

Paleoceanography and Paleoclimatology

PP51A MCC: Hall D Friday 0830h

Advances in the Development and Application of Paleoproxies I Posters (joint with A, H, OS, GC)

Presiding: A Eisenhauer, GEOMAR;
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PP51A-0262 0830h POSTER

Mo-Isotopes in the Oceans and a Case Study From the Black Sea

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Because of an increasing number of Mo isotope fractionation data, the geochemical cycle of Mo especially in the recent oceans is now better understood. Data presented here were determined using a Nu instruments MC-ICPMS and double spike techniques (external reproducibility generally below 0.1 permil (2s.d.) on 98Mo/95Mo). Mo isotopes are homogenous in the oceans (+2.3 delta 98Mo/95Mo relative to JMC in-house standard) at present day resolution. All data are therefore given in delta notation relative to Mean Ocean water Mo (MOMo). Mo-Sources: Continental rocks, assumed to represent the riverine input, show a narrow range of Mo isotope compositions (-2.0 to -2.3 permil) close to the in-house standard solution. Oxidic Mo-sinks: Pelagic sediments and recent Fe-Mn crust surfaces show lighter Mo isotope compositions (-2.7 to -3.2 permil). In addition, to depth profiles through thick sections of Fe-Mn crusts also yield uniform Mo isotope compositions (average of -2.9 and -3.2) over the last 60Ma implying a homogenous isotope composition in ocean water over this time period. This makes Mo different from other oceanic proxies since the large variations in environmental parameters seem to have not affected Mo. We explain the observed general offset of about 3 permil from ocean water with an equilibrium fractionation between major and minor Mo species in the water column, of which the latter are lighter and can be scavenged more efficiently due to higher coordination numbers. Suboxic Mo-sinks: The balancing heavier Mo isotope composition with respect to the input can be found in recent suboxic sediments from open ocean basins, which display variable values but are all heavier than the input (-0.7 to -1.6 permil). The influence of Low-T hydrothermal activity on the Mo isotope budget in the oceans is still to be tested.

Mo isotopes in the Black-Sea: Because of its limited water exchange with the open oceans, the high surface freshwater content (1/3) and its widespread bottom anoxia, Mo in the Black Sea is a special case. Mo isotopes from two drill cores show crustal values for limnic sediments (-2 to -2.2 permil), and a variation of -1 to -0.4 permil relative to MOMo for the marine settings. This isotope variation is positively correlated with Mo concentrations. Two possible explanations for the observed pattern would be: (1) increasing efficiency of the scavenging process under anoxic conditions or (2) various mixing between freshwater and ocean water and subsequent scavenging of all available Mo. This would lead to heaviest delta values for the most marine settings. The heaviest value (-0.4) can be explained by a mixture of 1/3 riverine input plus 2/3 open ocean water, a mixture presently reflected in the salinity of the distal Black Sea surface water.

PP51A-0263 0830h POSTER

Diagenetic and Isotopic Constraints for Molybdenum Geochemistry in Continental Margin Environments: Paleoproxy Potential

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Assessing the chemical composition of past oceans necessitates a reliance on sedimentary geochemical cues or proxies. Application of these paleo-chemical proxies relies on assumptions about their geochemical behavior. These assumptions are often limited by an inadequate understanding of proxy geochemistry, even for the most promising of paleo-oceanographic proxies. Despite their imperfections, without paleo-chemical tools verification and interpretation of past changes in oceanic chemistry are impossible.

Previous work has demonstrated that molybdenum may be concentrated in both oxic and anoxic environments. The details of Mo uptake in these systems remain unclear; however, the general sequence of Mo behavior in marine sediments is that (1) Mo is accumulated in oxic sediments in association with metal oxides; (2) Mo is then released during oxide reduction; (3) Mo is removed into anoxic sediments in the presence of HS⁻. Despite any uncertainties in Mo geochemistry, because of its low (lithogenic) background concentration in marine sediments and its relatively high authigenic concentration in reducing marine settings, Mo has attracted significant attention as a paleochemical tool.

We present pore water, benthic incubation chamber, and sediment solid-phase data from continental margin environments to assess Mo behavior within these environments. These data demonstrate that Mo uptake into sediments is roughly coincident with the intensity of sedimentary reducing conditions, governed by a combination of bottom water oxygen concentration and organic carbon decomposition rate. Pore water Mo isotopes demonstrate the build-up of an isotopically heavy pore water Mo pool relative to seawater implying that the solid-phase authigenic pool will be isotopically light relative to the pore waters. Sedimentary solid phases, from a number of different sites support predictions based on pore waters.

PP51A-0264 0830h POSTER

A DUAL PROXY OF OCEANIC WEATHERING INPUTS: RARE EARTH ELEMENT PATTERNS AND ND ISOTOPES FROM METALLIFEROUS SEDIMENT CORES

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Recent interest in reconstructing Nd isotopic distributions in the past ocean using Fe-Mn crusts, oxide coatings on sediment particles, foraminifera shells and fish teeth has raised questions about relative influence of water mass mixing vs. variations in weathering input. We have explored the utility of hydrothermal metalliferous sediments for generating high-resolution records of both Nd isotopes and rare earth element (REE) patterns in deepwater. We present a 135kyr record of high precision REE data, preliminary Nd isotope ratios, and $\delta^{18}\text{O}$ from a 2.3 m core collected at 3180m at 11S on the East Pacific Rise (EPR). REEs are

dominated (96%) by seawater REEs adsorbed to Fe particles in these metalliferous carbonates; the hydrothermal REE source itself is negligible. Downcore variations in Nd/Er (proxy for light/heavy pattern fractionation) are not large (10%) but are easily quantified by our ICP-MS method (precision 1%), and reproducibly correspond to $\delta^{18}\text{O}$ shifts. The largest Nd/Er excursions occur during deglaciations, e.g. Nd/Er=5.1 to 4.4 mol/mol between glacial MIS 6 and interglacial MIS 5e. If these variations reflect composition of ambient deepwater, then the results are opposite those expected by reduced influence of Atlantic component water (high Nd/Er) during glacials. Preliminary ϵ_{Nd} values for samples taken at Nd/Er extrema in MIS 1, 2, 5e and 6 are nearly invariant at -3.5 ± 0.4 , in excellent agreement with modern water column ϵ_{Nd} for Pacific deepwater at this depth. Thus, while paleo- ϵ_{Nd} shows virtually no change over 135kyr, REE pattern does carry information, but not, we believe, about water mass mixing changes. We suggest instead that Nd/Er reflects climatically-influenced weathering inputs to the Pacific REE pool. We propose a sea-level-driven mechanism: glacial low stand reduces the extent of estuarine environments in which the light-REE-depleted seawater pattern is imparted, causing 1) more direct input of unfractionated crustal REE sources, and 2) release of REEs during erosion of high Nd/Er shelf sediments. This mechanism, unlike tectonically-driven shifts in weathering sources, can occur on glacial/interglacial timescales, and is expected to result in negligible change in Nd isotopic input, consistent with observations. Alternative mechanisms could involve temporal variations in the flux and composition of water column particles. In a first application to longer timescales, a low-resolution Cenozoic record from DSDP Leg 92, shows much larger but smooth variation of 50% in Nd/Er between 28 and 1.5 Ma, with high values from 28 to 20 Ma, decreasing during the mid-Miocene to values similar to modern at <8 Ma. ϵ_{Nd} varies from -3 (near present deepwater value) to -6, but does not co-vary simply with Nd/Er. The combination of Nd/Er and ϵ_{Nd} constitutes a new tandem proxy that may reveal changes in the style and/or source of weathering inputs to the past ocean, not interpretable from ϵ_{Nd} alone. The results may have implications for climate-linked changes in the oceanic supply of biogeochemically important elements such as Fe and P.

PP51A-0265 0830h POSTER

Little Ice Age Recorded in Mn/Fe Precipitates by Pb and Nd Isotopes

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Ferromanganese precipitates of the Baltic Sea can be dated by the ²²⁶Ra_{excess}/Ba-method (Liebetrau et al., 2002). Recent investigations have shown that these precipitates may represent perfect archives for the post-glacial history of the circum Baltic area. In particular, these precipitates offer the possibility to study short term variations of the Scandinavian shield erosion and climate change during the Little Ice Age.

The Nd isotope record of a selected Mn/Fe crust from the Mecklenburg Bay of the Baltic Sea shows a significant change of the ϵ_{Nd} -value from around 13 for ages older than 1100 years AD to approx. 18 around 1600 years AD. This shift can be explained by increased erosion and input of Nd from Archean Scandinavian sources and/or a reduced inflow of North Atlantic water ($\epsilon_{\text{Nd}} = -13$) to the Baltic Sea. Comparison with a temperature reconstruction for Fennoscandia (Mann, 2001) documents a close relationship of the ϵ_{Nd} record with temperature variations during the Little Ice Age because negative ϵ_{Nd} -value tend to correlate with lower temperature during the last 1000 years. In contrast, the pattern of ²⁰⁷Pb/²⁰⁶Pb record closely correlates with historically known changes of anthropogenic activities during the industrial revolution and times of enhanced Ag and Pb mining.

Nd and Pb are correlated before 1100 AD but are decoupled after at about 1100 years AD. We propose that Pb appears to be more sensitive to anthropogenic activities since about 1100 AD.

Liebetrau V., Eisenhauer A., Gussone N., Wrner G., Hansen B.T., and Leipe T., 2002, ²²⁶Ra_{excess}/Ba

growth rates and U-Th-Ra-Ba systematic of Baltic Mn/Fe crusts, *Geochim. Cosmochim. Acta*, 66, 73-83.

Mann M.E., 2001, The Little Ice Age, in: *Encyclopedia of Environmental Global Change*

PP51A-0266 0830h POSTER

The Fe-isotopic Signature of Early Diagenesis: Implications for the Interpretation of the Geological Record

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It has been suggested that Fe-isotopic composition in low temperature environments may be used to assess the relative importance of bacterial and inorganic redox processes. In order to apply this isotopic tracer to the geological record it is vital to first understand the processes governing Fe-isotopic fractionation in modern environments. Iron in the sedimentary environment occurs in a wide range of ferric and ferrous minerals with varying reactivity. During early diagenesis these undergo a series of dissolution and re-mineralisation reactions which are controlled by both inorganic and microbially mediated processes. In this study we are examining the Fe and S reduction kinetics and isotopic compositions of a marine sediment core from an intertidal mud-flat. Porewaters from this study persistently show enrichment in the lighter isotopes with minimum $\delta^{56}\text{Fe}$ of -6.5 ‰, markedly lower than any previously reported data for natural systems. The processes governing the Fe-isotopic composition are believed to be the autocatalytic reduction of Fe by hydrogen sulphide, and potential fractionation effects during precipitation of pyrite. The bulk reductive dissolution kinetics of iron oxides and associated isotopic effects have been simulated in the laboratory with time-series extraction experiments. The rate of Fe reduction is largely controlled by the crystal structure of the iron oxide and the gross surface area of the minerals. The isotopic composition of extracted Fe in our experiment show considerable variation and becomes progressively heavier. This reflects dissolution of Fe-minerals of varying isotopic composition, as well as changes in the reduction rates during the experiment. A combination of different extraction experiments using cold HCl or ammonium acetate, has allowed us to distinguish between Fe(II) and Fe(III) phases in the sediments. This shows that Fe is gradually transferred from the Fe(III) pool to the Fe(II) pool with depth, as an increasing proportion of Fe is precipitated as Fe-sulphide. This is also reflected in the Fe-isotopic composition, where Fe(III) phases becoming progressively heavier with depth, indicating that the lighter Fe is incorporated preferentially into the pyrite. This is analogous to the S-isotopic system, where pyrite shows significant enrichment in lighter isotopes relative to the seawater source. Because of the considerable abiotic isotope effects that have been observed in this study, a detailed understanding of the kinetics of Fe-oxide reduction is instrumental in understanding the relative contributions of biotic versus abiotic Fe isotope fractionations.

PP51A-0267 0830h POSTER

Trace Element Pattern of Authigenic Pyrite: A Promising Proxy for the Redox State of Depositional Environment

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Authigenic pyrite is formed in a wide range of depositional conditions, including not only typically euxinic conditions (when it can precipitate as syngenetic pyrite already in the water column), but also the anoxic part of normal marine sediments, below the water/sediment

interface. We investigated the response in trace element composition of pyrite to such environmental differences in 49 pyrite separates prepared from the cores recovered by a 15.2 m deep drilling executed at Weilstetten, in SW of Germany. The drilling crossed a sedimentary sequence, encompassing the transition from normal marine sediments of the Lias Epsilon-I to the black shales of the Posidonienschiefer (Lower Toarcian, Lias Epsilon-II, and -III). The trace element composition of pyrite was analyzed by means of ICP-MS and the results were evaluated in a broader geochemical context, including the isotopic composition of S in Pyrite, the S-, C_{carbonate}- and C_{organic} content of the host rocks, as well as their isotopic composition (C and O). Results document a sudden change in trace element pattern of the pyrites, simultaneously with changes in other geochemical parameters and proxies at the transition mentioned above. The evaluation of the data by means of factor analysis shows that high contents of Co, Ni and Cu coupled with very low $\delta^{34}\text{S}$ values are indicative for early diagenetic pyrites formed in the low-redox environment of the sediment, which, however, was still open for sulfate supply, but in the same time also permitted a backwards diffusion and reoxidation of the not reacted H₂S. The open system conditions coupled with the disproportionation of sulfur species with intermediate oxidation states led to a strong fractionation of the S isotopes. In contrast, pyrites from black shales are characterized by relatively high concentrations of As, Mo and Sb and high $\delta^{34}\text{S}$ values. Together with other parameters (S/C_{org} ratios, $\delta^{13}\text{C}_{\text{org}}$ values) the data suggest that such pyrites were formed under closed system conditions. According to the proposed scenarios, they were formed either in the upper part of the sediment column, in which pores became rapidly isolated due to higher sedimentation rates, or it was precipitating from a thin layer of anoxic water which got isolated between the sediment and a compact layer of algal mat on the top (in part, acquiring similar features to syngenetic pyrites). This letter is in line with a model proposed on basis of paleontological evidences by Kaufmann (1978). Apparently, other trace elements have no paleoecological relevance. It is to be noticed that Mo and Re are decoupled in pyrite, their concentrations are not correlated in the samples investigated. Ref.: Kaufmann (1978): *N. Jb. Geol. Palnt. Abh.* 157:18-36.

PP51A-0268 0830h POSTER

An Intercomparison of Ba-Based Paleoproductivity Proxies: Results From the Equatorial Pacific

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Paleoproductivity reconstructions from the equatorial Pacific (JGOFS cores TT013 pc 72 and TT013 pc 114), using different Ba-based paleoproxies, generate inconsistent records. Accurate estimations of past ocean productivity are important in assessing global climate, since the supply and burial efficiency of organic carbon to the sediment affects the partitioning of CO₂ between the ocean and the atmosphere. Many paleoproductivity proxies draw on the relationship between elemental Ba concentrations and organic matter in the water column, including accumulation rates of barite (BAR) and Ba_{excess} (total Ba corrected for the terrigenous component), as well as Ba/Ti ratios. Here, we compare records of these proxies at several sites in the equatorial Pacific, and use published algorithms to calculate glacial-interglacial fluctuations in export productivity for the past 1 myr. The differences in the resulting productivity curves are evaluated in terms of robustness of each geochemical proxy, and validity of related assumptions. Results highlight the importance of a multi-proxy approach to paleoreconstructions.

PP51A-0269 0830h POSTER

Reconstructing upper ocean circulation using oxygen isotope measurements on *Globorotalia truncatulinoides*

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The deep dwelling planktonic foraminifera *Globorotalia truncatulinoides* provides important information

about water column properties at sensitive intermediate depths. Benthic and surface dwelling planktonic foraminifera reflect bottom and surface conditions, leaving a hole at crucial intermediate depths. Water column properties at intermediate depths can be used to deduce fundamental properties of upper ocean circulation; e.g., surface current patterns and the development of mixed layer and thermocline structure. Strong horizontal density gradients occur where strong ocean currents flow, reflecting the geostrophic balance between the horizontal pressure gradient force and the Coriolis term. The oxygen isotope ratio in the calcite tests of foraminifera is a proxy for water column density as both increase with decreasing temperature and increasing salinity. We compiled $\delta^{18}\text{O}$ measurements from *Gr. truncatulinoides* ($\delta^{18}\text{O}_{\text{trunc}}$) collected from surface sediments at 165 locations throughout the Atlantic Ocean. These $\delta^{18}\text{O}_{\text{trunc}}$ data closely approximate the $\delta^{18}\text{O}$ of calcite precipitated in equilibrium with seawater at 350 meters water depth and can be used to reconstruct density at this depth.

Surface sediment $\delta^{18}\text{O}_{\text{trunc}}$ maps reveal the density gradients associated with the major elements of the surface ocean circulation and structure; e.g. the subtropical gyres, the polar fronts, and the major boundary currents. The strong density gradients associated with the Gulf Stream are particularly well represented in the surface sediment $\delta^{18}\text{O}_{\text{trunc}}$ data. Down core $\delta^{18}\text{O}_{\text{trunc}}$ records indicate that the path of the Gulf Stream has not changed significantly from the last glacial maximum to the present. The $\delta^{18}\text{O}_{\text{trunc}}$ for both the Holocene and the last glacial maximum show that the density gradient associated with the Gulf Stream is confined within the Florida Straits. This suggests that the reduction in the geostrophic shear in the Florida Straits (Lynch-Stieglitz et al., 1999) did not reflect the diversion of some of the western boundary flow to the east of the Bahamas. Along the western margin of the North Atlantic there is a sharp increase in $\delta^{18}\text{O}_{\text{trunc}}$ where the Gulf Stream separates from the coast at Cape Hatteras. The separation latitude, as reflected in the $\delta^{18}\text{O}_{\text{trunc}}$ gradient, is the same for both the Holocene and the last glacial maximum. This supports the idea that the latitude of separation is determined strongly by the shape of the ocean basin.

PP51A-0270 0830h POSTER

Surface water versus coretop temperature calibrations of alkenone unsaturation (UK'37): Why the discrepancy?

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The widespread utility of the C37 alkenone unsaturation ratio as a paleotemperature proxy has prompted intense efforts to understand the generation of the alkenone temperature signal in the surface waters and to link this with the residual alkenone temperature signal recorded in the sediments. Here we present the global production temperature calibration of UK'37, derived from 400 surface water data from the Atlantic, Mediterranean, Pacific and Southern Oceans, and compare the integrated production temperature (IPT) recorded by UK'37 in coretop sediments with overlying sea surface temperature estimates.

The relationship between UK'37 and alkenone production temperature is tightly constrained over the entire range of present day oceanic environments. Regional deviations from the global trend exist but introduce biases of less than 2 C. The global calibration is nonlinear with a reduced slope at the temperature extremes. The temperature estimate is unbiased over the 1 - 30 C estimation range, with a mean standard error of 1.2C. The surface water calibrations were applied to coretop data to calculate the alkenone IPT recorded by sediment UK'37. Alkenone IPT deviates systematically from Levitus estimates of overlying annual mean SST at 0 m depth (Ann0). Although there are notable regional differences, IPT averages 2-3 °C warmer than Ann0 in mid- and high latitudes and converges to Ann0 at low latitudes. The deviation is best explained by a combined influence of seasonality in alkenone production and differential degradation of di- and tri-unsaturated alkenones.

PP51A-0271 0830h POSTER

Further Calibration of the Planktonic Foraminiferal Mg/Ca Paleothermometer: Sediment Trap Results From the Cariaco and Guaymas Basins

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Further calibration of the Mg/Ca paleothermometer is needed in order to better assess regional and inter-species differences in the temperature dependence of Mg uptake into planktonic foraminiferal calcite. We are measuring the Mg/Ca ratio in multiple species of foraminifera, including two surface dwelling species (*Globigerinoides ruber* and *Globigerina bulloides*) and two thermocline dwelling species (*Pulleniatina obliquiloculata* and *Globorotalia menardii*) from time-series sediment trap samples collected in the Cariaco Basin, Venezuela and Guaymas Basin, Gulf of California. The Mg/Ca values are compared with concurrent hydrographic data from each study site in order to determine how well this technique tracks measured temperature changes. The Guaymas Basin is particularly well suited for such a study since it undergoes a seasonal change in sea surface temperatures of over 15°C.

Our preliminary results indicate the Mg/Ca ratio in *G. ruber* accurately records the observed seasonal surface temperature cycle in both the Cariaco and Guaymas Basins, with the estimated temperatures typically being within 1.25°C of the observed values. At least some of this difference may be attributed to an offset between the time of calcification and the temperature measurements. The trace metal data will also be compared with oxygen isotope measurements made on the same suite of samples to resolve the internal consistency of these two temperature proxies.

PP51A-0272 0830h POSTER

Metal:Calcite Distribution Coefficients of Laboratory-Grown Bathyl Benthic Foraminifera

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Benthic foraminifera, collected from sediments off the Carolina coast, were maintained in mono- and multi-species cultures for four and a half months in a sediment-free culture system. The foraminifera were cultured in a closed system using a 1600-liter modified artificial seawater reservoir. The temperature, alkalinity, stable isotope ratios, and trace metal concentrations were held static in seawater medium during the experiment. The artificial seawater was circulated from the reservoir through nine 3 mL acrylic microcosms that contained 80-100 foraminifera living in ~1 mm thick silica substrate. Foraminifera were labeled with fluorescent calcein, prior to addition to the microcosms, to provide a clear demarcation between parent calcite and cultured calcite. At the end of the experiment juvenile *Bulimina aculeata* were harvested from the microcosms (~150-3000 specimens per microcosm). The cultured foraminifera were divided into two groups for separate trace metal analyses and stable isotope analyses. The foraminifera from the trace metal splits were cleaned and analyzed for Ca, Ba, and Cd by isotope dilution ICP-MS. Barium distribution coefficients were close to previously reported values of cultured foraminiferal calcite but remained lower than reported field data. Preliminary Ba:Ca distribution coefficients for *B. aculeata* do not appear to indicate strong life stage differences, even though there are indications of ontogenetic variations in $\delta^{13}\text{C}$ for this species (see McCorkle et al. abstract).

PP51A-0273 0830h POSTER

The Carbon and Oxygen Stable Isotopic Composition of Cultured Benthic Foraminifera (*Bulimina aculeata*).

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To study the controls on benthic foraminiferal shell chemistry, live benthic foraminifera were collected from a 750 m site on the North Carolina continental margin. Mono-specific (*Bulimina aculeata*) and multi-species (*B. aculeata*, *Discorbina berthelotti*, *Cibicides pachyderma*, *Lenticulina* sp., *Uvigerina peregrina*, *Hoeghunda elegans*) cultures were maintained for 4.5 months in an environmental chamber. Experimental microcosms contained a 1 mm layer of trace-metal free silica substrate, and were continuously flushed with water from a 1600 L seawater reservoir with known, constant temperature, $\delta^{18}\text{O}(\text{w})$, carbonate system chemistry and trace element concentrations. Each microcosm was seeded with 80-100 living foraminifera; *B. aculeata* was the most successful species in these cultures, with each microcosm producing hundreds of juvenile *B. aculeata*.

We determined the stable isotopic composition of the calcite from the cultured *B. aculeata*, and compared these $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values with the water chemistry of the microcosms, and with the shell chemistry of "free-range" *B. aculeata* collected and preserved from two sites on the NC and SC margin. The foraminiferal $\delta^{18}\text{O}$ values were close to the expected $\delta^{18}\text{O}$ of equilibrium calcite for both cultured and field *B. aculeata* ($\delta^{18}\text{O}$ offsets of -0.2 ± 0.1 ‰ and 0.0 ± 0.1 ‰, respectively). The $\delta^{13}\text{C}$ values of cultured *B. aculeata* were 0.7 ± 0.2 ‰ lower than microcosm dissolved inorganic carbon, with some evidence of smaller ^{13}C depletions in older juveniles (larger specimens). The foraminiferal water $\delta^{13}\text{C}$ offsets were larger for the field specimens (-0.8 ‰ at a 200 m site, and -1.4 ‰ at the 750 m site). These results suggest that the $\delta^{13}\text{C}$ values of *B. aculeata* include both "vital" effects (the offset observed in cultured specimens) and micro-habitat effects (the additional offset observed in field specimens).

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Calcium Isotopes in Foraminifera Shells: Evaluation for Paleo-temperature Reconstruction

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The Ca stable isotope ratio of foraminifera shells has been suggested as a potential paleo-temperature proxy and has recently been applied in several studies to reconstruct glacial interglacial fluctuations in seawater temperatures. The major advantage of using Ca isotopes for paleo-temperature reconstruction is the relatively long residence time of Ca in the ocean. Thus, no spatial or temporal change in the Ca isotopic composition of seawater is expected over time scales much shorter than a million years. Moreover, since Ca is a major constituent of carbonate, and an isotopic ratio rather than an element concentration or element-ratio (e.g. Mg/Ca, Sr/Ca) is measured, the Ca isotope proxy is much less likely to be affected by post depositional diagenetic alteration. However, preliminary results indicate that kinetic effects might largely control the Ca isotope fractionation involved in calcite shell formation. Before this new and exciting proxy

can be utilized routinely, a better understanding of the parameters controlling Ca isotope fractionation in carbonate minerals in general and in foraminifera and other carbonate-secreting organisms is required. We have measured the Ca stable isotope ratio of several foraminifera species from core top sediments from two well-studied sites to determine the inter-species and within-species variability in Ca isotopes. We assess the effects of water temperature, calcification rate, and vital effects on the Ca stable isotope ratio of modern foraminifera and evaluate the potential of this proxy for paleo-temperature reconstruction.

PP51A-0275 0830h POSTER

Genetic Evidence Reveals Species Dependent $\delta^{18}\text{O}$ Shift in *Neogloboquadrina pachyderma* (dextral) Between Glacial and Interglacial Times

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Genetic evidence shows that apparent single species records used in paleoceanographic reconstructions most likely contain an alternation in species concurrent with environmental change.

In this study the distribution pattern of small sub-unit (SSU) ribosomal (r)RNA genotypes of *N. pachyderma* (sin.) and (dex.) in the Nordic Seas are compared with surface sediment coiling ratios and isotopic values of *N. pachyderma* (sin.) and (dex.) for the same regions. The genetic evidence for *N. pachyderma* show that the morphological distinction of coiling direction is not sufficient to distinguish between genotypes and species. We have found morphologically right coiling specimens which are genotypically identical to *N. pachyderma* Type I (sin). These right coiling *N. pachyderma* Type I (sin) genotypes are specifically found in regions where $\delta^{18}\text{O}$ isotopes of *N. pachyderma* (dex.) and *N. pachyderma* (sin.) are identical in surface sediments; and they occur at a constant percentage of approximately 2-3% relative to the left coiling *N. pachyderma* morphotypes. On the other hand, morphologically and genetically right coiling specimens of *N. pachyderma* Type I (dex.) only occur in regions where $\delta^{18}\text{O}$ isotopes of *N. pachyderma* (dex.) and *N. pachyderma* (sin.) in surface sediments are different. In these regions the relative abundance of *N. pachyderma* (dex.) is always above the threshold value of 2-3%.

We then examine and discuss the potential alternation of genotypes of *N. pachyderma* (sin.) and (dex.) between glacial and interglacial conditions and its effect on the isotopic signature of paleo-records. Our analyses clearly show that the glacial-interglacial $\delta^{18}\text{O}$ signature in *N. pachyderma* (dex.) in the Nordic Seas contains a species-dependent isotopic shift of about 0.5‰ when relative abundances cross a certain threshold value. This finding not only enhances the calibrated use of $\delta^{18}\text{O}$ records of *N. pachyderma* (dex.), but also highlights the general need to genetically investigate other paleoceanographically important morphospecies in order to refine their use as paleoproxies.

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Determination of Intra-Test Variability of Trace Elements in Foraminifera by Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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Analysis of trace elements in fossil foraminiferal tests is widely used by palaeoceanographers to reconstruct past environmental conditions in the oceans. However, there remain a number of problems associated with the interpretation of these trace element data. Firstly, there is a lack of understanding as to the controls on the uptake of trace elements into foraminiferal tests. Secondly, fossil test chemistry may be influenced by post-depositional diagenesis, and thirdly, the impact of chemical cleaning techniques, used to remove contaminant detrital and authigenic mineral phases from the test surface, on test chemistry is uncertain.

In order to address these problems, information is required as to the variability of trace elements within individual foraminiferal tests. To this end, we have developed a technique for the analysis of trace elements in foraminiferal calcite by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). This technique is reproducible (<6 % for most elements), and has low detection limits. The accuracy of the technique is difficult to assess, but Mg/Ca, Sr/Ca and Li/Ca ratios for foraminiferal calcite are within the range reported elsewhere in the literature when normalised to a CaCO₃ standard.

Analysis of different types of calcite within a foraminiferal test shows that Sr/Ca and Li/Ca of calcite pustules surrounding the aperture of *Gr. tumida* are distinctly different from the chamber and keel calcite. Successive analyses of the same *Orbulina universa* test throughout a chemical cleaning procedure show that the Mg/Ca ratio of the test falls significantly after removal of ferromanganese oxide phases, but is unchanged after oxidative cleaning. Rastering of relatively flat parts of *G. sacculifer* has enabled us to investigate changes in chemistry through the test wall. High Li/Ca on the outermost part of the test can be attributed to contaminant phases, but Li/Ca is relatively constant at >5 μm depth. The depth of this contaminant layer is significantly shallower if the foraminiferal test is glassy, rather than opaque.

PP51A-0277 0830h POSTER

Records of planktonic foraminiferal shell weight provide insight into the controls on atmospheric CO₂ variability

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Records of planktonic foraminiferal shell weight from throughout the global ocean exhibit variability on glacial-interglacial timescales. Measured shell weights are a composite signal of dissolution related weight loss (Lohmann, 1995; Broecker and Clarke, 2001) superimposed upon initial shell weight variability (Barker and Elderfield, 2002). Differentiating between these signals provides a basis for describing the condition of carbonate saturation in surface waters as compared with bottom waters. The state of carbonate saturation in surface waters is related to surface-ocean pCO₂ via thermodynamic constraints but the pCO₂ difference (ΔpCO₂) between the surface ocean and the atmosphere is a more complex parameter. To build on our initial observation of foraminiferal calcification response to glacial-interglacial changes in atmospheric CO₂, we have measured shell weights in several cores from throughout the global ocean spanning the last termination from glacial to interglacial conditions, as well as a longer record from the Chatham Rise over the past 0.45 Ma. The amplitude of change varies between different planktonic species and probably reflects depth habitat differences. More importantly, results have been used to test whether shell weight records provide a consistent record of atmospheric CO₂ and/or whether, in comparison with the ice core record, they may be used to define regional differences in ΔpCO₂ on glacial-interglacial timescales.

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Seasonal δ¹⁸O Records From Submerged Fossil Corals in the Huon Gulf, Papua New Guinea

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We have generated seasonal δ¹⁸O records from submerged fossil corals from the Huon Gulf, Papua New Guinea, which lies in the West Pacific Warm Pool. The corals grew on the lower plate of an active convergent margin in the Huon Gulf and formed a series of 100-200 m high platforms occurring between depths of 240 and 2120 m. Previous studies suggest that the reefs build platforms during glacial/interglacial cycles and drown during periods of rapid sea level rise that follow low sea level events. Combining ²³⁰Th dates of corals from the 240 and 1950 m platforms with a model by Wallace et al. (this volume), platform ages have been estimated until more ²³⁰Th data is available. The model also suggests that all of the platforms were formed within the last 400 ka. Corals from the tops of the platforms, which grew just prior to rapid sea level rise according to the model, were collected by the ROV JASON.

Porites corals have been analyzed for δ¹⁸O and will be analyzed for Sr/Ca. Five corals, each spanning 5-12 years, were cut into slabs along the primary growth axis and sampled at 16-28 samples per year. The samples are from water depths of 853, 1277, 1631, 1977, and 2122 meters. The average δ¹⁸O values of these samples ranges from -2.1 to -3.7‰, 1.3 to 2.9‰ heavier than average modern (interglacial) *Porites* coral (that range from -4.8 to -5.0) growing nearby on the Huon Peninsula (Tudhope et al., 2001). The relatively high values of our submerged samples are similar to δ¹⁸O values of corals from MIS 3 and the penultimate deglaciation (Tudhope et al., 2001), suggesting that they grew during periods with low to intermediate sea levels. This result is consistent with the model of platform drowning described above.

Three to five years of seasonal δ¹⁸O changes have been measured in the five samples; they are listed here from lightest to heaviest average δ¹⁸O value. Sample 135 from 1977 m depth (²³⁰Th age of 348 ± 10 ka; Galewsky et al., 1996) has the lightest average δ¹⁸O value of -3.6‰ and an amplitude in the seasonal signal of 0.4‰. Sample 3 from 853 m (~180 ka from model), has an average value of -3.3‰ and a seasonal amplitude of 1.2‰. Sample 166 from 1277 m (~248 ka from model) has an average value of -2.8‰ and an amplitude of 0.6‰. Samples 244 from 1631 m and 303 from 2122 m (~295 ka and 375 ka, respectively, from model) have the heaviest average δ¹⁸O value of -2.1‰ and seasonal amplitudes of 0.3 and 2.5‰, respectively. Sample 3 is the only sample with a seasonal amplitude similar to that in the modern corals from the Huon Peninsula (Tudhope et al., 2001), while the other samples have lower amplitudes (sample 303 is likely altered). However, longer time series must be generated in order to make further conclusions.

Galewsky et al., *Geology* 24, 819 (1996). Tudhope et al., *Science* 291, 1511 (2001).

PP51A-0279 0830h POSTER

Novel Proxies Approach to Characterise Ice Rafting Events in the North Atlantic

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During the last glacial period, there have been several episodes of quasi-periodic iceberg discharge from the ice sheets into the North Atlantic (Heinrich Events) (Heinrich, 1988). These episodes are recorded in Quaternary sediments as layers of ice rafted debris (IRD). Properties of sediments in these Heinrich Layers (HLs) differ from those of adjacent ambient sediments. Heinrich Events (HEs) are associated with changes in global climate. To determine the cause of HEs, work on provenance of IRD was undertaken. Previous studies included analysis of bulk properties of lithic and organic matter in IRD and an attempt to correlate them with those of possible continental sources (e.g. Grousset et al., 2001).

We used biomarker approach to characterise the provenance of IRD in the North Atlantic, similar to oil-source rock correlation used in petroleum industry. In this work, biomarker composition of Heinrich Layers from several North Atlantic cores was compared with that of possible source areas. As a proxy for source of IRD, we analysed glaciogenic debris flows from trough mouth fans (TMF) that formed as a result of iceberg discharge (Vorren & Laberg, 1997). Those included samples from the Nordic Seas, Labrador Sea and Baffin Bay. Different classes of organic compounds (e.g. photosynthetic pigments and hydrocarbons) were characterised. Variability within each class, relative abundances of different components and isotopic signatures were considered. Biomarker fingerprints were compared within each core, within each TMF and between TMFs. Cluster analysis was performed to correlate sources of IRD (TMFs) and its sinks (HLs from several North Atlantic cores).

Grousset et al. 2001. Zooming in on Heinrich layers. *Paleoceanography*, 16, 240-259.Heinrich, H. 1988. Origin and Consequence of the Ice Rafting In Northeast Atlantic Ocean During the Past 130,000 Years. *Quaternary Research*, 29, 143-152.Vorren & Laberg, 1997. Trough Mouth Fans - Palaeoclimate and Ice-Sheet Monitors. *Quaternary Science Reviews*, 16, 856-881.

PP51A-0280 0830h POSTER

Assessed Potential of Conifers as Proxy Paleo-wind Stations

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A new method for extracting wind direction and velocity information from tree rings has been developed and applied to more than 60 conifers near two weather stations on the Olympic Peninsula of northwest Washington. Utilizing measurements from cores and full cross-sections, a mechanical wind-drag bending-moment model relates ring eccentricity to the horizontal component of unbalanced forces, principally wind, affecting the tree. Straight conifers on level ground typically develop thicker rings on the downwind side. The two study areas have very different wind patterns. At Port Angeles dominant wind is the westerly sea breeze, but at Quillayute dominant winds are south-east and southwest. Tested weather station record wind parameters include: annual (and seasonal) mean and summed velocity for hourly or peak daily observations. Sum velocity yields much higher significance than mean velocity in regressions against growth eccentricity, suggesting that tree response may be related to momentum transfer. Correlation significance increases when a 3-year running mean is applied to smooth out measurement error, delayed response to wind, and spatial wind variability; and when several trees are averaged, dispersing events such as limb loss. Linear regression of the vector resultants of eccentricity of Douglas-fir against annual sum velocity vector records at Port Angeles yields significant (P(t)<0.05) slope constants for R and θ in most cases. Vector assessment of Sitka spruce near Quillayute is limited by multimodal wind. Scalar sum velocity and ring-width eccentricity data from these and other species are significantly correlated at both areas. Seasonal assessment of eccentricity response to wind at the Pacific coast suggests that very high velocities, especially during growth season, promote thinner rings on the downwind side. In such cases predicted response is delayed by up to 8 years. Rainfall is a significant co-contributor to eccentricity only at the wetter coastal sites, and some delayed response there seems triggered by wet growth season conditions. Wavelet analysis of eccentricity of old trees reveals significant interannual (ca. 2-8yr), interdecadal (ca. 15-25yr), and secular spectral power since A.D.1580. Paleo-wind direction and velocity proxy data would have direct application to the evolving history of sea level pressure, aerosols, and coastal process.

PP51A-0281 0830h POSTER

Subannual Climate Records from Aragonite Stalagmites

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Bulk analysis of speleothems is an important means of reconstructing terrestrial environments at decadal scales for landmasses such as Southern Africa. However some of the most significant climatic events in the last few years in that region (such as the floods in Mozambique or current drought in Zimbabwe/Malawi) are much shorter period events that would not be resolved in such reconstructions. Trace elements in the aragonite stalagmites of Cold Air Cave, South Africa have the potential to provide high-resolution (perhaps monthly) climatic data for the region going back several ka if we understand 1) the relationship between geochemistry and climate and 2) the mechanism of stalagmite growth.

Here we report a SIMS study of these speleothems at 10 μm spatial resolution and ppm precision. Oscillations in Sr/Ca and Ba/Ca are observed parallel to the growth direction, and we interpret these to represent annual variations in rainfall. However, in addition we observe geochemical variation perpendicular to the growth direction. We infer the speleothem is laterally, as well as vertically, zoned.

By amalgamating several trace element profiles, we have produced a 45 yr trace element record that averages across the lateral zoning and we compare this with monthly rainfall. Droughts correspond to minima in Ca/Sr and Ca/Ba ratios and peaks to maxima in rainfall. However, in detail rainfall does not correlate linearly with geochemistry, indicating that kinetic factors, notably variation in growth rate, are central to trace element uptake. At present SIMS can provide qualitative evidence for drought or inundation events, but the goal of quantitative subannual climatic reconstruction remains elusive.

PP51A-0282 0830h POSTER

Extracting ENSO Records From Speleothems: A new Initiative in the South Pacific

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Recent studies have suggested that ENSO may have been switched off prior to 5 Ka raising the possibility that El-Niño waxes and wanes over the millennia. An understanding of ENSO past irregularity may give important clues to our climate future in a greenhouse world and therefore more proxy climate records are needed to test the suggestions of ENSO switch on/off events. Here we report initial results of a new initiative to acquire archives of ENSO and monsoon variability possessing at least decadal and possibly interannual resolution based on speleothems from limestone-capped islands in the Western Pacific Warm Water Pool. In the summer of 2002 we surveyed caves and drilled horizontal cores through both active and inactive stalagmites on the uplifted former atoll of Niue (19°00'S, 169°50'W) which has well developed karst features.

Century-long rainfall variability data on Niue agree remarkably well with ENSO events, hence speleothems in the caves should preserve the ENSO record. A fossil stalagmite sampled from a cave in the Pleistocene reef terrace yield ²³⁰Th ages of 62.6 and 65.2 Ka ($\pm 0.6\%$ 1 σ error) corresponding to early Isotope Stage 3. The stalagmite contains couplets (mean 250 μm thick) of alternating dark and light laminae which are likely annual growth increments. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ records representing about 120 years of continuous growth ($-5.4 \pm 0.4\text{‰}$ and $8.6 \pm 1.1\text{‰}$ PDB, respectively; n=54) show paired cyclicity between low and high value clusters. The trend and excursions of the $\delta^{18}\text{O}$ record are coherent with a model curve based on rainfall records and groundwater $\delta^{18}\text{O}$ values ($-4.6 \pm 0.51\text{‰}$ SMOW; n=19). $\delta^{13}\text{C}$ values are more negative and have higher amplitude excursions than a model curve based on groundwater DIC and $\delta^{13}\text{C}$ (1.34 to 3.62 mM and -4.8 to 11.0 ‰ PDB, respectively; n=19) and host rock $\delta^{13}\text{C}$ ($-0.4 \pm 0.9\text{‰}$ PDB; n=149). These results may indicate a larger past contribution from soil CO₂ relative to present. Our initial results suggest that ENSO was active during the last glaciation. Ongoing study of the recently drilled stalagmite cores aims to acquire long ENSO proxy records and seek confirmation of our initial results.

PP51A-0283 0830h POSTER

Rapid Analysis of Carbon Isotopic Compositions of Sedimentary Algal Sterols

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We are developing a new procedure to produce highly resolved records of the carbon isotopic composition of algal sterols. The procedure includes: (i) recovery of geolipids from dry sediments by extraction in organic solvents; (ii) chromatographic fractionation of the extract on silica gel; and (iii) removal of n-alcohols with Silicalite. Simplifications allow processing of 24 samples per day. Miniaturization has reduced the amount of sediment required to 300 mg. The carbon isotopic composition of the extract is measured using a moving-wire combustion system initially developed to accept the effluent of a liquid chromatograph (Brand and Dobberstein, *Isotopes Environ. Health Stud.* **32**, 275-283, 1996). Analyses are made at 25-sec intervals with an average standard error of 0.15 ‰ for samples ranging from 200 to 900 ngC. Comparison of the resulting records of the isotopic composition of algal lipids to parallel analyses of inorganic carbon allows calculation of the isotopic fractionation associated with primary production and thus provides information about conditions in the photic zone. It serves also to identify samples in which more detailed, compound-specific analysis would be worthwhile.

A highly-resolved record of ¹³C in polar lipids from a sediment core collected on the Oman Margin (ODP 723B) indicates fractionations between 20 and 25 ‰ . Events occurring on timescales of a few hundred years have caused variations as large as 4 ‰ . Increases in the fractionation could be caused by slowed rates of growth, an increase of the surface area/volume ratio of the community or an increase in the concentration of CO₂. Such changes could be related to varying strengths of upwelling, supplies of key nutrients, or to changes in the dominant population in the producer community. Characterization of the lipids present at selected depths, as well as the comparison of our profile with existing paleoceanographic records from the Oman Margin, should allow refinement of these possibilities.

PP51A-0284 0830h POSTER

The Neogene Nd and Hf Isotope Evolution of Pacific Deep and Bottom Water

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The oceanic residence times of Nd and Hf are believed to be on the order of the global mixing time of the ocean. This allows the application of Nd and Hf isotopes to trace water mass mixing and large-scale weathering/erosion processes. Neodymium is delivered to the oceans via riverine or eolian pathways, whereas the sources of dissolved Hf in the ocean are not well constrained.

We analyzed Nd and Hf isotope time-series of 5 ferromanganese crusts from strategic localities in the Pacific ocean. The goal of this study was to gain new insights of the past circulation patterns and input sources in the Pacific ocean beyond the existing records from the equatorial Pacific. Dating was obtained from ¹⁰Be/⁹Be ratios calculated by combining AMS-¹⁰Be profiles and ICP-MS Be measurements obtained for the same aliquots. Ages beyond 10 Ma were calculated applying a Co-constant flux model. Between 9 and 38 Myrs of seawater history are recorded in the investigated crusts.

A previously suggested vertical stratification of the equatorial Pacific water column could be confirmed

for Nd isotopes, but is not very well defined for Hf isotopes. Following a transect from the South Pacific to the North Pacific in 2000 m water depth, Nd and Hf isotopes become gradually more radiogenic, in line with continued dilution of Southern Ocean water masses with Pacific deep water. The most striking result is that over the past 20 Myr the differences between the south and the north Pacific have been larger than the variability within individual time-series. In detail, however, there are some important exceptions in the marginal southwestern and southeastern Pacific.

The coupling of Nd and Hf isotopes in all five records strongly suggests that hydrothermal Hf sources are not of ocean-wide importance, although they may be locally. The relative importance of eolian versus riverine inputs and the role of advected Southern Ocean water masses versus intra-basin mixing within the Pacific will be discussed. Our results provide an improved understanding of the potential of Hf isotopes as a tracer in paleoceanography and of the sources of Nd and Hf in the Pacific Ocean.

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Determination of Sediment Provenance at Drift Sites From Hydrogen Isotopes in Lipids

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Paleoclimate records with sufficient length and temporal resolution to study the occurrence and causal mechanisms of abrupt climate change are exceedingly rare. Rapidly deposited ocean sediments provide the best archive for studying these events through geologic time, but such sites in the open ocean are generally limited to sediment drift deposits such as the Bermuda Rise in the northwest Atlantic and the Cape Basin in the southeast Atlantic.

Using multiple climate proxies in a single core is becoming more common in high-resolution paleoclimate investigations, but a major potential concern with this approach arises from the possibility that the fine fraction of sediment (< 63 μm), and the climate proxies within it, may represent conditions far from the deposition site because it is the fine fraction that is easily advected. We hypothesize that hydrogen isotope ratios of lipids from phytoplankton may provide insight into the source of fine-grained sediment.

In pilot analyses of suspended particulate material collected on different days in June, 2000 from the Sargasso Sea, the δD of alkenones was $-160 \pm 7\text{‰}$ (n=8), similar to alkyl lipids from various plants reported by Sessions et al. (*Organic Geochemistry* 30, pp.1193-2000, 1999). We will compare the δD of lipid biomarkers from suspended particles and surface sediments between the Bermuda Rise and the Scotian Margin above which a large ($\sim 20\text{‰}$) δD gradient exists. In addition, we will compare the hydrogen isotopic difference between lipid biomarkers from suspended particulate samples and the water collected simultaneously. Lastly, we will examine the temporal variability of δD in suspended particles over short (day) time scales.

PP51A-0286 0830h POSTER

Uranium, Barium, Lead and Lead Isotopes in Sclerosponges: New Proxies in Sclerosponges

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We have used LA-ICPMS (Finnigan-Element) to determine U/Ca, Ba/Ca, Pb/Ca, and Pb-isotopic (²⁰⁶Pb/²⁰⁷Pb and ²⁰⁸Pb/²⁰⁷Pb) ratios in the skeleton of a sclerosponge collected from the Bahamas at a

depth of 146 m at increments of 0.02 mm. The concentrations of Mg, Sr as well as stable O and C isotopes were also determined along parallel transects and the skeleton dated using U/Th. Although the Ba/Ca, Mg/Ca, and Sr/Ca ratios are reasonably well correlated, only the Sr/Ca ratio exhibits a strong high frequency variation which we have interpreted as reflecting annual changes in temperature. The U/Ca ratio also exhibits apparent cyclicity on an intra-annual scale, but the overall variations are not correlated to changes in the concentration of Ba, Mg, or Sr. Changes in Mg/Ca and Ba/Ca may therefore be partially related to upwelling which may not always be seasonal in nature. The Pb/Ca ratio exhibits large variations related to the anthropogenic changes of lead in the environment with a maximum values occurring between 1970 and 1980. Superimposed on the changes in the Pb/Ca ratio is a 3-5 year cycle, perhaps related to climatic variables. The $^{208}\text{Pb}/^{207}\text{Pb}$ ratio shows a significant decline throughout the record from 2.47 prior to the increase in the Pb/Ca ratio to 2.44. In contrast the $^{206}\text{Pb}/^{207}\text{Pb}$ shows a significant decrease associated with the advent of Pb in gasoline followed by an increase back to early 1900 values associated with the decrease in Pb concentrations. The timing and magnitude of the change in $^{206}\text{Pb}/^{207}\text{Pb}$ ratio is similar to that previous reported for corals growing in the Atlantic (Shen and Boyle, EPSL, 82:1987) although lower than values reported in ice-cores (Rosman et al. EPSL, 176:2000). The $^{206}\text{Pb}/^{207}\text{Pb}$ ratio in the sclerosponge declines from background values ($^{206}\text{Pb}/^{207}\text{Pb} = 1.2147$) associated with the use of non-radiogenic sources of lead. A sharp increase around 1940 may relate to increase industrialization associated with World War II.

PP51A-0287 0830h POSTER

Stable Carbon Isotope Record in a Palau Sclerosponge

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The ratio of stable carbon isotopes ($\delta^{13}\text{C}$) deposited in the calcium carbonate skeleton of marine sclerosponges appears to record the carbon isotopic composition of seawater mixed-layer dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$). Thus the $\delta^{13}\text{C}$ signature chronicled in sclerosponge skeletons offers a promising multi-century proxy record of seawater mixed-layer $\delta^{13}\text{C}_{\text{DIC}}$ throughout the tropics. Here, a high-resolution (0.1 mm) $\delta^{13}\text{C}$ record for a 7.7 cm *Acanthochaetes wellsi* sclerosponge from Palau (7N, 134W) is presented. At a published growth rate of 0.45 mm per year, this record spans ~170 years beginning in July 2001 and going back to 1831. The $\delta^{13}\text{C}$ values for a definitive 10-year *A. wellsi* record spanning 1989-1998 were similar to $\delta^{13}\text{C}$ values here for the first 4.7 mm of the record providing supporting evidence for the growth rate. The sclerosponge $\delta^{13}\text{C}$ shows a distinct Seuss Effect. At the time this abstract was submitted, the analysis of the first 16 mm of the sclerosponge revealed a significant decrease in $\delta^{13}\text{C}$ with time [$\delta^{13}\text{C} = 0.02$ (distance) + 2.64, $r^2 = 0.73$, $p < 0.0001$, where time is marked by distance in millimeters from the growing edge] corresponding to a decrease in $\delta^{13}\text{C}$ of 0.076‰ per decade. For comparison, published low-frequency measurements in Australian, New Caledonian and Jamaican sclerosponges have yielded decreases in $\delta^{13}\text{C}$ of ~0.05 to 0.08 ‰ per decade over the past 40 years. Preliminary interpretation of the data indicates that the amount of atmospheric CO_2 contributing to the seawater $\delta^{13}\text{C}_{\text{DIC}}$ at Palau is intermediate to Australia and Jamaica. In addition, visual examination of the $\delta^{13}\text{C}$ record reveals regular fluctuation in $\delta^{13}\text{C}$ that may correspond to annual variability in $\delta^{13}\text{C}_{\text{DIC}}$. This research presents the first century or longer sclerosponge $\delta^{13}\text{C}$ record from the northwestern equatorial Pacific.

PP51A-0288 0830h POSTER

Radiocarbon Constraints on Oceanic Mixing, Banks Island Vanuatu: A Coralline Sponge Perspective

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Coralline sponges accrete a skeleton that is composed of calcium carbonate. They are common in shallow water environments as well as depths up to ~150m. They differ from hermatypic reef corals in that they secrete their skeleton in isotopic equilibrium with the surrounding seawater providing a distinct advantage over corals when reconstructing the surrounding seawater. A calcitic sponge *Acanthochaetes wellsi* collected from Banks Island, Vanuatu was analyzed for $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$. The carbon isotope records from this sample are consistent with the depletion of ^{13}C by fossil fuel derived CO_2 and an increase in $\Delta^{14}\text{C}$ due to atmospheric weapons testing. The sponge $\Delta^{14}\text{C}$ record peak in 1975 then gradually decreases due to dilution by oceanic mixing processes. The unique nature of coralline sponge isotopic equilibrium provides a strong constraint on the uptake of anthropogenic CO_2 . These results are also compared to a schematic ocean model in an attempt to quantify lateral and vertical diffusivity in this area of large air-sea CO_2 flux.

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The Oceanic Lead Trends Recorded by Sclerosponges.

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Lead profiles measured by ICP-MS in two Bahamian and three Jamaican sclerosponges display an increase in lead concentration during the last century, followed by a decrease since the seventies. This trend previously shown in polar ice and corals was explained by changes in atmospheric lead due to the use of leaded gasoline and the increasing use of unleaded gasoline since the seventies. Replicate profiles demonstrate the high reproducibility in single specimens. Different specimens from the same location display similar results, which demonstrates the reproducibility of the lead concentrations in different specimens. The similarity between the ICP-MS and LA-ICP-MS (Lazareth et al., 2000) measurements in two specimens from Acklins Island (Bahamas), confirms the reliability of laser ablation ICP-MS measurements. Regional differences, e.g. from 1930 to 1970 year AD a 2.5-fold increase in Jamaica (from 0.4 to 1.0 ppm), a 2.5-fold increase at Acklins Island (from 0.8 to 2.0 ppm) and a 4-fold increase at Turks and Caicos Islands (from 1.0 to 4.2 ppm) either reflect differences in intensity of the atmospheric and/or seawater pollution or is linked with a regional seawater distribution of lead due to the local organization of the oceanic currents.

An average growth rate of 233 micrometer per year was assumed, according to the work of Willenz and Hartman (1999). Since variations in the growth rate of the different studied sclerosponges is obvious, dating possibilities are explored in order to perfectly match the lead maxima. Between the maximum lead concentration and 1990, the lead curves display a ~1.3-fold decrease for the three Jamaican specimens and a ~2.3-fold decrease for the Turks and Caicos specimen. The specimens from Acklins Island, sampled in 1984 and 1981 recorded the onset of the decrease. Anomalous high values are obtained for the upper samples, where organic matter is present. These values are probably due to element enrichment in the dried tissues.

References: Lazareth C., Willenz Ph., Navez J., Kepkens E., Dehairs F. and André L., 2000. Sclerosponges as a new potential recorder of environmental changes: lead in *Ceratoporellanicholsoni*. *Geology* 28 (6): 515-518. Willenz Ph. and Hartman W.D., 1999. Growth and regeneration rates of the calcareous skeleton of the Caribbean coralline sponge *Ceratoporellanicholsoni*: a long term survey. *Memoirs of the Queensland Museum* 44: 675-685.

PP51A-0290 0830h POSTER

Biological Fractionation of Ge/Si by Antarctic Diatoms - JGOFs/AESOPS Trap Results

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Germanium (Ge) and silicon (Si) behave similarly both geochemically and biologically. As a result, today's oceanic Ge versus Si relationship is linear with a Ge/Si ratio of 0.7×10^{-6} (atom/atom). This same ratio is also observed in diatomaceous opal from core tops and from earlier interglacial periods. However, ratios in glacial sediments are ~30% lower: $(\text{Ge/Si})_{\text{opal}} \sim 0.5 \times 10^{-6}$. Two plausible mechanisms have been proposed for these glacial-interglacial shifts: 1) whole ocean changes in Ge & Si sources and/or sinks (changes in continental weathering sources or reverse weathering sinks inducing differential mass balance variations of Ge/Si); and 2) biological fractionation during diatom shell formation in surface waters coupled with incomplete utilization of Si (Rayleigh distillation and variable preformed Si). A statistically-significant positive Ge-intercept in the oceanic Ge vs. Si relationship can be interpreted as evidence of biological fractionation. On the other hand, the absence of significant fractionation in diatom cultures and the perfect linearity of the seawater Ge vs. Si relationship both argue against significant Ge-discrimination during opal formation.

Most diatom production and opal preservation occur in the Southern Ocean. To detect biological fractionation by diatoms, the Ge/Si ratio of intrinsic opal was measured in time-series trap samples from the southwest Pacific sector of the Southern Ocean - the JGOFs/AESOPS moorings across the Polar Front Zone along 170°W. Trap fluxes were collected for ~one year (1997), during which a doublet spring diatom bloom was captured in the 1000 m and 2000 m traps. Preliminary results show fractionation in the $(\text{Ge/Si})_{\text{opal}}$ ratio of the trapped diatom shells. The first bloom coincides with a decrease in the opal ratio from $(0.70 \pm 0.03) \times 10^{-6}$ to 0.55×10^{-6} and then a rapid return to the background oceanic ratio. The second bloom several weeks later displayed no fractionation - opal ratios do not differ from seawater. There are at least two explanations for the differences between the two blooms: 1) species' dependent Ge/Si diatom fractionation - perhaps the dominant diatom species changed between the two blooms; or 2) iron-dependent fractionation - perhaps the first bloom initiated under iron-replete conditions while the second bloom occurred in iron-depleted waters. Consequently, glacial-interglacial changes in $(\text{Ge/Si})_{\text{opal}}$ may record changes in the dominant diatom species or changes in surface water iron concentrations, rather than changes in local Si bio-limitation or whole ocean changes in the Ge/Si ratio of seawater. The plot thickens.

PP51A-0291 0830h POSTER

Molybdenum Isotopes & the Oxygenation of the Mid-Proterozoic Ocean

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Recently debate has arisen over the redox state of the mid-Proterozoic oceans. The occurrence of banded iron formations (BIF) in the Archean and Paleoproterozoic strongly suggests oceans with little dissolved O_2 or H_2S until ca. 1.8 Ga. The disappearance of BIF after this time is commonly taken to indicate ocean oxygenation. Alternatively, the extent of sulfidic conditions in the oceans may have increased after 1.8 Ga (Canfield, 1998). According to this view, ocean oxygenation did not occur until P_{O_2} approached modern levels after ~1 Ga. These different scenarios have important evolutionary implications (Anbar and Knoll, 2002). The molybdenum (Mo) stable isotope system may provide insight to this debate.

We previously observed systematic Mo isotope fractionation ($\delta^{97/95}\text{Mo}$) between recent oxic and sulfidic sediments (Barling et al., 2001; Arnold et al., 2001). The $\delta^{97/95}\text{Mo}$ of seawater and sulfidic sediments are essentially the same, suggesting that the Mo isotope composition of the oceans is largely controlled by fractionation during removal to oxic sediments. The extent of fractionation between adsorbed and dissolved Mo in laboratory experiments is comparable to the extent of

fractionation observed between Mn oxides and seawater ($\sim 1.7\text{‰}$), supporting this suggestion (Barling and Anbar, 2002; Siebert et al., 2001). The laboratory experiments indicate that adsorption of Mo onto Mn oxide particles is an equilibrium process with a characteristic $\alpha_{\text{solution-MnO}_2}$ of 1.0017. Therefore, $\delta^{97/95}\text{Mo}_{\text{seawater}}$ may reflect the global balance between Mo removal to oxic and sulfidic sediments and changes in this balance could be recorded as changes in $\delta^{97/95}\text{Mo}$ in ancient black shales deposited under sulfidic conditions. If the proportion of seafloor under oxic waters were smaller in the past, $\delta^{97/95}\text{Mo}$ in black shales should shift toward lighter values.

An investigation of Mo-rich black shales from the Wollgorang Fm. (~ 1.73 Ga) and Velkerri Fm. (~ 1.4 Ga) from the McArthur Basin, Australia reveals $\delta^{97/95}\text{Mo}$ lighter than in recent sulfidic sediments (0.22 to 0.79 ‰ vs. 1.0 to 1.5 ‰). Mo in these sediments is primarily authigenic. Therefore, these data are consistent with less extensive oxic deposition in mid-Proterozoic oceans.

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PP51A-0292 0830h POSTER

Accumulation Rates of Trace Elements in the Cariaco Basin: A 20-kyr History of Seawater Chemistry and Global Climate

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A sediment core from the Cariaco Basin on the Venezuelan continental shelf, which collected sediment as old as 20 kyr, was analyzed for its major-element-oxide and trace-element concentrations. The elements can be partitioned between a siliclastic, terrigenous-derived fraction and two seawater-derived fractions. The marine fractions are (1) a biogenic fraction represented by nutrient trace elements taken up mostly by phytoplankton in the photic zone, and (2) a hydrogenous fraction derived from bottom water via adsorption and organic matter from the photic zone, redox conditions and advection of bottom water, and the flux of terrigenous debris into the basin are used to calculate current trace-element accumulation rates. The sums of calculated accumulation rates of Cd, Cu, Mo, Ni, V, and Zn show excellent agreement with their measured bulk rates of accumulation in the uppermost surface sediment. This agreement between current measured and calculated accumulation rates of trace elements supports a model of trace-element accumulation rates in the subsurface sediment that gives a 20-kyr history of upwelling into the photic zone, bottom-water advection, and sediment provenance. Extrema in the trace-element accumulation rates and interpreted hydrographic properties of the water column correspond to changes in eustatic sea level and global climate.

PP51A-0293 0830h POSTER

Long-term, High-frequency Terrestrial Paleoclimatic Record from Carbon and Oxygen Isotopes of Pedogenic Carbonate from the Late Oligocene to Early Miocene John Day Formation at Longview Ranch, Central Oregon (28.7-23.6 Ma).

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Two hundred and eighty meters of continuously deposited section of Arikarean (Late Oligocene-Early

Miocene) volcanoclastic rocks with abundant calcareous paleosols exposed at Longview Ranch, Oregon provide a unique opportunity to examine a highly detailed and long-term terrestrial paleoclimatic record. The Longview Ranch sections preserve 354 calcareous paleosols over the 5.1 Ma period of the Arikarean, each representing an average of approximately 15 ka of deposition and soil formation. Such high frequency of soil formation allows for a detailed analysis of long-period Milankovitch-scale climatic change (frequencies less than the Nyquist frequency). Pedogenic carbonate nodules from calcareous (Bk) horizons of each paleosol have been analyzed for stable carbon and oxygen isotopic compositions, augmenting an already detailed terrestrial vertebrate paleontological and paleopedological record of this sequence, as well as the paleoclimatic record from the marine realm. Features of these stable isotopic records include Milankovitch-scale frequency oscillations, lulls in Milankovitch signal amplitude, unidirectional isotopic shifts, and short-term aberrations in both the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ records. Spectral power in the 41, 100 and 400 ka periods is exceptionally high throughout the record, except during a low amplitude interval between 27.5 and 26.7 Ma. Aberrations in the record occur sporadically, particularly prior to 28 Ma, and appear as single-paleosol isotopic excursions of up to 5 ‰ (negative). The major isotopic shift in the $\delta^{18}\text{O}$ record occurs rapidly at 25.5 Ma, from mean value from about 14 ‰ to 12 ‰. These records will be compared to major events in the regional vertebrate paleontological record, as well as the detailed global paleoclimatic record from marine foraminifera. A new variable of residual $\delta^{18}\text{O}$ will also be introduced as an indicator of terrestrial paleoprecipitation trends.

PP51A-0294 0830h POSTER

U-Th-Ra in Amazon rivers: New insights on Au-series fractionation during chemical weathering

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Seawater ($^{234}\text{U}/^{238}\text{U}$) has been proposed as a proxy for understanding past continental weathering conditions. Thus, it is crucial to constrain the parameters that control U-series fractionation during present day weathering in order to understand what they have recorded in the past. Additionally, U-series provide useful constraints for understanding chemical weathering as a function of environmental variables. We have analyzed ^{238}U , ^{234}U , ^{230}Th , ^{226}Ra compositions in the dissolved phase ($< 0.2\mu\text{m}$) of Amazon river and major tributaries. Two groups can be distinguished within Amazon tributaries: river draining mainly the Andes and the Brazilian shield; and rivers dominated by dissolved organic material. The latter are characterized by the absence of ^{238}U , ^{234}U fractionation and very high Th contents ($> 80\text{ng/l}$) whereas the former display ^{234}U excess over ^{238}U and lower Th contents ($< 30\text{ng/l}$). High Th concentrations for organic-rich waters are consistent with a previous study, which revealed the existence of strong complexes between Th and humic acids (Viers et al., 1997). The lack of ^{234}U , ^{238}U disequilibrium in organic-rich waters suggests that dissolved organic matter may play a role on ^{234}U , ^{238}U fractionation. However, as ($^{234}\text{U}/^{238}\text{U}$) ratio of the Amazon mainstream is dominated by Solimões and Madeira compositions, dissolved organic matter is believed to have minor consequences on the ($^{234}\text{U}/^{238}\text{U}$) input to the ocean. $^{232}\text{Th}/^{238}\text{U}$ of the source material based on ($^{230}\text{Th}/^{232}\text{Th}$) ratios range, for some rivers, between 5.5 and 8.7, which is higher than the estimated value based on $^{208}\text{Pb}/^{206}\text{Pb}$ systematics in Amazon rivers (ca. 3.8; Allegre et al., 1996). This may be the result of past U-removal during previous weathering events over time-scales longer than the half-life of thorium-230 (75 ka).

References: Viers J. et al. (1997) *Chem. Geol.*, vol. 140, pp. 181-206; Allegre C. J. et al. (1996) *Chem. Geol.*, vol. 131, pp. 93-112

PP51A-0295 0830h POSTER

Silicon Isotopic Measurements in Desolvated Samples by MC-ICP-MS

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Silicon, the most ubiquitous rock-forming element presents also a key role in biological processes. In particular, its biogeochemical cycle constitutes one of the most challenging issues in recent years due to its close relationship with the carbon cycle in marine environments (Tréguer et al., 1995; Ragueneau et al., 2000). The most recent silicon isotopic investigations on various natural samples have highlighted the great potential of this (palaeo)-proxy for oceanographers (De La Rocha et al., 1997, 1998). Better understanding the silicon isotope fractionation due to various biogeochemical processes can be achieved by facilitating its measurements through MC-ICPMS technique (De La Rocha et al., 2002; Alleman et al., 2002).

In this regard we have developed an original method to analyze silicon isotopes under dry plasma conditions. We demonstrate that coupling a Nu Plasma MC-ICP-MS with a Cetac Aridus desolvator allows the rapid acquisition of natural silicon isotope abundances with high sensitivity and accuracy. To adequately correct for the mass fractionation occurring at the interface between the plasma source and the mass spectrometer line, we combine external normalization using Mg as a dopant with standard-sample bracketing using NBS-28 as the reference. With the desolvating nebulization system, the measurement of ^{28}Si and ^{29}Si isotopes is not hampered by significant interferences. $\delta^{29}\text{Si}$ values are obtained with an accuracy and repeatability better than 0.1 ‰. The accuracy has been successfully calibrated against the laser fluorination line technique (De La Rocha et al., 1996; Alleman et al., 2002). We could demonstrate that the isotopic fractionation that might occur in the plasma or the desolvator was adequately corrected by combining Mg isotopes and the sample-standard bracketing procedure. Moreover, the preservation of the Si isotopic signatures of the samples is validated by the different chemical sample treatments required by these two techniques. This method presents clear advantages compared to the wet plasma technique described by De La Rocha et al. (2002), also using a Nu Plasma MC-ICP-MS, as being much more sensitive and less time consuming. We report here single $\delta^{29}\text{Si}$ data obtained within one hour and requiring less than $3\mu\text{g}$ Si per sample.

Preliminary results over a large range of natural samples including diatomite, large diatoms, sponge spicules, phytoliths and water from lakes and seawater will also be presented and briefly discussed.

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PP51A-0296 0830h POSTER

Does Differential Diffusion of Light Stable Isotopes Significantly Influence Their Pore Water Profiles?

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Nitrogen isotopes are a potentially powerful tool for paleoceanography, but their application requires an assessment of the extent of isotope fractionation during diagenesis. Measurement and modeling of the isotopic composition of ammonium in pore water profiles provides a means to determine the extent of diagenetic isotopic fractionation. However, the results of this modeling depend on accurately estimating the relative diffusivities of different isotopes. Most work to date using light stable isotopes of nitrogen and carbon has assumed that the diffusivities of different isotopes are not significantly different. This assumption may be incorrect for nitrogen isotopes in ammonium. In an open system at steady state, a diffusion-reaction model indicates that the effect of different diffusivities is to cause a systematic offset of pore water isotope ratios from the ratio released by diagenetic reactions. Diffusivity should be inversely proportional to the square root of the mass of the diffusing molecule. The ratio D15/D14 for $^{15}\text{NH}_4^+$ and $^{14}\text{NH}_4^+$ is likely to range from 0.973 if no waters of hydration are attached, to 0.995 if 5 waters

of hydration are attached to ammonium. These ratios predict offsets of +27 per mil to +5 per mil for pore water profiles, and this effect should be taken into account in diagenetic modeling. Laboratory experiments are underway to assess the importance of this effect.

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The Nitrogen and Oxygen Isotope Composition of Porewater Nitrate from Bering Sea Sediments

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We have measured the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate from sediment pore waters and the water column of the Bering Sea basin. The first high-resolution sediment porewater profile (with pore waters extracted by whole-core squeezing) shows an increase in nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ with depth in the sediment column (by 26‰ and 20‰, respectively) as the nitrate concentration decreases from 45 to 0.5 μM , due to denitrification at depth. However, the nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in the shallow zone of nitrification are equal to or slightly lower than those of bottom water, suggesting that the deep denitrification does not greatly alter the isotopic composition of the nitrate in the shallowest porewaters or, in turn, in the bottom water. These results appear to be consistent with results from *ex situ* incubation and *in situ* benthic chamber experiments by ourselves and other investigators (Brandes et al., 1997), which show that loss of nitrate due to sedimentary denitrification is not accompanied by an isotopic effect on the nitrate of the overlying water.

Measurements conducted during the GEOSECS and WOCE programs revealed the existence of a sizable deficit of remineralized nitrate in the deep Bering Sea, but water-column denitrification is not a likely mechanism for nitrate loss, since oxygen concentrations found in Bering Sea waters are too high (> 15 μM) to allow for bacterial nitrate reduction. Our water column measurements indicate that the nitrate deficit in the deep Bering Sea is not associated with nitrate isotopic enrichment. Together, our sediment and water column nitrate isotope analyses provide strong support for the earlier hypothesis that the deep Bering Sea nitrate deficit is due to sedimentary denitrification.

J. A. Brandes and A. H. Devol, *Geochim. Cosmochim. Acta*, 61(9), 1793-1801 (1997).

PP51A-0298 0830h POSTER

Endogenic Carbonate Sediment Flux in Lakes as an Indicator of Paleo-Groundwater Recharge

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Geochemical principles and field observations indicate that evaporatively concentrated alkaline lakes can become efficient calcium carbonate reactors, removing most Ca^{2+} from solution as endogenic mineral phases. In alkaline lakes where solute fluxes are dominated by ground-water processes, endogenic carbonate mineral formation is therefore expected to reflect rates of delivery of the limiting Ca^{2+} ion to lake waters by ground-water inflow. If changes in ground-water solute concentration are small relative to recharge-driven changes in

the rate of lake/aquifer fluid exchange, then the basin-integrated rate of endogenesis should reflect ground-water recharge rate and hence climate. Rates of endogenesis should show a positive correlation to recharge rates and climatic moisture, contrary to many interpretations of calcareous sedimentary records which emphasize solute concentration (rather than solute mass delivery) as a principal control.

Here we report on an investigation of 20th century endogenic carbonate flux in groundwater-dominated lakes of the Ovando Valley in western Montana. We use common elemental and mineralogical data sets and ²¹⁰Pb analyses of surface sediment cores to establish a history of carbonate endogenesis in two climatically similar but geochemically contrasting lake systems. We then compare these records (expressed as departures from the mean flux) to a common climatic metric incorporating parameters of relative land surface moisture (the Palmer Drought Severity Index). Our alkaline lake system (Evans Lake) shows strong correspondence between anomalies of climate and carbonate (aragonite) endogenesis. A nearby dilute system (Jones Lake), exposed to similar climatic forcing, displays a much weaker relation between carbonate formation and climate. Solute mass-balance analysis of alkaline lake water and ground water inflow demonstrates coherence between solute fluxes and endogenic sedimentation. This observation further supports the solute-limited model of endogenic production in this lake type.

We view endogenic mass flux in lakes as a valuable paleohydrologic proxy in areas of annual net evaporation, where ground-water dominance and elevated alkalinity are common features of perennial lakes. Where conditions are favorable, hydroclimatic signals may be recorded more clearly in this relatively simple relationship than in more commonly applied geochemical proxies.

PP51A-0299 0830h POSTER

Radiocarbon and Stable Isotopic Proxies in Deep-Sea Corals from Hawaii

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Recent observations of significant decadal to century-scale thermal variability at depths below 100 m in the Atlantic and Pacific Oceans have led to an increased interest in developing paleoenvironmental records from subsurface marine organisms. Azooxanthellate, or deep-sea corals, which have a large depth range and apparently long life spans, have the potential to integrate mid-depth ocean chemistry and record ocean processes on decadal and centennial time scales. Here, we present results from a detailed radiocarbon and stable isotopic study of two deep sea corals from Hawaii, *Corallium* (calcareous), and a proteinaceous zoanthid, *Gerardia*. These samples were collected live in the middle of the permanent thermocline at a depth of 400 m using the PISCES V submersible in 1997. Radiocarbon measurements along a radial transect near the base of each sample range from modern post-bomb (post-1950) values to 835 ¹⁴C years for the *Corallium* and 1200 ¹⁴C years for the *Gerardia*. Along a 12mm transect, the ¹⁴C ages in the *Gerardia* decrease in a linear fashion from a pre-bomb value of 445 ± 35 ¹⁴C years to 1200 ± 25 ¹⁴C years. If we assume a linear growth rate, the sample is 780 ± 30 years old and has radial extension rate of 0.015 mm/yr. The $\Delta^{14}\text{C}$ value of 71.3 ± 3.7 on the outer layer (0.5 mm thick) is equivalent to the surface bomb radiocarbon signature for Hawaiian waters. The presence of bomb ¹⁴C in the outer layer of the *Gerardia* suggests that surface-derived particulate organic carbon (POC) is the primary source of carbon to the skeleton. Thus, stable carbon (range 16.1 to 15.2‰) and nitrogen (range 8.7 to 10.8‰) isotopic measurements along the same radial growth axis likely provide a high-resolution (0.2 mm intervals) record of surface productivity and perhaps new primary production. In contrast, the 1 mm-thick outer layer of the *Corallium* has a $\Delta^{14}\text{C}$ value of 4.2 (2.2), equivalent to post-bomb radiocarbon values at 400 m depth. This suggests that the primary source of carbon for *Corallium* is the ambient pool of dissolved inorganic carbon (DIC) at the depth in which it lives. Over the outer 3.5 mm of an 11.3 mm radial transect, $\Delta^{14}\text{C}$ values decrease from 4.2 to 101.9 (±2.4), after which the values

remain constant within the error. Assuming that the changes in $\Delta^{14}\text{C}$ values represent the mixing of bomb carbon from the surface with older deep water which began in 1950, a linear growth rate of 0.06 mm/yr can be calculated over the outer 3.5 mm of the sample. Applying the radial growth rate to the entire sample yields a maximum age of 150 years. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ measurements on samples milled at 0.1 mm increments along the same radial growth axis of the *Corallium* have a range of 1.2‰ and 2.0‰, respectively. However, in contrast to most other deep-sea corals, these values do not exhibit any linear correlation. There are five decadal scale oscillations in the $\delta^{18}\text{O}$ record that may represent as much as a 4°C change in water temperature, most likely caused by changes in the depth of the thermocline. This is one of the first records of mid-depth temperature variations on decadal time scales.

PP51A-0300 0830h POSTER

High Resolution Glacial-interglacial Climatic Variations in the South China Sea during the Last 220,000 Years

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The Asian monsoon plays an important role of both regional and global climatic variations. The South China Sea (SCS) located between Southeast Asia continent and Western Pacific Ocean is an ideal place for studying oceanographic responses and changes of monsoon system in the past. Planktonic foraminiferal shells separated from two deep sea cores, ODP Site 1144 and SCS 15B, located near the northeast continental slope and the central ocean basin respectively were used to reconstruct high-resolution climatic records during the last 220 kyrs. Average of 20 individual foraminiferal shells were hand picked and cleaned thoroughly for high precision trace element/calcium ratios (i.e., Mg/Ca, Sr/Ca, and Ba/Ca) determination using a ThermoFinnigan Element II ICP-MS installed at NCKU. Isotopic compositions of oxygen, carbon, boron and strontium also were measured by stable isotope ratio or Triton TI thermal ionization mass spectrometer.

Mg/Ca and Sr/Ca in foraminiferal shells are sensitive proxies for sea surface temperature, chemical weathering and hydrothermal activity on seafloor. The SCS foraminiferal shells Mg/Ca and Sr/Ca show negative correlation with interesting glacial-interglacial variations. The calculated Mg/Ca SSTs varied as large as 6-7 °C with the highest temperature occurred at oxygen stage 5. The Sr/Ca ratios change about 16% (1.200-1.429 mmole/mole), possibly a result of periodic sea level changes which influencing terrigenous inputs or continental shelves weathering. On the other hand, the Ba/Ca display large variations (0.031-0.117 mmole/mole), possibly reflecting upwelling intensity or SCS bottom water chemistry. The boron isotopic compositions in planktonic foraminiferal shells are used to estimate pH in the surface ocean. Combining these proxies, high-resolution oceanic environmental records in the SCS were reconstructed for the last 220 kyrs. The results obtained from the SCS can be used to gain a better understanding of land-sea interaction in this region.

PP51A-0301 0830h POSTER

Biogeochemistry of Nitrogen Isotopes of Ammonia in the Pore Water of Sediments in the Eastern Tropical North Pacific; Implications for the Problem of Isotopic Fractionation of Sedimentary Nitrogen during Early Diagenesis

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Previous studies have indicated that the process of diagenesis alters the isotopic ratio in preserved organic matter. Published work by others has shown that: (1)

in an oxygenated environment, the $\delta^{15}\text{N}$ of preserved material is about 3 to 4 ‰ heavier than original isotopic composition of marine organic matter; and (2) bacterial degradation of organic matter leads to the preferential break down of ^{14}N containing bonds in peptides and amino acids. We address the issue of diagenetic alteration of the isotopic ratio of degrading organic matter by comparing the isotope composition of ammonium in the pore water to that of N in bulk sediments. Profiles of ammonium $\delta^{15}\text{N}$ were measured in pore waters of several cores obtained from the middle of the OMZ in the eastern Tropical North Pacific and the Gulf of California. Our prediction was that $\delta^{15}\text{N}$ of ammonia in the pore water should be lighter than bulk nitrogen isotopic ratio. However, the opposite was observed. At depth of several meters, $\delta^{15}\text{N}$ of ammonia is about 2-3 ‰ heavier than bulk N, and becomes up to 10-12 ‰ heavier than bulk N near the sediment-water interface. A diffusion-reaction-advection modeling was applied, and results indicate that observed pattern might be explained by a combination of three factors: lower diffusivity of $^{15}\text{NH}_4^+$ relative to $^{14}\text{NH}_4^+$, isotopic fractionation during bacterial degradation of organic matter, and preferential sink for lighter N isotopes in the upper 50-70 cm of sediment. The last factor might be related to either bacterially mediated anaerobic oxidation of ammonia, which would cause residual ammonia to become heavy, or bacterial uptake of ammonium during chemosynthesis. The extent of fractionation during diagenetic release of ammonium cannot be determined until relative diffusivities of $^{15}\text{NH}_4^+$ and $^{14}\text{NH}_4^+$ are established. Further modeling efforts and analytical work is being currently performed to address these problems. Preliminary analysis of $\delta^{15}\text{N}$ in bulk nitrogen show little change with depth, suggesting that the net diagenetic fractionation of bulk nitrogen isotopes is small at these sites.

PP51A-0302 0830h POSTER

Tracking ENSO with tropical trees: Progress in stable isotope dendroclimatology

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The terrestrial tropics remain an important gap in the growing proxy network used to characterize past ENSO behavior. Here we describe a strategy for development of proxy estimates of paleo-ENSO, via proxy rainfall estimates derived from stable isotope ($\delta^{18}\text{O}$) measurements made on tropical trees. The approach applies a new model of oxygen isotopic composition of alpha-cellulose (Roden et al., 2000), a rapid method for cellulose extraction from raw wood (Brendel et al., 2000), and continuous flow isotope ratio mass spectrometry (Brand, 1996) to develop proxy chronological, rainfall and growth rate estimates from tropical trees, even those lacking annual rings. The promise and pitfalls of the approach are illustrated in pilot datasets from the US, Costa Rica, Brazil, and Peru, which show isotopic cycles of 4-6 per mil, and interannual anomalies of up to 8 per mil. Together with the mature ENSO proxies (corals, extratropical tree-rings, varved sediments, and ice cores), replicated and well-dated stable isotope chronologies from tropical trees may eventually improve our understanding of ENSO history over the past several hundred years.

PP51A-0303 0830h POSTER

Freshwater Inflows to San Francisco Bay and Estuary, California From Ion Microprobe Analysis of Trace Elements in Estuarine Bivalve Shells

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In San Francisco Bay and Estuary, salinity and trace metal distribution are closely linked to freshwater inflow from the Sacramento-San Joaquin (S-SJ) Rivers. Because the magnitude and timing of precipitation and snow melt influence river flow, records of salinity and trace metal variations in SF Bay-Estuary may provide information about regional climate variability. Some trace elements are incorporated into growth-banded calcium carbonate bivalve shells in proportion to ambient water concentration, or with a dependence on environmental conditions such as temperature, salinity, or biological productivity. The work presented here will explore whether such geochemical tracers and proxy relationships exist in modern SF Bay and Estuary bivalve shells, with an ultimate goal of using these relationships to reconstruct past regional climatological and local environmental conditions.

A fast-growing euryhaline clam *Potamocorbula amurensis* was chosen for modern calibration studies because its physiology and ecology are well characterized, including tissue trace metal concentrations. High resolution trace metal records in *P. amurensis* shells may complement ongoing monthly monitoring efforts by providing information about short-term (weekly) changes in estuarine trace metal distributions, or by providing information about distributions before monitoring began. *P. amurensis* shells were collected near the confluence of the S-SJ Rivers (0-12 psu) and in northern SF Bay (up to 26 psu) following flood (1995) and drought (1991) years. B, Mg, S, V, Cr, Mn, Sr, and Ba concentrations were measured *in situ* across growth bands in shell cross sections by secondary ionization mass spectrometry (Stanford-USGSSHRIMP-RG). [M]/Ca_{shell} profiles were compared to records of calculated Delta outflow (an estimate of net S-SJ River discharge), salinity, and temperature.

S-SJ waters entering SF Bay and Estuary are naturally enriched in V. All V/Ca_{shell} profiles showed peaks corresponding to winter/spring S-SJ Delta outflow, defining a chronology for each shell. S/Ca_{shell} and Ba/Ca_{shell} profiles in shells collected near the confluence of the S-SJ Rivers showed highest correlations to Delta outflow (r=0.85 and r=0.73, respectively). Both V and S appear to be associated with shell organic matrix, and Ba/Ca peaks may indicate productivity events, suggesting *P. amurensis* feeding and shell growth are accelerated during freshwater inputs. B/Ca_{shell} ratios in the 1995 shell collected near the confluence of the S-SJ Rivers were positively correlated to both salinity and freshwater inflow. In summer/fall when freshwater inflow was low (sal >4 psu), B/Ca_{shell} followed variations in salinity (r=0.74). During peak river discharge in winter/spring (sal=0 psu), B/Ca_{shell} also reached peak values. $^{11}\text{B}/^{10}\text{B}$ measurements may help to distinguish the salinity component of B/Ca_{shell} records.

PP51A-0304 0830h POSTER

Spectral analysis of air and ground temperatures at Fargo, North Dakota: conduction dominated propagation of the annual frequency signal

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Surface air temperature (SAT) and ground temperature at various depths from 1 cm down to 1170 cm have been observed hourly for approximately the last twenty years at the North Dakota State University (NDSU) Microclimate Research Station (46°54' N, 96°48' W, elevation 273 m) in Fargo, North Dakota. Here we aggregate the NDSU SAT data and ground temperature data at each depth into time-series of daily means. We spectrally decompose each temperature time-series into Fourier components and then determine the phase and amplitude of the annual frequency component at each depth. The observed phase and amplitude of the annual signal versus depth are compared to expectations from

a model of conductive heat transport in a homogeneous medium. A harmonic temperature signal propagating conductively through a homogeneous medium will display a linear phase shift and an exponential amplitude attenuation with depth. We show that the behavior of the annual frequency signal within the ground is clearly conductive: linear regression of the phase shift and natural logarithm of the amplitude yield fits within R^2 values of 0.996 and 0.999, respectively. We use the best-fit regression coefficients from the amplitude and phase shift data to determine an average thermal diffusivity of the soil of $3.7 \pm 0.1 \times 10^{-7} \text{ m}^2/\text{s}$, and an average wave velocity of the propagating annual signal of $3.3 \pm 0.5 \text{ cm/day}$.

PP51A-0305 0830h POSTER

$\delta^{44}\text{Ca}$ in *N. pachy* (left): A Promising Tool for SST-Reconstruction in High-Latitude Oceans

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Reconstructions of sea surface temperatures (SSTs) by means of planktonic foraminifera are an essential tool in paleoceanography. Unlike to marine tropical environments where a number of established SST-proxies exist, information on paleo-SST of polar water masses is scarce. In these regions high-resolution records exist mainly for continental environments. Ca isotopes bear a high potential as SST proxies as they are insensitive to changes in global ice volume, evaporation or freshwater input. Here, measurements of the Ca-isotopic composition on calcite shells of *Neogloboquadrina pachyderma* (left coiling) - a dominant species in subpolar and polar surface waters - are presented. The genotype of individuals tests was determined at the University of Edinburgh. Subsequently the respective calcite shells were analysed for $\delta^{44}\text{Ca}$ at the University of Bern. The most complete data set is from the polar North Atlantic. All samples are from the same genotype and span a temperature (T) range from 1.9°C to 6.5°C. It was found that T correlates well with $\delta^{44}\text{Ca}$. The total $\delta^{44}\text{Ca}$ -variation results in a $\delta^{44}\text{Ca}$ -change of 0.2‰ per 1°C defined by a linear regression. In order to test whether the correlation is influenced by hydrographic or genotype differences a second set of a Southern Atlantic genotype of *N. pachy* (left) has been investigated. Preliminary observations point to T as the main factor controlling $\delta^{44}\text{Ca}$ variations and a T dependence very similar to that of Arctic specimen. Remarkably, this T dependence (although not the absolute values) is identical within errors to the one of tropical *G. sacculifer* (Nagler et al., 2000, G3). Thus, even though Ca isotope fractionation is known to be species-dependent, the increase of 0.2‰ $\delta^{44}\text{Ca}$ per 1°C seems to reflect a particular mode of biocalcification. While more calibration work is needed, it appears that T changes of polar surface waters will be quantitatively resolvable.

PP

PP51B MCC: 131 Friday 0830h

Interpreting Climate Change From Isotopic Records of Precipitation I (joint with A, H, OS, GC)

Presiding: J L Teranes, Scripps Institution of Oceanography; W Anderson, Florida International University

PP51B-01 0830h INVITED

ISOMAP - The Challenge of Mapping and Modelling Isotope Climate and Paleoclimate

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