



# Fourth Kaplan Symposium 2012 Jerusalem-Ein Gedi

Paleoceanography and Paleoclimatology: New Approaches to Old Problems

## Introduction

On behalf of the Institute of Earth Sciences we are pleased to welcome you to the fourth Kaplan Workshop. This series of exciting workshops in environmental geochemistry was made possible by a generous donation from Ian R. and Helen Kaplan. The present workshop, *Paleoceanography and Paleoclimatology: New Approaches to Old Problems* brings together leading figures in different aspects of paleoceanography and paleoclimatology. We hope that the intimate size and scenic location of the workshop will generate the right atmosphere for free exchange of ideas and initiation of future collaborations. In addition, the workshop aims to allow Israeli students and scientists to present their own research and be exposed to some of the new directions in paleoceanography and paleoclimatology research.

As noted in the introduction to the previous workshop booklets, Ian has been a teacher, a colleague and a friend of our institute for many years. Ian's first encounter with the Department of Geology at the Hebrew University (later to become part of the Institute of Earth Sciences) was during his stay in Jerusalem in 1962-1965 as a Jacob Ziskind Visiting Scholar and Guest Lecturer at the Department of Microbial Chemistry. It was at this time that students and faculty members at the Hebrew University were first exposed to the then emerging science of Biogeochemistry by one of its early leaders. The continuing contacts of Ian with Israeli science were primarily via his training a sequence of graduate students and post-docs from Israel in various aspects of low-temperature geochemistry. The Israeli graduates of the "Kaplan Group" on the fifth floor of Slichter Hall at UCLA returned to several Israeli universities, the Geological Survey, and industry. Ian's ties with the Hebrew University have never ceased. He is constantly there for many of us, always generous with mentoring and sound scientific advice. It goes without saying that these are but a small part of his achievements as a scientist and mentor. His contributions are many. His students are spread around the world. We regret that he was unable to join us this time, and we all hope that he will be with us in the next meeting to be held in 2014.

We would like to warmly thank the contributions of our invited speakers, who all made huge efforts to join us and share with us their knowledge. We also thank the poster contributors, showing the high quality science of Israel.

We thank you all!



## **Reorganization of the ocean overturning circulation at the Eocene-Oligocene transition – possible causes and consequences**

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It has been shown previously that northern component water (NCW) overflowing from the Nordic Seas started around the Eocene-Oligocene transition (EOT), and became part of the meridional overturning circulation (MOC) which was possibly initiated due to a shallow proto-Antarctic Circumpolar Current (ACC) by the late middle Eocene. We have shown previously that the onset of NCW occurred at a critical threshold during a rapid tectonic subsidence of the Greenland-Scotland Ridge (GSR) triggered by the suppression of the Iceland mantle plume. Here we show that the tectonically-induced NCW expanded the MOC to interhemispheric pattern with an observed deepening of its biologically-productive clockwise overturning cell. The interhemispheric MOC is implied from a recent compilation of global benthic foraminiferal  $\delta^{18}$ Oby a shift into a prominent global dispersion in interbasinal signal with an increase in the N-S differences at the EOT. The clockwise interhemispheric circulation cell is inferred from the recently observed  $\delta^{13}$ C increasing offsets between intermediate and deepwater (northward flowing intermediate waters in the North Atlantic) coupled with the increase in the NCW signal from the South Atlantic (Nd isotopes) throughout the Oligocene. These isotopic trends coincide with the history of the GSR subsidence and with the activity history of the Iceland mantle plume, and to a lesser degree with the ACC history. This result favors circulation models showing MOC limited to the Southern Hemisphere during a phase of shallow ACC prior to the EOT, and demonstrates the NCW role in modulating the MOC pattern. A possible consequence of this reorganized circulation is an enhancement of nutrients upwelled from the ocean interior which in turn increased the biological productivity and organic carbon burial, hence decreasing atmospheric  $CO_2$  which has led to the EOT cooling and glaciation. We demonstrate in two ways that the  $\delta^{13}$ C increase of the EOT phase (the phase dominated by cooling) reflects an enhancement of organic carbon burial and consequently a decreased atmospheric CO<sub>2</sub>: (1) by leads and lags relationships in the  $\delta^{18}$ O and  $\delta^{13}$ C increase, and (2) by a gross estimate of the amounts of organic carbon required to generate the signals of the  $\delta^{13}C$  increase and the CO<sub>2</sub> decrease recently estimated from alkenones and boron isotopes.

## What do tracers tell us about the deep ocean's role in glacial climate change?

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The deep ocean has at least two important roles to play in glacial-interglacial climate change. As the locus of nearly all the inorganic carbon in the atmosphere-ocean system, its behavior is the most important determinant of atmospheric CO2. In addition it is one of the only reservoirs in the system with a time constant long enough to explain the time lags seen between Antarctica and Greenland during terminations and marine isotope stage 3. I will review some approaches to using tracers to diagnose the modern deep ocean circulation state. The use of conservative tracers is especially important for diagnosing the last glacial maximum. I will try to summarize some main features of the LGM deep ocean and the offer a new idea for how the deep ocean can synchronize the hemispheres and play a driving role in pushing climate into a glacial from an interglacial.

## Radiocarbon constraints on the past ocean circulation, with an emphasis on the record from deep-sea corals.

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In my second talk I will concentrate on deep ocean radiocarbon and transient events during Termination 1. Much attention has been paid to the large changes in atmospheric D14C during the deglaciation (rightfully so) and I will try to unpack why I don't think the situation is quite so 'mysterious'. Towards the end I will show some new deep-sea coral data that includes temperature profiles of the intermediate-deep Atlantic from clumped isotope measurements.

### **Paleoredox proxies**

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The carbon cycle, climate and ocean oxygenation are linked through a web of interactions and feedbacks. These are sufficiently complex that basic relationships remain poorly understood. For example, a generation ago it was widely hypothesized that glacial climate should be correlated with deep ocean anoxia, and interglacials with enhanced oxygenation. Glacial-era anoxia would have been driven by increased oxygen consumption as carbon was moved from the atmosphere to the deep ocean via enhanced export production. More recently, attention has shifted to the possibility of the opposite correlation between oxygenation and climate, due to the well-understood relationship between temperature and gas solubility. By this logic, ocean anoxia should be correlated with warmer climates. This prospect has drawn increasing interest in connection with projected global climate warming. Additional factors, such as the rate of ocean ventilation, lead to additional uncertainty.

One way to assess the relative importance of these processes is to examine past changes in ocean oxygenation. This is an active area of research. However, most proxies for ancient ocean redox only provide information about local depositional conditions. This limitation is a serious handicap given the spatial heterogeneity of ocean redox conditions.

In recent years, several paleoredox proxies have been developed or proposed based on the isotope geochemistry of transition metals with long ocean residence times, such as Mo, U and Re. The promise of these proxies is that measurements at a single location could provide information about ocean redox change that is regionally or globally integrated. These proxies are being developed with the Precambrian and Paleozoic geologic record in mind, where the sparseness of the geologic record makes them particularly attractive. Additionally, because the hypothesized variations in ocean oxygenation during these eras are large and long-lived these proxies can provide useful information despite uncertainties about their systematics.

This presentation will review the development and status of these novel proxies with an eye toward their possible future application reconstructing more subtle and ephemeral redox changes in Cenozoic oceans.

## Tracing past climate changes in annually laminated lake sediments

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Annually laminated sediments are high-resolution recorders of climate and environmental variability on the continents because they provide both accurate chronologies based on varve counting and proxy data at decadal to seasonal resolution. This paper will give a general overview on varved sediments with a special focus on novel methodological approaches including non-destructive element scanning techniques in combination with micro-facies analyses allowing for reconstructing periods of rapid change even at seasonal resolution.

Applying element variations in sediment records as climatic proxies requires profound knowledge about element sources and reactivity. This is straightforward for some elements with a well-constrained geochemical signature like Ti, which is corrosion-resistant and hardly soluble and thus commonly considered as proxy for detrital minerogenic matter. For other elements, however, this is more ambiguous. Si, for example, can be a proxy either for diatom concentration (productivity) or for siliciclastic detrital matter. Another example is Ca, which occurs in dolomite (commonly detrital), calcite (endogenic or detrital), aragonite (endogenic), and gypsum (diagenetic, detrital, or authigenic). Since the sources for individual elements may change in time it is hardly possible to establish standard interpretation schemes for all types of lake records. These limitations in interpreting element scanner data can be reduced by complementary micro-facies analyses that have been proven a powerful tool to trace seasonal deposition changes and interprete these in terms of climatic and environmental processes. On the other hand, restrictions of microscope analyses in obtaining quantified data except for varve and seasonal layer thickness can be overcome by parallel element scanning. Consequently, a combination of micro-facies analyses and element scanning has a great potential to aid both, better quantification of micro-facies data and more sophisticated interpretation of element data. In result this will allow to trace the dynamics particularly of abrupt climatic and environmental changes at unprecedented resolution and precision. As an example this paper will discuss abrupt changes at the onset of the Younger Dryas as recorded in the Meerfelder Maar lake record and the approach to reconcile the lake record with the NGRIP isotope record from Greenland.

#### References

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Brauer, A., Dulski, P., Mangili, C., Mingram, J., Liu, J. (2009). The potential of varves in high-resolution paleolimnological studies. PAGES Newsletter 17: 96-98.

## The last interglacial in the central Mediterranean: Evidence from Lago Grande di Monticchio

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The record of finely laminated sediments from the Lago Grande di Monticchio maar lake in southern Italy provides detailed environmental and climatic reconstructions of the last climatic cycle (Brauer et al., 2007; Allen et al., 1999; Brauer et al., 2000). An independent chronology of the Monticchio record has been established by a multiple dating approach mainly based on (1) varve counting and sedimentation rate determination using detailed micro-facies data for non-laminated sections and (2) tephrochronology (Wulf et al., 2004). The site is particularly suitable for tephrochronology due to its location in a medial-distal and favourable downwind position to nearby explosive volcanoes of the Campanian, Roman and Sicilian-Aeolian Provinces, hence providing an ideal trap for tephra fallout material. A total of 344 distinct ash layers have been identified of which the most distinct ones have been analysed in detail through microscopic inspections and geochemical analyses using electron microprobe techniques in order to independently date the sediment sequence and represent essential marker horizons for linking the lacustrine palaeoclimate archive with other terrestrial and marine records in the Central and Eastern Mediterranean.

The basal sediments of the 102 m long Monticchio record are characterized by frequent slumping and turbidite deposition typical for an over-deepened maar crater in the initial phase of the lake formation. Dating of the basal sediments to ca 135 kyrs BP is in agreement with the assumed eruption age of the Monticchio maar lakes  $(132\pm12 \text{ kyrs BP})$ . This paper will focus on the predominantly organic sediments of the last interglacial including the penultimate glacial-interglacial transition (termination 2) developed between ca 80 and 90 m sediment depth. The interglacial deposits are continuously varved allowing microscopic varve counting and thus determination of the length of the last interglacial (17.7 kyrs) as defined by pollen data. Varve micro-facies variations reflect distinct changes during the last interglacial and especially the transitions. Major shifts from carbonate to diatom varves at the early interglacial and from organic diatom varves to clastic varves at the end of the interglacial occurred within decades. It is noticeable that there is no indication of a Younger Dryas-like oscillation during the penultimate deglaciation at Monticchio.

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## A Century of Improvements in Th-230 Dating Methods with Recent Applications to Cave Climate Records

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Thorium-230 dating has roots in the original discovery of radioactivity. Indeed, <sup>230</sup>Th was discovered prior to the discovery of isotopes. As an intermediate daughter in the <sup>238</sup>U decay chain,  $^{230}$ Th has extremely low concentrations in nature (as low as a part in  $10^{18}$  in surface seawater). The low abundances have limited by our ability to measure <sup>230</sup>Th precisely and therefore our ability to obtain precise <sup>230</sup>Th ages. Thus, every major improvement in  $^{230}$ Th dating has been tied to an increase in the fraction of  $^{230}$ Th atoms in a particular sample, which one can detect. In this regard, the biggest breakthrough was the original development of <sup>230</sup>Th dating methods in the 1950s, which utilized alpha-counting techniques and could detect one out of 10,000,000 <sup>230</sup>Th atoms. The next biggest improvement was the development of mass spectrometric methods (originally by thermal ionization) in the late 1980s, which could access one out of 1000 <sup>230</sup>Th atoms, an improvement of 4 orders of magnitude over alpha-counting methods. Since then, inductively-coupled mass spectrometric techniques (both with and without multi-collection), first replicated the thermal ionization value (in the 1990s), then improved that value by an order of magnitude (about 10 years ago), then in the last year or so by another factor of 3. The current value is about one in 25. I will discuss the implication of these improvements for age precision and age range.

Parallel to improvements in dating have come the development of long high-resolution stable isotope records from cave deposits, including Israeli and Chinese Cave records. Although the dating improvements clearly played an important role in stimulating this work, this sort of research could have been done much earlier, albeit with poorer age control. Ironically, an elegant piece of work by Chris Hendy in 1971, may well have slowed this line of research. In a series of forward models, Hendy demonstrated that the interpretation of cave stable isotope values could be complex. Although we have, in many cases, worked our way around these complexities, it would serve us well to keep Hendy's study in mind as we move forward.

## Monsoons and Meltdowns: the Story from Chinese Cave Climate Records

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We have reconstructed most of the last 400,000 years of Asian Monsoon history from the oxygen isotopic composition of three Chinese Caves: Hulu, Dongge, and Sanbao. The average oxygen isotope resolution of the record is a few to several decades. The record is, in essence, a history of the oxygen isotopic composition of meteoric precipitation through time, which, in turn, is related to monsoonal precipitation in the region. The chronology is established with precise <sup>230</sup>Th ages.

The monsoon is dominated by orbital-scale variability throughout, and millennialscale variability during glacial periods. At orbital scales, the monsoon follows northern summer insolation with no discernable phase shift, supporting a direct link between seasonal heating and the monsoon, as originally predicted by John Kutzbach. At millennial scales, the last glacial record correlates strikingly with that observed in Greenland, with Chinese correlatives to all 25 Greenland interstadial events, and broadly similar millennial-scale sequences observed and established for the penultimate and antepenultimate glacial periods.

The monsoon exhibits remarkable relationships with the ice core atmospheric gas record. A tie to the oxygen isotopic composition of atmospheric oxygen supports the idea that shifts in the monsoon and low latitude hydrology change the Dole Effect, likely through a combination of changing terrestrial productivity and changes in the average isotopic composition of waters used by land plants. A close tie to methane confirms links among atmospheric methane, the low latitude hydrologic cycle, and the extent of low-latitude wetlands.

We are able to correlate features in the monsoon record to ice core, marine, and other cave records, thereby establishing, for key periods, the timing and sequence of events recorded around the globe in different surface environments. Correlation strategies include the methane-monsoon relationship to correlate cave and ice core records, a link between Heinrich Events and the monsoon to correlate cave and North Atlantic marine records, and a link between the monsoon and positions of surface currents to correlate cave and Northwest Pacific marine records.

Using these strategies, we have determined the timing and sequence of events during the terminations of the last 4 glacial cycles. Our correlations place new constraints on the causes of glacial terminations, a problem that still remains unsolved despite decades of study. The relationships that we observe suggest that terminations are caused by orbitally-induced changes in the seasonal distribution of insolation, coupled with positive feedbacks involving atmospheric  $CO_2$ 

## An introduction to paleoproxies: history and developments

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In general there are two types of paleoceanographic proxy. One type tells us from inspection of the marine geological record what processes have occurred in the oceans in the past. A second type of proxy allows us to inspect the composition of seawater, or processes that have occurred within oceans, in the past. For this, it is common to use the chemical or isotopic composition of biogenic calcium carbonate as the proxy archive and this talk will focus on foraminiferal trace element and isotope geochemistry. I will describe some history and conflict, setting the scene for what follows.

## Glacial-interglacial cycles of ocean composition over the past 1.5 million years

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The Earth's climate underwent a fundamental change between 1250 and 700 thousand years ago, the Mid-Pleistocene Transition (MPT), when the dominant periodicity of climate cycles changed from 41,000 to 100,000 years in the absence of significant change in orbital forcing. Over this time, an increase occurred in the amplitude of deep ocean sediment oxygen isotopic ratios, traditionally interpreted as defining the main rhythm of ice ages although containing large effects of changes in deep-ocean temperature. We have separated the effects of decreasing temperature and increasing global ice volume to define a distinct sequence of events in a 1.5 million year record over and since the MPT period.

### **Tracing Continental Inputs through the Oceans**

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The products of long-lived radioactive decay systems are important tools for tracing Earth processes. This lecture focuses on Nd isotopes, whose value has been increasingly recognized over the past decade as a tracer of ocean- and paleo-ocean circulation. Nd isotopes are designated as a "key *trace element and isotope*" (*TEI*) by the international GEOTRACES Program (the successor of GEOSECS), whose mission is to identify the processes and quantify the fluxes that control the distributions, sources, sinks and internal cycling of TEIs in the oceans. The residence time of Nd in the oceans is long enough its isotopic signal to be advected by moving water masses far from input sites, but short enough to prevent homogenization of the Nd isotope ratios. Thus Nd isotopes are useful tools for *tracing continental inputs through the oceans*.

In the oceans, Nd isotopes covary with conservative water mass tracers such as salinity, and lateral and vertical gradients coincide with changes in water mass boundaries. The values of the Nd isotope ratios often approximate the expected value based on the mixture of water masses, and thus they are described as behaving "quasi-conservatively". On the broadest scale, in the North Atlantic they reflect the low values of the old continental crust that surround that basin; they show much higher values in the Pacific, reflecting input from volcanics surrounding that basin, and they are intermediate in the Circum-Antarctic, broadly reflecting inputs from the two northern components. On more regional scales, North Atlantic Deep Water moving southward in the South Atlantic retains its "old continent" isotopic fingerprint, and the Circum-Antarctic-derived water masses flowing northward (Antarctic Intermediate and Antarctic Bottom Water) retain their "intermediate" isotopic fingerprint.

At least sometimes. There are major gaps in our knowledge of Nd sources, sinks, and internal cycling that limit its applicability as a water mass tracer, in large part due to the small number of seawater data available for large areas of the oceans. As a result there is an ongoing debate regarding the degree that Nd isotopes in the oceans behave conservatively.

The most prominent *non-conservative* explanation for the Nd isotope variations in the oceans is control by inputs along water mass transport paths, through exchange between seawater and sediments, especially along continental margins (often termed "*boundary exchange*"). Recently published GCM models of Nd isotopes in the oceans have come to a range of conclusions as to their sources and sinks, with the Toulouse group<sup>1</sup> advocating the idea that throughout the oceans the variability can be explained by boundary exchange, the Lamont group<sup>2</sup> concluding that the global oceans can be explained mainly by circulation, and the Bern group<sup>3</sup> falling somewhere in-between. Clearly, the value Nd as a circulation and paleo-circulation tracer depends on our understanding of the sources and sinks.

Ultimately, our lack of understanding of the marine Nd cycle reflects the sparseness of published seawater Nd isotope data, and over the next half-decade the GEOTRACES programs will take care of this need. This lecture will summarize the current evidence, for and against, the "quasi-conservative" behavior of Nd as a circulation tracer.

**References:** <sup>1</sup>Arsouze, T., Dutay, J.-C., Lacan, F., Jeandel, C. Modeling the neodymium isotopic composition with a global ocean circulation model. *Chem. Geol*, 239, 165-177 (2007); <sup>2</sup>Jones, K.M., Khatiwala, S.P., *Goldstein, S.L., Hemming, S.R., van de Flierdt, T.* Modeling the distribution of Nd isotopes in the oceans using an ocean general circulation model. *EPSL*, 272, 610-619 (2008); *Rempfer, J., Stocker, T.F., Joos, F., Dutay, J.-C., Siddall, M.*. Modeling Nd-isotopes with a coarse resolution ocean circulation model: Sensitivities to model parameters and source/sink distributions. *GCA*, 75, 5927-5950 (2011).

## New Perspectives on the history of Lake Lisan (the last ice age Dead Sea)

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The Dead Sea, as a closed basin terminal lake, is subject to large lake level fluctuations in response to climate changes, reflecting the degree of aridity in the Levant. It shows a general pattern of lower lake levels during interglacials (like the present day Dead Sea) and higher levels during glacials. For example, glacial Lake Lisan reached a maximum lake level of ~240 meters higher than the typical Holocene levels (of ~400 meters below sea level), flooding the Jordan-Arava Valley and including the Sea of Galilee. The sediments deposited are exposed along the margin of the Dead Sea and the Jordan River Valleys, ranging in age from ~70-14 ka (encompassing MIS4 through MIS2) and dated by U-series and  $^{14}C$ .

These large glacial-interglacial lake level fluctuations reflect the connections between climate patterns in North Atlantic-Europe and the Eastern Mediterranean-Levant regions, with the glacial high levels a consequence of relatively greater wetness in the Dead Sea catchment during glacials. Nevertheless, as a consequence of large and abrupt climate shifts during MIS4-2, major lake level shifts might be expected, and recent investigations of the history of Lake Lisan levels<sup>1,2</sup> have reached contrasting conclusions.

We have undertaken a new evaluation and synthesis of the history of Lake Lisan levels, taking into account geological and chronological data from throughout the Dead Sea basin. This new synthesis will be presented for the first time during the Kaplan Meeting<sup>3</sup>.

Our results show that the general wet glacial conditions were perturbed by large, rapid millennial-scale lake level fluctuations of up to ~100 meters. Moreover, the millennial pattern is opposite the glacial-interglacial pattern, whereby Greenland abrupt interstadial warmings are associated with high-stands, and stadial coolings with low-stands. The high stands can be identified for nearly every Greenland interstadial warming.

Why are the millennial time-scale patterns opposite the orbital time scale patterns? Our interpretation is that the glacial high-stands reflect the expansions in Northern Hemisphere ice sheets over Europe, which deflected the Saharan-Mediterranean front southward, as well as westerly storm tracks to the Eastern Mediterranean, increasing evaporation and moisture delivery to the Levant. The millennial-scale lake level decreases associated with Greenland stadials are most extreme during Heinrich events and reflect cooler Atlantic to Eastern Mediterranean atmosphere and sea-surface temperatures, which weaken the cyclogenic rain engine bringing moisture to the Levant, resulting in droughts. The increased temperatures associated with warmer Greenland interstadials allow the Eastern Mediterranean-Levant climate to resume typical glacial conditions, resulting in enhanced Levant precipitation and high Lake Lisan levels. *References:* 

<sup>1</sup> Bartov, Y., Goldstein, S.L., Stein, M. & Enzel, Y. Catastrophic arid episodes in the Eastern Mediterranean linked with the North Atlantic Heinrich events. *Geology* **31**, 439 (2003). <sup>2</sup>Lisker, S., Vaks, A., Bar-Matthews, M., Porat, R. & Frumkin, A. Stromatolites in caves of the Dead Sea Fault Escarpment: implications to latest Pleistocene lake levels and tectonic subsidence. *Quaternary Science Reviews* **28**, 80-92 (2009). <sup>3</sup>Torfstein, A., Goldstein, S.L., Stein, M., & Enzel, Y. Impacts of abrupt climate changes in the Levant from last glacial Dead Sea levels. *Submitted to Nature*.

### Past Changes in the Atlantic Ocean Circulation

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In this overview talk I will review what we know about changes in Atlantic Ocean Circulation during the past, with a special emphasis on the Last Glacial Maximum, the deglaciation and the Holocene.

## **Ocean Circulation Response to Heinrich Events**

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Sediments in the North Atlantic suggest that glacial periods are punctuated by purges of the Northern Hemisphere ice sheets (Heinrich Events). The input of freshwater from the melting icebergs is thought to have interrupted the Atlantic Meridional Overturning Circulation. I will review evidence from various proxies for water mass properties and ocean circulation over the Heinrich Events, and introduce new records of upper ocean properties from the Florida Straits over the most recent Heinrich Events. It appears that not all of the Heinrich Events were associated with large changes ocean circulation. For the two Heinrich Events that occurred during the coldest part of the glacial cycle, many records ocean circulation and water mass properties show a much muted or non-existent response.

## North Atlantic Multidecadal Variability: looking back from present-day climate analysis and modeling into Holocene climate variability

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Atlantic multidecadal variability (AMV, a.k.a. AMO) is the name given to the spatially coherent, slow changes in North Atlantic sea surface temperatures (SSTs) that were displayed in the instrumental record during the last century and a half. Early investigators of these changes noted that the spatial character of these changes is different than that of North Atlantic interannual SST variability and its relation to atmospheric variability is also unique. Later it was found associated with wide spread impacts on temperature and rainfall in land regions surrounding the North Atlantic and beyond. The observed characteristics of the AMV and growing evidence from coupled climate models reinforced the notion that AMV is associated with variations in the ocean circulation, in particular, in the rate of meridional mass overturning and associated poleward heat transport in the Basin. In this talk I will describe recent findings regarding the AMV including the mechanisms linking it to ocean circulation changes and to its associated observed impacts. Finally, I will discuss its possible influence on hydroclimate variations in the Levant during the Holocene.-

### The geological record of ocean acidification

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The future consequences of ocean acidification for marine ecosystems are difficult to assess, in part because laboratory experiments are limited by their necessary short time-scales and reduced ecologic complexity. In contrast, the geological record is replete not only with a variety of global environmental perturbations that may include ocean acidification, but also associated biotic responses including adaptation and evolution. I review the past ~300 My of Earth history and highlight a number of events exhibiting evidence for elevated  $pCO_2$ , global warming and ocean acidification, some with contemporaneous extinction or evolutionary turnover amongst marine calcifiers. Although valuable insight can be gained, no event perfectly parallels future projections in terms of the balance of carbonate chemistry changes – a consequence of the unprecedented rapidity of  $CO_2$  release currently taking place.

## Causes and consequences of massive CO<sub>2</sub> release at the Paleocene-Eocene boundary

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From the late Palaeocene to the early Eocene (~59-50 Myr), the Earth's surface and oceans went through an interval of progressive warming, culminating in the early Eocene climatic optimum. Superimposed on this gradual warming trend are a series of `hyperthermal' events – geologically abrupt (<10 kyr) warmings of Earth's surface and deep ocean, the most prominent of which was the Palaeocene-Eocene Thermal Maximum (PETM, ~56 Myr). Associated with the hyperthermals are large negative carbon-isotope excursions observed in all surficial carbon reservoirs together with the dissolution of deep-sea carbonates, consistent with massive injections of 13C-depleted carbon into the ocean-atmosphere system. Although understanding the causes of hyperthermals is important, not least because the amount of the carbon release and magnitude of global warming can be used to estimate climate sensitivity, a variety of different potential sources for this carbon have been proposed but with no current consensus on their relative role. Here I will focus on the original and arguably the most contentious idea – marine hydrates.

## Atmospheric circulation over Asia and its impact on paleoclimatic records.

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Asia, the largest continuous landmass on Earth, experiences the greatest seasonality and climate gradients on Earth, and induces an atmospheric circulation that each year draws more than half the airmass of a hemisphere across the equator. Tibet, the largest topographic feature outside of poles, sits square in the middle of the jet stream and creates atmospheric circulation patterns that affect climate around the globe.

Within Earth Sciences, and also many textbooks, the climate of Asia is often deconstructed into two semiannual components: a wintertime, dry cold monsoon, associated with the Siberian high pressure system; and a summertime, warm wet monsoon associated with a thermal low pressure system over the continent. In the extreme of this cartoon, the whole Indian-Asian monsoon system is depicted as a single dynamical system, driven by the thermal contrast between land and ocean.

In actuality, this vast tract of real estate experiences a rich spatial structure of atmospheric circulation and related weather. In many cases these varied phenomena have largely independent causes. Moreover, some of the most interesting features of the climate dynamics defy a simple deconstruction into two monsoonal seasons. This presentation will review a few cases studies of these phenomena that have paleoclimate implications: the role of the Tibetan Plateau in driving the monsoon; the atmospheric mechanisms leading to loess transport and deposition; the spatial pattern of glacier sensitivity to climate change; and the response of precipitation and precipitation isotopes to orbital forcing.

## What do glaciers tell us about climate variability and climate change?

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Glaciers respond to long-term climate changes and also to the year-to-year fluctuations inherent in a constant climate. Differentiating between these factors is critical for the correct interpretation of past glacier fluctuations and for the correct attribution of current changes. Previous work has established that century-scale, kilometre-scale fluctuations can occur in a constant climate. This presentation asks two further questions of practical significance: how likely is an excursion of a given magnitude in a given amount of time, and how large a trend in length is statistically significant? A linear model permits analytical answers wherein the dependencies on glacier geometry and climate setting can be clearly understood. The expressions are validated with a flowline glacier model. The likelihood of glacier excursions is well characterized by extreme-value statistics, although probabilities are acutely sensitive to some poorly known glacier properties. Conventional statistical tests can be used for establishing the significance of an observed glacier trend. However, it is important to determine the independent information in the observations which can be effectively estimated from the glacier geometry. Finally, the retreat of glaciers around Mount Baker, Washington State, USA, is consistent with, but not independent proof of, the regional climate warming that is established from the instrumental record.

## Sea level chronology and the rapidity of ice-volume changes in climate change

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The highly evaporative, semi-enclosed, marginal Mediterranean and Red Seas are excellent places for palaeoclimate studies with a high signal to noise ratio. This is because of the residence time of waters within these basins is strongly determined by the amount of exchange with the open ocean. The residence times are primarily a function of sea level, as can be demonstrated through hydraulic control calculations for the exchange flows through the narrow and shallow straits (284m deep at the Camarinal Sill in the Mediterranean opening, and 137 m deep ay the Hanish Sill in the Red Sea opening). Both basins therefore have a first-order sensitivity to sea-level change, which is more extreme for the Red Sea than for the Mediterranean, but which is recognizable in stable isotope records of both basins. In the Mediterranean, there is a much more complicated hydrological cycles than in the Red Sea, which perturbs the primary sea-level signal.

In this first presentation, I will present a detailed new U-series based chronology for eastern Mediterranean and Red Sea records of the last 150,000 years. With this, our Red Sea studies have delivered a physically well-constrained and stratigraphically highly resolved, continuous, and now well-dated record of sea-level variations. This can now be compared on an entirely independent footing with well-dated climate proxy data from other regions. The comparisons reveal very fast (order of a century) correlations between both the variability and the rates of polar climate and ice-volume changes. Also we can now determine rates of sea-level change throughout the last 150,000 years. These show rates of rise of typically 2 m/century for all episodes of significant ice-volume reduction, and rates of sea-level lowering that are typically up to 1 m/century. The last interglacial sea-level highstand reached above 0 m between 131 and 121 ka BP, with a peak highstand between 130 and 126 ka BP (85% confidence limits). The onset of Last Interglacial African monsoon maximum clearly (stratigraphically) started after the highest sea-level position was achieved (~128 ka BP), and lasted until ~120 ka BP.

## Mediterranean and Red Sea connections to global palaeoclimate scenarios

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In this second presentation, I will focus on records of wind-blown dust from the same samples as the records discussed in my first presentation (hence, on the same chronologies). Here I focus more on the long records over several glacial cycles. Dust records from the central Red Sea are found to show excellent signal agreement, down to millennial variability, with grain-size (ablation) records from the Chinese Loess plateau; it appears that the easternmost African/Arabian dust flux history was very similar to that of the Asian/Chinese deserts. Both show maximum dust fluxes during terminations. In the eastern Mediterranean, and also off NW Africa, dust records reveal a different signal, which suggests that Saharan dust fluxes were subject to different controls. This suggests significant differences in the African versus the Arabo-Asian monsoon variabilities, likely due to complex interplays between soil moisture and wind direction/intensity changes. We are currently studying northern Red Sea records, where we anticipate a mixture of the two signals. We are setting up statistical un-mixing studies to reveal phase relationships, but this northern Red Sea work is for future talks.

### Climate variability in the equatorial Pacific since the last glacial maximum: regional and global implications.

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Oceanographic conditions along the equatorial Pacific are a key element of tropical climate with broader global implications. Studies over the past decade have used variations in equatorial Pacific sea surface temperature (SST) and salinity (SSS) patterns, based on measurements of planktonic foraminiferal  $\delta^{18}$ O and Mg/Ca as well as the alkenone unsaturation index, to determine changes in the tropical mean climate state and their possible implications to equatorial Pacific dynamics. The results from these SST reconstructions provide, however, somewhat inconclusive picture as to the changes in the equatorial Pacific zonal gradient. Yet, these reconstructions point out to substantial changes in the tropical hydrological cycle. A synthesis of published and new records of the  $\delta^{18}$ O of seawater suggests that at the last glacial maximum, hydrologic conditions along the equatorial Pacific were similar with late Holocene. In contrast, enrichments in  $\delta^{18}$ O of seawater of similar magnitudes are recorded in most sediment cores on both the eastern and western sides of the tropical Pacific during Heinrich Stadial 1 and Younger Dryas, suggesting hydrological changes consistent with the migration of the Intertropical Convergence Zone (ITCZ). These changes occur on various time scales and are likely driven by climate variability in the high latitudes.

Focusing on the western equatorial Pacific, our work shows that following deglacial warming of about 3°C, the entire western sector of the Western Pacific Warm Pool reached maximum warmth during the Holocene Thermal Maximum, from ~10,000 to 6,000 yr BP, subsequently cooling by  $\sim 0.5^{\circ}$ C toward the present. The observed long-term surface cooling of WPWP appears to be in contrast with expectations from changes in radiative forcing throughout the Holocene implying additional controls on WPWP SSTs. Our reconstruction indicates a relative freshening of the southern Makassar Strait ~9,500 yr BP when rising sea level reconnected the South China and Indonesian Seas. The permanent reduction of mixed layer salinity in the southern Makassar Strait arguably initiated the current thermoclineenhanced Indonesian Throughflow. However, the uniformly warm early Holocene surface temperatures and subsequent cooling both up and downstream of the Indonesian Throughflow suggest that the Holocene SST trends in this region are not directly related to reduced Indonesian Throughflow heat transport through the Makassar Strait. A compilation of SST records from the Makassar Strait, the main path for North Pacific water to enter the Indonesian Throughflow (ITF), and the Savu Sea, where Indonesian Throughflow exits into the eastern Indian Ocean, and of temperature changes in the underlying water, suggests that a sustained oceanic connection between the Southern Hemisphere and Indonesian surface water may occur through vertical mixing in the Banda Sea and likely elsewhere. This hypothesized link provides a mechanism for Southern Source Water to influence not only the local surface water but also the entire Indo-Pacific Warm Pool. These observations highlight the intimate links between high and low latitude climates.

## Krypton and Xenon in Air Bubbles from Ice Cores as Tracers of Past Ocean Temperature

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The heavy noble gases krypton and xenon are quite soluble in liquid water, with a strong temperature-dependence of the solubility. Because the total inventory of these gases in the ocean-atmosphere system is constant, an increase in the oceanic inventory must be accompanied by a complementary decrease in the atmospheric inventory. Dinitrogen (N) gas is much less soluble and so its atmospheric inventory is little affected by ocean temperature change. Sources and sinks of N<sub>2</sub> may be neglected due to the great abundance of this gas in the atmosphere, and the fact that the entire denitrifiable inventory of N comprises less than 0.01% of the atmospheric pool. Thus the ratios Kr/N<sub>2</sub> and Xe/N in the past atmosphere should predominantly reflect past ocean temperature change. These parameters may be estimated from measurements of trapped air composition in ice cores, making appropriate corrections for gravitational settling and thermal fractionation that occurred in the snow layer (firn) at the ice core site. Measurements are done by classical dual- dynamic-inlet electron impact mass spectrometry on air melt-extracted from 1 kg of ice, and encompass the krypton isotope pair <sup>86</sup>Kr/<sup>82</sup>Kr and <sup>15</sup>N<sup>14</sup>N for the purpose of making the gravity and thermal corrections.

This new proxy reflects mean ocean temperature change, albeit slightly weighted toward the cold end of the temperature distribution due to the greater solubility of these gases in cold water. Because the ocean's heat and gas burdens are set at the outcrop where air-sea equilibration last occurs, and they travel through the ocean interior nearly adiabatically and conservatively, there is no time lag between changes in ocean heat content and changes in atmospheric noble gas burden. Consideration of the solubilities and relative volumes of the reservoirs leads to the prediction that a 1°C warming will produce a +0.5‰ increase in atmospheric Kr/N<sub>2</sub>. Current measurement precision is around 0.2‰ for a 1-kg piece of ice, suggesting a precision of about 0.4°C for this proxy. Reconstructions over the past glacial cycle suggest a glacial mean ocean temperature about 3°C colder than present, with a rapid warming of about 2°C between 18-15 ka. This was a time period of rapid atmospheric CO<sub>2</sub> increase, consistent with the hypothesis that atmospheric CO<sub>2</sub> lowering in the glacial episodes was caused by sequestration in a poorly ventilated, dense, cold deep water layer.

### **Return Flow of the Global Overturning Circulation**

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The ocean's overturning circulation is divided into upper and lower cells. The upper cell includes the formation of deep water in the North Atlantic and the Atlantic Meridional Overturning Circulation (AMOC), while the lower cell includes the formation of bottom water around Antarctica. The upwelling in both cells takes place along the southern flank of the Antarctic Circumpolar Current (ACC). My subject today is the return flow of the upper cell. In my two lectures I will be describing an aspect of the return flow that has not been described before, an aspect that readily explains why the strength of the upper cell varies along with the precessional cycle.

My first lecture is based on a new analysis of surface radiocarbon measurements from the 1940s and early 1950s and from the WOCE and CLIVAR Eras in the 1990s and early 2000s. These observations show that the return flow of subantarctic water from the ACC back to the North Atlantic is routed through coastal upwelling regions off Costa Rica and Peru in the Pacific and similar regions off Africa in the Atlantic. The upwelling in these areas is small in scale and, of course, is entirely wind-driven. Coupled climate models have a hard time resolving these features. My first lecture is focused on a comparison of observed and simulated <sup>14</sup>C distributions in the Pacific. The model in this case fails to resolve the upwellings off Costa Rica and Peru and produces a very different kind of return flow as a result.

### **Reorganization of the Return Flow**

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My second lecture begins with paleo observations which show that the strength of the upper cell varies with precession with a particular phase: it is relatively strong when the insolation during northern summers is weak and it is relatively weak when the insolation during northern summers is particularly strong, i.e. when perihelion occurs near the summer solstice. The link with precession comes about when upwelling in the equatorial Atlantic transforms subantarctic water into warm and salty surface waters that are more easily converted into dense overflow waters in the North Atlantic. In this regard, McIntyre et al. (Paleoceanography, 4, 19-55, 1989) shows that times with weak northern summer insolation produce equatorial winds that are more zonal and more favorable for upwelling. It would appear that more upwelling in the equatorial zone = more deep-water formation in the North Atlantic. A recent attempt by Jochum et al. (Paleoceanography, 25, 2009PA001856, 2010) to force a coupled climate model with the opposite phases of the precessional cycle actually produces the wrong result.

A stronger AMOC shifts the warmest sea surface temperatures into the Northern Hemisphere and leads to cooler SSTs in the Southern Hemisphere. But warmer SSTs in the north also lead to a second kind of seesaw between the Atlantic and Pacific through their influence on the return flow. This second seesaw seems to have been active over the last 100 years at a relatively low level. It was active at a higher level during the millennial events of stage 3. It was active in a more sustained way during the strong precessional cycles during stage 5. And it is especially active during glacial terminations when the rising summer insolation leads to a discharge of meltwater that shuts down the AMOC completely. In this case, a cold North Atlantic and shifted southern westerlies (Anderson et al., Science, 323, 1443-1448, 2009) leads to the intense deglacial warming in and around Antarctica and a release of  $CO_2$  from the deep ocean.



## Respiration of Amazon tree stems greatly exceeds local CO<sub>2</sub> emission

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Respiration in tree stems is an important component of forest carbon balance. The rate of  $CO_2$  efflux from the stem has often been assumed to be a measure of stem respiration. However, recent work has demonstrated that stem  $CO_2$  efflux can either overestimate or underestimate respiration rate, because of emission or removal of CO<sub>2</sub> by transport in xylem water. Here we used the ratio between CO<sub>2</sub> efflux and O<sub>2</sub> influx in stems of tropical forest trees to better understand respiration in an ecosystem that plays a key role in the global carbon cycle. This ratio, which we defined here as ARQ (Apparent Respiratory Quotient), is expected to take a value of 1.0 if carbohydrates are the substrate for respiration, and the transportation of  $CO_2$  in the xylem water is negligible. However, we found values of  $0.66\pm0.18$  using a stem chamber approach to quantifying ARQ. These low ARQ values indicate that a large portion of respired CO<sub>2</sub> (~35%) is not emitted locally, and is probably transported upward in the stem. Our results indicate the existence of a considerable internal flux of  $CO_2$  in the stem. Our results indicate, in agreement with previous work, that the widely used CO<sub>2</sub> efflux approach for determining stem respiration is unreliable. While they are more difficult to make, we demonstrate estimates of O<sub>2</sub> uptake as a more appropriate method to estimate stem respiration rates.

## Multiple sea-ice states and abrupt moc transitions in a general circulation ocean model

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Sea ice has been suggested, based on simple models, to play an important role in past glacial-interglacial oscillations via the so-called ``sea-ice switch" mechanism. An important part of this mechanism is that multiple sea-ice extents exist under the same land ice configuration. This hypothesis of multiple sea-ice extents is tested with a state-of-the-art ocean general circulation model coupled to an atmospheric energy-moisture-balance model. The model includes a dynamic-thermodynamic sea-ice module, has a realistic ocean configuration and bathymetry, and is forced by annual mean forcing. Several runs with two different land ice distributions represent present-day and cold-climate conditions. In each case the ocean model is initiated with both ice-free and fully ice-covered states. The presentday runs converge approximately to the same sea-ice state for the northern hemisphere while for the southern hemisphere a difference of about three degree latitude between the sea-ice extents of the different runs is observed. The cold climate runs lead to meridional sea-ice extents that are different by up to four degrees in latitude in both hemispheres. While approaching the final states, the model exhibits abrupt transitions from extended sea-ice states and weak meridional overturning circulation, to less extended sea ice and stronger meridional overturning circulation and vice versa. These transitions are linked to cooling and warming of the North Atlantic high-latitude deep water. Such abrupt changes may be associated with the Dansgaard-Oeschger events, as proposed by previous studies.

### Ocean circulation under snowball earth conditions

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The dynamics of ocean circulation under Snowball conditions is still largely unexplored. Here we study oceanic circulation under a complete ice cover using the MIT oceanic general circulation model. We use idealized aqua-planet conditions with meridionally variable sea glacier depth and surface temperature, and spatially constant geothermal heating. We examine convection and meridional circulation developing due to brine rejection associated with ice production and freezing temperature variations, due to the dependence of freezing temperature on pressure and thus on the ice thickness. We show that variable freezing temperature and salinity have a crucial role on ocean circulation. These two factors may therefore have a significant effect on sea glacier dynamics as the heat flux at the bottom of the ice, and hence ice melting, is strongly affected by ocean circulation.

## An assessment of the distribution, concentration and transport processes of mercury offshore from Haifa based on sediment cores

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The Haifa Bay region is affected by industrial and municipal discharges introducing mainly particulate matter, nutrients and heavy metals. Mercury (Hg) that has potentially severe health consequences for the marine environment was detected above eastern Mediterranean background levels in the Haifa Bay surface sediments. Hg levels in shallow water sediments and biota are monitored by the Israel Oceanographic and Limnological research as part of the Israel's National Monitoring Program, showing elevated levels compared to the rest of the coast and few cases in which Hg levels in fish exceeds the safety standards. Two main point sources of Hg pollution were found in Haifa Bay: (1) a chlor-alkali plant effluent discharge at the northern part of the bay that was operated until 2004; and (2) the Qishon estuary which contains effluent from nearby industries. These are in addition to diffusive sources as atmospheric deposition and runoff. Though Haifa Bay is considered a terminal basin for sediments being supplied from the Nile delta, it is possible that sediments are eroding and continuing further, carrying pollution on. In this study, geographically representative sediment cores and grab samples in and off Haifa Bay area were collected and analyzed for Hg concentrations to assess Hg re-distribution and transport.

Two cores were collected by box corer in 2009-2010 from Bustan HaGalil calcareous ridge north of the bay (B3, water depth 36m) and from the continental shelf off Haifa bay (G1, water depth 66m). A third core (ST9, water depth 6m) was collected by divers using Perspex tube in 2011 at the northern part of Haifa Bay.

The core from inner part of the bay shows a decrease of Hg content in the upper few centimeters with respect to last years' concentration in the same station. Its Hg profile demonstrates the decreasing trend of anthropogenic Hg in the bay. On the other hand, the other two cores taken outside of the bay, show significant Hg enrichment (6-fold and 2-fold of background levels) towards the upper few centimeters, reflecting the re-suspension and seaward transport of enriched Hg particles.

Hg analysis of grab samples which were collected this year, will give more information on Hg distribution in the surface sediment at the bay and offshore. Further Lead-210 dating and grain-size analysis will enable calculating changes in Hg fluxes in time and reveal transport mechanisms.

## Geochemical proxies for changes in dust sources in Negev desert loess

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The loess of the Negev desert of Israel was deposited mainly during the late Pleistocene. It is characterized by a bimodal grain-size distribution with modes between 2-8 micrometer (fine silt) and 50-60 micrometer (coarse silt) that represent two different sources of dust, one distal and one proximal.

Here we investigate the carbonate-free samples of the two size fractions and search for a geochemical signature of the distal and proximal sources of the loess in three OSL-dated primary loess sequences along a climatic transect: Hura village ( $\sim$ 250 mm/yr) and Ramat Beka ( $\sim$ 150 mm/yr) in the northern Negev and Mt. Harif ( $\sim$ 100 mm/yr) in the central Negev. The fractions are separated and analyzed for major and trace elements and for Sr and Nd isotopic composition. Preliminary results show differences between the fine and coarse fractions that agree with the observation of two different sources contributing to loess in the Negev. Sr-Nd isotopic ratios of both silt fractions suggest contribution from several distal (e.g. Sahara, Arabia) and local proximal sources (e.g. Sinai deserts, Nile delta sediments, and the Sinai-Negev sand dunes). Moreover, changes in loess sources over time were detected in shifts in Sr and Nd isotopic values of the fine fractions, these shifts occurred at  $\sim$ 60-70 kyr in Mt. Harif and Ramat Beka sites and at  $\sim$ 20 kyr at Hura site.

These results support the formation model of primary desert loess by eolian abrasion of sand dunes and suggest that the loess chemical and isotopic composition reflect changes of dust sources over time.

## Influences of atmospheric and oceanic circulation systems on South African coastal and inland climate as inferred from speleothem stable isotope records

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The position of South Africa at the intersection of subtropical trade winds and temperate westerlies creates a highly variable climate with strong east - west gradients in rainfall amount and seasonal distribution. During summer, the south easterly trade winds bring warm and moist air mainly to the east, during winter the westerlies bring high amounts of rainfall mainly to the south western corner of the country. Because the oceanic rainfall source regions off the south-east (summer rainfall) and west (winter rain) coasts strongly vary in physical properties, the oxygen isotopic compositions ( $\delta^{18}$ O) of rainfall in summer and winter also differ. The different rainfall and temperature conditions during the main growing season also create a specific pattern in the vegetation distribution. The summer rainfall region is dominated by plants following C4 photosynthesis; whereas C3 plants are more common in the winter rainfall region. These differences most probably are recorded in the speleothem  $\delta^{18}$ O and  $\delta^{13}$ C records.

Speleothem records from Crevice Cave on the South African south coast (near Mossel Bay) cover the interval between ~111 and ~53 ka<sup>1,2</sup>. Their isotopic record is compared to a speleothem record from a cave situated in the Klein Karoo (E-Flux Cave) about 90 km inland of Mossel Bay. At present, precipitation in both areas occurs throughout the year, but with lower amounts at the inland site. The vegetation on the coast contains higher amounts of C3 plants, while the vegetation inland is richer in C4 grasses. Different  $\delta^{13}$ C values in the paleorecords indicate that this vegetation difference also existed in the past. The  $\delta^{18}$ O values at the two sites vary within similar ranges, but reveal striking differences during glacial MIS 4: whilst in Crevice Cave both the  $\delta^{18}$ O and  $\delta^{13}$ C shift towards more positive values, the E-Flux records shift to more negative values. The development of the Crevice Cave curve shown here reveals a close resemblance to the development of Antarctic temperatures<sup>3</sup> and sea surface temperatures in the Agulhas Retroflection area<sup>4</sup> and the Cape Basin<sup>5,6</sup>. The steep steps in late MIS 5 and at the end of MIS 4 in the inland record correspond with Obliquity changes<sup>7</sup> and are probably related to a threshold in the position of the meridional movement of the trade wind belts over Southern Africa.

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## Rapid expansion of oceanic anoxia immediately before the end-Permian mass extinction

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**Introduction**: Periods of oceanic anoxia had a major influence on the evolutionary history of the Earth and are often contemporaneous with mass extinction events. Due to the geochemical properties of U, the ratio of  $^{238}U^{235}U$  can be used as a tool to investigate the history of ocean oxygenation at a global scale. The low-temperature redox transition of U (from U<sup>6+</sup> to U<sup>4+</sup>) is the primary cause of  $^{238}U^{235}U$  fractionation on Earth, with the reduced species preferentially enriched in  $^{238}U$  [1-5]. During times of oceanic anoxia, the flux of reduced U to anoxic facies (such as black shales) increases, preferentially removing  $^{238}U$  from seawater. The loss of isotopically heavy U drives seawater to lighter isotopic compositions [6], where it is recorded in the rock record. In this study, we examined the  $^{238}U^{235}U$  and Th/U ratios in a carbonate section spanning the end-Permian extinction horizon (EH) to evaluate the extent and timing of ocean anoxia. Samples for this study were collected from the Dawen section of the Yangtze Block in southern China.

**Results and Discussion**: In the Dawen section, the average U isotopic composition of samples deposited prior to the EH ( $\delta^{238}$ U=-0.37‰) is very close to that of modern seawater ( $\delta^{238}$ U = -0.41±0.03‰[2]). This observation suggests that the fraction of U removed to reducing sinks during the late Permian was similar to that of the modern ocean. However, at or immediately preceding the EH, the Dawen section exhibits an abrupt and significant change in  $\delta^{238}$ U to values averaging -0.65‰ after the EH. This shift toward lighter U isotopic compositions is consistent with an increase in the deposition of isotopically heavy U in anoxic facies, and represents an approximate sixfold increase in anoxic sedimentation.

*Timing of anoxia*: Previous hypotheses concerning the end-Permian extinction have called on an extended period of whole-ocean anoxia prior to the EH. However, the combined Th/U and U isotope data demonstrate that pervasive whole-ocean anoxia did not exist until at, or immediately preceding the EH, suggesting that any redox fluctuations that may have occurred well before the EH would have been localized in extent. Further discussion on the development of these conditions is given in [7].

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- [4] Brennecka et al. (2010) *EPSL* 291:228–233
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## Seasonal to decadal climatic change recorded by a modern speleothem, Soreq Cave, Israel: Taking steps towards understanding high-resolution past climate in the Eastern Mediterranean

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Laser ablation Inductively Coupled Plasma Mass Spectroscopy (LA-ICP-MS) and Secondary Ion Mass Spectrometry (SIMS) enable stable isotope and trace element analysis at high spatial resolution. These new micro-sampling techniques provide the opportunity to reconstruct past climatic change recorded in speleothem laminae down to sub-annual timescale. However, to better interpret these high-resolution (HR) data we first need to understand the seasonal to decadal response of the modern hydrological system to climate by examining the relationships between rainfall, soil, host rocks, cave water and modern speleothems.

First we have established a HR sampling strategy for the Soreq Cave. Rain-water and cave drip- and pool-waters are collected weekly during winter. Modern cave deposits are collected by placing etched glass plates in pools and under slow drips or by harvesting calcite precipitated on manmade objects installed in the cave. All samples are analyzed for trace element composition and oxygen, hydrogen and carbon isotopic composition. The new HR data, combined with the existing Soreq Cave database spanning the last 20 years, are used to characterize the response of the modern hydrological system to annual weather. We were able to determine end member parameters for the Soreq Cave associated with extreme wet and dry climate conditions, respectively. It is also noted that various sites inside the cave record the climate variations in different scales thus requiring site specific calibration.

In parallel, we examined a modern speleothem that precipitated on a sampling device that was placed in the cave in 1990 (sample 5-3-best from the deeper part of the cave at >40m rock cover). This sample was analyzed in high resolution for trace element concentrations (using LA-ICP-MS) and oxygen isotopic ratio (using the WiscSIMS). The geochemical record from the speleothem together with the direct measurements of rain and cave drip waters show that modern calcite indeed records seasonal weather as well as extreme events.

This work will serve as a basis for interpretation of HR paleoclimate records from preinstrumental speleothems.

## A combined high-resolution oxygen and carbon diatom isotope records of Holocene changes off Adélie Land, east Antarctica

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Antarctica and its ice sheets have played, and continue to play, a major role in the global ocean-atmosphere system and specially the East Antarctic Ice Sheet (EAIS). The EAIS stores 79% of the global Antarctica ice volume, and thus directly influences both Antarctic and global climate, due to its influence on the albedo of the Southern Hemisphere, thermohaline circulation and atmospheric circulation. A better understanding of the impact of glacier systems and the associated climate feedbacks of the east Antarctic region, particularly through the sea ice cycle and the magnitude of deep water formation is important for future climate predictions [1 and references therein]. Moreover, coastal and continental shelf zones (CCSZ) of Antarctica, among the most productive ecological provinces of the Southern Ocean [2], have largely been ignored in terms of late Quaternary oxygen isotope studies. In the frame of a three cores study, all located on the CCSZ off east Antarctica and designed to trace melt water input from the continent, we present here  $\delta^{18}O_{diatom}$  and  $\delta^{13}C_{diatom}$  data from piston core MD03-2601 (66°03.07'S, 138°33.43'E, 746 m water depth) retrieved off Adélie Land. The core, 40 m long, presents an undisturbed sequence of diatom ooze that covers the Holocene period from 1000 cal yr BP to 11,000 cal. yr BP. Isotopic measurements were done every 32 cm (~80-100 yrs resolution).  $\delta^{18}O_{diatom}$  analysis were performed using Infra Red laser extraction technique in line with a Finnigan Delta Excel mass spectrometer which allows the analysis of very small samples (200 µg) as required for high-resolution paleoenvironmental reconstructions. Absolute calibration was achieved by using NBS28 and PS diatom standard [3].  $\delta^{13}C_{diatom}$  measurements were performed using an elemental analyzer in line with a Finnigan MAT 252 mass spectrometer.  $\delta^{18}O_{diatom}$  record shows maximum variation of 3‰ with mean analytical reproducibility less than  $\pm 0.38\%$  and small but continuous depletion through the Holocene interpreted as little change in glaciers melting.  $\delta^{13}C_{diatom}$  shows maximum variation of 5% with mean analytical reproducibility less than  $\pm 0.11\%$ .  $\delta^{13}C_{diatom}$  record shows three distinct periods between 1050-2700 cal. yr B.P., 2900-7700 cal. yr B.P and between 7900-11000 B.P. with heavier values between 2900 and 7700 cal. yr B.P. These results are in the range of values expected for the Southern Ocean [4,5]. Combined with diatom population and species counts, geochemical data ( $^{230}$ Th<sub>excess</sub>,  $\delta^{15}$ N<sub>bulk</sub>, Fe measurements) and biomarkers (HBIs) from the same sediment core, sensitivity of  $\delta^{13}C_{diatom}$  and  $\delta^{18}O_{diatom}$  records to changes in environmental parameters (nutrient utilization, sea ice coverage, sea-surface temperature, ocean currents in the uppermost part of the water column, freshwater input from glaciers) give insights on glaciers melting and the impact of the melt water influx on the surface seawater characteristics during the Holocene off Adélie Land, east Antarctica.

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## Climatic variations over the Red Sea region since the Last Glacial Maximum: regional and global lessons

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The Red Sea is connected to the Indian Ocean via a narrow and shallow strait. It is extremely sensitive to climatic changes, including sea-level variations and changes in atmospheric conditions, and therefore it is an ideal place to study climate variability. We used an ocean general circulation model in conjunction with proxy records to investigate regional and global climate changes during the Last Glacial Maximum (LGM) and during the Holocene.

Our results for the LGM show that the conditions within the Red Sea are very sensitive to sea level reduction and there is only a mild atmospheric impact. The best correlation between the model results and reconstructed conditions exists when the water depth at the Hanish Sill is  $\sim$ 33, which would be effected by a sea level lowering of  $\sim$ 105m. A local relative sea level reduction of  $\sim$ 105m also closely agrees with the inference of the LGM low sea level at the location of the sill based on the ICE-5G (VM2) model.

During the Holocene, the Red Sea was characterized by high sea level and extreme changes in the hydrological cycle at both Mediterranean and the Monsoons climatic domains. Therefore, the Red Sea was sensitive to changes in atmospheric conditions, and it only showed a relatively mild response to sea level change. Sea surface temperature reconstructed from proxy records and our model results suggest prevailing humid conditions during early Holocene and arid conditions during late Holocene. The gradual decline in Red Sea temperature between these two time periods suggests a gradual decline in the summer monsoon strength. Because Monsoon-driven changes in the exchange flow through the Strait of Bab el Mandab affected the crenarchaea population structure, their molecular fossil distribution in the sediments of the Red Sea potentially provides an index for the summer monsoon strength during the Holocene.

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## Development of a Fast Throughput Method for Ca Isotopes using MC-ICP-MS

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Calcium (Ca) isotope measurements have applications in paleoceanography, climate studies and biomedicine. Many applications, such as high-resolution chemostratigraphy or clinical monitoring of bone mineral balance, would benefit from an increase in sample throughput. Traditional ion exchange techniques utilized in carbonates is insufficient to properly purify samples of more complex matrices, such as urine or high K/Ca ratio phases. We describe a new chemical separation method to isolate Ca from other matrix elements in biological samples, developed with the long-term goal of making high- precision measurement of natural stable Ca isotope variations a clinically applicable tool to assess bone mineral balance. A new two-column procedure utilizing HBr achieves the purity required to accurately and precisely measure two Ca isotope ratios (<sup>44</sup>Ca/<sup>42</sup>Ca and <sup>44</sup>Ca/<sup>43</sup>Ca) on a Neptune multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS) in urine. Purification requirements for Sr, Ti, and K (Ca/Sr > 10 000; Ca/Ti > 10 000 000; and Ca/K > 10) were determined by addition of these elements to Ca standards of known isotopic composition. Accuracy was determined by (1) comparing Ca isotope results for samples and standards to published data obtained using thermal ionization mass spectrometry (TIMS), (2) adding a Ca standard of known isotopic composition to a urine sample purified of Ca, and (3) analyzing mixtures of urine samples and standards in varying proportions. The accuracy and precision of <sup>TM44/42</sup>Ca measurements of purified samples containing 25 µg of Ca can be determined with typical errors less than ~0.2% ( $2\sigma$ ). The protocols discussed here have the potential to be modified for automated sample preparation of large numbers of samples in the future.

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# The use of phosphate Oxygen isotopes For identifying airborne-P sources to Lake Kinneret

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Lake Kinneret (LK) in northern Israel suffers from excessive Phosphorous (P) inputs, which can lead to eutrophication of this essential fresh water body. Lately, it was shown that dust deposition provides most of the dissolved inorganic Phosphorous (DIP) and total Phosphorous in the annual nutrient load. Here we suggest that the oxygen isotopic composition of inorganic phosphate ( $\delta^{18}$ Op) in dust may reflect the source  $\delta^{18}$ Op. In order for  $\delta^{18}$ Op to be a useful tool for P tracking from source to sink, the  $\delta^{18}$ Op values in the dust sources must be unique. We performed a detailed resin-P (anion-exchange membrane extractable)  $\delta^{18}$ Op values (from +17.2 to +22.7‰) for the various soils, where a distinct isotopic footprint was observed in agricultural soils. Temporal variation in the anthropogenic P fractions was observed in airborne particles, collected over LK, during the summer and autumn of 2011. Our results suggest the source of the airborne-P arriving LK may reflect varying P fluxes from adjacent croplands. This proof of concept enables us to estimate directly atmospheric-P sources to LK. Extending this research can pave the way for more accurate P tracing on larger scales.

### Measuring near-equilibrium rates of silicate mineral dissolution and secondary phase precipitation using silicon isotopes

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One of the most basic problems in studying weathering kinetics is the apparent discrepancy between dissolution rates of silicate minerals measured in the field and dissolution rates measured in laboratory experiments. The rate measured in the laboratory is faster by few orders of magnitude than the rates in the field. The many differences between experimental conditions in the laboratory and natural conditions in the field include: solution/mineral contact, duration of weathering, aging of surfaces, presence and depth of defects and etch pits, formation of leached layers, surface coatings, degree of under saturation, and solution chemistry in micro-pores.

Methods of determination of dissolution rates of silicates are usually based on differences between measurements of Si concentrations. However, the change in solution concentration is affected by both the dissolution of the primary mineral and the precipitation of secondary minerals. Moreover, these concentration differences are small relative to the high concentration of the solutions, under near to equilibrium conditions. As the change in concentration is lower than the uncertainty on ion concentration measurement, the error on the measured rate is large. As a result, the slow rates of mineral dissolution that are observed in the field cannot be determined using standard laboratory methods (Ganor et al., 2007).

This research project proposes and tests a novel method for measuring slow rates reactions of silicate minerals by using stable isotopes of Silicon. This new method overcomes the analytical difficulties by lowering the absolute error on dissolution rates. Moreover, with this method one can eliminate the effect of secondary phase precipitation on the determination of dissolution rate of a primary mineral and it is possible to approximate the precipitation rate of the secondary phase minerals.

Simulations of albite dissolution, at low temperature ( $3.6^{\circ}$ C,  $25^{\circ}$ C and  $50^{\circ}$ C), near equilibrium conditions and with precipitation of kaolinite using PHREEQC code were carried out. Simulation results verified the tremendous effect of measuring Si isotope ratio of the experiment solution on reducing reactions rates error. The absolute error on rates reduced to less than one order of magnitude significantly better than the traditional method of change in solution concentration. Furthermore, Simulations of the experimental system showed negligible effect of possible fractionation during secondary phases (clays as kaolinite) precipitation on measured dissolution and precipitation rates in wide range of fractionation factors ( $0.5^{\circ}_{\circ} - 20^{\circ}_{\circ}$ ).

### Calcification processes in the benthic foraminiferan *Planogypsina acervalis* and the possible role of amorphous calcium carbonate (ACC)

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The flat attached benthic foraminiferan *M. acervalis* belongs to the calcitic-radial perforated group. It is a shallow water dweller often attached to stones or stems of the high plant *Halophilla* found in the Gulf of Eilat, Red Sea. It has a cyclic camber arrangement and builds a whole rim of chambers when it grows. Because of its attached nature, when cultured in a Petri dish over a cover slip, it is possible to observe its cellular processes using the confocal laser scanning microscope. Below we describe the process of calcification in this species as observed using the fluorescent dye Calcein. Pulse-chase incubations for 20 days showed that out of 10 live and active specimens only two added a rim of new fluorescent chambers at their margins. This happened at the course of not more then 24 hours. The specimens that did not calcify were loaded with numerous fluorescent Calcein containing small (µm size) vesicles that were cycling in the cytosol. These vesicles showed bright Calcein fluorescence (brighter then the incubation medium, but did not show any birefringence under crossed polarization. On the other hand the specimens that did calcify did not contain much Calcein vesicles and looked dark compared to the non-calcifying ones.

Based on these observations we propose the following model to describe the calcification processes in *M. acervalis*: This species precipitates large amount of calcite when it adds a rim (or a cycle) of chamberlets. This occurs in a short period and hence required large reservoir of CaCO<sub>3</sub> prior to the calcification event. It seems that these organisms are spending most of their time accumulating CaCO<sub>3</sub> in the forms of ACC vesicles that are highly fluorescent. The non-calcifying specimens were therefore in a phase of accumulation of ACC prior to chamber formation. During the growth of a new rim of chambers, the ACC containing fluorescent vesicles are consumed to provide Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> for the newly formed chamberlets. I parallel the cytosol lost its fluorescence. Specimens that did not calcify are still in the phase of accumulating ACC.

In addition to the above we observed large (more then 10  $\mu$ m) fusiform symbiotic algae within the cytosol. These symbionts showed clear red chlorophyll fluorescence but in addition contained also Calcein. The Calcein seems to be concentrated in vesicles and this observation requires further investigation.

#### Groundwater-lake interaction in the Dead Sea area

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The Dead Sea hypersaline water system is unique in terms of its unusual geochemical composition, rapid lake level changes and water composition of the brines discharging along its shoreline. The Dead Sea can be used as a natural lab for studying groundwater-seawater interaction and saline water hydrological circulation along the aquifer-sea boundary. It provides an opportunity to follow the geochemical processes along a flow path from the lake into the aquifer and back into the lake. The lake level has been dropping since the 1960's due to human interference in its water budget, reaching a rate of 1 m/yr in recent years.

Saline water circulation in coastal aquifers may be a major process that governs trace element mass balances in coastal areas. This study uses radium isotopes in order to quantify the lake water circulation in the Dead Sea aquifer. There are four naturally-occurring radium isotopes, with half-lives ranging from 3.7 days to 1600 years which are chain products of uranium and thorium isotopes. Radium isotopes are usually enriched in saline groundwater and therefore are good candidates for estimating seawater or hypersaline lake water circulation in the aquifer.

Compared to most natural water bodies, the Dead Sea is extremely enriched in radium and barium, where both  $^{226}$ Ra and  $^{228}$ Ra activities and Ba concentration (145, 1-2 dpm/L and 5 mg/L, respectively) are 2-3 orders of magnitude higher than in ocean water, whereas the salinity of the Dead Sea is only 10 times higher.

Circulated Dead Sea water in the aquifer contains decreased concentrations of <sup>226</sup>Ra (60 dpm/L), Ba (1.5 mg/L), Sr (300 relative to 340 mg/L in the Dead Sea) and Sulfate (250 relative to 392 mg/L). We suggest that the low <sup>226</sup>Ra and Ba concentrations are due to precipitation of barite and celestine from the supersaturated Dead Sea water on entering the aquifer. <sup>228</sup>Ra and the shorter-lived <sup>224</sup>Ra and <sup>223</sup>Ra, which have much lower activities in the Dead Sea (up to 1.8, 3 and 0.8 dpm/L, respectively), are enriched in the circulated Dead Sea water (up to 25, 100 and 30 dpm/L, respectively) due to recoil and desorption. This implies that the circulation of Dead Sea water in the aquifer removes <sup>226</sup>Ra and contributes <sup>228</sup>Ra, <sup>223</sup>Ra and <sup>224</sup>Ra to the lake. Therefore, a major source with relatively high <sup>228</sup>Ra/<sup>226</sup>Ra ratios is added to the Dead Sea mass balance.

Following a flow path of saline water from the Dead Sea inland, barium and  $^{226}$ Ra decrease gradually and  $^{228}$ Ra increases gradually. This provides a method for calculating the DS mass balance, groundwater age or velocity and the rate of barite and celestine precipitation.  $^{228}$ Ra ages are around 2 and 13 yrs at 10 and 80 m from the shore inland, respectively. With this velocity (5-6 m/yr), the first order precipitation rate constant is 0.23 1/yr.

Based on <sup>226</sup>Ra and <sup>228</sup>Ra mass balances in the Dead Sea, the calculated amount of Dead Sea water circulation is 200-300 million m<sup>3</sup>/yr, which is of the same order of magnitude as all other known Dead Sea water sources at present (160-340 million m<sup>3</sup>/yr) and therefore is a significant component in the Dead Sea mass balance.

### Calcein incorporation into the shells of foraminifera: A new tool to study their biomineralization processes.

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The eukaryotic unicellular marine foraminifera populate most of the oceanic environments and play a major role in the global carbon cycle. They are major producers of calcium carbonate (the mineral Calcite) which preserves well in the sediments and they serve as an excellent archive for paleoceanographic research. Understanding foraminiferal biomineralization is therefore important both for ocean acidification studies and in order to wisely and reliably interpret paleoceanographic proxies. The incorporation of the fluorescent probe Calcein into the shells of live Amphistegina lessonii was studied using confocal laser microscopy (LSM). Calcein is readily incorporated into newly precipitated CaCO3 in these and in other foraminifera. This in itself is a surprising observation because the molecular weight of Calcein is 622 g mol<sup>-1</sup> and it is known to be membrane impermeable. These observations can be explained by seawater vacuolization that supply  $Ca^{2+}$  and  $CO_3^{2-}$  together with Calcein (and other similar fluorescent dyes) directly into the site of biomineralization (Erez 2003, Bentov et al 2009). The amount of Calcein incorporated into the shells is proportional to the calcification measured independently by direct weighing or by alkalinity depletion. Thus Calcein may be used quantitatively to estimate calcification rate. However the distribution coefficient of Calcein in foraminifera is very low in the order of 10<sup>-4</sup> with a significant increase with salinity and calcification rate. These observations have wide implications for understanding of Rayleigh type fractionations processes for stable isotopes and trace elements in the modified seawater calcification reservoirs in foraminifera (sensu Elderfield et al 1996, Erez 2003, Bentov et al. 2009).

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### Paleoclimate variations during the Holocene as recorded in Levantine continental shelf sediments

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Sediments deposited on the south eastern continental shelf of the Levantine Basin are sensitive recorders of climatic and oceanographic variability affected by the north Atlantic and indirectly, through the variations in the Nile River discharge, by monsoonal climate systems. In order to reconstruct the influence of these systems on Holocene sediments two cores were taken off shore southern (V115) and central (V101) Israel coast at water depths of  $\sim$ 35 m, within the Nile littoral cell. The sediments were radiocarbon dated and analyzed for grain size, major and trace elements, and Sr isotopes. The cores, dated to 8,540 and 7,600 years BP respectively, show two distinct sedimentation regimes with high rates, of 190-140 cm/ka in the early Holocene, and significantly lower rates of 50-60 cm/ka during the last 5,500 years. Humid climate prevailed in the early Holocene and an aridification process started about 6,000 years ago and continues to these days. Two periods are also reflected by the <sup>87</sup>Sr/<sup>86</sup>Sr values: i) high values, ~0.71, in the early Holocene, reflecting a dominant signature of the White Nile and local streams and ii) much lower values,  $\sim 0.7074$  in the southern core compared to ~0.7080 in the northern core, during the last 5,500 years, reflecting a strong finger print of the Blue Nile on the sediments adjacent to the Nile cone that rapidly disappear northwards. Additionally, the northern core shows ~1,500 years cycles that correlates with cold events known as the north Atlantic Bond cycles and with times of low monsoon activity in the Arabian Sea. Between those cycles, higher influence of the eastern Mediterranean climate system appears in the northern core despite the high activity of the monsoonal system, mainly because of its more distal location relative to the Nile Cone and its proximity to the Cyprus Low depression system.

# Fine detritus material in Red Sea cores as indicator of dust transport and regional climate conditions during MIS6/5 and MIS2/1 transitions

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The Red Sea (RS), located in the midst of the Arabian-Sahara desert belt, comprises an ideal archive for reconstructing dust transport and atmospheric circulation in this region during the late Quaternary. The information is recovered from deep sea cores that were drilled at the bottom of the RS by the Meteor. Here, we present data recovered from core KL-23, which was drilled in the northern RS (25°44' 88N 35°03' 28E). Interpreting the fine-grain (<63µm) detritus in the cores as desert dust we explored the mineralogy, grain-size distribution, major and trace elements chemistry and Sr-Nd-Hf isotope composition of the silicate residue (insoluble in acetic acid). Initial core chronology was based on the SPECMAP  $\delta^{18}$ O age model indicating that the core spans nearly 370 ka. The core chronology was improved by matching the  $\delta^{18}$ O patterns with those of core GeoB- 5844-2 (north to KL-23) that was dated by radiocarbon and  $\delta^{18}$ O patterns of the densely dated (by U-Th) Soreq Cave (Israel) speleothems. We focused on two glacial interglacial transitions: MIS 6 to 5 and MIS 2 to 1 (at  $\sim$  150/130 kyr BP and  $\sim$ 20/8 kyr BP, respectively). Nd-Sr-Hf isotopic ratios indicate contribution from two main lithological sources: "granitic" material, which is common in the Arabian and Sahara crustal terrains and "basaltic" material, which possibly originated from the Cenozoic basaltic terrains at the southern margins of the Red Sea. The "granitic" source was more dominant during glacials, while enhanced supply of detritus from the "basaltic" source occurred immediately after glacial terminations and transitions to interglacials. Major elements probably record weathering processes at the source regions where enhanced alteration of basaltic source occurred during interglacials.

Glacial intervals in the core are characterized by uni-modal grain-size distribution with a mean value at  $\sim 20 \ \mu m$ , while the interglacials show bi-modal distribution that reflects a change of the wind regime and the additional "basaltic dust" source. We suggest that the "basaltic dust" probably originated from the Ethiopian highlands due to higher frequencies of Red Sea trough. Stronger activity of the African monsoons may have caused the enhanced weathering of the dust sources as evident in the major element chemistry of the interglacial samples. This observation is consistent with the timing of deposition of sapropel layers in the Eastern Mediterranean.

# Precipitation Kinetics of Sulfate-Bearing Minerals under Environmental Condition of CO<sub>2</sub> Geological Storage

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Carbon Capture and Storage (CCS) has been widely recognized as one of the main technologies to mitigate climate changes. Deep-saline aquifers are the preferred potential repositories for excess  $CO_2$ , currently being emitted to the atmosphere from anthropogenic activities, Large-scale injection of  $CO_2$  into subsurface reservoirs would induce a complex interplay of multiphase flow, capillary trapping, dissolution and chemical reactions that may have significant impacts on both short-term injection performance and long-term fate of  $CO_2$  storage. To ensure the viability of geologic  $CO_2$  storage, we need a holistic understanding of reactions at supercritical  $CO_2$  water-rock interfaces and the environmental factors affecting these interactions.

The major objectives of the research are to study the kinetics of  $CO_2$  brine-rock interactions and derive respective rate laws under the typical conditions of  $CO_2$  storage sites. These rate laws may be used in modeling the storage sites and operating them in a way that will minimize scaling and consequence reduction of injectivity.

A new experimental system was set up at the BGU Water-Rock interaction laboratory allows studying the interaction between  $CO_2$ , brine and minerals under  $CO_2$  supercritical conditions. Consisting of a 300ml continuous stirred reactor combined with two 30m long plug flow reactors, both fully capable to deal with high pressure, temperature and corrosive conditions maintaining a continuous and computerized data acquisition of various variables including: pressure, temperature, stirring, in-situ pH, and ORP. The experimental setup allows the measuring of dissolution and precipitation rates of diverse minerals under a wide range of environmental conditions as found in  $CO_2$  storage sites (pressure, temperature, pumping rates, brine and rock composition) offering the possibility to sample liquid and solid samples for further chemical and morphologic analysis.

# Significant Climate-Driven Ocean Anoxia on Millennial Timescales

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One important impact of global climate change may be a significant increase in ocean anoxia. Warming decreases oxygen solubility in seawater by 3-8  $\mu$ M/°C depending on the water temperature [1]. Given warming projections of 2-5°C over the next 200 years [2], we can expect a decrease O<sub>2,sat</sub> of 10-40  $\mu$ M. This decrease may be even more extreme if polar warmer exceeds global average warming, as is expected.

The significance of decreasing  $O_{2,sat}$  for oxygen concentrations in the deep ocean is not agreed upon by the scientific community, since deep ocean oxygen concentrations are a complicated function of gas solubility, physical ocean mixing, and biological effects [3-5]. Here, to demonstrate the potential significance of this effect, we present the results of calculations that assume temperature-driven changes to oxygen solubility are the single dominant process. Our use of simple but illustrative calculations is analogous to early models of  $CO_2$ -driven warming [6]. Decades of scientific advances and millennia of CPU hours spent modeling global climate change have shown that simple estimates of global warming based on fundamental physical processes were surprisingly accurate [6]. The same may be true here.

Assuming 2-4°C of warming, our results predict that the areal extent of dysoxic water masses (defined as  $<5 \mu mol O_2 kg^{-1}$ ) will increase by 20-50 million km<sup>2</sup>, an area 2-5 times larger than the USA. This expansion would occur primarily in the eastern Pacific. Based on the reservoir-corrected conventional radiocarbon ages of the affected water masses, this expansion would occur on a time scale of about 500 - 1000 years. This time scale is dictated by apparent age of the oxygen-depleted water masses, and is much longer than the time spans typically considered in climate modeling. We show that our results agree well with recently published results from Earth system models [3] and can even be used to explain patterns of redox variations compiled for the last glacial maxima [5].

The implications for such a large increase in ocean anoxia would be profound, particularly for the marine nitrogen cycle. Assuming that current oxygen utilization rate estimates can be used to predict future denitrification rates, we estimate that pelagic denitrification would increase by 25-100 Tg N/year. Clearly, changes of such magnitude will invoke a cascade of feedbacks which can only be fully understood through numerical modeling. Long numerical simulations (>1000 years) will be required to resolve important effects of climate changes occurring in the deep ocean. Consideration of this millennium time scale may be important for understanding the links between the century-scale climate variations of the late 20<sup>th</sup> century and millennial-scale events recorded in the geologic record.

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# Dust and mineral iron utilization by the marine diazotroph Trichodesmium

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Trichodesmium, a filamentous N2-fixing cyanobacterium, forms extensive blooms in nutrient-poor tropical and subtropical ocean waters. Trichodesmium significantly contributes to biological fixation of nitrogen from the atmosphere in these waters, and thereby fuels primary production and influences nutrient flow and the cycling of organic and inorganic matter. These blooms require large quantities of iron, which are partly supplied by the influx of wind-blown Yet the processes and mechanisms associated with dust acquisition are poorly dust. understood. Here, we incubate natural populations and laboratory cultures of Trichodesmium with isotopically-labelled iron oxides and desert dust, to determine how these cyanobacteria collect, process, and utilize particulate iron. We show that, like most phytoplankton, Trichodesmium acquire only dissolved iron. However, unlike other studied phytoplankton, we show that *Trichodesmium* accelerates the rate of iron dissolution from oxides and dust, via as yet unspecified cell-surface processes, and thereby increases cellular iron uptake rates. Natural puff (ball-shaped) colonies of Trichodesmium are particularly effective at dissolving iron from oxides and dust. We attribute this to efficient dust trapping in their intricate colony morphology, followed by active shuttling and packaging of the dust within the colony core. We thus suggest that colony formation in *Trichodesmium* is an adaptive strategy which enhances iron acquisition from particulate sources such as dust.

# A numerical model of the Red Sea circulation during Marine Isotope Stage 5e

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The Red Sea is, due to its unique properties of excess evaporation and limited exchange of water with the open ocean, of particular interest to oceanographers and paleoclimatologists. Using an oceanic general circulation model (MITgcm), we have developed a regional model of the Red Sea and investigate its circulation during Marine Isotope Stage (MIS) 5e, the peak of the last interglacial, 125 ka before present, a climatic period which can serve as a analogue for recent (and future) climate. Compared to present-day conditions, MIS 5e was characterized by higher northern hemisphere summer insolation, accompanied by increases in air temperature of more than 2 °C and global sea level approximately 7 m higher than today. As a consequence of the increased seasonality, intensified monsoonal conditions with increased winds, rainfall and humidity in the Red Sea region are evident in speleothem records and supported by model simulations. We applied conservative estimates of atmospheric parameters obtained from various published modelling studies as the boundary conditions for our MIS 5e simulations. Preliminary results of this simulation show evaporation and water exchange rates through Bab al Mandab reduced by  $\sim$ 50%. Differences between present day and MIS 5e in annual average temperature of the Red Sea are negligible, while annual average salinity is reduced by 0.7 psu. Winter SST are almost unchanged, the only significant differences being a cooling of the shelf areas in southern Red Sea. Winter SSS are lower by  $\sim 1$  psu in the northern and central Red Sea. Differences in the summer conditions are more pronounced and centered on the central area of the basin which was subject to the largest differences in rainfall and air humidity. Summer SST are higher by up to 2 °C in the central and 1 °C in the northern Red Sea, while SSS are lower by ~1.5 psu in the central part of the basin. Sensitivity experiments, investigating the individual effects of the different forcing parameters (humidity, insolation, wind speed) during MIS 5e on the Red Sea hydrography are forthcoming.

# Last millennium changes in the eastern Mediterranean SST and carbonate system reconstructed from stable isotopes of vermetid reefs

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We have developed a high-resolution proxy for estimating variation in Sea Surface Temperature (SST), stable carbon isotopes composition of the dissolved inorganic carbon  $(\delta^{13}C_{DIC})$  and Mean Sea Level (MSL) by measuring stable oxygen and carbon isotopes and radiocarbon age in the aragonite shells of the Mediterranean reef forming vermetid Dendropoma petraeum. The Last Millennium reconstruction is based on composite record, which results from splicing five vermetid cores, drilled from the Israeli coast: Hof - Dor, Shikmona, Atlit and Acre. Age control was established with 18 accelerator mass spectrometer radiocarbon dates of homogenized samples of ~20 vermetid units. Each core was continuously sub-sampled at 0.5cm interval using 1 mm drill. The resulting record consists of a continuous record of 157 points spanning from 975 AD to the present, with sampling resolution of 6.5yr. The transformation of the vermetid isotopic record to SST and  $\delta^{13}C_{DIC}$  is based on a two years sampling scheme of living reef tops and surface water. Our findings show that the vermetid reef surrounding SST,  $\delta^{18}O_{SW}$  and  $\delta^{13}C_{DIC}$  reflect the open water conditions of the continental shelf. Taking into account that the annual average of seawater  $\delta^{18}O_{SW}$  is 1.62±0.12‰, the average  $\delta^{18}O$  of living reef tops (0.52‰±0.13‰) corresponds to average deposition temperature of 25.3°C, 2°C higher than the average SST of the Eastern Mediterranean (EM). Hence, average annual SST was calculated by employing constant correction of 2°C. Living vermetids show mean offset of 1.2‰ between the skeletal  $\delta^{13}$ C and the seawater  $\delta^{13}C_{DIC}$ . Therefore, the  $\delta^{13}C_{DIC}$  reconstruction is based on this constant offset.

The reconstructed SST and  $\delta^{13}C_{DIC}$  variations reveal preindustrial to present day warming and depletion trends, respectively, compared to moderate fluctuations during the early record. The SST record shows low fluctuations during the Midlevel Climate Anomaly (1000-1300 AD) and long moderate cooling during the Little Ice Age (1300-1700 AD) with amplitude of only 1°C. The recent warming of 1.6°C from 1830-2004 (0.008°C/yr; R<sup>2</sup> = 0.98), which accounts for 70% of the last millennium amplitude, is also accompanied by MSL rise of ~1mm/yr. The recent trend of  $\delta^{13}C_{DIC}$  mirrors the increase in atmospheric CO<sub>2</sub>, reflecting large shift in the EM carbonate system. Based on the high correlation between SST and  $\delta^{13}C_{DIC}$  in the period 1870-2004 (R<sup>2</sup> = 0.93) the accelerated warming since the mid 19<sup>th</sup> century is attributed to the global rise in greenhouse gases. This period also exhibits a decrease in productivity and acidification of 0.16-0.18 units, calculated from the present relationship of  $\delta^{13}C_{DIC}$  and  $^{25°C}pH_{Total}$ .

#### Can fish farms sequester atmospheric CO<sub>2</sub>?

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During the last decade several open sea iron fertilization experiments were conducted in regions of the ocean where iron is the limiting nutrient to test the hypothesis that enhancing phytoplankton productivity increases atmospheric  $CO_2$  sequestration. These experiments were unsuccessful because despite the increase in productivity, most of the carbon fixed in the surface mixed layer was re-mineralized and released back as  $CO_2$  to the atmosphere. Fishfarming in the oligotrophic (low nutrients high iron) northern Gulf of Aqaba (GOA) that was operating intensively between the years 1997-2007 provided a long-term "natural" fertilization experiment supplying available nitrogen (mainly as ammonia N) and phosphate. This ocean fertilization increased the primary productivity of northern GOA by ~2.5 fold compared to the previous long-term values. Unlike the case of the short-term fertilization experiments, the "chronic" nature of this fertilization allowed for the pelagic ecosystem to adapt to the enhanced productivity by increasing the grazers population. This resulted in increased carbon export to depths below the photic zone (export production) as suggested by the increase in nitrate and phosphate of the deep water.

It is very likely therefore that re-mineralization of the excess organic matter flux reaching the sediment/water interface of northern GOA will produce  $CO_2$  that should enhance dissolution of CaCO<sub>3</sub> at the bottom. The alkalinity increase due to this CaCO<sub>3</sub> dissolution increases the  $CO_2$  retaining capacity of the bottom water. Hence, when bottom water re-equilibrates with the atmosphere during winter mixing, it releases less  $CO_2$  into the atmosphere than lower alkalinity waters. Here we analyze sediment pore water from different locations at the northern GOA and show that indeed CaCO<sub>3</sub> is dissolving despite significant bottom water supersaturation. The sediments at depth of ~700 m show clear dissolution of CaCO<sub>3</sub> at the top few centimeters as reflected by alkalinity increase. Below, at a depth range of 5-10 cm, rhodochrosite (MnCO<sub>3</sub>) precipitation forms an alkalinity minimum. Deeper in the sediment, porewater alkalinity increases again due to anaerobic respiration. At shallower depths porewater Mn concentrations are too low to allow for rhodochrosite (MnCO<sub>3</sub>) precipitation and formation of alkalinity minimum. In summary, we conclude that the increased organic flux to the sediments at 700m indeed caused  $CO_2$  sequestration in response to the nutrient enrichment.

# Metal contamination in wetland deposits at the coast of Israel

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The coastal plain, the most populated area in Israel, has been exposed to contaminating trace metals, since the beginning of the Industrial Revolution and the Zionist Settlement. Wetlands sediment may be a very good recorder of this metal pollution, as metals reaching the ponds surface and water body, via airborne particles and terrestrial run-offs, will tend to be sequestered in the sediment, due to the affinity of metals to depositing organic matter and to oxides and minerals.

We aim to reveal the geochemical record of anthropogenic contamination in sediment profiles from the Israeli coastline wetlands in order to evaluate metal fluxes to the most populated area in Israel and identify pollution sources. This is done mostly by tracking down-profile changes in the concentrations of lead (Pb) and mercury (Hg), good representatives of metals pollution, together with a pool of other trace metals; identifying Pb isotopic composition in different fractions of the sediment, as tracers of sources; <sup>210</sup>Pb dating and granulometeric description of the sediment. In this stage, we focus on sediment profiles from Dora pond, a seasonal winter pond near Netanya.

Preliminary results indicate the study is feasible and a continuous decreasing trend was recorded for Pb and Hg occurrence from top to bottom of the tested profiles from the north and center of the pond, implying background levels (i.e., before anthropogenic pollution) were reached. As expected, trace metal contaminants were found correlated to OM and to fine particles. A large range of Pb isotopic composition was observed and there are clear differences among samples from the north and center of the pond, which points to different sources of Pb.



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