OS32A HC: Hall III Wednesday 1330h

Biogeochemical Evolution of the Phanerozoic Ocean I

Presiding: **A PAytan,** Geological and Environmental Sciences

OS32A-118 1330h POSTER

Continental Drift and Basin Formation During the Phanerozoic: Geotectonics under 2-Body Mantle Convection

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During the Phanerozoic the distribution of continents has varied from the singleton Pangea aggregation to the complicated distribution of post-Paleozoic times, providing biogenetically favorable marine basins and shorelines at all latitudes. Accounting for continental drift, thermal convection within the Earth's mantle is known to be inevitable, but fails to account for major features of plate motion.

The tectonic record is here examined in terms of 2-body convection. Of its essence convection is a gravity phenomenon, of necessity a function of total ambient gravity. The field within the Earth member of Kuiper's Earth/Moon double planet consists not only of the terrestrial field but that of its satellite, uniquely massive relative to that of its primary and in continuous close orbit [1]. The action of the mobile tidal bulges, some tens of cm in geocentric height at the Equator, is to induce vorticity dimensionally similar to that in convection of purely internal origin, but asymmetrical and peaked strongly in low latitudes. Convection under the joint field is of a two-body type, internally powered under Earth's highly supercritical Rayleigh number, but of form determined jointly by the internal plus external field. Heuristically it may be viewed as taking place under a minute permanent tilt, delimited by the departure from the geocentric vertical of phase-delayed water and solid-earth masses, averaged over one revolution. As measured by the tidal phase lag including that in the oceans, in low latitudes the asymmetric fraction of the convection may represent a large fraction of the whole [2].

Under this regime it is to be expected, for instance, that when a 'Pangea' aggregation breaks up the drift of its fragments resembles the development of an 'Atlantic Ocean', with absolute motion of the Americas towards the Pacific realm, encroaching on the Pacific realm [3]. Similarly asymmetric displacement is evident in the form of the western equatorial embayment of the Pacific towards Sundaland.

References: [1] RCB, 2000. Tectonic Consequences of Earth's Rotation (Oxford UP): 48-49. [2] Cartwright, D.E. and R.D. Ray, 1991. Energetics of global ocean tides from Geosat altimetry. JGR 96(C9); fig. 9. [3] Wilson, J.Tuzo, 1970. Some possible effects if N America has overridden part of the East Pacific Rise. Geol. Soc. Amer. Abstr. w. Programs 2; 7 pp. 722-723.

OS32A-119 1330h POSTER

Cenozoic Seawater Sr/Ca Ratio Curve from Marine Barite: A Preliminary Investigation

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On geologic timescales (1 million years), the relative weathering of carbonate versus silicate minerals, as well as metamorphic/hydrothermal processes, have the potential to influence the long-term carbon cycle. Consequently, perturbations affecting the rate or efficiency of these mechanisms may cause significant fluctuations in atmospheric CO2 concentrations. Since the relative intensity of these processes affect both the Sr isotope composition and Sr/Ca ratio of seawater, a combined, paleoceanographic record of fluctuations in seawater 87-Sr/86-Sr and Sr/Ca ratios may provide quantitative information about the roles of weathering and hydrothermal activity in long-term C cycling.

Several workers have attempted to develop a seawater Sr/Ca ratio paleocurve using biogenic calcite as a paleosource. However, variations in the resulting Sr/Ca ratio data can only be interpreted in terms of changes in the oceanic Sr concentration, since Ca is a primary component in both calcite and aragonite. Moreover, vital and diagenetic effects cannot be completely eliminated as a factor influencing the Sr/Ca ratio.

In previous work, it has been demonstrated that marine barite is a potential alternative to biogenic calcite for some geochemical paleoproxy work (e.g. 87-Sr/86-Sr, Paytan et al., 1993). Both Sr and Ca substitute for Ba in the barite crystal structure, thus, it is possible that marine barite may record ambient (i.e. seawater) Sr and Ca concentrations. Here, we present results from a preliminary investigation to determine whether marine barite records paleoseawater Sr/Ca ratios, by analyzing the Sr/Ca ratio of barite from several Cenozoic age, ODP cores.

OS32A-120 1330h POSTER

Geochemical Evidence for Variations of Northwest Pacific Subarctic Front during the Last 400-KY

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We investigate the late Quaternary hydrography of NW Pacific to clarify how it was sensitive to the past climate changes. The sediment core taken from Suiko Seamount (44° 47.2'N, 170° 09.6'E, Water Depth: 1784m), located at midpoint of Emperor Seamount chain, was used for reconstructing sea surface temperature (SST) change and consequent variations of Northwest Pacific Subarctic Front.

Foraminiferal δ^{18}O, Mg/Ca ratio and alkenone SST indicate that this site was situated under influence of subtropical water at Marine Isotope Stage 9-11. Average SST difference between the last glacial cycle and MIS 9-11 was as much as 5°C, indicating poleward shifting of NPSF at MIS 9-11. Slightly heavier values of planktonic δ^{13}C (*G. bulloides*) at MIS 9-11 also imply the presence of warm subtropical water in this region. This warming at MIS 9-11 coincides with previously reported the period of high carbonate accumulation in NW Pacific. After MIS 8, subpolar water was gradually advanced into equatorward, and supply of ice-rafted materials was accelerated in this region.

OS32A-121 1330h POSTER

Deepwater circulation changes in the North western Pacific during the last 300 kyrs: Results from the metal/Ca ratio in benthic foraminifera

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Trace elements incorporated in foraminiferal shells in marine sediments provide us the essential information to clarify the paleo-oceanograpic condition. We investigated the thermohaline circulation changes in the north Pacific during the last 300 kyrs using metal/Ca ratio of benthic foraminifera in sediment core samples recovered from the Emperor Seamounts (44°47.2' N, 170°9.6' E, water depth: 1,784 m). Trace metals (Cd, Sr, Mg, Ca) were analyzed by the magnetic sector field inductively coupled plasma mass spectrometry (HR-ICP-MS). Cd/Ca ratio showed the glacial-interglacial variations: higher values in interglacial periods and lower values in glacials. Glacial Cd/Ca values are approximately 10 - 20 % lower than interglacial ones. It suggests that the glacial Pacific deepwater (PDW) was fresher than today. The difference between the carbon isotope records in planktic and benthic foraminifera was large in interglacial and small in glacial periods. These results suggest that the ventilation between surface and deeper water was relatively activated during the glacial periods.

On the other hand, Mg/Ca and Sr/Ca ratio shows different result between each other. Mg/Ca shows similar image with the oxygen isotope record of foraminiferal shells, however, Sr/Ca record shows inconsistent pattern with oxygen isotope record. Moreover Sr/Ca values decreased gradually at the middle to lower part of the core, and this pattern is similar with CaCO3 contents of the core. It might suggest that Sr/Ca record represented the carbonate dissolution history rather than the temperature of seawater.

OS32B HC: Hall III Wednesday 1330h

Biogeochemical Processes in Anoxic and Suboxic Environments I

Presiding: **M Scranton,** State University of New York**; J Murray,** University of Washington

OS32B-122 1330h POSTER

Does Sulphurization Create an Early Diagenetic Link Between Trace Elements and Organic Matter? - Evidence From the Southeast Atlantic

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The remineralization of organic matter is one of the most important biogeochemical processes and its impact on the distribution of trace elements has been shown in many studies. However, it is not the only possible reaction in the sedimentary organic carbon cycle. In anoxic marine sediments sulphurization, i.e. the reaction of organic matter with reduced inorganic sulphur species, is another important mechanism during the early stages of diagenesis. It works as an antagonist to remineralization since the intra- and intermolecular incorporation of sulphur supports the preservation of organic compounds. While in the last two decades numerous studies have investigated possible mechanisms for sulphurization and provided hypotheses for various reduced sulphur species and classes of organic compounds (e.g., Sinninghe Damsté and de Leeuw, 1990) little attention has been paid to its consequences for the fate of trace elements.

In this contribution we present data from the Southeast Atlantic that indicate a close relation between the sulphurization of organic matter and the distribution of trace elements in the upper tens of meters of diagenetically active sediments (Heuer et al., submitted). Our observations are based on a high resolution (5 cm steps) survey of 16 trace elements in the solid phase of two gravity cores that were taken from the highly productive upwelling region off Namibia and from the Niger deep sea fan. The gravity cores are 10.7 m and 20.2 m long and record the last 135 and 245 ka. The influence of productivity related primary input and the potential effects of early diagenesis are checked with Ba as a proxy for paleoproductivity and porewater analysis, respectively.

References:

Heuer V., Kasten S., and Schulz H. D. (submitted) Does sulphurization create an early diagenetic link between trace elements and organic matter? - Evidence from the upwelling region off Namibia, Southeast Atlantic. Geochimica et Cosmochimica Acta.

Sinninghe Damst J. S. and de Leeuw J. W. (1990) Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: State of the art and future research. Advances in Organic Geochemistry 1989 (eds. B. Durand, F. Behar) Organic Geochemistry 16, 1077 - 1101.

URL: http://www.geochemie.uni-bremen.de

OS32B-123 1330h POSTER

Preservation of Terrestrial and Marine Organic Matter in an Intermittently Anoxic Coastal Fjord; Effingham Inlet, BC.

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W E D

Using bulk analyses, stable carbon isotopes, and mineral surface area measurements, we evaluated the preservation of marine and terrestrial organic matter in a semi-pristine coastal fjord. Effingham Inlet extends from Barkley Sound in the western side of Vancouver Island, British Colombia. It has two inner sills formed by glacial means, which allow the formation of two different marine environments, over a short geographic distance. A narrow and shallow sill at the opening restricts circulation resulting in deep waters within the inlet that are depleted and/or devoid of dissolved oxygen. This results in the deep middle basin being anoxic, the innermost basin is suboxic, and the outermost is oxic. Sediments samples from fifteen stations were compared to endmembers and simple linear models were used to relate preservation to either mineral surface area or source. Carbon contents ranged from 3.6-10.3% organic carbon. The carbon to nitrogen ratios ranged from 11.1 to 21.5. The surface area of the sediments varies from 13.1 to 45.7 m2/g, and OC/SA were 0.90to 4.50. The d13C ranged from -22.6 to -26.6. The percent terrestrial organic matter ranged from 20% at the mouth to 95% at the head of the inlet, irrespective of the redox conditions of each basin. After accounting terrestrial organic matter, the marine organic matter showed a strong relationship to mineral surface area. OC:SA ratios were highest in the middle (anoxic) basin, suggesting that while the terrestrial organic matter preservation is related to distance from its source, the marine organic matter preservation is related to both mineral surface area and redox condition.

URL: http://boto.ocean.washington.edu/aog

OS32B-124 1330h POSTER

Accumulation of Redox-sensitive Trace Metals in Continental Margin Sediments and Their Paleo-applications

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The accumulation of redox-sensitive trace metals in sediments can be affected by many factors (i.e., bottom water oxygen, organic carbon accumulation and sedimentation rate). To explore the impact of such factors on trace metal accumulation a suite of multicores from the continental margin off western Canada was studied. This information was then used to interpret the paleo-record obtained from a piston core from the same region.

Under suboxic conditions Re and U should accumulate in sediments. As sediments become more reducing (i.e., anoxic) Ag, Cd and Mo are expected to accumulate given their affinity with sulphide. However, despite the development of reducing conditions within millimetres of the sediment-water interface, there is little accumulation of Re, U, Mo, Cd or Ag in the near surface sediments off Vancouver Island. These trace metal data are consistent with Mn/Al and I/Organic carbon ratios that suggest near surface sediments (0 to 15 cm) are only slightly reducing. Deeper in the sediment (i.e., >15 cm) trace metal enrichment is observed. Rhenium is enriched by up to 60 ppb in those multicores collected from within and below the oxygen minimum zone. In comparison, U and Cd enrichment only occurs in multicores from the oxygen minimum zone. Molybdenum concentrations remain low (i.e., <1.5 ppm) in all multicores. The lack of Mo enrichment is consistent with other data that indicate very little net sulphate reduction and sulphide formation.

The behaviour of Ag differs significantly from that of the other trace metals. The concentration of Ag increases with increasing water depth, such that shelf sediments have the lowest Ag concentrations (<100 ppb) and sediments from the deepest location (1750 m) have the highest (up to 580 ppb). There is also a strong positive correlation between Ag and Ba concentrations. We hypothesize that Ag, like Ba, is scavenged from seawater by settling organic particles. The higher concentrations of Ag in sediments from deeper locations most probably reflects the higher dissolved Ag concentration in deeper waters and the longer residence time of organic particles in seawater before they reach the sediment.

In piston core JT96-09 (920 m water depth) trace metal concentrations peaked during the last deglacial (13.4 to 12.7 kyr B.P.) and again between 11.2 and 7.1 kyr B.P.. At the same time the benthic foraminiferal assemblage shifted to an assemblage dominated by species that typically live under very low oxygen conditions (e.g., Bolivina argentia). These data suggest a shoaling of redox boundaries within the sediment, possibly due to increased organic flux to the sediment and/or lower oxygen concentrations in the overlying water.

OS32B-125 1330h POSTER

The Effects of Microbiological Process on Physicochemical Properties of Clayey Sediments

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To understand the fundamental biogeochemical processes in anoxic/sub-oxic sub-bottom sediments that may affect re-suspension and deposition of clayey sediments, several batches of sediments were microbially reduced with Shewanella oneidensis MR-1, and then examined for the physicochemical properties. Analyses of X-ray diffraction (XRD) show that smectite-like clays are dominant mineral components with little illite and chlorite, and Fe(III)-reduced smectite plays an important role in changing the physicochemical properties of sediments. Hundreds of Transmission Electron Microscopy (TEM) images were used to investigate fabrics and size distributions of clay aggregates. Most clay aggregates in Fe(III)-reduced clayey sediments show face-to-face contacts and skewed size distributions to a larger aggregate size resulting in less pore spaces in clay fabrics. The unaltered (oxidized) clay aggregates show edge-to-edge and edge-to-face contacts with normal size distributions of clay aggregates. Mean clay aggregate size increases by about 40 nm in Fe(III)-reduced clayey sediments. An attempt of measuring the effective settling velocity of suspended sediments were made indicating that clay aggregation or flocculation induced by microbial activities in this study is an important mechanism for speeding the removal of sediments from the water plume.

Keywords: flocculation, re-suspension, Shewanella oneidensis MR-1, smectite, TEM, XRD

OS32B-126 1330h POSTER

OMZ-Sediments in the Peruvian Upwelling Region: Organic Matter Composition and Bottom Water Oxygen Content

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The Peruvian upwelling region is characterized by high surface water productivity leading to an oxygen minimum zone (OMZ) that extends from 30 m to 600 m water depth. During RV SONNE cruise 147 in June 2000 several sediment cores underlying bottom waters with varying oxygen contents were sampled. A comparison of their bulk composition showed exceptionally high organic carbon contents in sediments underlying the center of the OMZ. Further investigations were carried out to assess the quality of the organic material. We focused on selected compound classes of the labile fraction, mainly lipids, chlorins and amino sugars. Each of these parameters provides information about the origin as well as the degradation state (freshness) of the organic material deposited at the investigated sites. The molecular composition seems to be related to the oxygen conditions in the surface sediments and the overlying water column. A comparison between sulfate reduction rates and the organic matter composition provides further insights into organic matter degradation in these environments.

OS32B-127 1330h POSTER

Geochemical Records of Seasonal Redox Change in Holocene Laminated Sediments from the Baltic Sea.

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Within the deep basins of the Baltic Sea, finely laminated diatomaceous sediments characteristic of anaerobic conditions have been deposited at intervals throughout the last 8,000 years. Scanning electron microscope studies have revealed the regular recurrence of bundles of laminae that commonly take the form of couplets or triplets of diatomaceous and lithogenic material. Examination of the diatom assemblages and analogy with modern depositional processes in the Baltic suggests that these bundles represent varves. Superimposed on these varved sediments are distinctive laminae of Ca-rhodochrosite. Energy dispersive X-ray microanalysis (EDS) combined with backscattered electron imagery enables the placement of Ca-rhodochrosite laminae within an annual cycle of deposition showing that Ca-rhodochrosite deposition is a rapid phenomenon occurring on seasonal time scales. The occurrence of these distinctive laminae as a winter/ early spring deposit is in close agreement with the seasonality of flushing of the Baltic with oxygenated waters as recorded in instrumental records. This finding provides supporting evidence for the assumed direct causal link between saline inflow events propagated from the North Sea and Ca-rhodochrosite deposition. The common occurrence of hexagonal Mn-sulphide pseudomorphs and the ubiquitous presence of S in EDS further suggests that the initial formation of Mn-sulphide may be a common step in the process of rhodochrosite formation.

OS32B-128 1330h POSTER

Methane Distributions Along the Western Mexican Shelf and Eastern Tropical North Pacific

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The eastern tropical North Pacific Ocean (ETNP) is an area of rich surface-ocean productivity due to coastal upwelling. The decomposition of organic matter results in extremely low levels of dissolved oxygen in the upper ocean. Methane cycling in these suboxic/anoxic conditions was investigated during the East Pacific Redox Experiment (EPREX) in May-June 2000. EPREX sampled at six stations starting just north of Hawaii (Station 1), and extending across the ETNP to 110 km off the coast of Mexico (Station 6). Dissolved methane concentrations increased dramatically in the upper water column from Station 1 to Station 6 as the dissolved oxygen concentrations dropped to anoxic levels. Station 6 methane concentrations reached 28 nM at 350 m, as compared to 2-3 nM at the same depth at Station 1. Rough estimates of the meridional extent of these elevated methane concentrations make the ETNP site of the largest pool of oceanic methane reported to date. Methane stable carbon isotopic ratios (δ^{13}C-methane) at Station 6 showed vertical stratification with isotopically light methane above 400 m and isotopically heavy methane below 400 m. The isotopically light methane indicates an in situ biogenic source. The isotopically enriched methane below 400 m is assumed to have its source elsewhere and to have undergone fractionation due to oxidation. This source is assumed to be either the organic-rich sediments or oxygen depleted waters of the western Mexican shelf.

A second cruise in November 2001 is occupying stations along the western Mexican shelf, between San Diego and Manzanillo, Mexico. The early stations are positioned north of the ETNP and progress southward into increasingly suboxic/anoxic waters. Water column samples and sediment porewater samples are being collected at each station and analyzed for dissolved methane concentrations. These data in conjunction with the EPREX data set will help determine the source of the highly concentrated, isotopically heavy methane found at Station 6. In addition, it will define the northern extent, along the Mexican coast, of the methane rich pool from the ETNP.

OS32B-129 1330h POSTER

A Record of Water Column Dysoxia in Shelf Waters of the Mississippi Prodelta Over the Past 100 Years

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Seasonal hypoxia occurring in shelf waters west of the Mississippi Birdfoot Delta results from increased nutrient loads from the Mississippi River when certain oceanographic and climatological conditions are met. However, it remains unclear if similar hypoxic events have occurred in the water column east of the Mississippi River Delta along the Louisiana-Mississippi shelf. A record of shelf hypoxia over the past 100 years was evaluated from gravity cores collected during the summer of 2000 from this area. Two proxies of anoxia/dysoxia were used: framboidal pyrite size distributions and benthic foraminifer assemblages. Typically, framboids which develop in anoxic water columns and settle on the seabed to be incorporated into the sediments are smaller in size, whereas framboids which result from nucleation in anoxic sediments overlain by oxygenated and sulfide-free water columns are larger in size. A series of scanning electron microscope images and image analysis techniques were analyzed to identify and measure individual framboids. A census of benthic foraminifers was made and the following indices were used as indicators of low oxygen conditions: the ratio of infaunal to epifaunal species; the percentage of anoxia tolerant to intolerant species; and overall changes in assemblages.

A sedimentation accumulation rate of 0.2 cm/yr, was obtained from ^{210}Pb analysis, which allowed for the examination of framboidal pyrite size distributions and benthic foraminifers at five-year intervals. Framboid size distributions downcore averaged $\sim$ 10 μm in diameter. The species composition of benthic foraminifer assemblages remained similar downcore, and was dominated by dysoxia-tolerant species. Results from framboidal pyrite size distributions and benthic foraminifer species suggest no significant change in the concentration of oxygen in the water column. This implies that the study area has not experienced hypoxic events during the last 100 years.

OS32B-130 1330h POSTER

Hyperthermophiles of the hydrothermal vent subsurface: limits of life

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Hyperthermophilic archaea, isolated from deep-sea hydrothermal vents, survive and grow under extreme heat, pressure, and chemical toxicity. Although it has been assumed that their environmental tolerance range sets the extreme limits for life, particularly in deep, hot subsurface environments, many critical factors and components of this tolerance have not been systematically tested. Defining the critical chemical and physical environmental extremes that limit growth and survival of hydrothermal vent archaea allows us to determine the likelihood of a deep subsurface biosphere, and has implications for understanding the ecology and evolution of prokaryotic life on Earth. We have tested growth and survival of two heterotrophic (elemental sulfur reducers) archaea under relevant (simulated in-situ) environmental conditions - acidic pH, high pressure and temperature, and high sulfide and metal concentrations, individually, and together in ways that approximate natural conditions. Both Pyrococcus strain GB-D and Thermococcus fumicolans are capable of growth at 90°C and pH down to 4.5 at both one atmosphere and 250 atm pressure over a period of 24 hours. At 100°C and one atm pressure Pyrococcus and Thermococcus grow down to pH 4.5, but at 250 atm and 100C grow only at pH 7.5. The deep subsurface is a very heterogeneous environment, and hydrothermal activity can displace organisms temporarily from their niches where conditions are favorable for growth. We tested survival of these two organisms under starvation conditions, and determined that survival decreased with higher pressure. At 100°C and 250 atm, only Pyrococcus is able to survive. Interesting synergistic effects of temperature, pH and pressure have been noted for these two organisms. At 90°C and pH 7, both organisms demonstrated 100% viability after exposure to starvation conditions in the presence of up to 30 mM sulfide over a 24 hour period. Pyrococcus survived in the presence of 80 mM sulfide for 18 hours, and Thermococcus survived up to 10 hours in the presence of 60 mM sulfide, although percent viability was reduced for both organisms. Under growth conditions, Pyrococcus and Thermococcus exhibited growth in the presence of up to 30 mM and 80 mM sulfide, respectively at both 90 and 100°C. These sulfide concentrations far exceed those found in situ at hydrothermal vents, although they may be encountered in the deep subsurface. We have found that sulfide partially ameliorates the effect of metal toxicity. Both Thermococcus and Pyrococcus can survive exposure to as much as 10-3 M Cu and Zn, and 10-2 M Co, in the presence of 0.4 mM or 2 mM sulfide. Without some sulfide, survival is greatly reduced or nonexistent. These experiments demonstrate intriguing possibilities for potential habitat ranges in the deep subsurface.

OS32B-131 1330h POSTER

Evidence for Persistent, Hydrothermally-Stimulated, Sulfur-Dependent Chemosynthesis in Mary Bay Canyon, Yellowstone Lake, WY.

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The Yellowstone Lake geoecosystem harbors evidence of past geochemical activity on a wide variety of time scales. Relic chimneys and siliceous spires provide copious solid-phase evidence of dissolved mineral seepage and vigorous venting on the hundreds to thousands of years ago range, with corroborating laminations of iron, manganese, and sulfur crusts on surfaces facing extinct vent sites. Mass balance between sulfate- and chloride-depauperate river and creek inflows and many-fold enriched outflow unequivocally document minimum levels of in-lake ventwater inputs, even though precipitation (Fe, Mn, S), evasion (CO_2, CH_4), and biological transformation (all) reduce the apparent enrichment of non-conservative chemical species. Present-day lakewater enrichment of these species in the face of dilution from inflows and *in situ* consumption requires a persistent contribution of geothermally-altered fluids at the decadal scale.

Chemosynthetic bacteria include species that oxidize reduced sulfur, iron, and manganese peculiar to many hydrothermal fluids yet are otherwise uncommon in open water ecosystems. Physiological and molecular characteristics of these organisms can be used to trace plumes as well as to quantify activities in active vent fields. In the steep-sided, narrow Mary Bay canyon (z_{max} = 55m) of Yellowstone Lake, bottom vents release sulfide at near-millimolar concentrations but removal to less than micromolar levels occurs within a meter of the orifice. Ventwater chemosynthesis is vigorous, commonly about 5μgC/L/hr at bottom-water temperatures, but also falls off rapidly just above the vent mouth. However, potential chemosynthesis assessed with thiosulfate addition remains nearly constant at 3-4μgC/L/hr for 35m from the bottom, decreasing only when breaching the depth of the sill to the main floor of the bay (20m). These rates are very similar to surface water photosynthetic CO_2 fixation, and have been documented annually for 4 years. Combined with unusually high enrichment of ^{222}Rn in canyon waters measured in the 1980s and early 1990s, there is strong evidence for persistent release of geothermally-produced reduced sulfur at this site, slowly welling out of the confined canyon into overlying waters. Relatively continuous activity of deep-dwelling sulfur-oxidizing bacteria may thus contribute significantly to overall biogeochemical transformation and possibly even ecosystem carbon cycling. Based on geological evidence for longer-term reduced iron and sulfur venting, chemosynthesis may be relevant to Yellowstone Lake biogeochemistry over millenial time scales.

URL: http://www.uwm.edu/Dept/GLWI

OS32B-132 1330h POSTER

Nitrate-Accumulating Sulfur Bacteria in Shallow Coastal Marine Environments: Annual Pattern of Intracellular Nitrate Pool in Surficial Sediment

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Hypoxia of bottom water during stratification period is a universal feature in eutrophied coastal environments, and nitrate-accumulating sulfur bacteria (Beggiatoa) occur abundantly in the surficial sediment and appear to play a dominant role in the nitrogen cycle of such environments by coupling anaerobic sulfide oxidation with the reduction of nitrate to ammonium. The intracellular nitrate pool (intra-NO_3) in the sediment (depth, 0 to 100 mm), estimated from the concentration difference before and after freezing (-30°C) the samples of sliced sediment, were measured seasonally at a 20-m-deep station in the central part of Tokyo Bay. The central part of Tokyo Bay is characterized by strong eutrophication, and dissolved oxygen in the bottom water (DO_{bw}) was totally depleted (anoxia) during mid-summer. As destratification was initiated in early fall, DO_{bw} gradually increased and recovered to air-saturated conditions during winter and early spring (mixing period). DO_{bw} started to decrease again from middle spring with water column stratification following a phytoplankton bloom. The bottom water NO_3 were around 10-20 μM throughout the year except during mid-summer when DO and NO_3 were absent in the bottom water. The intra-NO_3 in the surficial sediment showed a remarkable seasonal change in response to the anoxic-suboxic-oxic conditions in the bottom water. During mid-summer, there was neither visible mat of Beggiatoa on the sediment surface nor intra-NO_3 in the sediment. As destratification was initiated in early fall, NO_3, not DO was first supplied to the anoxic bottom water. At the beginning of October when NO_3 was present in the suboxic bottom water, the sediment surface was already covered in patches with white mats of Beggiatoa but the intra-NO_3 was still very small (3.0$\pm$4.7 nmol N cm^{-2}). At the end of October when DO_{bw} was half air saturation, the sediment surface was coated with massive mats of Beggiatoa and the intra-NO_3 increased dramatically and a huge pool of 358$\pm$226 nmol N cm^{-2} was found just at the sediment-water interface. At the middle of December when DO_{bw} was air saturation, there was no visible mat of Beggiatoa on the sediment surface, but there was still a large pool of the intra-NO_3 (287$\pm$98 nmol N cm^{-2}) and subsurface peak of the intra-NO_3 was found at a depth of 5 to 10 mm. During late winter and early spring there was neither visible mat of Beggiatoa on the sediment surface nor significant pool of the intra-NO_3 in the sediment. As stratification was initiated in middle spring, DO_{bw} started to decrease again. At the middle of April when DO_{bw} was half air saturation, there was no visible mat of Beggiatoa yet, but there was already a small pool of the intra-NO_3 (23$\pm$14 nmol N cm^{-2}) at the sediment-water interface. At the end of April when DO_{bw} was 40% air saturation, there was no visible mat of Beggiatoa yet, but the intra-NO_3 increased rapidly and a large pool of 130$\pm$25 nmol N cm^{-2} was found at the sediment-water interface. At the beginning of July when DO was still present in the bottom water at 30% air saturation, the sediment surface was coated with massive mats of Beggiatoa again and a large pool of the intra-NO_3 (161$\pm$98 nmol N cm^{-2}) was found at the sediment-water interface. These results indicate that the anoxic-suboxic-oxic conditions in the bottom water has drastic influence on the nitrogen cycle of eutrophied coastal environments through the regulation of the population dynamics of Beggiatoa in the surficial sediment.

OS32B-133 1330h POSTER

Benthic Nitrogen Cycling Under the Minimum Oxygen Zone in the Coastal Upwelling System of Centrql Chile

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The benthic nitrogen in upwelling areas could impact the pelagic nitrogen inventory and consequently contribute to higher productivities. How can benthic processes control if the sediment acts as a nitrogen source or sink to the water column along the year, under high organic matter deposition and minimum oxygen conditions?

To address this question a study was conducted during two years (1999, 2000) at two different stations in the Chilean upwelling area (36°S) located on the continental shelf (87 m) and in a semi-enclosed bay (27 m). *In situ* measurements of water column (oxygen, nutrients, temperature) and sediment properties (Chl-*a*, NO_3^-, NH_4^+, Eh) were combined with laboratory experiments in order to determine N fluxes across the sediment-water interface (NO_3^- and NH_4^+), as well as to estimate rates of N cycling, such as the rate of ammonification, denitrification, and dissimilatory NO_3^- reduction to ammonium (DNRA) associated to mats of giant bacteria (*Beggiatoaceae*) .

Even if the two places are under similar oceanographic conditions and close benthic pelagic coupling,

our results indicate that sediments have a different behavior associated with nitrogen cycling. The continental shelf appear as an ammonium sink (-3 $\pm$ 4 mmol m^{-2} d^{-1}) during winters periods and a source (8 $\pm$ 2 mmol m^{-2} d^{-1}) during spring-summer. While sediments in the bay, act all the year over as an ammonium source, in average 5 times higher in summer than in winter (5 mmol m^{-2} d^{-1}). Both places appear as a sink of nitrate all the year.

Higher oxygen levels underlying the sediments and low quantity and quality of organic matter (*i.e.* Fep/Chl-*a* ratio, C:N > 9) are correlated with ammonium fluxes to the sediment suggesting assimilation and/or nitrification processes, as during winter in the shelf. Anoxic conditions and high content of fresh organic mater, determine significant ammonification rates and positive ammonium fluxes (net ammonium release to the water column), in both places and a significant DNRA (17-20 % of the total ammonium fluxes) by conspicuous mats of *Beggiatoa* sp. in the bay. During summer, the continental shelf sediments, lost an important quantities of nitrogen due to high denitrification rates (3 $\pm$ 1 mmol m^{-2} d^{-1}) while is not significant in the bay (< 0.5 mmol m^{-2} d^{-1}) .

Benthic areas under high organic matter input and minimum oxygen conditions, during summer are important sources of nitrogen, as ammonium to the water column. This areas could also to be important sites of denitrification and a net nitrogen lost for the pelagic system. However, our results suggest that when the sediment chemical conditions are very reduced, as during summer in the bay, the denitrification could be inhibited and an other dissimilative nitrate reduction process, the DNRA could be important, contributing with the sediment ammonium source.

OS32B-134 1330h POSTER

Stratification Produces Productivity, and Other Processes you Haven't Seen Before: An Anoxic Pond Challenges our Understanding of Lacustrine Geochemistry

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Conventional understanding of lake dynamics tells us that when a closed lake becomes stratified, bottom waters will stagnate and putrefy as they are cutoff from atmospheric contact, while productivity in surface waters will slow as nutrients are sequestered into settling organic matter. Productivity increases when stratification breaks down and remineralized nutrients in the bottom waters are recirculated back to the surface. Here we present a different kind of system, an anoxic pond where stratification actually promotes productivity and reduced waters produce some unusual sediments.

Located on the island of Oahu, Hawaii, Ordy Pond is a 5 m deep eutrophic, murky, brackish, pond in which productivity is light-limited. A time series analysis of the water column and sediment production from April, 2000 through May, 2001 revealed high productivity, with chlorophyll on the order of 150 μg/L, and organic carbon fixation rates on the order of 530 mgC/m^2, despite a euphotic zone of less than a meter depth. Thermal stratification in the summer preceded a bloom of productivity that occurred presumably as photosynthesizers were able to remain longer in the euphotic layer. During the bloom, surface water oxygen exceeded saturation by 83% (O_2 = 0.381 mM, 12.21 mg/L). Bottom water sulfide was <0.5μM before stratification but exceeded 1.5μM 8 weeks later, coincident with similar increases of inorganic nitrogen, phosphorous, and carbon resulting from remineralized settling organic matter. In winter, as the vertical temperature gradient relaxed and diffusive mixing increased, surface waters became suboxic upon mixing with bottom waters that never exceeded 4% of oxygen saturation over the year.

Increased sediment production followed surface water productivity. Carbonate ^{18}O and ^{13}C are controlled by evaporation and productivity, respectively; ^{18}O is 2 per mil heavier and ^{13}C is 1.5 per mil heavier in summer than in winter. XRD analyses of trapped material found the carbonate to be a mixture of kutnahorite - $(CaMn)(CO_3)_2$ - and calcite. Kutnahorite was unexpected as it was not measured in the sediment cores collected from the pond. However, Ordy's chemistry is well within the zone of nitrate reduction where Mn(II) is stable, and the pond is oversaturated with respect to kutnahorite. We believe that somewhere within the sediment water interface (a 1.5 m thick unconsolidated layer), the kutnahorite is recrystallized to calcite in a process preserving the isotopic signature of the original carbonate.

OS32C HC: Hall III Wednesday 1330h

Paleoceanography of Warm and Cold Climates During the Cenozoic Cooling Trend

Presiding: **B J Haupt,** Penn State University

OS32C-135 1330h POSTER

Modeling the effect of changes in atmospheric CO_2 content on decadal climate variability and of large-scale orography on global teleconnections: Cenozoic case studies

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Reconstructions of atmospheric CO_2 partial pressure (pCO_2) indicate considerable variations of this greenhouse-gas concentration during the Cenozoic. We employ an atmospheric general circulation model (AGCM) of intermediate complexity to study how different pCO_2 values may affect decadal climate variability on a global scale. Moreover, sensitivity experiments for idealized changes in orography are used to assess the effect of Cenozoic plateau uplift on atmospheric teleconnection patterns. The employed AGCM is the PUMA-II model, which is based on the standard hydrodynamic equations. It includes a radiative transfer calculation with interactive clouds, large-scale and convective precipitation and surface fluxes of momentum, heat and moisture. The land-surface module includes the evolution of a temperature profile in the soil, soil hydrology and snow pack over land. Over oceans, sea-surface temperature (SST) is calculated from the energy balance and weak restoring to modern SST. Sea-ice is diagnosed from the SST field. The model resolution is approximately 5.6° × 5.6° in the horizontal (T21) with five equidistant terrain-following sigma levels defining the vertical coordinates. Despite its reduced complexity, the PUMA-II model represents the internal variability of the atmosphere, including midlatitude synoptic eddies, reasonably well. We will present results from 200-year model integrations for various pCO_2 values, ranging from 200 to 1000 ppmV. Based on an analysis of the low-frequency components of the global sea-level pressure and SST fields, we address the question to what extent pCO_2 changes may have induced variations in decadal climate variability during the Cenozoic. A set of additional sensitivity experiments is performed to investigate how the uplift of the Himalaya and Tibetian Plateau and of the Western Cordillera of North America affected large-scale atmospheric circulation patterns. Experiments with leveled Himalaya-Tibetian orogen and Western Cordillera are used to estimated atmospheric teleconnection patterns by means of eigen techniques.

OS32C-136 1330h POSTER

Diatom assemblage changes during the last 300 kyrs in the western subarctic North Pacific

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Sedimentary records spanning the last 300 kyrs were obtained from the Emperor Seamount (ES: 49° 44' N, 16° 19' E) and in the southern part of the Bering Sea (BOW-8A: 54° 47' N, 17° 55' E). Diatom assemblages in the records were analyzed in order to reconstruct paleoceanography in the western subarctic North Pacific. A secular change in diatom assemblages indicated mainly three things; 1) total diatom accumulation rates at site ES showed generally higher values than those at BOW-8A during the last 300 kyrs; 2) *Neodenticula seminae* is a dominant taxon in the region; 3) abundance of *Thalassiosira gravida*, known as an ice-edge indicator, at ES was relatively high as compared with that in the southern part of Bering Sea during the glacial period. The western subarctic North Pacific tended to have had a higher production of diatoms than the southern part of the Bering Sea in spite of the open ocean condition during the Late Quaternary. Sea-ice coverages had a stronger effect in the western subarctic North Pacific than the southern part of Bering Sea during the glacial period.

OS32C-137 1330h POSTER

Seasonal diatom succession across the Antarctic Polar Front: the key to high-resolution Southern Ocean paleoceanography?

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The Southern Ocean is a centerpiece in global biogeochemical cycles and ocean circulation. Recent drilling in the Atlantic Sector (ODP Leg 177, Shipboard Scientific Party, 1999) has recovered laminated diatom ooze sediments, spanning intermittently throughout the last 1.6 My (Pearce, unpublished), which potentially record a seasonal surface water productivity signal (Grigorov et al., in print).

An array of sediment traps, as part of the AESOPS program, deployed in the Indian Sector samples marine snow on its way from the surface waters to the sediment (Honjo et al., 2000). These are complimented by fluff layer and top 0.5 mm sediment surface samples. Analysis of the sinking diatom assemblage, demonstrates how the surface water productivity signal is altered before it is recorded into the sediments and thus a more critical examination of the sediments can be achieved.

The aim of this combined study is two fold: to establish the seasonal change in the diatom assemblage across the Polar Front and its alteration through the water column; use the diatom seasonal succession to test the hypothesis that laminated sediments from the Atlantic Sector contain an annual signal, and potentially act as a long-term sediment trap of seasonal flux.

Grigorov, I., R. Pearce & A. Kemp. Southern Ocean laminated diatom ooze: potential for paleo flux studies, ODP Leg 177, Site 1093. Deep-Sea Research, in print

Honjo, S., R. Francois, S. Manganini, J. Dymond, R. Collier, 2000. Particle fluxes to the interior of the Southern Ocean in the Western Pacific sector along 170 W. Deep-Sea Research II, 47 p.3521-3548

Shipboard Scientific Party, 1999. Leg 177 summary: Southern Ocean Palaeoceanography. In Gersonde, R., Hodell, D.A., Blum, P. et al., 1999. Proceedings of the Ocean Drilling Program, Initial Reports, vol. 177. College Station, TX (Ocean Drilling Program). 1-67

OS32C-138 1330h POSTER

Glacio-Eustatic Control on Plio-Pleistocene Sedimentation Along the Northern California Ocean Margin

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Over the last 3.5 million years major climatic and tectonic changes have resulted in high frequency fluctuations in relative sea level adjascent to the northern California shoreline. A detailed record of these changes is preserved in two sedimentary sequences currently exposed along the coast – the neritic to nonmarine Merced Formation near San Francisco and the bathyal to neritic Rio Dell Formation north of Cape Mendocino. With the goal of deciphering the Plio-Pleistocene paleoenvironmental histories of these expanded ocean margin sequences, detailed stratigraphic sections were measured and described from the lower portion of the Merced Formation and from the Upper Rio Dell Formation. Samples taken approximately every 4 meters have been analyzed for benthic foraminiferal assemblage, palynological assemblage, stable carbon and oxygen isotope composition of foraminiferal carbonate, and organic geochemistry (polycyclic aromatic hydrocarbons, alkanes). Variation in these parameters appears to demarcate glacial and interglacial cycles. These results generally support previous interpretations of glacio-eustatic control on the cyclicity of sedimentary facies within the Merced and Rio Dell formations.