from this site and potentially sites in other semi-arid / arid environments.

Deuterium was used as an artificial tracer for the irrigation water in the cave and allowed for the calculation of the amount of dilution by stored water in the system. These calculations demonstrated that we observed a significant level of dilution of the irrigation water.

For each irrigation several sites activated and the dripwater was collected for trace element characterisation and organic matter analysis via fluorescence. In-situ measurements were also taken of pH and EC. Principal component analysis was to identify the trace elements that were bedrock-derived and/or soil-derived. The soil component was identified based on correlation with fluorescence representing the dissolved organic matter. Barium, magnesium, copper and nickel were also associated with the soil component. The bedrock component comprised the traditional elements such as calcium, strontium, magnesium.

In this semi-arid environment barium and magnesium, elements traditionally believed to be derived from the bedrock show different behaviour. Barium is derived from the soil and magnesium is derived from both the bedrock and soil. An important observation is that magnesium, traditionally a reliable proxy for effective rainfall, may not be suitable tracer in semi-arid environments, due to the additional contribution from the soil. However this study has identified the potential of barium as a soil tracer in stalagmites.

The conclusions from these irrigation experiments have been applied to the interpretation of the trace element records present in stalagmites collected from this site. These trace element records have then been compared to climate records and the conclusions from the infiltration experiments were confirmed.

RECONSTRUCTION OF PRECIPITATION VARIABILITY IN THE CARIBBEAN DURING THE LAST GLACIAL (80 - 7 KA BP)

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During the Last Glacial period, climate in the North Atlantic area was subject to large and rapid changes, which are, for instance, evident in Greenland ice core records (NGRIP members, 2004). In recent years, several high-resolution speleothem records from Central America covering the Last Glacial have been published (e.g., Lachniet et al., 2009; 2013), documenting a close link to North Atlantic climate variability on both orbital and millennial time scales. For the Caribbean, however, high-resolution terrestrial climate records are mainly available for the Holocene. For instance, Fensterer et al. (2012; 2013) presented a high-resolution stalagmite record from Cuba covering the last millennium and a lower-resolution record covering almost the entire last 12 ka. Other speleothem studies from the Caribbean (Mangini et al., 2007; Winter et al., 2011) only cover a few millennia.

Here we present two speleothem records from Puerto Rico and Cuba, which cover the period between 80 and 7 ka BP. The speleothems have been precisely dated by MC-ICP-MS ²³⁰Th/U-dating, and stable oxygen and carbon isotope ratios as well as trace element concentrations have been determined at high resolution. Stalagmite CM from Cuba is ca. 50 cm long and grew, interrupted by a few short-term hiatuses, between 80 and 7 ka BP. Stalagmite Larga 1 from Puerto Rico is 2 m long and grew between 50 and 15 ka BP.

The Larga 1 record shows a clear response to North Atlantic climate variability, which is documented by hiatuses during Heinrich events 3 and 4 as well as substantially higher $\delta^{18}\text{O}$ values during Heinrich events 2 and 5. Elevated $\delta^{18}\text{O}$ values during Heinrich events are accompanied by elevated $\delta^{13}\text{C}$ values and Mg content. This pattern is interpreted as reflecting drier conditions on Puerto Rico during North Atlantic cold events confirming the relationship observed on shorter time-scales using Holocene stalagmites from Cuba (Fensterer et al., 2012; 2013). However, the lower-resolution CM stalagmite record from Cuba does not show pronounced changes in $\delta^{18}\text{O}$ values and other climate proxies during Heinrich events. This may either reflect a different response of precipitation variability on Cuba to North Atlantic climate change – possibly related to the shorter distance to the Gulf of Mexico and the Pacific – or a generally lower sensitivity of the CM speleothem record.

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STALAGMITE SURVIVAL: NATURAL ATTRITION AND CYCLICAL GROWTH PATTERNS OF STALAGMITES IN SOUTHWEST SULAWESI OVER THE PAST 530,000 YEARS

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Numerous speleothem studies have analysed the age distribution of stalagmites harvested from multiple caves and inferred important changes in paleoclimates to explain stalagmite growth phases. However, stalagmites take tens to hundreds of thousands of years to grow, and thus the twin desires to preserve the cave condition for future generations and advance palaeoclimate science are often in conflict. In this study, we show that paleoclimate information can be extracted from a cave system without the removal of stalagmites. Our novel approach utilizes the ages of non-destructive mini-cores extracted in situ from the bases of stalagmites, thus keeping the intrinsic value of the cave intact.

Our case study is based on U/Th dates for 77 individual stalagmites drilled in situ in thirteen caves located in and around Bantimurung-Bulusaraung National Park, South Sulawesi, Indonesia. The stalagmites grew over the last ~530,000 years, and analysis of their age distribution shows an exponential decrease in the number of older stalagmites surviving to the present day. The exponential age distribution indicates that the rate of natural attrition of stalagmites is approximately constant through time, probably in response to a number of natural processes, including downward erosion of the karst terrain, cave collapse, in-cave erosional processes, in-cave sedimentation covering stalagmites, and dissolution of stalagmites by undersaturated waters. Natural attrition of stalagmites is likely to be a general cave phenomenon, and has important implications for cave conservation because it highlights that random removal of stalagmites without prior knowledge of their ages will result in unnecessary collection and failure to sample the full length of the available paleoclimate record.

Departure from this “normal” exponential profile shows that significant deviations are produced by periods of more frequent stalagmite growth, inferred here to reflect increases in monsoon rainfall over Sulawesi. By adjusting the record to account for stalagmite attrition, more statistically robust paleoclimate information can be inferred.

Crucially, these insights on past climates have been obtained entirely from reconnaissance-style basal mini-core ages. The data collection process is therefore non-destructive and does not require the removal of stalagmites from the cave. This novel technique is suitable for caves where the removal of stalagmites would cause irreparable damage, or jeopardize local cultural and tourism potential.

A RECONSTRUCTION OF PLIOCENE CLIMATE USING SPELEOTHEMS FROM THE NULLARBOR PLAIN, SOUTHWEST AUSTRALIA

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The Pliocene (~2.5-5 Ma) is an important time interval for study of the Earth's climate system due to its potential as an analogue for future climates. However, there is a significant lack of terrestrial archives of palaeoclimate information for this period, and even fewer reliable estimates of palaeotemperature. There is also a distinct lack of data from Southern Hemisphere locations. This project is part of a larger study that aims to address these gaps by providing palaeohydrological and palaeotemperature reconstructions for the Pliocene using speleothems obtained from caves beneath the Nullarbor Plain, southern Australia.

U-Pb dating of numerous Nullarbor speleothems shows that their growth spans from the late Miocene, through the Pliocene, and into the Pleistocene (Woodhead et al. in prep). This project aims to complement the broader study by focussing on long speleothem sections (>1m), potentially spanning complete Pliocene “stadial-interstadial” cycles. Internal chronologies will be established, allowing interpretations to be made regarding climatic changes during stadial-interstadial cycles.

Both fluid inclusion mass spectrometry and clumped isotope carbonate palaeothermometry will be used to produce palaeohydrological and palaeotemperature estimates. Fluid inclusion analyses will provide a direct proxy for the isotopic composition of past precipitation, which can be used to reconstruct regional rainfall patterns. Modern rainfall samples from the region will be used to isotopically fingerprint dominant sources of precipitation, informing interpretations of conditions at the time of speleothem deposition.

Clumped isotope carbonate palaeothermometry is a relatively new technique, based on the statistics of ¹³C-¹⁸O bonds in carbonate minerals (“ Δ_{47} ”). Although clumped isotopes in modern speleothems generally appear to be affected by significant isotopic disequilibrium effects, it has been suggested that such disequilibria can be accounted for by combining Δ_{47} analyses with fluid inclusion $\delta^{18}\text{O}$ data, potentially allowing for independent measurements of continental palaeotemperatures.

This research will provide a unique dataset of terrestrial temperature estimates during the Pliocene that will have practical applications in informing the next generation of climate models future climate change.

A HIGH-RESOLUTION EAST ASIAN MONSOON RECORD AROUND 2.8KA B.P. FROM MT.SHENNONJIA, CENTRAL CHINA

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Abstract: Here a newly retrieved stalagmite oxygen isotope ($\delta^{18}\text{O}$) record from the Yongxing Cave in Hubei province, central China is presented to provide an Asian monsoon history spanning 4.4 to 1.8 kyr BP with an average 4-yr-resolution (up to 2 yr in some part), based on 8 U/Th dates, about 603 pairs of stable isotope data and lithological studies. Our high-resolution $\delta^{18}\text{O}$ record reveals a striking weak summer monsoon event between 2.92-2.74kaB.P., lasting about 180 years. At the onset, the $\delta^{18}\text{O}$ values progressive increase by 2.5‰(from -10.48‰ to -7.98‰) within ~50 years, and drop by 2.4‰ (from -7.68‰ to -10.09‰) within~30 years at the end, forming a double peak and three plunging structure. These characteristics were consistent with the structure of “8.2ka” event recorded by Stalagmite H4 from Heshang Cave in Hubei. Dynamically, these two abrupt monsoon events might be related to a distinct decrease in the solar activity and the North Atlantic Ocean ice-raftering events. This probably suggests that they are controlled by the same driving mechanism. As previously suggested, the stalagmite-based “8.2 ka” event from the Asian monsoon area likely reflects the response of East Asian monsoon climates to ice-raftered events in the northern Atlantic. A comparison of Cave $\delta^{18}\text{O}$ and Greenland temperature records indicates that there is a strong link between high- and low-latitude climates at centennial scale. In addition, spectral analysis of our $\delta^{18}\text{O}$ record shows significant periodicities of 222yr□196yr□58yr□16 yr, which suggests that variation of the monsoon intensity are possibly influenced by the solar forcing.

LATEST MIOCENE-EARLY PLIOCENE VEGETATION AND CLIMATE OF THE NULLARBOR PLAIN: NEW INSIGHTS FROM FOSSIL POLLEN RECORDS OF U-Pb DATED SPELEOTHEMS

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The late Neogene environmental history of southern Australia remains poorly understood, largely because aridification has destroyed most biological evidence. Moreover, estimation of the ages of late Neogene terrestrial fossil assemblages almost always relies heavily on (imprecise) biostratigraphy. Hence for this long period which set the scene for more familiar late Quaternary environments, we don't really know what happened, or when.

The arid karst Nullarbor Plain (with c. 250 mm annual rainfall) separates mesic biotas of southeast and southwest Australia. Establishment of this biogeographic barrier is usually attributed to late Miocene uplift of the Plain. However, new pollen records recovered from U-Pb dated Nullarbor speleothems demonstrate a more dynamic vegetation and climate history. Pollen assemblages straddling the Miocene/Pliocene boundary (c. 5.6 to 5.0 Ma) dominated by Gyrostemonaceae, Casuarinaceae and Haloragaceae imply very open vegetation reflecting a semi-arid climate, but evidently slightly wetter than today. Early Pliocene pollen assemblages dominated by Myrtaceae (*Eucalyptus*, *Corymbia/Angophora*, and other types of uncertain generic affinity) and *Banksia* (Proteaceae), imply substantially higher rainfall than modern, and the presence of pollen attributable to *Doryanthes* (Doryanthaceae) by 4.89 Ma and *Geniostoma* (Loganiaceae) by 4.20 Ma imply rainfall three or four times higher than today (≥ 800 mm annual rainfall). We have not been able to recover pollen from speleothems younger than c. 3.5 Ma, probably reflecting increasing aridity after this date. The single exception is a Pleistocene sample from 0.4 Ma dominated by Chenopodiaceae pollen, indicating that modern chenopod shrubland, which characterises the Nullarbor today, was in place by the Middle Pleistocene. Our results imply that warm and wet Pliocene climates had a profound effect on currently arid central Australian environments.

Interpreting climatic signals from stalagmite trace element and isotopic records using simple geochemical models and growth rate constraints

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Fully exploiting the climatic information from speleothem trace element and isotopic records requires a quantitative approach for resolving the multiple parameters influencing geochemical signals. For example, monitoring data and simple models show that the degree of prior calcite precipitation (PCP) – a prime contributor to variation in speleothem Mg/Ca, Sr/Ca, and Ba/Ca – is driven by both the drip interval as well as the degree of oversaturation of the drip with respect to CaCO₃ at cave pCO₂. We show how this generates a temporally variable relationship between Mg/Ca and drip interval which must be accounted for in interpreting time series of PCP-sensitive trace elements.

In laboratory and monitoring experiments, the oversaturation state of dripwater has also been shown to affect oxygen isotopic fractionation in calcite.

To resolve these effects in natural cave settings, we present new data from hydrochemical monitoring and from comparisons of sets of coeval stalagmites from MIS 5 to MIS 1 from cave systems in a small geographic region which is expected to have uniform climatic forcing. In addition, the I-STAL model [1], is used to confirm the stalagmites with strongest and weakest sensitivity to drip rate variation in PCP. The I-STAL model is also used to compare the growth rate variations predicted from inferred saturation states using standard kinetics of speleothem growth with geochronologically constrained growth rates. We show how this approach can be used to identify the oxygen isotopic signals most likely to reflect primary variations in dripwater d18O and cave temperature, from components strongly influenced by kinetic effects.

SPELEOTHEM RECORDS OF CLIMATE VARIABILITY FROM OIS 5 TO THE LATE HOLOCENE FROM THE CROATIAN LITTORAL (MANITA PEĆ CAVE)

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Littoral part of Croatia, recognized as transitional climatic zone between the continental Europe and Mediterranean, hosts thousands of caves, but speleothem-based palaeoclimate and palaeoenvironmental studies are still scarce.

We present the study conducted in Manita peć Cave (44°18' N, 15°28' E, 570 m a.s.l.) formed in Upper Jurassic limestone of Velebit Mt. Study has encompassed characterization of microclimate settings, dripwater hydrology and environmental conditions for modern calcite precipitation. For the palaeoclimate interpretation, two stalagmites (MP2 and MP3) were recovered and their O and C stable isotope time series were constrained by U-Th dating method.

Regional response to the global climate changes was revealed for the periods between ~106 ka and ~46 ka and from ~13 ka to ~5 ka. The most prominent changes that had led to growth interruption of MP2 and significant change in deposition of MP3 were preceded by considerable $\delta^{13}\text{C}$ increase from -7‰ to 0‰ (VPDB) in both speleothems, indicating deterioration of climatic conditions. Interestingly, $\delta^{13}\text{C}$ of modern calcite from this cave is ca. -11‰ implying the presence of vegetation and soil microbial activity, although the present plant cover is quite deprived.

In order to assess potential causes of climate signals and dominant influences regarding continental and maritime air masses, we compare our results with the records from the same time periods from Villars Cave, France (Genty et al., 2010), Sofular Cave, Turkey (Fleitmann et al., 2009), Soreq and Peqin Cave, Israel (Bar-Matthews et al., 2003) and from north Alpine caves (Boch et al., 2011).

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ASSESSMENT OF THE HYDROLOGICAL BEHAVIOUR IN CAVE ENVIRONMENTS AT VARYING ALTITUDES ON THE EASTERN ADRIATIC COAST (CROATIA)

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Croatian eastern Adriatic coast, with the Dinarides as orographic barrier, occupies a key position between eastern and western Mediterranean basins and delimits central European and the Mediterranean regions. This boundary region is influenced both by Atlantic and Mediterranean air masses, and during past climate changes it has probably been shifting, leaving the palaeoclimate signals records within the speleothems.

In order to characterize cave environments eligible for the reconstruction of the palaeoenvironmental settings, we selected three caves at the different altitudes along the transection from Dalmatian islands to Velebit Mt peaks (Croatia): Strašna peć Cave on Dugi otok Island (70 m a.s.l.), Manita peć Cave in Velika Paklenica canyon (Velebit Mt, 570 m a.s.l.) and Spilja u Zubu Buljme Cave (Velebit Mt, 1305 m a.s.l.). We have conducted cave microclimate and dripwater monitoring to select representative site/speleothems for palaeoclimate reconstruction, and analyzed isotopic composition of precipitation and cave dripwater. The aim of the latter was to estimate contemporary regional and local influences of Atlantic and Mediterranean air masses and differences between coastal and continental, and between low- and high-altitude sites.

As for the water isotopic imprints, altitude effect was noted both in precipitation and in dripwater isotopic composition. Two lower caves, in spite of the altitude difference of 500 m, have local meteoric water line (LMWL) of similar slope and intercept. Slopes lower than that of the global meteoric water line (GMWL) indicate enhanced evaporation during the warm season. As expected, the LMWL of the highest cave region resembles the GMWL by the slope, but obtained values of deuterium excess for all three caves ($d_{ZB} = 16.0\text{‰}$, $d_{MP} = 14.6\text{‰}$ and $d_{SP} = 14.5\text{‰}$) do not match neither Atlantic (10‰) nor Mediterranean (22‰) values, indicating both continental and maritime influences.

According to the cave microclimate conditions, two lower caves showed potential for the studies to come with their stable cave environments (temperature amplitudes of 1.7 and 1.8 °C, and RH of 100%), and drip sites with corresponding speleothems which showed stable discharge mode with only weak response to the rain events. Unfortunately, the highest cave has too large air temperature amplitude (5.3 °C), so the isotopic signal in already sparse calcite precipitation is surely affected by kinetic fractionation.

TRACKING THE CLIMATE SIGNAL IN STALAGMITE DRIPWATERS FROM HARRIE WOOD CAVES, SE AUSTRALIA

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Monitoring cave environments is a valuable approach to assist in the interpretation of speleothem paleoclimate records. Multi-year studies of cave drip water permits an assessment of the climate signal in speleothems, as well as the potential for its modification by karst hydrology. Data presented here are from three drip water monitoring sites in Yarrangobilly Caves (NSW, SE Australia) collected on a fortnightly sampling program launched in 2006.

The relationship between the stable isotopic composition of the precipitation to the drip water, temporal variations of the discharge and chemical changes in the drip water were investigated. Stable isotope analysis showed that the drip water was sourced from local meteoric waters. Low temporal variability of the cave drip water isotopic composition in comparison to the range observed in the rainfall reflects attenuation of the seasonal rainfall isotopic variation and of two distinctly depleted rainfall events. As there is a strong buffering of the rainfall isotopic signal, this attenuation suggests mixing and storage in the karst system. All drip sites sustained a base flow during multi year periods of water deficit, further confirming a storage component.

Our studies spanned two contrasting recharge episodes during the El Niño (2006-2009) and the La Niña (2010 – 2012). Specifically, prior to 2010, during the El Niño where there was persistent rainfall deficit, infiltrating meteoric water was at a minimum and stored for at least three years; spending sufficient time to equilibrate and reach saturation with respect to calcite. After the first main precipitation event during this phase the stored supersaturated water was evacuated whereby the drip rate, Ca concentration, EC and calcite saturation indices tracked together and increased sharply reaching maximum levels. Again after a relatively dry 12 month period in 2011, the drip rate, Ca concentration, EC and SI_C simultaneously increased as the result of above average rainfall but not to the same levels reached previously reflecting the reduced degree of saturation due to a shorter storage time.

This research highlights the importance of understanding the influence of the karst on the stable isotope and chemistry of drip waters and the relationship to the climate signal prior to interpreting paleoclimatic information preserved in speleothems.

A PRELIMINARY STUDY ON GLACIAL TERMINATION-II IN NORTHERN CHINA

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Using the stalagmite XL4 collected from Xinglong Cave in Hebei province, China (40°29'N, 117°29'E, 591 m a.s.l.), we explore the climate variability of glacial termination-II (T-II) in Northern China. The stalagmite is columnar in shape and formed by pure calcite. No hiatus is found within the study period. We obtained 15 ²³⁰Th ages along the growth axis with MC-ICP-MS at the Isotope Laboratory in Xi'an Jiaotong University. The range of uranium concentration of the dating subsamples is from 259 to 718 ppb. In order to improve the accuracy of dating, powder subsamples were drilled as much as about 500mg for each along the deposit layers, hence yielding rather small errors less than 2‰. We then measured stable isotope samples along the growth axis to generate the $\delta^{18}\text{O}$ time series, and 36 isotope subsamples are preliminarily analysed using a Kiel-IV device attached to the Thermo Scientific MAT 253 stable isotope ratio mass spectrometer system at the same Laboratory mentioned above. Covering about the period of 126,500 to 134,300 yr BP, the isotope series reveals several interesting findings, of which two points were most worthy of discussion:

(1) The most rapid decrease (MRD) in the $\delta^{18}\text{O}$ of XL4 occurred after about 129,561aBP, prior to the occurrence of the same event in the $\delta^{18}\text{O}$ of stalagmite SB25 from Southern China (Cheng et al, 2009) for about 520 years (129,561aBP-129,040aBP). Even giving full consideration to the errors in the data, the phase difference also reaches more than 200 years ($[129,040+70]_{\text{SB25}} - [129,561-240]_{\text{XL4}}$).

(2) A very clear T-II pause (Lototskaya et al, 1999) occurred after the MRD in the $\delta^{18}\text{O}$ of XL4, which is rather unique comparing the stalagmite $\delta^{18}\text{O}$ profile from Southern China.

In summary, the pattern of climate variability of the T-II in Northern China is significantly different from that in Southern China, and the signal of climate change during the T-II is most likely transported from the north to the south.

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WESTERN MEDITERRANEAN OCEAN-ATMOSPHERE EVOLUTION ALONG THE LAST INTERGLACIAL ENDING

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This study aims to examine in parallel the marine and atmospheric changes that occurred in the Western Mediterranean region at the ending of the last interglacial stage (Marine Isotope Stage, MIS 5e) and initiation of the last glaciation. Geochemical measurements (stable isotopes and trace elements) have been produced in both terrestrial (speleothems) and marine (planktonic foraminifers) climatic archives. Two speleothems have been analysed, one was collected from Menorca island (Indiana) and the other from the Central Pyrenees (Judith). The studied marine sediment cores are ODP Site 977A from the Alboran Sea and core MD99-2343 from the Balearic Sea. Chronologies for the speleothems are based in their U/Th dates while marine chronologies are based on isotopic stratigraphy. Paired analyses of $\delta^{18}\text{O}$ and Mg/Ca in the planktonic foraminifer *Globigerina bulloides* from the Mediterranean cores have allow to reconstruct the evolution of both Sea Surface Temperature (SST) and changes in the $\delta^{18}\text{O}$ of surface marine water. These marine records are compared with carbon isotopes ($\delta^{13}\text{C}$) and Mg/Ca ratios measured in the speleothem calcite.

Intervals with relatively high $\delta^{13}\text{C}$ values in the speleothems coincide with high $\delta^{18}\text{O}_{\text{sw}}$ values in the marine record, supporting that conditions of low soil humidity occurred when evaporation-precipitation balance was increased in the Western Mediterranean basin. These results indicate that the MIS 5e ended with abrupt shift toward arid conditions, which consisted in a two pulses event, and another strong aridification event occurred at MIS 5b. Comparison with the SST records indicates that these humidity changes were not always coupled with the major SST transitions, for instance, the major cooling phase ending MIS 5e occurred after the aridification event had initiated. These results ultimately highlight the close connection between humidity patterns in the southern central Pyrenees and western Mediterranean Sea conditions.

EIGHT-YEARS OF CAVE MONITORING AT GOLGOTHA CAVE, SW AUSTRALIA: IMPLICATIONS FOR SPELEOTHEM PALEOCLIMATE RECORDS

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Speleothems are an important archive of paleoenvironmental information but a thorough understanding of processes are necessary for their interpretation. In order to better understand speleothem records from the climatically-sensitive southwest region of Western Australia, we have conducted a detailed eight-year monitoring study at Golgotha Cave, southwest Western Australia.

Oxygen isotopic data demonstrated that the majority of water moved through the relatively porous Quaternary calcarenite as matrix-flow via preferential vertical pathways, with an inferred transit time of less than one year. A zone of high-flow dripwater is preferentially fed by high-magnitude rainfall events (Treble et al., 2013). Geochemical modelling indicates that dripwater carbonate chemistry is largely unmodified until dripwater enters the cave, owing to the simple karst hydrology. Prior calcite precipitation signals of increased Mg/Ca and Sr/Ca in dripwater are attributed to stalactite deposition. This signal is enhanced at low-flow sites and minimised at the high-flow site as degassing and subsequent stalactite deposition are a function of drip interval.

Long-term rising trends are found in most solutes that we attribute via a mass-balance approach to increasing forest bioproductivity. These results are consistent with an increase in forest understorey following a low-intensity burn six months after monitoring commenced.

A fundamental message from this study is that individual speleothem records from within Golgotha Cave will differ, e.g. speleothem $\delta^{18}\text{O}$ at our high-flow site is biased to recording high-magnitude rainfall events, whilst prior calcite precipitation will be the main driver of speleothem Mg/Ca and Sr/Ca at low-flow sites. Forest biomass appears to be modulating transpiration-sensitive ions and these may serve as an indicator of fire history.

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Treble et al. (2013) An isotopic and modelling study of flow paths and storage in Quaternary calcarenite, SW Australia: implications for speleothem paleoclimate records. *Quaternary Science Reviews* 64: 90-103.

WHEN CRYSTALS BECOME DUST: SPELEOTHEM DEGRADATION PROCESSES IN PRAILEAITZ I CAVE (NORTHERN SPAIN)

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Introduction

Praileaitz I Cave is located in Gipuzkoa (Basque Country, Spain). An important network of caves has been identified in this area with archaeological materials from the Upper Palaeolithic. In addition to archaeological materials, in August 2006 a series of red painted signs was discovered inside the cave.

Purpose and methodology of study

Within the cavity there are evident signs of deterioration of different types and generations, affecting both the host rock and the speleothems. The supports of many of the paintings, specifically the drapes, are in a clear state of deterioration due to disintegration of the texture of the speleothem, resulting from selective dissolution of the crystals and the creation of intercrystalline porosity. To analyse and study the different types of degradation and their causes, we gathered a total of 14 samples of speleothems and rock throughout the cave. The speleothems sampled are of different types and come from different growth phases. In order to monitor the parameters that may be causing the pathologies of degradation, a protocol was drawn up for measuring the environmental parameters and the condensation water and drip water in the cave. To analyse the water from the cave, samples were taken at four representative drip points in the cave and from condensation water.

The protocol established for addressing the problem of the different pathologies in the speleothems includes a combination of various techniques: (1) Conventional optical microscopy, (2) Scanning electron microscope, (3) X-ray diffraction analysis, (4) isotopic analyses of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ from micrite, speleothem and host rock and (5) water chemistry and isotopic analysis.

Pathologies in the speleothems of Praileaitz I

The pathologies fundamentally develop on speleothems that are now inactive or sporadically active with weak dripping, regardless of their morphology and formation phase. In Praileaitz I cave we distinguish three types of “pathologies” with clearly distinguishable zoning throughout the cave: (1) through organic activity, (2) generation of micrite or “moonmilk” and (3) sheeting/dissolution.

Degradation resulting from organic activity (root colonisation and bioturbation) has only been detected at the entrance to the cave, which receives direct sunlight.

Micritization and formation of “Moonmilk” cover different types of support including the host rock and the different types of speleothems and are white and porous in

texture. It is normally millimetric, formed by a network of matt white calcite crystals of less than 4 μm .

Dissolution/sheeting alteration affects inactive speleothems, mainly of drape type and stalactites, and the host rock, creating intercrystalline porosity or hemispheric dissolution. This pathology involves an alteration in the textural features of the speleothems through sheeting or loss of material from the surface layers (“onion-skin”) along the growth lines.

Causes of the Pathologies

The two main internal pathologies described in Praileaitz I cave are simply a differential reflection of a single process: condensation of the humidity in the interior of the cave. The greatest proliferation of the alteration of a micritization/ “moonmilk” formation type takes place in the near entrance chambers, where there are very sharp fluctuations in temperature and humidity between spring-summer and autumn-winter, leading to humidification-dehumidification (evaporation) cycles that determine the greater and lesser creation of condensation water on the walls and speleothems of the cave. This variability in the ambient conditions in the most external area of the cave results in neof ormation of acicular micritic calcite during the months of greatest temperature and a fall in humidity in the cave, from the dissolved carbonate (speleothem) in a period of greater condensation. In contrast, in the inner chambers of the cave, both the temperature and the humidity (close to 100%) remain constant throughout the period with sharp increases in CO_2 concentrations in the months of May-November, increasing the dissolution effects from the condensation water.

A narrow passage at different elevations between external and internal chambers serves as a climatological barrier to energy/mass fronts from the exterior. This particular physiography is important because it prevents the energy fronts (heat-cold) from entering the internal sector and allows constant climatic conditions in this interior sector of the cave. At the same time, however, these conditions are aggressive for the speleothems, due to the high concentration of CO_2 and the constant availability of condensation water, which means that the alteration processes described occur with greater intensity and duration.

Acknowledgements

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CORALLOID SPELEOTHEMS ASSOCIATED WITH NEANDERTHAL SKELETON IN ALTAMURA CAVE (SOUTHERN ITALY): ENVIRONMENTAL CONSTRAIN AND PALEOCLIMATE SIGNIFICANCE

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Coralloid speleothems or “cave popcorns” originate from spray phenomena and/or carbonate-rich aerosols. The nucleation of coralloids generally occurs upon protuberances of the cave walls and their growth is controlled by air currents and cave geometry and, possibly, by microbial activity. However, being their mm-size dimensions and complex grape-like shape, their growth mechanisms as well as their paleoclimate significance is still poorly understood.

In this work we present the first petrographic, micro-stratigraphic and geochemical study of three coralloid groups that coat an exceptionally well preserved Neanderthal skeleton found in Lamalunga Cave (Altamura, Southern Italy). The results are important to reconstruct the regional climate setting during the Last Glacial cycle and its possible relationship with Neanderthalian migration and dwelling in Southern Italy (Lari et al., in prep).

Petrography and micro-stratigraphy reveal that coralloids are characterised by elongated columnar and open columnar fabrics, and their different growth phases are separated by organic-rich dark layers and micrite intervals which correspond to condensed intervals and/or sedimentary hiatuses (Frisia et al., 2012).

Preliminary dating by ICP-MS U/Th technique revealed that coralloids formed during four distinctive warm episodes during the last glacial/interglacial cycle (last 130 ka) suggesting that coralloids, unlike other speleothems, record only the major favourable climatic events and can, therefore, be utilised as benchmark for the warmest/wettest climate intervals.

The small size and complex undulated morphology make these samples particularly apt for Synchrotron Radiation X-ray Microfluorescence (SR- μ XRF) analyses allowing the acquisition of high resolution trace element data not easily achievable with other analytical techniques (Borsato et al., 2007).

SR- μ XRF mapping and scanning coupled with U/Th dating and micro-stratigraphy permits the environmental characterisation of the different growth phases and condensed intervals and provides a valuable tool for the precise correlation between different samples.

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A BELGIAN SPELEOTHEM FROM THE LAST INTERGLACIAL: INSIGHTS IN THE ONSET OF GLACIAL CONDITIONS IN NORTHERN EUROPE

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The Han-stm-9 (or ‘Triptyque’) speleothem is a broken, 68 cm long and candle-shaped stalagmite from the Han-sur-Lesse cave system in the south of Belgium. The stalagmite was collected in summer 2013 within the southern part of the cave network and was dated between ~125 and ~99ka. Most likely, climate optimum conditions during the 130-125ka interval are linked to the growth of this and other speleothems from Belgian caves. This particular speleothem gained interest because of the partial conformity with the continental interglacial period in northern Europe (130 – 118ka), referred to as the Eemian, and its dense calcite composition with visible layering, excluding post-depositional deformation. Furthermore, the stalagmite displays a complex growth history, with large variations in growth rates and periods of ceased speleothem formation. Two hiatuses, with a distinct macroscopic expression, occur. The first one starts at 118.4ka and lasts until 113.0ka. A second hiatus is situated between ~108ka and 103.7ka. A trend in growth rate, consisting of slow growth gradually increasing towards very fast speleothem formation before both hiatuses, is observed. These intervals with very high growth rates, for instance around 118ka, enable high-resolution climate reconstructions via stable isotopes ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) and trace elements (Mg, Sr, Ba and P), down to centennial and decadal scale.

The occurrence of the first hiatus around 118ka is interesting given its correspondence with the generally accepted termination of the Eemian in northern Europe at 119-118ka. Though, after this, other intervals of speleothem growth alternating with non-deposition suggest a more complicated structure of the transition towards the Last Glacial period. Other Belgian speleothems, collected in the Han-sur-Lesse cave and at other locations in Belgium, show similar trends of increasing growth rates and ceased speleothem formation.

The analysis carried out on this stalagmite, combined with similar studies on other Belgian speleothems from that time interval, will add to the knowledge of how glacial climate conditions were established on the north European continent.

THE END OF THE LAST INTERGLACIAL AS REGISTERED IN SPELEOTHEMS FROM CAVES IN BELGIUM

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Three stalagmites from the Remouchamps and Han-sur-Lesse caves (Belgium) grew from ~124 to 100ka with growth rates going from 0.8mm/century to 3cm/century. Stable isotopic ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) and growth-rate analyses suggest a rather stable climate from 122.0 to 115.8 ka. A clear climate deterioration is observed at ~115.8 ka and lasts until 111.2ka ($\pm 0.5\text{ka}$, 2s), which corresponds well with Greenland Stadial 26. Several short-term but clear changes are observed in the stable isotopic composition at ~121.5, 119.5, 118.4, 117.6 ($\pm 0.5\text{ka}$, 2s) and are interpreted as climatic events of ~several hundred years long. They correspond with changes in stalagmite diameter and growth rate. Depending on the combination of changes in the $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, growth rate and stalagmite diameter, the events are interpreted as corresponding to changes in rainfall amount or temperature.

The RSM17 stalagmite exhibits visible seasonal layering during the entire 120-115ka period on which changes in Mg, Sr, Ba en P have been observed. This well pronounced lamination, likely annual as suggested by the U-Th data demonstrates a strong seasonal character of the climate and/or vegetation activity during this period. We compare these MIS5 seasonality to the present day calcite layering observed in the cave.

The stalagmites, with a growth-rate increase after 125ka, globally corresponding to the so-called Eemian optimum, seem to start later than other southern stalagmites from France, Italy or Spain. This observation raises the question of a possible late onset of interglacial conditions in north-west Europe and a progressive S-N advance of warmer conditions between 130 and 125ka through western Europe.

ISOTOPE ANALYSIS OF FLUID INCLUSION WATER IN SPELEOTHEMS

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Techniques for stable isotope analysis ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of fluid inclusion water in rock samples have advanced rapidly over the past ten years. Recent progress is fuelled by the development of new techniques, facilitating rapid and high-precision analysis of <1 microliter water samples. Isotope analysis of fluid inclusion water still is time consuming, but worth the effort, as it provides valuable information on paleo-fluids that formed rock and minerals in various geological settings.

In speleothem studies, fluid inclusion isotope values provide key paleoclimate parameters. Such data are a direct proxy for the isotopic composition of paleo-rainfall, because cave drip water captured in the fluid inclusions isotopically approximates rainwater above the cave. Particularly in monsoonal settings, fluid inclusion isotope variation can be substantial, due to changes of rainfall amount or moisture source area. Combining $\delta^{18}\text{O}$ values of fluid inclusion water and host calcite allow us to separate the effect of changes in rainwater isotope composition and cave temperature, on the assumption that speleothem calcite grew in (some sort of) isotopic equilibrium. In this presentation some recent work done in our stable isotope lab in Amsterdam is lined up to highlight the precision and temporal resolution that this technique offers. Further examples will be given to outline some of the remaining problems and complications for the isotope analysis of fluid inclusions and the proper interpretation of the data. I will finally try to provide an outlook on future developments in fluid inclusion isotope analysis.

THE ONSET OF MEDITERRANEAN CLIMATE CONSTRAINED USING COMPUTED TOMOGRAPHY-DERIVED DENSITY VARIATIONS IN AN IBERIAN STALAGMITE

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Previous pollen-based studies^{1,2} subdivide the Holocene climate in the western Mediterranean region into three intervals: a humid phase (12-7 ka BP), a transition phase (7-5.5 ka BP), and an aridification phase (5.5 ka BP until present) that represents the onset of Mediterranean climate. However, substantial chronological uncertainty is associated with these pollen-based reconstructions and precludes the deconvolution of climate- from possibly anthropogenic-driven vegetation shifts. Moreover the mechanisms controlling these shifts, if indeed climate-induced rather than anthropogenic, are unclear.

Here, we present a high-resolution, accurately-dated Holocene palaeoclimate record from El Refugio Cave in southern Iberia, constructed using computed tomography-derived stalagmite density variations. This record represents the first precise radiometric stalagmite chronology created without sectioning the sample that tracks the growth axis in three dimensions, thus increases confidence in the climatological interpretations. Additionally, the tomographic visualisation allows enhanced detection of growth hiatuses and axis shifts, which may correspond with regional seismic events. The El Refugio Cave record considered together with other Northern Hemisphere proxy records reveals that insolation-driven southward displacement of the North Atlantic Subtropical High from its early Holocene position that underlies the inception of a Mediterranean climate in southern Iberia at 5.2 ka BP.

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HYDROCLIMATE CHANGE IN THE AMAZON LOWLANDS: A TALE OF TWO CAVE RECORDS

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Study on speleothems from Paraiso cave (04°04'S, 55°27'W), a site proximate to the equator in eastern Amazon, provides the first absolute-dated, high-resolution record on the regional precipitation history through the last 50,000 years. Oxygen isotopic analysis on the samples reveals millennial-scale variations during the last glacial period. The variations share a similar magnitude (~2 ‰) to, but are anti-phased with those in the Hulu-Dongge cave record from eastern China. Therefore, the observation is consistent with the previously reported millennial-scale meridional shift of the tropical rainfall belt. From the last glacial to Holocene, the Paraiso record however presents a distinct decrease in calcite d18O, with a magnitude up to 7 ‰. When it is compared to the record from Diamante cave in western Amazon, we found that the d18O values in two records have a large offset during the glacial, but not in Holocene. We suggest that the Amazon Basin was relatively dry in the glacial time. Therefore, rainfall d18O in the basin was dominated by a typical continental fractionation along a moisture trajectory. During the Holocene, higher rainfall and denser rainforest in the lowlands may have resulted in more water recycling through transpiration. Therefore, moisture d18O gradient would be reduced between the east and the west in the basin. Despite the drier conditions inferred for the glacial Amazon lowlands, d13C values in the Paraiso record never reach high values; thus ruling out vegetation dominated by C4 plants.

SEASONAL- TO DECADEAL-SCALE MONSOON VARIABILITY OVER THE LAST TWO CENTURIES DERIVED FROM CHINESE CAVE RECORDS

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Abstract: Using ^{230}Th dating and annual-layer counting techniques, we constructed precise timescales of the last two centuries for several annually-banded stalagmites from cave sites affected by the East Asian Monsoon or partially mixed with Indian Monsoon. A proxy of $\delta^{13}\text{C}$ along the different stalagmite profiles displays either distinctly seasonal or ENSO-scale cycles, depending on local climate conditions and different geochemical cycles of carbon in the cave system. Stalagmite $\delta^{18}\text{O}$ profiles in central and SW China are incomparable on decadal time, suggesting complex factors that control the short-term variations of stalagmite $\delta^{18}\text{O}$ at different sites. We detected a dominant periodicity of 50~60 years for monsoon precipitation, agreeing with the drought/flood index from historical documents. A significant monsoon failure occurred at ~AD1840', timing of the Taiping Heavenly Kingdom Movement. A Sr/Ca record in SW China is in line with the Northern hemisphere temperature (NHT) and the tropical Pacific sea surface temperature (SST) over the last two centuries, indicating atmospheric(soil) CO_2 and mean annual cave temperature have dominated the Sr geochemical behaviors in that karst system. The different proxies, placed on a common timescale, provide evidence for assessing respective contributions of natural climate and anthropogenic effect to the current global warming.

2 YEAR, HIGH RESOLUTION SPELEOTHEM GROWTH, CO₂, CAVE VENTILATION AND METHANE DEPLETION RECORD RESPONDING TO SEASON AND WEATHER

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Speleothem palaeo-climate records offer valuable insight into regional climatic variations at mid-latitudes distinct from polar climatic records. An assumption of regular speleothem growth between 2 age dates is usually applied. This time period between dates may be 10s, 100s or 1,000s of years leading to an assumed average speleothem growth which may be hiding growth hiatuses or changes to speleothem hydrology. Counting annual isotopic or compositional bands due to seasonal variation provides one solution to separate speleothem growth rate as a variable over time. However, most speleothem records have insufficient spatial resolution to distinguish annual growth bands.

Direct physical measurement of in-situ speleothem growth is difficult because of instrument resolution and speleothem morphological vagaries. We have taken a different approach here based on the associated CO₂ liberated when speleothems grow. To discriminate CO₂ due to speleothem growth from other sources of CO₂, particularly high CO₂ from soils, the stable isotope $\delta^{13}\text{C}$ is used. The 3 principal sources of CO₂ are external air, speleothem growth and soil-air. Each of these sources has a distinctive $\delta^{13}\text{C}$ signature allowing calculation of the relative proportion of CO₂ derived from each source at each sampling location for every hour over a 2 year period. When combined with CO₂ concentration and sensitive air-flow velocities a rate of CaCO₃ accumulation, or speleothem growth, is calculated. This 2 year speleothem growth record from Chifley Cave shows large seasonal and diurnal speleothem growth biases. Transient weather patterns also strongly influence speleothem growth.

Cave air CO₂ shows a seasonal (summer maximum) and often a diurnal cycle, from a minimum late morning to a maximum in the late evening caused by ventilation of external low CO₂ air. Differences between the external temperature and the near constant cave air temperature causes a buoyancy contrast which drives bi-directional cave air ventilation. On hot days cool cave air (11°C) sinks into the Grand Arch and is replenished by sucking external air from the Plughole cave opening. The slightly lower cave atmospheric pressure on hot days also causes soil-air rich in CO₂ to seep into Chifley Cave, notably at the bottom of Katies Bower. On cold winter days

relatively buoyant warm cave air escapes via the Plughole 70m above and through minor fissures reversing the summer pattern.

Ambient air drawn into Chifley Cave is depleted in methane by a maximum of 90%. Karst soils both within the limestone caves and on the surface constitute a significant net methane sink. Clear seasonal patterns are present with a consistent average summer methane concentration of 0.5 ppmv (~70% depletion) highly correlated with high concentration (7,000 – 12,000 ppmv) low $\delta^{13}\text{C}$ CO_2 (-24 ‰ PDB). This gas composition is consistent with surface soil gas drawn into Chifley Cave through myriad small fissures during summer.

This extreme methane depletion is produced by high-affinity methanotrophs in surface soils as well as internal cave soils at Jenolan Caves. A seasonal pattern of methane depletion is observed, implying a seasonal variation from exogenous methane depletion in summer to in-situ microbial activity in winter. An investigation of extracted bacterial DNA targeting type I methanotrophs and type II methanotrophs revealed a large diversity of methane monooxygenase genes from a total of 178 operational taxonomic units (OTUs). The DNA sequences fell into six clades (branches) within the *pmoA/amoA* evolutionary tree. Two of these clades are potentially novel (ie. they represent undiscovered diversity within the *pmoA* gene family).

MAJOR REORGANIZATION OF THE NORTH ATLANTIC OSCILLATION DURING THE EARLY HOLOCENE DEGLACIATION

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The North Atlantic Oscillation (NAO) controls the strength and position of the westerlies (Hurrell, 1995) and is associated with a clear dipole precipitation pattern over NW Europe and the W Mediterranean/NW Africa. However, this teleconnection pattern is not stationary (Wang et al., 2012). Furthermore, the true natural variability of the NAO is still unknown due to a lack of instrumental data extending back beyond the Anthropocene. It also remains a question how the NAO will develop under the influence of the melting Greenland ice sheet. This requires climate reconstructions from key NAO regions covering the Early Holocene deglaciation. Since the longest NAO reconstruction only extends back to 5.2 ka before present (Olsen et al., 2012), there is a strong need for longer records.

Here we present a precisely-dated, high resolution speleothem oxygen isotope record from Grotte de Piste, NW Morocco (a key NAO region) covering the time period from 11.6 to 2.6 ka BP. Carbon and oxygen isotopes were analysed at 15-year resolution. A multi-proxy approach provides solid evidence that the $\delta^{18}\text{O}$ values reflect rainfall variability.

We calculated correlations between our Moroccan rainfall record and another speleothem rainfall record from NW Germany (Fohlmeister et al., 2012). Under present-day NAO conditions, these records should show a negative correlation. However, we observe a positive correlation during the Early Holocene, which changes into a negative correlation towards the Mid Holocene. Simulations with the earth system model COSMOS (Wei and Lohmann, 2012) indicate that this change in the NAO teleconnection pattern is related to the changing ice-sheet configuration and the deglaciation.

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SPELEOTHEM ARAGONITE PARTITION COEFFICIENTS FOR Mg, Sr, Ba AND U ASSESSED FROM CALCITE-ARAGONITE TRANSITIONS

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Carbon and oxygen stable isotope ratios recorded in calcitic and aragonitic speleothems are widely applied as proxies for past climate conditions. Whereas numerous studies of trace element variability in calcite speleothems have been published (e.g., Tremaine and Froelich, 2013), only very little information on trace element variability in aragonite speleothems is available (e.g., Wassenburg et al., 2013). Since aragonite contains high amounts of U compared to its calcitic counterparts, it can be dated with very high precision and accuracy. Thus, detailed investigation and exploration of the full potential of speleothem aragonite trace element variability for palaeoclimate reconstruction is of great importance.

Recently, Stoll et al. (2012) published a simple model that facilitates quantitative evaluation of speleothem trace element variability. Quantitative interpretation heavily relies on how well constrained the partition coefficients are for the trace element of interest. Although many laboratory precipitation experiments studying aragonite trace element partitioning are available, none of them reflects specific cave precipitation conditions (i.e., low ionic strength, thin water films). Trace element partition coefficients for speleothem calcite are available for Mg, Sr, Ba and U (among other elements; Day and Henderson, 2013).

Here we present approximation of trace element partitioning coefficients in speleothem aragonite. We analysed the trace element composition of nine well-preserved stratigraphical and lateral calcite-aragonite (Cc-Ar) transitions. Using the “known” trace element partition coefficient for the calcite, the solution composition can be derived. Assuming that the solution composition did not undergo major changes during the time interval when speleothem mineralogy changed, the trace element composition of the aragonite can be used to determine aragonite trace element partition coefficients. The stratigraphical Cc-Ar transitions indicate that speleothem aragonite partition coefficients approximate $8.4 (\pm 1.8) \times 10^{-5}$ for Mg, $1.0 (\pm 0.2)$ for Sr, $0.4 (\pm 0.2)$ for Ba and $5.6 (\pm 6.4)$ for U.

We also present Cc/Ar ratios for other elements (Al, Si, P, Mn, Y, Pb) where no calcite partition coefficients are available.

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PALEOCLIMATE STUDY BASED ON HIGH TIME RESOLUTION ANALYSES OF STALAGMITE FROM JAVA ISLAND, INDONESIA

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In the last decade, geochemical records in stalagmites have been widely recognized as a powerful tool for the elucidation of paleoclimate/environment of the terrestrial areas. The previous data are mainly reported from middle latitude. However, this study aims at reconstructing past climate variations in the Asian equatorial regions by using oxygen and carbon isotope ratios recorded in Indonesian stalagmites.

First of all, in order to assess the reliability of stable isotopic ratios of stalagmites as climate proxies, we conducted time series comparison between precipitation and $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of two modern stalagmites from western and eastern Java Island, Indonesia. We analyzed CIAW15a and BRI10a stalagmites and found that the number of growth bands is coincident with the uranium series disequilibrium age within the error, showing that the growth bands are dominantly annual. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations of the stalagmites are primarily inversely correlated with precipitation data on annual/monthly scale. In particular, there are higher correlations between 2-years moving averages of isotopic values and precipitation during the rainy season, suggesting that $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of stalagmites are useful as ancient precipitation proxies in this study site.

Then, we measured $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations of the stalagmites over the last 1000 years for CIAW15a and the last 400 years for BRI10a, and acquired isotopic time-series was compared with various climatic proxy data. There is multi-decadal to centennial variability in the isotopic data of two stalagmites, and it is likely to be related to the position/strength of the Intertropical Convergence Zone.

An abrupt drying event in southern Turkey early in the last interglacial recorded by speleothem stable isotope and trace element data

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Stable isotope and trace element data from a fast-growing last interglacial stalagmite (Dim 1) from Dim Cave, near the coast of southern Turkey, strongly suggest that the climate became increasingly dry at around 128 ka. Strong isotopic enrichment and coincident increases in Sr/Ca ratios culminate in cessation of growth at about 127±1 ka. The length of the hiatus is uncertain but may have been only a few decades. Precise dating of the stalagmite by U-Th methods has proved difficult because most of the original aragonite fabric has recrystallised to calcite, probably soon after deposition, and consequent uranium mobilisation has given rise to spurious and inverted ages. However, dating the surviving primary aragonite has allowed the construction of a coherent age model. Possible correlatives of this brief but striking event may be the strong positive stable isotope excursions in the Corchia Cave record from Italy at ~126.5 ka (Drysdale et al., 2009) and in Bourgeois-Delaunay Cave, southwest France, at ~128 ka (Couchoud et al., 2009). The latter, like Dim 1, also has a growth discontinuity just after the isotope maximum. These episodes may be coincident with a meltwater event recorded in the Labrador Sea which has an interpolated age between tie points of ~127 ka (M. Chapman, pers. comm., 2014).

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A REVIEW OF NEW ZEALAND PALAEOCLIMATE FROM THE LAST INTERGLACIAL TO THE GLOBAL LAST GLACIAL MAXIMUM

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Results from terrestrial and marine palaeoclimate proxies are integrated to reconstruct palaeoclimate variations in New Zealand from the Last Interglacial to the global Last Glacial Maximum (gLGM). By combining data from 21 speleothems we have constructed composite O-C stable isotope sequences from 0-88.5 ka BP and from 107.8-128.2 ka BP. The gaps in the sequence (a 19.3 ka break in coverage in MIS 5b/c and a 2.97 ka gap in MIS 5a) preclude the construct of a continuous record; so data were referenced to a common scale by normalizing individual records (subtracting means and dividing by standard deviation). Overlapping records were then merged chronologically. These records were compared to integrated summer insolation for 45°S and to terrestrial and marine environmental proxies available for the New Zealand region.

The MIS 5e thermal maximum in New Zealand was around 128-122 kiloyears BP (ka BP) and therefore similar in timing to the Last Interglacial in Australia, southern Europe and Greenland. Temperatures in parts of North Island may have been 2°-3°C warmer than present and the sea rose 3-5 m above modern level. In MIS 5d and 5b cool conditions with glacial advances occurred in South Island, but from about 87-73 ka in MIS 5a warmth within 2°C of present characterised most of the interstadial (locally termed the Otamangakau Interstadial).

Conditions then cooled rapidly and culminated in a MIS 4 glacial advance that was the greatest of the Last Glacial Cycle (nzLGM). The climate was cool to cold and while wet in westerly windward locations may have been dry in the east. Combined Australian and New Zealand evidence suggests glacial culmination around 67-61 ka. This regional LGM coincided with severe cooling in Europe.

During MIS 3 conditions were very variable. The climate in eastern North Island (Hawke Bay and the Bay of Plenty) at the start of MIS 3 was similar to the Holocene, and the period 61-43 ka was relatively mild overall and is termed the Aurora Interstadial, although it contained a short interval of mountain glacier expansion around 49-47 ka. After 43 ka conditions cooled again with a glacial advance from 42-38 ka, before a return to milder but still cool conditions during the Moerangi Interstadial from 37 - 31 ka. After this conditions deteriorated at the lead in to the global LGM (gLGM). The maximum glacial advance occurred in late MIS 3 around 31 ka. The glacial onset was abrupt with the Te Anau Glacier in Fiordland, one of the largest in the Southern Alps, taking only about 2000 years to achieve its maximum gLGM depth, probably because conditions were wet as well as cold. But stable isotope data suggest that the climate then became drier, while remaining cold, and the glacier progressively ablated such that its surface had lowered 390 m by the start of MIS 2 and by >600 m by ca. 18 ka.

The onset of the gLGM in New Zealand led glacial onset in the Northern Hemisphere by a few thousand years, possibly because alpine glaciers respond more rapidly to climate change than continental ice sheets. The culmination of the gLGM in NZ occurred in MIS 3 about 12 000 years before global ice volume reached its peak as determined by the marine stable isotope record. By the time global ice was at a maximum (19 ka) glaciers had almost disappeared from major Fiordland valleys in New Zealand. Whereas polar ice sheet records have revealed a “bi-polar see-saw”, this is not so evident in the mid-latitudes, because some temperate zone inter-hemispheric climate events coincide closely in time.

THE U-Pb IN SPELEOTHEM CHRONOMETER: CURRENT PROGRESS AND FUTURE PROSPECTS

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The chronology of speleothems by the U-Pb method has reached the point of a robust analytical methodology with enormous, but as yet largely unexplored, potential. Applications are beginning to appear in the literature relating to climate change, tectonics and human evolution – examples from the Melbourne laboratory will be presented here. The next decade will likely see a major expansion of these activities.

When coupled with other emerging technologies, the U-Pb chronology of speleothems from key sites now has the potential to provide novel insights (both palaeotemperature and palaeohumidity) into ancient climate from around the globe and throughout much of Earth history. Meanwhile studies of included pollens and microscopic animals, and associated fossil remains offer insights into floral/faunal diversity and change through geological time.

On a local scale, within-cave studies provide the opportunity to date palaeo-seismic events, while on a regional scale, age compilations allow estimation of rates of uplift and karstification.

The ramifications of these many developments will be significant across diverse fields of research, from human evolution, palaeontology and ecosystem development, through studies of weathering and erosion, to the influence of tectonics on landscape evolution.

DECADAL-SCALE VARIABILITY OF EAST ASIAN MONSOON DURING LGM REVEALED BY AN ANNUALLY-LAMINATED STALAGMITE FROM HULU CAVE

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Abstract: An annual layer-counted and ²³⁰Th-dated stalagmite (No:H98) oxygen isotope record from Hulu Cave, eastern China, provides a detailed East Asian summer Monsoon (EASM) history between 24.04 and 21.12 ka with an average 3-year resolution. The $\delta^{18}\text{O}$ record exhibits several multi-decade- to centennial- scale oscillations, analogous in timing and structure to Greenland ice core temperature records. This resemblance between the two regions also supports the idea that changes in speleothem $\delta^{18}\text{O}$ largely represent variations of regional precipitation isotopic composition associated with large-scale atmospheric circulation changes. The idea is further confirmed by our comparison of $\delta^{18}\text{O}$ record with $\delta^{13}\text{C}$ and other hydrologically sensitive proxies such as Sr/Ca, annual layer thickness and gray level. Based on a general pattern of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records, we divided the whole growth period into four sub-stages: (I) gradually increased EASM strength and humidity between 24.04 and 23.29 ka; (II) relatively stable EASM (23.29 to 22.60 ka) in the studies time interval except a minor part of the relatively dry; (III) EASM evidently weaken but relatively complicated hydrological response process (22.60 to 22.02 ka); (IV) the strongest EASM and the most humid stage (22.02–21.12 ka). This local hydrologic condition is partly coupled to variations in the EASM, consistent with a modelling simulation that speleothem $\delta^{18}\text{O}$ mainly reflects summer monsoon intensity as a whole rather than the amount of local precipitation. Cross-spectral and spectral analyses reveal centennial- and decadal-scale periodicities of solar activity, which might initiate changes in EASM and further amplified by coupled atmospheric and oceanic circulations.

Key words: Nanjing stalagmite; Decadal-scale variability; East Asian summer monsoon; Last Glacial Maximum

HOLOCENE CLIMATE VARIABILITY RECORDED IN AN ARAGONITE-CALCITE SPELEOTHEM FROM SUMATRA, INDONESIA

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The Indo-Pacific Warm Pool (IPWP) is the largest body of warm water on Earth, playing a key role in the global distribution of heat and precipitation. It lies at the intersection of climate variability influenced by the Australasian monsoon, El Niño-Southern Oscillation (ENSO), and Indian Ocean Dipole (IOD). Speleothem records have provided precisely dated records of past rainfall variability over the IPWP region, however, no records currently exist for the Indian Ocean region of the IPWP.

Here we present high-resolution (~15-year sample interval) stable isotope and trace element data in an aragonite stalagmite from western central Sumatra. Located in the eastern sector of the IOD, this is the first speleothem record that can directly address rainfall variability associated with the IOD. Laser ablation ICP-MS trace element analysis is shown to be a powerful tool for identifying speleothem mineralogy and demonstrates rapid transitions between aragonite and calcite that cannot be resolved by traditional XRD methods. The trace element information allows the oxygen isotope record to be corrected for mineralogical effects, and also provides additional evidence for environmental conditions above the cave.

The speleothem indicates a prominent dry excursion during the Younger Dryas, in contrast to speleothem records from the central IPWP. An overall wetter Holocene period is punctuated by centennial-scale events, which may coincide with climate anomalies recorded in records from the western Indian Ocean.

Hydrologic variability during the Younger Dryas and Holocene based on speleothems from Laos

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Rainfall in the tropical Indo-Pacific region is controlled by a suite of complex ocean-atmospheric phenomena, such as the Intertropical Convergence Zone (ITCZ), the Asian monsoon system, and the El Niño Southern Oscillation. Whilst the evolution of the East Asian Summer Monsoon (EASM) through the Holocene has been well documented from proxy records in China, very few high-resolution paleo-records exist from farther south in Mainland Southeast Asia. Here we present the first high-resolution Holocene record of Southeast Asian Monsoon (SEAM) evolution compiled from $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements conducted on four U-Th dated speleothems from Tham Mai Cave in northern Laos (20.75 N, 102.65 E), a key site at the interface between the Indian and East Asian monsoon systems.

The speleothem oxygen isotope records are tied to robust chronologies constructed utilizing >50 U-Th ages, and indicate the records span from ~0.853 to 14.36 ka with sub-decadal resolution. During the Holocene, the Tham Mai speleothem $\delta^{18}\text{O}$ records are characterized by lower values during the early to mid-Holocene with increasing values towards the late Holocene. This is similar to trends seen throughout the Asian monsoon region, reflecting the strong insolation control on monsoon strength and ITCZ position. The Younger Dryas is characterized by an abrupt $\delta^{18}\text{O}$ increase beginning ~12.8ka and lasting until ~11.5ka when $\delta^{18}\text{O}$ values decrease by almost 4 ‰. The timing of the Younger Dryas is close to that observed in Dongge Cave and in Greenland ice cores. This suggests that similar to EAM, the SEAM weakened in sync with high latitude abrupt cooling event. $\delta^{18}\text{O}$ displays a sharp 2 permil increase at ~8.2 ka indicating that SEAM also weakened in response to this event. The speleothem $\delta^{18}\text{O}$ record from Tham Mai Cave in Laos shows strong similarities to other records of Asian monsoon strength, including a strong insolation driven weakening since the mid-Holocene and abrupt decreases during the Younger Dryas and 8.2 kyr event. However, our results from Holocene “time-slice” experiments with the GISS ModelE2-R of precipitation $\delta^{18}\text{O}$ from the grid point closest to our study site show both decreased $\delta^{18}\text{O}$ values and decreased precipitation amount in Laos at 6 ka relative to the control run. This suggests that $\delta^{18}\text{O}$ of precipitation of our location is not directly related to local precipitation but may reflect other processes.

Given the potential convoluting influence of moisture source region, transport history, and other factors on speleothem $\delta^{18}\text{O}$ in this region, we utilize speleothem $\delta^{13}\text{C}$ as an additional proxy that may better reflect local hydrology. Many studies have demonstrated that speleothem $\delta^{13}\text{C}$ shifts often reflect changes in vegetation cover,

the degree of microbial activity in the soil, and/or the effective water balance within the karst system, all of which are related to climate in such a way that higher $\delta^{13}\text{C}$ values are indicative of drier conditions at the study site and vice versa. During the Younger Dryas, changes in Laos speleothem $\delta^{13}\text{C}$ tracks the $\delta^{18}\text{O}$, indicating that the Younger Dryas was likely characterized by extremely dry conditions in Southeast Asia. $\delta^{13}\text{C}$ records follow the trend of $\delta^{18}\text{O}$ until the middle Holocene when the proxies begin to diverge. $\delta^{13}\text{C}$ records display a negative trend from middle to late Holocene, indicating a wetter local environment. This may reflect increasing rainfall towards the Late Holocene as the ITCZ migrates southward in response to decreasing Northern Hemisphere summer insolation. In line with previous results from Asian monsoon region, our results suggest the Holocene evolution of Laos speleothem $\delta^{18}\text{O}$ may be influenced by changes in moisture source region and/or upstream rainout and not simply monsoon strength or rainfall amount.

Tropical Indo-pacific modern and paleo-hydrology : comparison of paleoclimate modeling and speleothems data

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The complexity of Asian monsoon region speleothem $\delta^{18}\text{O}$ may be introduced from monsoon strength, moisture source region, transport history, local precipitation, cave hydrology and other influences on speleothem $\delta^{18}\text{O}$ in this region. In order to provide a more robust interpretation of speleothem $\delta^{18}\text{O}$ data from southeast Asian region, we utilize existing simulations with two isotope-enabled GCMs, GISS ModelE and IsoGSM, to investigate the climatic controls on precipitation $\delta^{18}\text{O}$ in Laos and in the broader Indo-Pacific/Asian Monsoon region. We also utilize the KarstFor karst hydrology model (Baker et al., 2013) to investigate potential cave hydrology influences on speleothem $\delta^{18}\text{O}$ from Laos. Our new and first composite speleothem records from Laos, which is a key site at the interface between the Indian and East Asian monsoon systems, will be used as a case study for interpreting SouthEast Asian Monsoon (SEAM) speleothem $\delta^{18}\text{O}$.

We investigate the MERRA nudged GISS ModelE2 simulations and the 20th century reanalysis nudged IsoGSM simulations of precipitation $\delta^{18}\text{O}$ from the grid point closest to Laos for modern climatology and $\delta^{18}\text{O}$ systematics. Results show a significant correlation with Pacific SSTs over the Niño-3.4 region and in the western and northern Indian Ocean, suggesting that the $\delta^{18}\text{O}$ of annual rainfall may be influenced by climate modes such as ENSO and the IOD. Furthermore, correlations with OLR, SLP, and vertical zonal wind shear over the tropical Indo-Pacific all suggest a strong relationship with the Indian monsoon intensity and convection over the Indo-Pacific warm pool, which likely contribute to “pre-fractionation” of moisture advected to our study site. In addition, statistical analysis of Laos precipitation $\delta^{18}\text{O}$ from IsoGSM shows a decreasing trend of $\delta^{18}\text{O}$ since 1900AD, which is consistent with an “amount effect” or “monsoon intensity” control on precipitation $\delta^{18}\text{O}$. After detrending, $\delta^{18}\text{O}$ is moderately correlated with the NINO3.4 index ($r=0.53$) and with the IOD index at a lag of 1 year ($r = -0.35$). This indicates that interannual variability of precipitation $\delta^{18}\text{O}$ from our site may be controlled by ENSO, while the lower frequency precipitation $\delta^{18}\text{O}$ variations may be controlled by monsoon intensity and/or local precipitation.

In addition to modern reanalysis data, we utilize results from Holocene “time-slice” experiments conducted for 9, 6 and 0 ka with the GISS ModelE2-R. The initial results show that at 6ka, southeast Asia is dryer than today which is opposite than changes over India and East Asia. However, the speleothems record from our site show a

similar increasing $\delta^{18}\text{O}$ values from middle Holocene to Late Holocene as other speleothems through out Asian monsoon regions. These results, therefore, verify that our records from Laos reflect the strong insolation control on monsoon strength and ITCZ position while not necessarily reflecting local precipitation.

To determine the relative influence of climate, hydrology, and precipitation $\delta^{18}\text{O}$ on the $\delta^{18}\text{O}$ of speleothem calcite, we use IsoGSM results as input to the KarstFor model which is a forward model of speleothem $\delta^{18}\text{O}$ (pseudoproxies). The results suggest that in Southeast tropical indo-Pacific hydrologic variability could potentially introduce 0.5-1 permil variations, in the absence of abrupt climatic changes at the surface .

In summary, we tentatively interpret the increasing $\delta^{18}\text{O}$ values through the Holocene as reflecting precession related decreases in SEAM monsoon strength and/or convective precipitation over the Indian Ocean and Bay of Bengal. Finally, through time-series analysis and comparison with climate indices, we assess the potential influence of coupled climate modes on our record, and we tentatively interpret the high frequency variability may reflect the response to dynamical modes such as ENSO or the Indian Ocean Dipole.

TROPICAL HYDROCLIMATE CHANGE DURING THE LAST DEGLACIATION: A STATISTICS STUDY ON SPELEOTHEM OXYGEN ISOTOPIC RECORDS

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The tropical hydroclimate has endured dramatic changes through the last deglaciation, approximately 20,000 years ago to 11,000 years ago. Although it has been extensively studied, its underlying mechanisms remain debated, mainly because that a large body of the paleoclimate records from the tropics have relatively poor chronological controls and coarse sampling resolution. Here, we selected 15 well-dated, high-resolution speleothem records obtained from caves located in the low-latitudes of both hemispheres, and applied a statistics approach to explore the driving mechanisms of the tropical hydroclimate during the deglaciation.

We found a strong appearance of Heinrich Event 1 (H1) and Younger Dryas (YD) in most of the records. The two events are registered as a dry climate in speleothem records from eastern China, the Arabia Peninsula, Borneo and New Zealand, while they consistently appear as a wet climate in southwest US, eastern South America, Flores of Indonesia, and South Africa. However, the two abrupt events are absent in the records from the Mediterranean region, probably due to growth hiatus or low sampling resolution.

The observed patterns were reassured by applying Empirical Orthogonal Functions (EOF) analysis to all the speleothem records. Three modes (Principal Components - PCs) explaining more than 80% of the variances from all the records were generated, and the single first mode contributes 47% of the variance explained. The overall loading pattern does not change if removing or adding a few records. But the ratio of variances explained, especially for the first mode, increases if records with strong local influences (such as records from the Mediterranean region) are excluded in the comparisons. The first mode resembles a combined signal of insolation and Atlantic meridional overturning circulation (AMOC), suggesting tropical precipitation is mainly controlled by these two factors during the last deglaciation period. Further statistic analysis is however needed to single out the contribution from each forcing.

MILLENNIAL AND ORBITAL CHANGES OF ASIAN MONSOON INFERRED FROM CHINESE STALAGMITE DATA

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Abstract: Here we focus three important issues quoted on the published Chinese stalagmite data. Firstly, new evidence from replicate tests between remote cave records in central China and modern rainfall data further supports for Chinese stalagmite 18-O signal as a good proxy of Asian Monsoon changes. Secondly, we re-interpretd some unexpected features of the past 400ka cave records at millennial and orbital changes based on the mechanism of Asian monsoon and its global linkages. Relative low monsoon intensity at Marine Isotope Stage 5e, 7e and 9e could be affected by deceases in atmospheric heat and moisture transport from Southern Ocean. The southern hemisphere climates also exert an important impact on millennial-scale monsoon changes. Thirdly, we here provided new decadal-resolution stalagmite18-O data continuously spanning ~16000 years dated within MIS10 that shows a large amplitude of millennial-scale variability. A detailed feature of millennial-scale events identified from the record lends a strong support for a persistent feature of the DO and Heinrich events, not only in the last glacial period but also in the old glacial periods. The similar magnitude of stalagmite 18-O oscillation between the last glacial and the old glacial period suggests that millennial-scale oscillations were frequently triggered by re-organization of atmospheric/oceanic circulations at glacial conditions of intermediate ice-volume values, as predicted by modelling simulations.

CLIMATE VARIATION IN THE ASIAN MONSOON FRINGE OVER THE PAST 60 KA

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The climate variability over the past 500 ka has been well characterized by speleothem records from typical Asian monsoon regions, such as Hulu, Dongge and Sanbao records. However, it remains unclear what climate pattern dominates the current summer monsoon fringe areas. Here we present a precisely-dated composite speleothem $\delta^{18}\text{O}$ record from Wanxiang cave, the southwestern Chinese Loess Plateau, covering the most portion of the past 78 ka with resolutions of 1-5 years. The cave is located in the modern Asian summer monsoon fringe area with annual mean rainfall of ~ 500 mm occurred mainly during summer. The new Wanxiang record shows broad variations undistinguished from the speleothem record from typical Asian monsoon regions, which tracks northern Hemisphere summer insolation on orbital timescale and thus dominated with precessional cycles. Superimposed on the long-term trend are millennial-scale events that can be correlated to Greenland ice core and Hulu records. However, different from speleothem records from typical Asian monsoon regions, the Wanxiang record shows hiatuses during the Last Glacial Maximum (26 to 19 ka BP), the Younger Dryas, as well as Heinrich events 3, 4 and 6. We suspect that the large global ice volume and/or the cold North Atlantic events might significantly weakened the Asian summer monsoon with its fringe retreated southeastward away from the cave site, resulting the observed hiatuses. Notably, the Wanxiang record spans across the Heinrich event 1 with a $\delta^{18}\text{O}$ gradually increase trend, rather than an abrupt event as documented in the Hulu record. This may suggest that the climate during the time period might dominate with the Westerlies instead of the Asian monsoon.

A DETAILED EAST ASIAN MONSOON HISTORY SURROUNDING THE MYSTERY INTERVAL DERIVED FROM THREE CHINESE SPELEOTHEM RECORDS

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The Mystery Interval (MI, 17.5–14.5 ka) was the first stage of the last deglaciation, a key interval for understanding mechanisms of glacial-interglacial cycles. To elucidate possible causes of the MI, here we present three high-resolution, precisely-dated oxygen isotope records of stalagmites from Qingtian and Hulu Caves inside China, reflecting changes in the East Asian summer monsoon (EASM) around the MI. Based on well-established chronologies using precise ²³⁰Th dates and annual-band counting results, the two-cave $\delta^{18}\text{O}$ profiles of ~ 7 -yr-resolution match well at decadal timescales. Both of the two-cave records document an abrupt weakening (2‰ of $\delta^{18}\text{O}$ rise within 20 yr) in the EASM at ~ 16.1 ka, coinciding with the transition of the two-phased MI reconstructed from New Mexico's Lake Estancia. Our results indicate that the maximum southward displacement of the Intertropical Convergence Zone and associated southward shift of polar jet stream may generate this two-phase feature of the MI during that time. We also discover a linear relationship among decreasing EASM intensity, rising atmospheric CO₂ and weakening Atlantic Meridional Overturning Circulation between the MI and Younger Dryas episodes, suggesting a strong coupling of atmospheric/oceanic circulations in response to the millennial-scale forcing, which in turn regulates global climate changes and carbon cycles.

A 700-YR SPELEOTHEM RECORD OF ANNUAL BANDS AND GEOCHEMICAL PROXIES IN THE MID-HOLOCENE FROM QINTIAN CAVE, CENTRAL CHINA

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The high-resolution palaeoclimate records of cave secondary carbonate have been broadly used to explore the detail structures of the palaeoclimatic millennial oscillations and the to interpret the driving mechanism for the decadal or centennial climate variability. one stalagmite(named QT33) collected from Qintian Cave(31.5°N,110.4°E;1630m above sea level),Shennongjia, Central China. This sample is 118mm in height, composed of pure calcite deposition, without evident porous on the polished surface. QT33 is confirmed developing during the mid-Holocene. Between 5500 to 4800aBP, by ²³⁰Th dates and counting data of annual layer-thickness. Three samples for ²³⁰Th dating were conducted at the Isotope Laboratory of Geology and Geophysics Department Minnesota University, USA. During its formation, the circumstance conditions of the cave were relatively stable and the annual layers were continuously developing with the average thickness of 120μm so we can perform high-resolution measurements for it by multi-proxies such as the grey level, annual layers' thickness, trace element and the stable isotope composition, etc. A total of 236 samples for δ¹⁸O measurements were analyzed with on-line automated carbonate preparation system linked to Finnigan MAT-253 ratio mass spectrometer at the Isotope Laboratory of College of Geography Science, Nanjing Normal University. The QT33δ¹⁸O record is broadly similar to those documented by Dongge Cave and Heshang Cave. This suggests that Chinese stalagmite δ¹⁸O can reflect regional climate change. In the study of the decadal and centennial scale climate change, δ¹⁸O record will be significantly effect by ambient noise. the real climate sign can be extracted by the multi-proxies analysis. We found that the QT33δ¹⁸O recorded three similarity <file://localhost/app/addword/similarity> dry period: 5550 to 5500a BP, 5260 to 5200a BP, 5000 to 4940a BP. But the mechanism caused the drought phenomenon is unclear. Currently, study on the record is behind the starting line, has not formed the complete system. We plan to conduct further studies over the next few months.

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Century-scale monsoon climate fluctuations from a middle Holocene stalagmite record in Yunnan, China

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Abstract:

We developed a 1875-year (6060-4185 a BP) high resolution record from stalagmite (FL4) in Hulu cave, Huaping, Yunnan, China, to clarify Indian Monsoon climate changes during the middle Holocene on the basis of ICP-MS-²³⁰Th series dating and carbon and oxygen isotope analysis. Carbon and oxygen isotope records, with an average resolution of 3~10 a, indicated that a series of decadal-scale abrupt climate changes were superimposed upon the century-scale monsoon climate changes, exhibiting a sawtooth-shaped pattern. The $\delta^{18}\text{O}$ record revealed three century-scale events of weak monsoon causing three drought events in 6060-5950 a BP, 5380-5140 a BP and 4810-4620 a BP. Serious deficit ($\sim 2.5\text{‰}$) on $\delta^{13}\text{C}$ within 5503-5433 a BP implied a heavy rainfall event, similar to $\delta^{18}\text{O}$, demonstrating an enhance monsoon system. FL4 record on century-scale monsoon climate fluctuations is similar to the records from Residual Delta $14\text{C}(\Delta^{14}\text{C})$ of tree ring and ice cores, demonstrating that monsoon climate changes recorded by stalagmites in lower latitudes are comparable to those in the Arctic regions. The $\delta^{18}\text{O}$ spectral analysis revealed about 500 year periodic fluctuations during the past 1875 years, which is related with periodic change in solar activity and Greenland temperature change. FL4 stalagmite records reflect that rapid strengthening or weakening of the Indian monsoon and century-scale climate fluctuations resulted from changes in solar insolation and solar activity.

