

## OS11C-58 0830h POSTER

### Characteristics of alkenone synthesized at the *Emiliana huxleyi* bloom in the Bering Sea

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In order to realize connection between alkenone production and modern sea surface environment, we investigated alkenones produced in 2000 *Emiliana huxleyi* (*E.huxleyi*) bloom at the eastern Bering Sea. Alkenone in surface water was detected in a limited area ranging from 57°N to 63°N, where was low phosphate and high ammonium/nitrate ratio. This nutrient condition was similar as that in the surface Atlantic water when *E.huxleyi* bloom occurred. Total alkenone content (C<sub>37:2</sub>, C<sub>37:3</sub> and C<sub>37:4</sub>) per a gram of suspended particles ranged from 22.0 to 349 μg/g dry weight. For surface sediment samples, total alkenone content per a gram of sediment ranged from 0.109 to 1.42 μg/g. These results suggest that large part of particulate alkenones synthesized in the surface water was immediately degraded through the water column and/or in the interface layer between bottom water and ocean floor despite of shallow water depth of 70m on the shelf. However, the alkenone content in the surface sediment was 2-20 times higher than those of the pelagic area in the North Pacific, therefore the bloom would be important as an effective event for transportation of organic carbon to the ocean floor. We also analyzed δ<sup>13</sup>C alkenone value for some suspended particulate samples. As a result, δ<sup>13</sup>C alkenone produced at bloom strongly depended on the growth rate of *E.huxleyi* rather than [CO<sub>2</sub>(aq)]. This finding implies that δ<sup>13</sup>C alkenone would be useful as an indicator of paleo growth rate of alkenone producer at high seasonality area for primary productivity (it means area that large part of annual primary production is produced in a very short term such as bloom). Alkenone temperatures for a part of suspended particulate samples did not correspond to observed sea surface temperature (SST). On the other hand, alkenone temperature of the surface sediment ranged from 6.78 to 8.19°C corresponding to the average of SST in September, 7-8°C. The difference between particulate alkenone temperature and observed SST might be caused by the *E.huxleyi* bloom status in logarithmic phase, because alkenone synthesis system is unstable in logarithmic phase. The reason why alkenone temperature recorded in sediment corresponded to the in-situ SST might be that alkenone temperature of sediment is integrated value through at least year order containing the logarithmic and the stable phases. In addition, the alkenone temperature recorded in sediment suggested that large part of alkenone was mainly synthesized in autumn in the eastern Bering Sea. The most characteristic thing in this study is that the relative amount of C<sub>37:4</sub> in total alkenones were extremely high ranging from 18.3 to 41.4%. Such high C<sub>37:4</sub> % is common feature in C<sub>37:4</sub> detectable area where is susceptible to fresh water, and sea surface salinity (SSS) of this study area was also low, <32 psu during the observation. The relationship between C<sub>37:4</sub> % and SSS was a linear. This finding expects C<sub>37:4</sub> % in the sediment to become as a paleo SSS indicator.

## OS11C-59 0830h POSTER

### Production and turnover rates of C37 alkenones during an *Emiliana huxleyi* bloom in the Bering Sea

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As a molecular geochemical indicator, alkenone unsaturation index (Uk37) has been applied to reconstruct surface paleo-seawater temperature associated with global climate change. The objectives of this study are as follows: (1) to examine the production and turnover rates of C37 alkenones during the *Emiliana huxleyi* blooms in the eastern Bering Sea, (2) to compare the in situ seawater temperature with the Uk37 based seawater temperature for particulate matter and Pr-Uk37 or for newly biosynthesized cells, the letter estimated using a 13C labeling technique, and (3) to investigate the relationship between the alkenone unsaturation index (Uk37) and the physiology of phytoplankton. The production rates of C37 alkenones are highly variable in the surface water of the Bering Sea (during *Emiliana huxleyi* blooming), ranging from 0.074 - 0.17 for C37:2 and 0.23 - 0.66 for C32:3 respectively. The temperature difference (dT\*\*) between in situ temperature and Uk37 based temperature for particulate matter is generally larger than the temperature difference between in situ temperature and Pr-Uk37 based temperature. Turnover rates of C37 alkenones in particulate matter might be related to the physiological changes of *Emiliana huxleyi*, which may be attributable to nutrient deficiency near the slope area (BR00-10). The turnover rate of C37:3 seems to be an indicator describing the temperature discrepancy (dT\*\*) between the in situ sea water temperature and the C37 alkenone temperatures estimated by using Uk37. The C37 alkenones concentration (12.5 μg/L) at BR00-10 is 3 fold larger than the concentrations (0.77-3.07 μg/L) at other three stations. In addition, the Uk37 based seawater temperature at BR00-10 (3.96°C) is much lower than the in situ temperature (7.51°C), showing the largest seawater temperature difference (dT\*\*). This low temperature and large abundance of C37 alkenones may be due to turbulent mixing like eddy or tidal mixing on the slope area, considering the existence of very low temperature and high ammonium concentration with the water mass beneath the surface mixed water mass. The uncoupling between the in situ temperature and Uk37 based seawater temperature at the slope area (BR00-10) may designate the nutrient supply mechanism related to the long duration of the *Emiliana huxleyi* bloom in summer (July to September, 2000). From these results, we suggest that Uk37 based temperature for particulate matter should be a fingerprint of the water mass origin, but the use of Pr-Uk37 can be a new way to make correction for the difference between Uk37 based temperature and the in situ temperature in the various ocean environments.

## OS11C-60 0830h POSTER

### Diatom Fluxes in the Western Subarctic Pacific, 1997-2000

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Time-series sediment trap samples were collected during December 1997 to April 2000 at 1000 m, 3000 m, and 5000 m at Station KNOT (44°N 155°E; water depth 5500 m) in the northwestern subarctic Pacific. Components of diatom fluxes at three depths have been measured and compared each other in this study. Major diatom taxa at each depth were *Neodenticula seminae*, *Thalassiosira* spp., and *Chaetoceros* spp.. *Chaetoceros* resting spores represented relatively high values. The dominance by the major taxa indicates high productivity. However, their diatom components were different from the one of surface samples obtained in September 1999. Moreover, the temporal flux patterns were different between 1000 and 3000 m. The mean total diatom flux at 3000 m was 1.9 times higher than that at 1000 m. In particular, the mean flux of *Hyalocheate* spp. at 3000 m was 4.7 times higher than that at 1000 m. This may be linked with a possible lateral or oblique transport through intermediate water containing *Hyalocheate* spp. from hemipelagic or coastal regions. The high contents of *Chaetoceros* resting spores suggest that part of the particles arriving at 3000 and 5000 m were originated from hemipelagic or coastal regions.

## OS11C-61 0830h POSTER

### Boundary-Layer Structure and Air-Sea Fluxes Over the Japan/East Sea During Winter Cold-Air Outbreaks

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Episodic N-NW wintertime "cold-air outbreaks" occur over the Japan/East Sea (JES) as a result of dry and cold air masses incursions from the Eurasian continent. During such events, the air-sea interaction over JES is greatly enhanced. In particular, an area about 150 km in diameter off Vladivostok referred to as the "Flux Center" (FC) experiences very large fluxes of momentum, sensible and latent heats.

The study of meteorological forcing over JES was an important objective of the ONR-sponsored winter 2000 JES experiment in which the NPGS/CIRPAS Twin Otter aircraft was a key component. To obtain turbulence measurements, the aircraft was instrumented with fast-responding wind, temperature, humidity and motion and navigation sensors. IR sea surface temperature sensors were also installed. Thirteen research flights, were flown from Misawa NAF, Japan, over the Japan/East Sea during the month of February.

Three basic research goals were addressed with different flight patterns: Internal Boundary-Layer Growth: after transit to the FC South of Vladivostok, a line of soundings from 100 to 3000-5000 feet was flown following an approximate streamline across the JES. Flux Mapping: after transit to the FC south of Vladivostok, the surface-layer fluxes were mapped in a grid pattern at 100 feet with soundings to 5000 feet. Flux Divergence: after transit to the FC south of Vladivostok, a vertical stack pattern was flown to determine the flux divergence profile in the boundary layer.

Results of turbulent air-sea fluxes and boundary-layer structure obtained from the three type of flights will be presented. A dramatic growth of the internal boundary layer (IBL) and a subsequent jump or second IBL as the JES SST front was crossed were observed. The IBL warmed, moistened and lost momentum along the streamline. Enhanced fluxes were also observed in the "Flux Center". COAMPS model results will be compared to the observations.

## OS11D HC: Hall III Monday 0830h

### Chemical Processes in Lakes and Oceans

**Presiding:** B Sundby, Institut des Sciences de la Mer de Rimouski, Université du Québec à Rimouski

## OS11D-62 0830h POSTER

### Evidence of Surface Reactions of Ca<sup>2+</sup> and Inorganic Carbon Species on Calcite in Seawater

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The stoichiometric ratio between the release of Ca<sup>2+</sup> and carbonate alkalinity (Ac) during CaCO<sub>3</sub> dissolution has been assumed to be 0.5 in previous solubility determinations. As is shown here, recent and previous laboratory and field studies where both Ca<sup>2+</sup> and Ac were measured demonstrate that this stoichiometric ratio is not strictly observed. We hypothesize that sorption of Ca<sup>2+</sup> and inorganic carbon species may cause variations from the expected stoichiometric ratio. Although surface complexation models have been

proposed and linked to CaCO<sub>3</sub> dissolution kinetics in simple solution systems, the significance of sorption of Ca<sup>2+</sup> and inorganic carbon species on the CaCO<sub>3</sub> surface has not received much attention in marine chemistry studies. Comparisons between this work and previous work suggest that high pCO<sub>2</sub> may promote adsorption of inorganic carbon species and Ca<sup>2+</sup> desorption, whereas low pCO<sub>2</sub> may promote desorption of inorganic carbon species and Ca<sup>2+</sup> 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 saturation-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 65 μM and less in the bottom 50 m of the water column. This is below published values of the oxygen concentrations in this region (90 μM) 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<sup>2</sup>. 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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Anomalous 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)<sub>3</sub>, 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<sup>-</sup>), a major, conservative constituent of seawater (> 1ppm), either competes with other anions (e.g., HAsO<sub>4</sub><sup>2-</sup>, HPO<sub>4</sub><sup>2-</sup>) for the OH<sup>-</sup> 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<sub>2</sub>; 10 mM CaCl<sub>2</sub> + 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<sub>2</sub>) 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 δ18O 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 δ18O 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 (Paul 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 CO<sub>2</sub>. 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 preferential 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 therefore has to be considered as an 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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