

the GOA and PWS may also occur at Montague Strait. However, due to the shallower depths over the Continental Shelf in this region it is less likely to occur there. Although the frequency and magnitude of deep water exchange vary from year to year, past measurements of currents at HE indicate that a complete flushing of the bottom water (> 250m) can occur within one month time due to intrusions from the GOA. Broad-scale advection of GOA water around PWS has also been inferred from stable isotope data ( $\delta^{13}\text{C}$ ).

Although surface water from the GOA could potentially reach many fjords in PWS, hydrographic data collected from 1994 to 1997 indicate that deep water intrusions potentially reach only basins that lack entrance sills. Deep advection into these fjords was evident from increases in both temperature and salinity (hence density) at intermediate depths (100-300 m) from late spring to early fall that were correlated with similar temporal changes in the deep T/S properties of +1 to 2 (C and psu) within nearby passes. The changes in deep density within the smaller fjords indicated that deep water exchange is potentially linked to large scale circulation processes in PWS. In contrast, fjords with intermediate to shallow depth sills exhibited either very minor changes or none at all in deep T/S properties during the same time period. Exchange within these basins appears to occur in the late winter, similar to renewal of the deep water within Unakwik Inlet and other shallow silled fjords around the GOA. This renewal process prevents stagnation and anoxic conditions from developing within the inner basins of all shallow-silled fjords in PWS. Also, the seasonal variation in the timing of deep advection among fjords in conjunction with differences in freshwater content may influence the species composition of zooplankton available to juvenile fish within these nursery habitats; in particular Calenoid copepods and other oceanic holoplankton species.

OS22L-11 1630h

### Mechanisms Affecting Spring Zooplankton and Pink Salmon Fry in Prince William Sound

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The distribution and abundance of zooplankton and fish have been monitored for several years in Prince William Sound, first through the efforts of the Sound Ecosystem Assessment (SEA) program (1994-98), and more recently as part of the Nowcast/Forecast Information System (NFIS) program of the Oil Spill Recovery Institute (OSRI). The SEA program documented the importance of large-bodied copepods, mainly Neocalanus, as prey, and walleye pollock (*Theragra chalcogramma*) and Pacific herring (*Clupea pallasii*) as the numerically most abundant competitors and predators of juvenile pink salmon in the early spring. We conducted eight acoustical-net sampling surveys in the Sound during the spring bloom periods of 2000-01 to document the physical and biological conditions in the Sound that influence juvenile pink salmon growth and survival. A five-fold difference in zooplankton biomass was observed between the two years. Dense schools of herring were observed to reduce nearby zooplankton abundance, but in general fish abundance in the zooplankton layer was low. It appears possible to explain the spatial distributions from the deep-water sources of Neocalanus combined with physical features. However, more information is needed to understand the substantial interannual differences.

OS22L-12 1645h

### Climate, Chaetognaths, and Copepods: Interactions on the Southeast Bering Sea Shelf

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During 1995-99, the abundance and community structure of zooplankton on the southeast Bering Sea Shelf reflected interannual variability in climate conditions. We examined the interactions of an invertebrate predator, the chaetognath *Sagitta elegans*, and its copepod prey, by comparing chaetognath and copepod abundances during 1995-1999, and evaluating effects of chaetognath predation on copepods during

spring of 1995 and 1997. The percent of prey standing stock consumed was estimated from ambient chaetognath and prey concentrations, gut content analysis, and experimentally-determined digestion rates. Chaetognaths consumed a range of prey sizes that encompassed all local copepod species and stages. The mean feeding rate was 0.7 prey chaetognath<sup>-1</sup> day<sup>-1</sup>, and the copepod standing stock removed daily was more than 0.4%. The most frequently consumed prey types were the copepods *Calanus marshallae* and *Pseudocalanus* spp. *Pseudocalanus* abundances were relatively low in cool years, while spring *C. marshallae* abundances appeared to be related to the timing of the spring phytoplankton bloom, which was influenced by ice cover. Chaetognath concentrations did not covary with climate indices, but increased from 1995-99. *C. marshallae* generally produces only one generation a year, and is more vulnerable to cumulative predation effects than *Pseudocalanus*, which has multiple generations within a year. In 1997, an average spring in terms of temperature and ice, when copepod abundances were low and chaetognath abundances were high, predation effects were much greater than in 1995, a cold year in which chaetognath abundances were relatively low and copepod abundances high. Low abundances of *C. marshallae* in 1997 may have resulted in part from heavy predation by chaetognaths.

OS22M HC: 317 B Tuesday 1330h

### Linking Modern and Past Biogenic Fluxes II

**Presiding:** R Francois, Woods Hole

Oceanographic Institution; R A

Jahnke, Skidaway Institute of

Oceanography

OS22M-01 1330h

### Can the Al/Ti ratio be used as a tracer of export production in biogenic marine sediment? An examination of the compositional associations of excess metals in biogenic sediment.

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Many studies have focused on interpreting the record of biological productivity in the oceans using a variety of chemical and sedimentological tracers preserved in marine sediments. Murray et al. (1993) and Murray and Leinen (1996) showed that changes in Al/Ti in bulk carbonate sediment from the equatorial Pacific coincide with changes in the bulk accumulation rate, and proposed that the high ratios (~3 times higher than average shale values) are caused by scavenging of dissolved Al. Because the excess Al component accounts for up to 50% of the total sedimentary Al, the Al/Ti may be a sensitive tracer of particle flux and/or export production. As interest in this potential tracer evolved (i.e. Dymond et al., 1997; Banakar et al., 1998; Timothy and Calvert, 1998), the question progressed from Does it occur? to What is it recording? To address this question, we performed sequential extractions targeting the chemical signatures of the loosely-bound, carbonate, oxide, organic, opal, and residual fraction of surface samples along the JGOFS cross-Equator transect at 140W, and from downcore samples at critical glacial/interglacial intervals. While Al was detected in all extracts, Ti was only detected in extracts of the oxide, organic, opal, and residual phases. The greatest percent of Al (in samples with >75% CaCO<sub>3</sub>) was tied to the oxide (~30-70%) and organic fractions (~5-40%). Only 10% of the Al was associated with the opal phase and 20% with the residual phase. The results for Ti indicate that between 30-70% of the Ti in high-carbonate samples is in the organic phase, 2-8% is in the opal phase, and 20-30% is in the residual phase. All of the Ti in low-carbonate, high-terrigenous samples is associated with the residual fraction. Although the percentages of Al and Ti in the opal phases are lower than in other phases, the correlation between Al and Ti is strongest ( $r^2=0.97$ ) in this phase. The Al/Ti of the total excess components shows an equatorial maximum not only confirming the importance of the excess phases, but also highlighting the possible role of an excess Ti component in the system.

OS22M-02 1345h

### A Proxy for Benthic Carbon Oxidation Rate Reconstructions

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We present a new geochemical proxy for determination of past changes in organic carbon (C-org) oxidation rates (C-ox) on the sea floor. The method employs the  $\delta^{13}\text{C}$  of two co-existing benthic foraminifers; *Bolivina argentea*, a near-surface dwelling species and *Buliminella tenuata*, a species that calcifies at between 4 and 6 mm below the sediment-water interface in suboxic, laminated sediments in the North Pacific. The  $\delta^{13}\text{C}$  values of their tests accurately record pore water  $\delta^{13}\text{C}$  values at their respective habitat depths. Paired analyses of these two species allows us to reconstruct the magnitude of the pore water  $\delta^{13}\text{C}$  gradient from sediment samples representing near annual resolution for the past few hundred years. Because the pore water isotopic gradient is directly proportional to the TCO<sub>2</sub> pore water gradient, it is possible to relate the magnitude of the  $\delta^{13}\text{C}$  gradient to values of C-ox. On the sea floor of Santa Monica Basin, C-ox has fluctuated between 0.6 - 2.5 mmolC m<sup>-2</sup> d<sup>-1</sup> and generally increased from 1600 to 1980 AD. Between 1920-1970, C-ox increased from 1 to 2 mmolC m<sup>-2</sup> d<sup>-1</sup> and then decreased into the 1980's. By adding C-ox to a high resolution record of C-org burial rate we have derived the pattern of C-org rain to the sea floor; it fluctuated between 3 and 4 mmolC m<sup>-2</sup> d<sup>-1</sup> over the last 80 years. Estimates of primary productivity at this location for the past 80 years reconstructed from SST measurements are compared to our estimates of C-org rain derived from the isotopic proxy measurements. The ratio of C-org rain at 900m to primary carbon production has remained constant at 10±1% despite a 40% change in mean annual primary productivity. Of the 10% of the carbon reaching the sea floor in Santa Monica Basin ~50% accumulates as buried organic carbon. However, there is a trend toward lower burial efficiency with higher productivity and rain rate.

OS22M-03 1400h INVITED

### Paleo-Sediment Trap Insights into the Significance of Subsurface Production for Ocean Flux

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The emerging mismatch between satellite-derived surface water productivity and benthic fluxes highlights the current lack of understanding of the contribution of sub-surface production to export flux. Although oceanographic sampling with closing nets employed as early as the 1898-1899 Valdivia cruise led to suggestions of the existence of a shade flora, very few experiments have targeted subsurface phytoplankton. Recent SEM-led research on laminated diatomaceous sediments from a wide range of deep-sea and marginal settings has focussed on a species-based interpretation of the annual cycle of diatom production and export. Reinforced by examination of selected sediment trap data, these studies demonstrate that a number of diatom species, hitherto regarded as a typical sparse flora of oligotrophic settings are capable of major carbon export forming organic-carbon rich sediments such as the Mediterranean sapropels (1,2). The styles of production and mechanisms of export undergone by these diatoms contrast with the received spring bloom or upwelling scenario. Rather, these diatoms appear to have a number of adaptations which allow them to exploit a deep nutrient source including a) the adaptation to grow rapidly in low light conditions; b) the ability

to regulate their buoyancy to migrate to deep nutrient pools and c) symbiosis with Nitrogen fixing bacteria. Massive flux of these diatoms appears to be generated either by the termination of summer water column stratification by winter mixing or by interaction with oceanic frontal systems. There are few oceanographic observations of subsurface concentrations of such diatoms but one such diatom mass was observed and sampled in the Southern Ocean. The timing and nature of this occurrence may point the way for the future oceanographic experiments required to improve our understanding of this hitherto neglected process. (1) Kemp, A.E.S., Pearce, R.B., Koizumi, I., Pike, J. & Rance, S.J. 1999. The role of mat forming diatoms in formation of the Mediterranean sapropels. *Nature* 398, 57-61. (2) Kemp, A.E.S., Pike, J. Pearce, R.B. & Lange, C.B. 2000. The "fall dump": a new perspective on the role of a shade flora in the annual cycle of diatom production and export flux. *Deep-Sea Research II*, 47, 2129-2154.

## OS22M-04 1415h INVITED

### Reconstruction of Paleoproductivity and Paleo-Calcite Flux for the Eastern Equatorial Pacific: proxy comparisons

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The Eastern Equatorial Pacific is a major center for chemical exchange between the deep and surface ocean, and between the ocean and the atmosphere. In terms of the global carbon cycle, surface ocean biological productivity and calcite production have the potential to promote, or mitigate, significant change. The ratio of organic carbon and calcite fluxes to the deeper ocean may play a part in regulating atmospheric carbon dioxide content. We examine methods for reconstructing changes in this ratio over the late Quaternary in the EEP. For organic carbon, proxies based on benthic foraminiferal assemblages and on ratios of Ba/Al and Al/Ti in sediments show a coherent record. This record differs significantly from that obtained by calculating accumulation rates of biogenic sediment components. We examine reasons for the difference between ratio based and accumulation rate based proxies for productivity. For paleo-calcite flux we have developed a new way to find the percent of calcite dissolved from sediments. This permits calculation of flux if sediment accumulation rates can be correctly estimated. We examine paleo-calcite flux records based on simple and Th-230 normalized accumulation rates and compare these to proxies of paleoproductivity.

## OS22M-05 1430h

### Sedimentary Corg Accumulation Under the Benguela Upwelling: Implications for Budgeting Glacial/Interglacial Corg Fluxes in Coastal Upwelling Areas

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Sediments accumulating on continental shelves and slopes beneath coastal upwelling areas are very rich in organic carbon. Most of modern organic carbon is reported to accumulate on the shelves in shallow water depths. During sea-level lowstands most parts of these areas were exposed while increases in organic carbon accumulation have been observed in many cores from continental slopes under high productivity systems, and a strongly increased productivity was inferred for glacial periods. However, with increasing numbers of sedimentary records becoming available for certain upwelling areas, often a glacial decrease in organic carbon accumulation can be recognized for the same coastal area. This feature indicates much higher spatial and temporal heterogeneity in the Corg accumulation underneath such coastal upwelling systems than has been considered before, both, for glacial and interglacial periods.

This heterogeneity has to be taken into account when attempting budgets for coastal upwelling systems.

Based on an extensive grid of surface samples and sediment cores, we investigated the modern distribution and accumulation budget of organic carbon for the shelf and slope off Namibia. This was compared with organic carbon accumulation on the slope during the mid-Holocene and during the Last Glacial Maximum. We found the modern inner shelf to be the most important site of organic carbon accumulation. The total amount of organic carbon buried annually in sediments of the Benguela system was estimated to be in the order of 2.5 Mio tons of carbon. For the Last Glacial Maximum we observed a 75 percent increase in organic carbon accumulation with respect to the Holocene on the slope, while accumulation on the outer shelf during the LGM remains very difficult to estimate. Nonetheless, taking together all this new information for the Namibian upwelling system, it seems very unlikely that paleoproductivity was two to four-fold higher during glacial periods compared to interglacials. Further problems with estimating regional budgets arise from sediment distribution patterns that are influenced by the complex interaction of sedimentation, near-bottom currents and sea-floor morphology.

## OS22M-06 1445h

### Toward an Understanding of Ocean-Atmosphere CO2 Flux in the Coastal Oceans and its Role in Global Climate Change: Evidence from the Santa Monica Basin, Offshore, California

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Coastal upwelling zones are the most productive regions in the world's oceans, and they can exert a significant control on global carbon cycling by regulating the incursion or excursion of CO<sub>2</sub> across the water-atmosphere interface. In the event of increasing atmospheric CO<sub>2</sub> concentrations due to fossil fuel burning, it is important to understand how the coastal oceans respond to this change biologically and physically by changing the flux of CO<sub>2</sub> between atmosphere and the ocean waters.

In this talk we focus on the role of the bioproductivity in Santa Monica Basin (SMB) surface water in controlling the air-sea CO<sub>2</sub> exchange and the long-term variation of DpCO<sub>2</sub> (pCO<sub>2</sub> difference between ocean surface water and the atmosphere). In order to assess whether this coastal ocean is a sink or a source to atmospheric CO<sub>2</sub> and how this sink/source characteristic would change at different climatic conditions, we examine existing water column hydrographic measurements to characterize the seasonal cycle of surface water CO<sub>2</sub> disequilibrium with respect to atmospheric CO<sub>2</sub>. Organic and isotopic geochemical data (utilizing  $\delta^{13}C$  of foraminifera shells and alkenones and Uk37 sea-surface temperature reconstruction) from SMB sediments are used to reconstruct historical surface water [CO<sub>2</sub>(aq)] for the past 400 years. We also evaluate DpCO<sub>2</sub> changes at different oceanographic conditions as a result of climatic variations or anthropogenic influence.

Major conclusions from this research are 1) Air-sea CO<sub>2</sub> disequilibrium in this coastal ocean responds quickly to changes in variations in the intensity of upwelling and abrupt climatic variations. During the Little Ice Age (and at times of stronger upwelling), surface water is undersaturated with respect to atmospheric CO<sub>2</sub> and behaves as a sink for atmospheric CO<sub>2</sub> (DpCO<sub>2</sub> = -50 uatm). During weak upwelling, when surface water temperature is higher, primary production is not strong enough to draw down surface water CO<sub>2</sub>, and surface water serves as a source of atmospheric CO<sub>2</sub> (DpCO<sub>2</sub> = +75 uatm). Anthropogenic eutrophication of coastal waters can be as influential as abrupt climate/oceanographic fluctuations, depleting surface water [CO<sub>2</sub>(aq)] and increasing possible air-sea CO<sub>2</sub> flux. 2) The changes in source/sink characteristics may be a result of enrichment of nutrients (PO<sub>4</sub> or NO<sub>3</sub>) relative to [CO<sub>2</sub>(aq)] in the upwelling source waters. 3) Reconstruction using empirical relationship between Ep (isotopic fractionation between dissolved CO<sub>2</sub> and POC) and [CO<sub>2</sub>(aq)] may be valid in this coastal upwelling environment even though growth rate is thought to be an important control on Ep values. Growth rate factor is considered in the empirical relationship, and variations in growth rate during the entire period may have been small possibly due to integrated sedimentary signals. Reconstructions with growth rate consideration using PO<sub>4</sub> or NO<sub>3</sub> as the limiting nutrient appear to underestimate [CO<sub>2</sub>(aq)] and yield unrealistic results. 4) The magnitude of CO<sub>2</sub> disequilibrium (DpCO<sub>2</sub>) in this coastal ocean both from water column hydrographic study and the historical reconstructions suggests coastal ocean may have been very important in controlling the air-sea CO<sub>2</sub> flux. By comparison with other coastal oceans environments, including the Cariaco Basin, it is evident that marginal

settings could have been a significant CO<sub>2</sub> sink for the last glacial interval and they may also have the ability to mediate the increasing release of CO<sub>2</sub> from fossil fuel burning.

## OS22M-07 1520h

### Advances in Development and Application of the <sup>15</sup>N Paleo-Proxy for Marine N-Cycle Processes

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Over the last decade, there has been substantial improvement in our understanding of the processes that create nitrogen isotopic signals in the water column and the conditions that lead to their preservation in the sediments. After numerous studies in a variety of marine environmental settings, a picture has emerged of only a few dominant processes which are typically well separated in time and/or space, particularly if focus is on the N-isotopic signal that ultimately reaches the sediments.

In non-HNLC regions including upwelling zones, the average  $\delta^{15}N$  of sinking particles is driven by the weighted-average  $\delta^{15}N$  of new nitrogen sources. Despite the importance of recycling in the euphotic zone, overall mass balance between euphotic zone new nitrogen sources and sinks drives this equivalence in  $\delta^{15}N$ . In most non-HNLC regions, the vertical transport of NO<sub>3</sub><sup>-</sup> is the principal source of new nitrogen and comparison between NO<sub>3</sub><sup>-</sup>  $\delta^{15}N$  and annual average-sediment trap  $\delta^{15}N$  falls on a 1:1 line. Much of the regional variation in NO<sub>3</sub><sup>-</sup>  $\delta^{15}N$  comes about through isotopic enrichments produced by water column denitrification with a fractionation factor of 20 to 30 ‰. Isotopic depletions do occur in regions with significant N fixation which introduces new nitrogen with a  $\delta^{15}N$  of -1 to -2 ‰ relative to the oceanic average NO<sub>3</sub><sup>-</sup>  $\delta^{15}N$  of near 5 ‰. HNLC regions, which have neither local denitrification or N fixation, are characterized by their partial annual euphotic zone utilization of NO<sub>3</sub><sup>-</sup>. Under these conditions, isotopic fractionation during partial NO<sub>3</sub><sup>-</sup> uptake is expressed as <sup>15</sup>N-depleted sinking POM. Recent results from the Southern Ocean, show average sediment trap  $\delta^{15}N$  to fall within values predicted from surface ocean measurements of the fractionation factor (5 to 8 ‰) and NO<sub>3</sub><sup>-</sup> drawdown.

Down-core fidelity of the N isotopic signal is highly dependent on the overall state of organic matter preservation. Where preservation is moderate to excellent such as on continental margins overlaid by oxygen-poor waters, core-top  $\delta^{15}N$  matches average sediment trap values. In deep, open ocean settings with poor preservation, a diagenetic enrichment of up to 5 ‰ is evident. This offset may be overcome by isolating unaltered fractions such as diatom-bound organic matter.

There is now a substantial literature applying the <sup>15</sup>N paleo-proxy on a variety of time-scales demonstrating coupling between climate change and N-cycle processes. Examples of reconstruction of denitrification (Arabian Sea) and surface NO<sub>3</sub><sup>-</sup> drawdown (Southern Ocean) will be discussed.

## OS22M-08 1535h

### Influence of Environmental Factors on Nitrogen Isotope Fractionation in Marine Phytoplankton

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The utilization of nitrate by marine phytoplankton can be accompanied by a significant isotope fractionation of the stable isotopes of nitrogen. The  $\delta^{15}N$  value of phytoplankton that results from isotope fractionation can be used as a measure of relative nitrate utilization in the euphotic zone and as an indicator of trophic level in the marine food web. Previous work has shown that the magnitude of isotope fractionation can differ between different species of phytoplankton, as well as in a species whose growth rate is being limited by different abiotic factors. In this study we have measured the isotope fractionation value for a variety of marine phytoplankton under laboratory conditions that range in light levels, light/dark cycles, temperature, and iron availability. The fractionation factor changes predictably with changes in light level and

light/dark cycle, especially for diatoms. Low temperature and low iron conditions reduce growth rate, but have only a small influence on the isotope fractionation factor. Our findings suggest that different strategies of nitrate utilization in different environments can cause fractionation values to range from 2-18 ‰ when growing on nitrate as the sole nitrogen source, but not as a simple function of growth rate. Although the extremes are rarely seen in nature, the patterns seen in the laboratory allow us to make important generalizations about isotope fractionation by diatoms and other marine phytoplankton in a variety of ecologically important regions of the ocean. This is relevant to studies of modern biological processes in the water column and for the accurate interpretation of  $\delta^{15}\text{N}$  in the sedimentary record.

## OS22M-09 1550h

### Relationship of Nitrogen Isotope Fractionation to Phytoplankton Size and Iron Availability During the SOIREE Southern Ocean Iron Release Experiment.

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The  $^{15}\text{N}$  composition of sediments has been used as a proxy for nitrate utilization in Southern Ocean surface waters to investigate the contribution of Southern Ocean productivity to glacial/interglacial changes in atmospheric  $\text{CO}_2$  concentration. Interpretation to date has relied on a temporally constant isotope fractionation factor  $\epsilon$  associated with uptake and assimilation of nitrate by phytoplankton. To investigate the reliability of this approach, during SOIREE we examined the relationships between the  $^{15}\text{N}$  compositions of dissolved nitrate, size-fractionated (200, 70, 20, 5, 1  $\mu\text{m}$ ) suspended particulate organic nitrogen (PON), and sinking particles caught in traps suspended below the mixed layer. We found evidence for variations in  $\epsilon$  with both cell size and iron availability.  $\delta^{15}\text{N}_{\text{PON}}$  increased by several ‰ with increasing cell size, both within and outside the iron-enriched patch.  $\delta^{15}\text{N}_{\text{PON}}$  was a further 3-4 ‰ higher in size fractions dominated by large diatoms collected from within the iron-fertilized patch. Comparing the  $\delta^{15}\text{N}$  of the large diatom dominated size fractions to the  $\delta^{15}\text{N}$  of the nitrate suggests relatively low  $\epsilon$  values of 4-5 ‰, in contrast to values of 7-9 ‰ estimated from both enrichment of  $\delta^{15}\text{N}$  of nitrate above the seasonal pycnocline and comparison of mixed layer nitrate  $\delta^{15}\text{N}$  with sinking-particle  $\delta^{15}\text{N}$ . We speculate that several factors contributed to this iron response, including the increase in abundance of large diatoms, higher growth rates, and an iron-stimulated shift from ammonium-based to nitrate-based production. To the extent that large diatoms are responsible for a large fraction of  $\text{NO}_3^-$  utilization, variation in  $\delta^{15}\text{N}_{\text{PON}}$  and  $\epsilon$  with size can affect the  $\delta^{15}\text{N}$  recorded in diatom-dominated Southern Ocean sediments. Higher glacial  $\delta^{15}\text{N}$  in Southern Ocean sediments may reflect increased iron availability, cell size, and growth rate along with increases in nitrate utilization; these effects must be considered in any quantitative scaling of  $\delta^{15}\text{N}$  variations to extent of nitrate utilization.

## OS22M-10 1605h

### Holocene Variations in Saharan Dust Input to the North Atlantic and its Influence on Upper Ocean Nitrate

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The link between iron supply and surface ocean productivity has been explored in the modern ocean by a variety of experiments. However, both purposeful additions from boats and laboratory incubations require unnatural perturbations to the in situ biochemical system. We have measured the accumulation flux of dust in ODP core 658c to monitor the history of natural variations in dust supply from north Africa over the last 14 ka. Over 120 excess  $^{230}\text{Th}$  measurements were made down core to normalize the dust percentage record for variations in the accumulation of other sedimentary components. This record shows a dusty Sahara/Sahel during the Younger Dryas and an abrupt shift to wetter environments at the beginning of the Holocene. The end of the African Humid period is marked by a sharp increase in dust accumulation at 5.5 ka.

These abrupt shifts in dust supply to the North Atlantic represent a large deviation from the modern situation. Productivity in the nutrient starved Sargasso Sea and the Gulf of Mexico had much less total iron available in the early Holocene than these areas do today. In these nutrient poor surface waters, the  $\delta^{15}\text{N}$  of the sinking nitrate reflects a measure of nitrogen fixation relative to other processes, including local mixing and global denitrification. We use a high-resolution record of bulk sedimentary  $\delta^{15}\text{N}$  from the Orca Basin, a saline anoxic depression in the Gulf, to constrain the balance between nitrogen fixation and these other processes in the overlying waters. At the start of the African Humid period there is a 1.5 per mil increase in  $\delta^{15}\text{N}$ . This value stays high until the mid-Holocene when it falls back to about 2.5 per mil. These data are consistent with decreased nitrogen fixation, relative to denitrification, when iron supply drops, and the inverse when iron supply resumes at 5.5 ka. Using changes in boundary conditions from the paleo record, our study is in a sense a natural iron removal/addition experiment. The implied result is that iron is an important component of the surface marine ecosystems ability to fix nitrogen and can therefore play an important role in determining the limiting nutrient in the ocean.

## OS22M-11 1620h

### $\text{U}_{37}^{\text{K}'}$ and the Physiological Condition of Alkenone-Producing Cells Exported to Marine Sediments

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Alkenone unsaturation patterns ( $\text{U}_{37}^{\text{K}'}$ ) are now commonly measured stratigraphically in marine sediments as a record for paleo sea-surface temperature (SST). Strong statistical correlation between nearly global measures of  $\text{U}_{37}^{\text{K}'}$  in surface marine sediments and overlying mean annual SST underpins the method. Nonetheless, this statistical calibration displays considerable variability in the  $\text{U}_{37}^{\text{K}'}$  value represented by a given SST, adding uncertainty to its use in paleothermometry. In this study, isothermal batch culture experiments were conducted with a key alkenone-producer, *Emiliania huxleyi*, to evaluate to what extent cell physiology could contribute to the observed variability in this empirical field calibration. In strain CCMP 55a, alkenone content and composition remained constant throughout exponential growth when nutrients (ortho-phosphate, nitrate) were replete. Stationary phase (nutrient-starved) cells continued to produce alkenones, amassing concentrations three or more times higher than those dividing exponentially (1.5-2 pg/cell). The  $\text{U}_{37}^{\text{K}'}$  of the 'excess' alkenone was significantly lower (0.12 units) than expected. Alkenone content and composition of exponentially growing cells placed in darkness also changed significantly. Five days of darkness resulted in 80% decrease in cellular alkenone concentration and a 0.12 unit increase in  $\text{U}_{37}^{\text{K}'}$ . Given the established temperature response of  $\text{U}_{37}^{\text{K}'}$  in exponentially growing cells of CCMP 55a (i.e. 0.034 units/°C), the range of physiological variability in alkenone unsaturation pattern noted in our experiments corresponds to a temperature uncertainty of  $\pm 3.5^\circ\text{C}$ . This magnitude of variability is not unlike the range observed in the statistical  $\text{U}_{37}^{\text{K}'}$ -SST calibration for surface marine sediments which begs the question: what is the physiological condition of alkenone-producing cells exported to marine sediments? The answer to this question may depend on the particular ocean location considered and have substantial bearing on how stratigraphic  $\text{U}_{37}^{\text{K}'}$  records in marine sediments are interpreted paleoceanographically.

## OS22M-12 1635h

### Generation and Transfer of the Alkenone-Based Sea Surface Temperature Indicator in the Cariaco Basin Water Column: A Study of the UK'37 Index in Sediment Trap Materials from the CARIACO Time Series

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Monthly changes in water column temperature, primary production (PP), and biogenic fluxes were investigated through several annual upwelling cycles in the Cariaco Basin as part of the on-going CARIACO time series. The compositions of long-chain C37 alkenones in settling particles were determined in order to assess the reliability of these biomarkers as indicators of past sea surface temperature (SST). Seasonal upwelling caused significant and rapid changes in SST, PP and biogenic fluxes. Alkenone fluxes were poorly co-related to PP and organic carbon export from the euphotic zone. However, the alkenone unsaturation index (UK'37 ratio) closely followed the variations of SST in terms of timing and magnitude. Such data indicate that alkenone-synthesizing algae in the Cariaco Basin live near the surface during most of the year and rapidly adjust the unsaturation of these compounds in response to changes in temperature independently of variations in PP and plankton composition. Additionally, there was close agreement among the UK'37 ratios obtained from trap samples collected at different depths during the same period, indicating that the transfer of this signal to the sediments via particle settling occurs with little diagenetic alteration. The relationship between the UK'37 signatures of sediment trap materials and SST was generally consistent with the calibration equation developed by Prahl et al. (1988). The average alkenone-based temperatures derived from cumulative alkenone fluxes collected each year yielded values that were within 0.5 °C of the annual mean SST measurements. Such reliability between the alkenone-based and actual temperature estimates bode well for the application of the Prahl et al. (1988) equation to reconstruct past SST variability in the Cariaco Basin.

URL: <http://organic.geol.sc.edu/cariaco.htm>

## OS22N HC: 323 A Tuesday 1330h

### Western Pacific Marginal Seas IV

Presiding: S Ramp, Dept. of Oceanography

## OS22N-01 1330h INVITED

### Kuroshio Intrusion In Northern South China Sea

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Data recorded by three subsurface Acoustic Doppler Current Profilers (ADCPs) in the Luzon Strait (LS) showed the Kuroshio Current (KC) intruded steadily and persistently into the South China Sea (SCS) through the central LS. The monsoon had little impact on the intruded KC. Moored current velocity measurements about 240km west of central LS showed a persistent westward velocity component indicating that the KC intruded further westward into the northern SCS. The composite current velocity, calculated from shipboard ADCP measurements in 1991-2000, showed the intruded KC mostly curved clockwise and flowed out of the SCS through the northern LS. A northward current, originating from the west of northern Luzon, interacted with the intruded KC. The current was generally in a westward flow. Only a small branch flowed eastward through the southern LS out of the SCS. Across the LS,