proposed and linked to CaCO3 dissolution kinetics in simple solution systems, the significance of sorption of Ca2+ and inorganic carbon species on the CaCO3 surface has not received much attention in marine chemistry studies. Comparisons between this work and previous work suggest that high pCO2 may promote adsorption of inorganic carbon species and Ca2+ desorption, whereas low pCO2 may promote desorption of inorganic carbon species and Ca2+ adsorption. While alternative explanations of the mechanism of surface exchange reactions may be presented, these surface reactions can significantly influence the interpretation of previous studies such as saturometer-based solubility determinations and the interpretation of dissolution mechanisms in deep-sea sediments.

OS11D-63 0830h POSTER

Rainwater Flux of Fossil Fuel Derived DOC Determined via 14C Analysis

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Preliminary measurements of the 14C content of rainwater DOC (dissolved organic carbon) was used to quantify the amount of fossil fuel carbon removed from the atmosphere via rainwater. The magnitude of a rainwater sink for fossil fuels is extremely important because currently there is no measured removal mechanism for these incompletely combusted organic compounds. We have determined rainwater DOC flux to be a significant part of global carbon cycling equal to approximately 6 percent of the fossil fuel carbon flux to the atmosphere. 14C measurements of rainwater DOC can be used to quantify fossil fuel fractions because DOC originating from fossil fuels is devoid of 14C and hence distinguishable from organic carbon of modern biogenic origin. As part of NOSAMS (National Ocean Sciences AMS Facility) research initiatives program, five rainwater samples were prepared for isotopic analysis. Incompletely oxidized fossil fuels accounted for a significant percentage (11-17 percent) of DOC, with fossil fuel carbon concentrations as high as 66 μM.

OS11D-64 0830h POSTER

Hypoxia in the Deep Waters of the Laurentian Trough, Lower St. Lawrence Estuary

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During a recent cruise to the Lower St. Lawrence Estuary, measurements of dissolved oxygen revealed concentrations of 65μM and less in the bottom 50 m of the water column. This is below published values of the oxygen concentrations in this region(90μM) and suggests that we may be experiencing a trend towards hypoxia. The area of the seafloor that is bathed in low oxygen water may cover more than 1000 km^2. This observation is cause for concern because of the effects low oxygen will have on benthic and epibenthic fauna and on nutrient release and subsequent primary production. Hypoxia in the Laurentian Trough is not a seasonal phenomenon. The bottom water is isolated from the atmosphere because the more than 300 m deep water column is permanently stratified. New oxygen cannot be supplied from the atmosphere but has to be delivered to the region by the slow flow of deep water from the Atlantic Ocean along the bottom of the 2000 km long Laurentian Trough. The oxygen concentration at a given location is determined uniquely by the oxygen concentration in the water that flows landward toward the head of the Trough and by the local rate of oxygen consumption. At present, the bottom water oxygen concentration in the Estuary is 15% of saturation, compared to 60% in the Cabot Strait near the seaward end of the Trough.

OS11D-65 0830h POSTER

The Influence of Ionic Strength and Fluoride ion Concentration on the Adsorption Properties of Gibbsite: Phosphate and Arsenate Adsorption

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Anomalously high concentrations of arsenic and phosphate are found in the sediments of the Saguenay Fjord relative to those of the Gulf and St. Lawrence Estuary. Whereas the source of phosphate is likely anthropogenic, arsenic appears to be scavenged from the bottom marine waters. The adsorption of phosphate and arsenic to various mineral oxides is well established but the precise scavenging agent(s) in this particular environment is not known.

The surface waters of the Saguenay Fjord show a particulate aluminum anomaly that decreases downstream or with increasing salinity. The aluminum is introduced as a result of the activities of the aluminum refining facilities and harbor activities upstream. The most likely solids introduced to the waters from these activities are bauxite, the ore mineral, and gibbsite $Al(OH)_3$, an intermediate product of the refining process. A recent study carried out in our laboratories revealed that the adsorption capacity of gibbsite for phosphate and arsenate is decreased significantly in seawater relative to freshwater. These observations imply that trace elements adsorbed onto aluminum oxides in freshwaters will desorb and be released to the solution upon mixing with marine waters.

We propose that fluoride (F^-), a major, conservative constituent of seawater (> 1ppm), either competes with other anions (e.g., $HAsO_4{}^{2-}$, $HPO_4{}^{2-}$) for the OH^- surface sites or substitutes for the hydroxyl on the surface of gibbsite. On the basis of this working hypothesis, we measured the adsorption capacity of gibbsite for arsenate and phosphate in pure water; 0.67 M NaCl; 10 mM $CaCl_2$; 10 mM $CaCl_2$ + 0.64 M NaCl and in seawater in the absence and presence of the fluoride ion. In the latter case, the fluoride activity was buffered by the addition of a fluorite (CaF_2) crystal to the solution. Results of the adsorption and fluorite equilibration experiments will be presented.

OS11D-66 0830h POSTER

Cell Surface Proteins Induced by Copper Toxicity in the Marine Diatoms *Thalassiosira pseudonana* and *Cylindrotheca fusiformis*

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Copper pollution is a significant problem in the coastal marine environment. Harbors and estuaries are especially impacted by inputs such as wastewater runoff and anti-fouling paint on boats. Typically in seawater, copper is strongly complexed by organic ligands reducing its biological availability and making it difficult to predict its biological effects. In order to address the biological availability of copper to diatoms, cell-surface proteins have been identified as markers for the organism's exposure to copper. These proteins were observed by labeling cell surface proteins with succinimidyl 6-(biotinamido) hexanoate (SBH), extracting the proteins, and performing western blots. Three glycosylated, cell-surface proteins have been identified in the marine centric diatom *Thalassiosira pseudonana* and two cell-surface proteins have been identified in the pennate diatom *Cylindrotheca fusiformis* when cultures were copper "shocked", but not in control, zinc, or cadmium "shocked" cultures. In an effort to characterize the genes responsible for the induced proteins, several fragments of internal amino acid sequence have been obtained for two of the proteins through de novo sequencing methods. These fragments were used to develop degenerate primers, and a DNA fragment corresponding to one of the proteins has been successfully PCR amplified and sequenced. Additionally, polyclonal antibodies have been made against the induced *T. pseudonana* proteins, and the applicability of using these antibodies in a bioassay for detecting copper stressed diatoms is currently being evaluated.

OS11D-67 0830h POSTER

Oxygen Isotopic Composition of Particulate Phosphatic Compounds in Sediment Trap Samples

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The oxygen isotopic composition of particulate phosphatic compounds in sediment traps from different depths and from different oceanic settings may reflect the degree of regeneration of phosphate in the water column. Accordingly this may be used as a tracer for the extent of phosphate turnover in the water column.

The oxygen isotopic composition of phosphatic compounds in organic matter has been attributed to kinetic fractionation during metabolism (Longinelli et al., 1976) and is not significantly affected by temperature (Paytan, 1983). Thus, the isotopic composition of particulate organic matter within the water column should reflect variations in the source and/or recycling of phosphate within the system, where the closer the d18O of organic phosphate approaches isotopic equilibrium with the seawater the greater the recycling of phosphate within the system.

We have analyzed the oxygen isotopic composition of inorganic and organic P fractions extracted from sediment traps and core top sediments to determine how the d18O changes spatially (coastal Pacific Ocean, Central Pacific Gyre, and Southern Ocean) and temporally. These results will be compared to the composition of P containing organic compounds in the same sediment traps determined using 31P-NMR spectroscopy (Paytan et al., 2002) and sequential phosphate extractions (Faul et al., 2002) to gain a better understanding of how phosphate is cycled in the water column.

OS11E HC: Hall III Monday 0830h

Marine Geosciences

OS11E-68 0830h POSTER

Diatoms in Volcanic Ash Layers: Enhanced Fertilization or Preservation?

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In a recent study Frogner et al. (2001) have shown that the initial dissolution of volcanic ash in seawater provides an external nutrient source for primary production in ocean surface waters that may stimulate biological drawdown of CO2. We investigated diatom assemblages in a sediment core from the Norwegian-Greenland Sea, which shows prominent ash layers. One of these ash layers reveals a tremendous increase in diatom abundance and accumulation rates. A diatom dissolution index was established to investigate the influence of preverential dissolution or preservation in this sediment core. Although the preservation of diatoms is good within the ash layer and there is microscopic evidence for silica leaching of volcanic glass, similar preservation of diatoms is observed in samples outside the ash layer, indicating, that indeed a fertilizing effect has caused the huge increase in diatom sedimentation during deposition of the volcanic ash. In a preliminary study ash layers and their diatom content from various oceanic regions have been investigated to check if volcanic ash deposition in general causes enhanced diatom productivity and therfore has to be considered as a important factor in the global carbon and silica cycle.

OS11E-69 0830h POSTER

Three-dimensional Walk-through Panoramic Animation for Bottom Topography

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We developed 46 animations of 3D panoramic view for bottom topography near Japan. The animations are made by a high performance visualization tools with new technology for 3D surface modeling, rich lighting and realistic rendering, using mainly J-EGG500 (JODC Expert Grid data for Geography at 500m intervals around Japan) and higher resolution data based on high special and quality echo sounding in several coastal region. One of the most features of the animation is that a user can control direction of viewpoint spherically. We also developed 16 walk-through movies like a camera moves along fixed paths. The user can playback and feel like viewing from an airplane or submarine. The animations and movies are distributed by CD-ROM with several detailed descriptions by HTML, and they can be displayed using Web browser installed browser plug-in.

OS11E-70 0830h POSTER

Environmental Factors Affecting Ferromanganese Crust and Nodule Composition in the Tropical South Pacific Ocean

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In the study area (140 W-180 and 0-25 S), comprising parts of the oceanic equatorial high productivity zone and oligotrophic central gyre, primary productivity is a significant regional environmental control on crust and nodule compositional variability, which is much stronger latitudinally than longitudinally. Three productivity-related environmental factors, O2 concentration in and depth of the O2 minimum layer and CCD, vary similarly latitudinally with productivity. The significant correlation of crust and nodule compositional variability with them throughout the study area mirrors that of productivity. The effects of these environmental factors differ with metal and deposit type. In crusts, Mn, Ni and Co increase and Fe decreases equatorward with rising productivity, decreasing O2 level in and depth of O2 minimum layer; Cu correlates with none of these variables and negatively with Co. In nodules, Mn, Ni, Cu and Mn/Fe increase with rising productivity and at depths near the CCD on the margin of the equatorial high productivity zone; Fe, Co and Co/Mn increase with declining productivity and rising CCD southward from the equator. In nodule formation, the decay of labile organic matter concentrated in sediments near the CCD under productive waters fuels diagenetic reactions which preferentially mobilize Mn, Ni and Cu and enhance their enrichment; Fe and Co are less diagenetically mobile. As productivity decreases southward and at depths below the CCD, diagenetic conditions weaken and hydrogenetic conditions similar to those favoring crust deposition occur. In crust formation, metal remobilization in the O2 minimum layer in the water column enriches crusts similarly to but less strongly than diagenesis in the case of nodules. This partly explains the weaker positive correlation between productivity and Mn and Ni in crusts than in nodules. Co's correlation with productivity may be related to its incorporation in weak organic complexes in the surface waters from which it is easily remobilized in the O2 minimum layer. Cu's lack of correlation with productivity is partly ascribed to its greater tendency to form strong organic complexes from which it is not easily remobilized in the O2 minimum layer.

OS11E-71 0830h POSTER

Initiation of Subduction, Forced Changes in Absolute Plate Motion and the Development of Rifting: A Pacific Perspective

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In the process of examining Pacific Basin reconstructions and new Absolute Plate Motion (APM) models, it became evident that the initial alignment of all subduction zones, i.e. the strike of the newly formed trench axis, consistently seemed to roughly parallel the APM of the adjoining oceanic plate during the time the zone was being formed. Every major subduction zone, whose original alignment relative to APM could be established, invariably exhibited this relationship. Furthermore, two types of subduction zone initiation could be recognized: A) those that preceded, and may have been responsible for subsequent, major, long-lived changes in APM and B) those that followed major changes in the APM, whose development may have enabled the accommodation of the ensuing convergent stress build-up following the change. In the latter situation, APM changes appeared to have occurred concomitant with terrane collision and/or accretion and, although sometimes impressive, were often short-lived. In both situations, however, subduction zone alignment roughly paralleled the APM at the time of the initiation of subduction. For example, the Japan, Yukon - Tanana, and Izu - Bonin - Mariana (IBM) arcs all appear to have formed spontaneously and roughly parallel to plate motions prior to long-lived changes in APM that occurred at 125, 100/96, and 45/43 Ma. Whereas the Melanesian, Tonga/Maramuni - Trobriand, and New Britain - New Hebrides arcs, as well as the incipient Micronesian Trench, also formed parallel to plate motions after the changes in APM that occurred at 45/43, 27, 18, and 6-2.6 Ma. The significant but short-lived change in Pacific APM, between 27 and 23 Ma, probably was triggered by the collision of the newly formed and buoyant Caroline plate and Euripik Ridge with the Manus forearc at the western end of the Melanesian Trench, which caused Melanesian Trench subduction to end and spreading on the Caroline plate to be shut down. The next short-lived change in Pacific APM, between 18 and 12 Ma, probably was triggered by the sinistral wrenching along the New Guinea portion of the Maramuni - Trobriand Arc. Finally the most recent changes at 6 and 2.6 Ma appear to be due to collision of the Ontong Java Plateau root with the subducting Australia slab and the actively spreading, buoyant Woodlark Basin with the Solomon Islands Forearc. In similar fashion, plate reconstructions and new APM models also suggest that the alignment of rift axes/spreading ridges at the time of initiation of rifting/spreading also paralleled the APM of the plate on which they formed. For example, at 96 Ma the developing Australia - Antarctic rift appeared to be aligned parallel to the combined pre-rift APM. Rifting next appears to have developed at 84 Ma in the Tasman Basin and possibly south of the Campbell Plateau along the Pacific Antarctic Ridge, again parallel to the combined pre-rift APM. Likewise, at 34 Ma, Caroline Basin spreading appears to have been initiated on the Pacific Plate with the spreading center aligned parallel to the Pacific APM. Finally, at 10 Ma, North Fiji Basin spreading appears to have been initiated on the Pacific Plate, in the New Hebrides backarc, with the spreading center again aligned parallel to the Pacific APM.

OS11E-72 0830h POSTER

Molecular level radiocarbon dating of surface sediments from the western North Pacific

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Compound-specific radiocarbon analysis (CSRA) as well as bulk organic matter and foraminifera was conducted on surface sediment from the western North Pacific. The three sediment core samples were recovered from southern Okhotsk Sea, a marginal sea of the western North Pacific. The CSRA results of fatty acids, hydrocarbon, sterols and long-chain ketones (alkenones) extracted from the same horizon of sediment core showed a radiocarbon age diversity. A large radiocarbon age variation were attributed from assuredly different origins from both autochthonous (marine) and allochthonous (terrestrial) products. However, in some compounds there was unconsistence of radiocarbon ages despite the same marine sources. This study will aim to realize organic compound-based chronology for marine sediment, particularly in the westeren North Pacific, where is difficult to obtain sufficient amount of planktonic foraminifera for AMS analysis due to dissolution of calcium carbonate in relation to CCD. The molecular level radiocarbon dating approach had analytical problems in relation to difficulties of recovering target compounds with higher purities and realistic amount from sediment samples, and extremely small amount AMS radiocarbon analysis (20 100mgC). To date we have achieved successfully these problems as the result of technical modifications of a preparative capillary gas chromatography (PCGC) system and individual organic carbon graphitization of compounds for AMS analysis.Our results of CSRA using the marine sediments would provide the possibility as an chronology tool for estimating the real age of sedimentary seaquences using organic matter for paleoceanographic study.

OS11E-73 0830h POSTER

Changes in Pacific Plate Motion in the Hotspot Reference Frame Since 125 Ma

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Numerous changes in Pacific Absolute Plate Motion (APM) are indicated by the copolar alignment of penecontemporaneous segments of western Pacific hotspot trails. A few of the trails also seem to be collinear, formed by overprinting from successive hotspots. The various trails also appear to be separated by coeval bends, with each of the bend times associated with obvious Pacific Rim tectonism. For example, at 125 Ma, a major APM change is reflected in the Shatsky Rise Papanin Ridge bend and the initiation of the northern and southern Wake trails as subduction ended along the northeastern margin of Gondwana and accelerated along the eastern margin of Eurasia. Phoenix Ridge spreading also was shut down, evidenced by the reversal in anomalies M3-1. The APM change At 110 Ma, visible in both the Wake trails, was accompanied by initiation of Yukon Tanana arc volcanism. The Northern Hess Rise formed and Nauru Basin basalts were emplaced. At 96 Ma another major change in Pacific APM occurred accompanied by initiation of Australia-Antarctic slow spreading followed by an APM change at 82 Ma, which was associated with the initiation of the Emperor trail and the beginning of spreading in the Tasman Basin and south of the Campbell Plateau. Spreading also began in the Stewart, Ellice, and Central Pacific Basins and possibly along the Osbourn Trough. About 75/74 Ma, a change in APM may have occurred as spreading ended in the Stewart, Ellice, and Central Pacific basins, and along the Osbourn Trough; began in the New Caledonia Basin; and increased in rate in the Tasman Sea Basin. At 65 Ma an APM change occurred as the Louisville trail was initiated and spreading ended in the New Caledonia Basin and began in the Coral Sea Basin. At 56 Ma a minor change in APM occurred as Aleutian Arc volcanism was initiated. About 45/43 Ma, the major APM change that produced the prominent bend in the Hawaiian-Emperor chain and a minor bend in the Louisville chain immediately preceded the start of Melanesian Trench subduction and ridge propagation was initiated both north and south of the Murray FZ. About 36/34 Ma, a change in Pacific APM occurred as subduction began along Loyalty - Three Kings Ridges and spreading was initiated in the Caroline, Déntrecasteaux, and South Fiji basins. A brief northward APM shift between 27 and 23 Ma, reflecting the Caroline basin-Manus arc collision that ended subduction along the Melanesian Trench, may have caused the separation of Cocos and Nazca plates from the Farallon plate, Wrangell arc volcanism, and northward ridge propagation in the Parece Vela basin. Between 18/16 and 12 Ma, a northward clockwise APM rotation perhaps was initiated by the Chile Ridge-Trench collision. This change also may have been responsible for fracture zone separation and North Chile Ridge propagation, as well as enhanced explosivity of circum-Pacific arcs. The dramatic APM change in the Late Neogene that began at 6 Ma and intensified at 2.6 Ma appears to have forced the Pacific plate to pivot counter-clockwise around the Ontong Java Plateau. This change, apparently initiated by the collision of the plateau with the subducting edge of the Australia plate, also appears to have triggered the development of extensional transform faults, formation of clockwise-rotating microplates, oblique linear volcanic ridges such as Hollister near the Louisville hotspot and several unnamed ridges near the Foundation hotspot, as well as intra-arc extension in the Aleutian arc.

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