

## Pre-Workshop Community Statements

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I am responding to the OCTET web page invitation for community participation in the upcoming OCTET workshop.

1. My concern is about arriving at the mechanistic understanding of the biological pump, subheading: the form of organic carbon exported. To my knowledge, the credo for the open sea is:

Export of POC from the upper layers is especially associated with a temporary imbalance between the rates of phytoplankton cell division and mortality, the latter principally by grazing; the export of POC is especially favored when and where medium-sized or large diatoms build up higher concentrations; sometimes, in heavy blooms, there may even be sinking of aggregated diatoms, without having gone through the stomach of a grazer.

My incomplete knowledge of the sediment trap literature is that sometimes, in some regions, much collected material occurs as fecal pellets, but

elsewhere the mass is unstructured and, perhaps, has arrived as flocs. Also, I newly note for the Arabian Sea (mostly referring to the Indo-German results) that a large percentage of the annual flux arrives at times of the year when the climatology of the hydrography does not lead one to expect much of a temporary imbalance between the rates of phytoplankton cell division and mortality (cf. also the Color Scanner data).

So, what determines the relative (as percentage of primary net production left over after 24 h) and the absolute flux from the upper layers? The difference between flux by fecal pellets and other means is that the large diatom cells will be broken when being swallowed. So, I urge that the trap materials which, I am sure, are being stored, be studied more intensively with the microscope than, to my knowledge, has been the case during JGOFS. I realize, of course, that broken frustules do not prove that they had arrived at the trap in a pellet: The original pellet may have been ingested while still in the photic zone (models by Gus Paffenhöfer and, I think, also Eileen Hofmann) or have decayed "on its own" from bacterial action, and the debris then may have been incorporated in flocs.

My first question therefore is: How often do unbroken diatom frustules occur? How important is grazing by higher animals?

2. What goes on below the upper layers, aside from a statistically reasonably predictable decline of POC flux with depth - what goes on, mechanistically speaking? There is the statement by Su Honjo (I believe, based also on the Arabian Sea experience) that the color of the trap content changes dramatically between two trap levels, which were separated by a long distance. Also, the Soviet observations of 4 decades ago of mesozooplankton biomass, when plotted on a double-logarithmic scale, indicate in typical ocean regions a significant break of slope somewhere below the transition from the meso- to the bathypelagial, suggesting a different balance between food supply and maintenance needs.

The "statistically reasonably predictable flux", which to my knowledge does not address those two observations, may at any depth easily differ by a factor of two between, if not stations, then regions. In either case, only a few percent of the primary production are at issue, and the accurate prediction will be very difficult, to say the least. But looking from "bottom-up", a factor of two makes 100% difference in food supply for the layers below, as well as for the permanent burial of carbon.

So, given a certain flux from the zone below the upper layers, what are the major processes leading to the further decay of flux with depth? A few years back (and actually, during the Woods Hole GOFs planning meeting of 1984 immortalized in the Blue Book), the study of a controlled mesopelagic volume was briefly ventilated, that is, to try to understand mechanistically the difference between the flux into and the flux out of a layer of a few hundred meters thickness. The investigation would require a truly major effort of several, or rather many, years of experimental and field work - where do we stand on that?

I think that an initiative for work as under (2) should come from the EDOCC group, but would you want to keep the issue in mind?

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## Linkages between Ocean Biogeochemistry and Climate Variability

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### *Introduction*

We have learned from JGOFS and other studies that variability in physical forcing substantially influences ocean biogeochemistry and ecosystem structure. Many oceanic regions are influenced by substantial variability of large-scale ocean-atmosphere interaction which are related to climate patterns such as El Niño-Southern Oscillation (ENSO), North Atlantic Oscillation (NAO), Arctic Oscillation (AO) and Pacific Decadal Oscillation (PDO). The oceanic response to these climate patterns will manifest itself, for example, as changes in the air-sea flux of CO<sub>2</sub>, nutrient supply to the euphotic zone, community structure, partitioning of DOM and carbon fluxes. In planning future OCTET activities, longer term integrated field and modelling studies that capture the biogeochemical responses to climate variability and changes in physical forcing should be one element of the program.

As background for discussion at the OCTET meeting, I present data which demonstrates that ocean biogeochemistry at the BATS site in the North Atlantic subtropical gyre is influenced by both NAO and ENSO (Bates, 2000).

### *Interannual variability*

The JGOFS time-series sites and Equatorial Pacific have provided datasets which can be used to decipher the processes responsible for interannual variability in ocean biogeochemistry (Michaels and Knap, 1996). For example, interannual ecosystem changes in the North Pacific subtropical gyre appear related to ENSO variability (Karl *et al.*, 1995; Karl, 1999). At the BATS site, interannual trends at BATS can be examined by determining how hydrographic and biogeochemical anomalies, or deviations from a mean state, vary over time. A six month running mean is applied to deviations from the mean of specific physical or biogeochemical parameters each cruise. Cross-correlation coefficient analysis can then be used to determine whether there are significant correlations between biogeochemical anomalies at the BATS site and natural large-scale climate patterns such as ENSO or NAO.

These statistical analyses reveal that upper-ocean temperatures are inversely correlated with parameters such as mixed-layer depth, rates of integrated primary production and total carbon dioxide (TCO<sub>2</sub>). During negative (cooler) temperature anomaly periods over the decade, mixed-layer depths were deeper by up to 20 meters; rates of integrated primary production were higher by up to 200 mg Cm<sup>2</sup>d<sup>-1</sup>, and TCO<sub>2</sub> concentrations were higher by up to 5 μmoles kg<sup>-1</sup> (Figure 1). During periods with positive (warmer) temperature anomalies, mixed-layer depths were shallower, and rates of primary production and TCO<sub>2</sub> concentrations were lower. These analyses reveal that the year-to-year variability of biogeochemical parameters such as TCO<sub>2</sub> and primary production at the BATS site was substantial compared to seasonal variability. The next step is to determine whether there are potential linkages between the observed interannual variability and larger scale climate variability.

### ***The NAO Connection***

As Table 1 shows, anomalies of temperature, salinity, mixed-layer depth, primary production and  $\text{TCO}_2$  are correlated with variation in the NAO, a periodic shift in the strengths and positions of sub-polar high and low pressure cells in the North Atlantic and the winds associated with them. The coefficients of variability range from 0.32 to 0.52. This correlation is surprisingly high, given the inherent mesoscale variability of the Sargasso Sea (McGillicuddy *et al.*, 1999).

The correlation between ocean temperature and salinity anomalies and the NAO in the Sargasso Sea is not a new finding. Many other research groups have found a connection between ocean temperatures and the state of the NAO in this region. During positive NAO periods, the westerlies that usually prevail in the region between Florida and Cape Hatteras west of the Azores High weaken, reducing wind stress and heat exchange and leading to warm ocean temperature anomalies. During negative NAO periods, storm tracks appear to shift southward, cooling surface waters and deepening mixed layers. It makes sense that ocean biogeochemistry are linked to these regional changes. Only now, with BATS observations continuing into a second decade, can the connections between ocean biogeochemistry and climate patterns begin to be demonstrated.

### ***The ENSO Connection***

The anomalies of salinity and alkalinity shown in Figure 1 are significantly correlated with each other. They are also correlated with variation in ENSO state. Periods of lower salinity and alkalinity followed El Nino events by approximately six months, while a positive (high) salinity anomaly followed the 1997 La Nina event. Other researchers have found a similar lag between ENSO events and salinity anomalies in the Caribbean Sea and tropical North Atlantic.

As Table 1 shows,  $\text{TCO}_2$  and alkalinity normalized for salinity levels are inversely correlated with the Southern Oscillation Index (SOI). On BATS cruises along the  $64^\circ\text{W}$  meridian between  $25^\circ\text{N}$  and  $36^\circ\text{N}$ , we have found that normalized  $\text{TCO}_2$  and alkalinity decrease southwards across the Sargasso Sea. The correlations between normalized  $\text{TCO}_2$ , normalized alkalinity and the SOI suggest that water masses passing through the BATS area change with time. Furthermore, changes may occur in the circulation patterns of the subtropical gyre that contribute to interplay between ocean biogeochemistry and climate variability.

This analysis indicates that both NAO and ENSO play a role in modulating interannual biogeochemical variability at BATS. This influence likely extends to changes in ecosystem structure, the dynamics of the microbial community and DOM cycling, and the distribution of nitrogen fixation in the Sargasso Sea. Future ocean carbon cycle studies should be conducted over the full cycle of dominant modes of climate variability (e.g., ENSO, NAO) thereby capturing the range of biogeochemical responses to interannual changes in physical forcing.

Bates, N.R., 2000. Interannual variability of oceanic  $\text{CO}_2$  and biogeochemical properties in the western North Atlantic subtropical gyre. *Deep-Sea Research II* (in press)

Karl, D.M., 1999. A sea of change: biogeochemical variability in the North Pacific subtropical gyre. *Ecosystems*, **2**, 181-214.

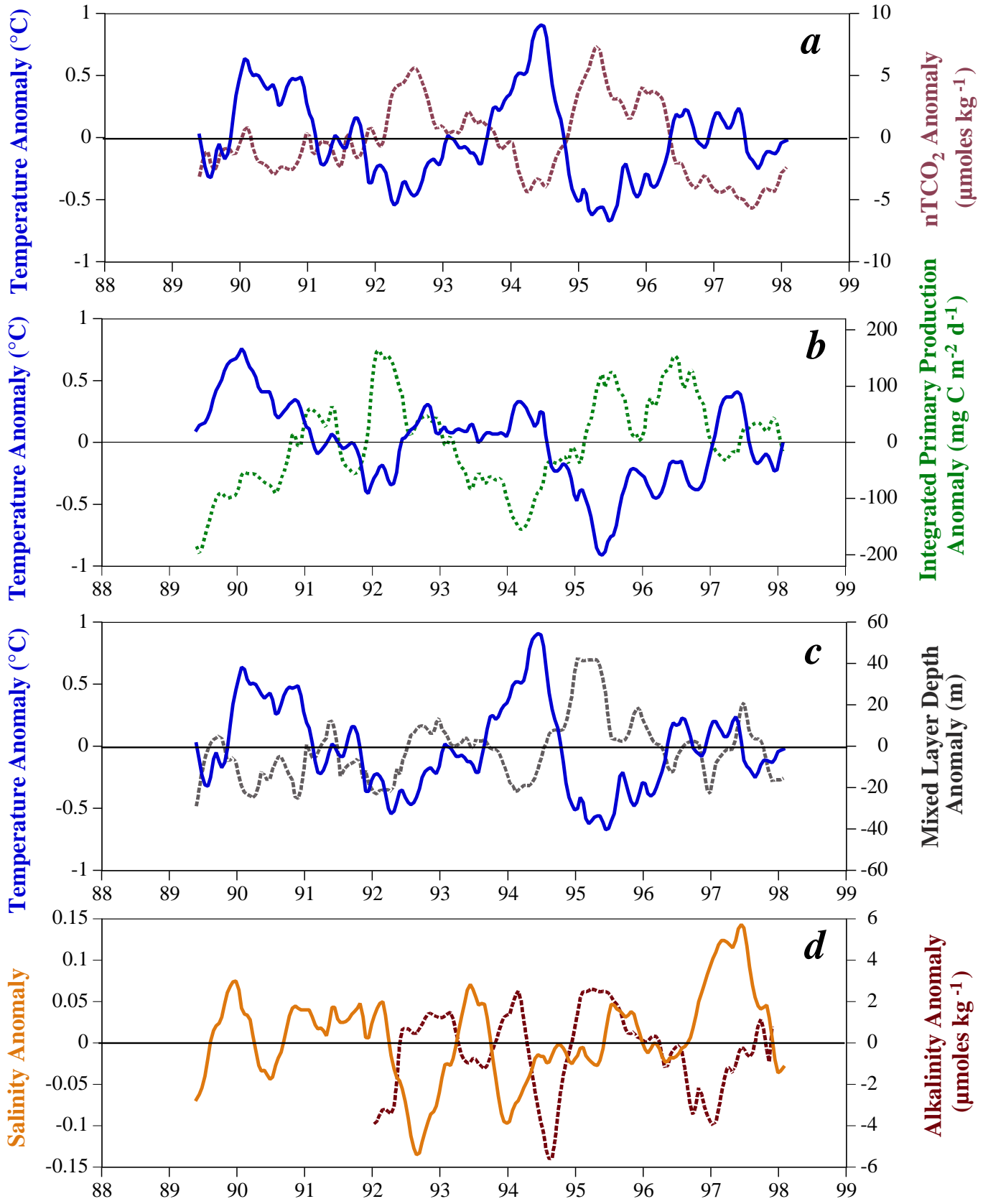
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**Table 1.** Correlation coefficients for hydrographic and biogeochemical anomalies at the BATS sampling site (1988-1998) and large-scale climate patterns, represented by the Southern Oscillation Index (SOI) and the North Atlantic Oscillation (NAO) Index. Coefficients of less than 0.2 were not reported. All figures represent a six-month running mean of the anomaly. A six-month lag with respect to the SOI gives the best correlation between that index and hydrographic and biogeochemical parameters.

	SOI <sup>2</sup>	NAO	SST	Temp.	Salinity	TCO <sub>2</sub>	nTCO <sub>2</sub>	TA	nTA	ML	PP
	(0-100 m)										
SO Index <sup>1,2</sup>	—	—	—	—	—	—	—	—	—	—	—
NAO Index <sup>1</sup>	-0.43	—	—	—	—	—	—	—	—	—	—
Surface Temperature (SST) <sup>1</sup>	0.28 <sup>2</sup>	0.40	—	—	—	—	—	—	—	—	—
Temperature (0-100 m) <sup>1</sup>	0.35 <sup>2</sup>	0.42	-0.66	—	—	—	—	—	—	—	—
Salinity <sup>1</sup>	0.52 <sup>2</sup>	-0.48	—	—	—	—	—	—	—	—	—
TCO <sub>2</sub> <sup>1</sup>	—	-0.46	-0.54	-0.38	0.44	—	—	—	—	—	—
nTCO <sub>2</sub> <sup>1</sup>	-0.53 <sup>2</sup>	—	-0.65	-0.45	-0.39	0.64	—	—	—	—	—
Alkalinity (TA) <sup>1</sup>	0.34	-0.52	—	—	0.69	0.25	—	—	—	—	—
nTA <sup>1</sup>	-0.41	—	—	—	-0.37	-0.39	0.38	—	—	—	—
Mixed Layer (ML) <sup>1</sup>	0.35 <sup>2</sup>	-0.32	-0.56	-0.45	—	0.40	0.49	—	—	—	—
Primary Production (PP) <sup>1</sup>	-0.21 <sup>2</sup>	-0.33	-0.51	-0.64	—	0.35	0.32	—	—	0.20	—

<sup>1</sup>6 month running mean of anomaly

<sup>2</sup>A lag of 6 months to the SOI Index gives the best correlations between SOI, hydrographic and biogeochemical parameters.



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## Support for Ocean Margins Component within OCTET and CCSP

### **James Bauer**

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This letter is intended to convey both my enthusiasm and urging for the inclusion of an explicit ocean margins initiative in the Carbon Cycling Science Plan upcoming planning efforts. Indeed, the nearly complete omission of a margins component, or even a modest emphasis on one, in these early discussions is of concern for a number of reasons. First, the absence of such a component de-emphasizes what may arguably be *the* most biogeochemically dynamic and diverse region of the oceans. Second, some of the *major* unresolved terms in global ocean and coupled continental - oceanic fluxes of bio-active elements, and especially of organic matter, are mediated by processes in ocean margins. As a single representative example, the fluxes of terrestrial organic matter from the continents to the oceans are known to be more than great enough to account for the radiocarbon-based residence times of oceanic organic C (almost exclusively as dissolved organic carbon, DOC). Yet we find negligible amounts of this terrestrial material in any part of the ocean, including its margins, which consequently implicates them as highly efficient “filters” and transformers of organic matter. The question of what happens to the vast amounts of terrestrial organic material discharged to the oceans still, after years of research, represents a significant gap in our fundamental understanding of the ways that ocean margins function and how they serve as the key interface between the continents and greater ocean.

The multitude of complex physical, chemical and biological processes in ocean margins - which in aggregate are much more difficult to decipher than the largely 2-dimensional world of recent open ocean flux studies - are only recently being recognized and pursued through multi-disciplinary approaches. Our rapidly evolving understanding of the critical processes regulating transformations and fluxes in margins are still largely qualitative, and demands that global land-ocean fluxes be more quantitatively evaluated. The processes in margins that affect net fluxes to the ocean interior ocean must be better defined and constrained.

It would be a disservice to the larger community of earth scientists if we as oceanographers did not at least attempt to grapple with these issues regarding ocean margins, which fall almost wholly under our purview. We should not allow this key region of global land-sea interaction, so critical to helping complete our understanding of *global* (not just open ocean) fluxes, fall between the cracks, as it so often has in past programs. The demise of some traditional sources of funding (e.g., DOE) for large-scale margins biogeochemistry studies makes this situation all the more pressing. If oceanographers and marine biogeochemists are not prepared to invest in this effort, certainly no other part of the geosciences community can be expected to do so. The inclusion of a component such as RiOMar (River-dominated Ocean Margins) in the CCSP would be an important step toward ensuring that ocean margins and the rivers

that supply them (and that are at the same time so susceptible to human influence and alteration) receive their due attention in the grand scheme of global carbon flux studies.

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## Importance of benthic-pelagic coupling in the ocean carbon cycle

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Two new initiatives in U.S. ocean carbon cycle research are OCTET (Ocean Carbon Transport, Exchanges, and Transformations) and EDOCC (Ecological Determinants of Ocean Carbon Cycling). A main goal of these two initiatives is to quantify the "biological pump" (for organic carbon and calcium carbonate) in sequestering carbon in seafloor sediments. Major oceanographic research efforts over the past two decades have concentrated on processes affecting carbon cycling within the water column. However, processes occurring at, just above, and below the sediment-water interface can have a serious impact on the diagenesis of deposited organic matter and the subsequent storage of carbon within the sediments. These processes, which I group under the theme "benthic-pelagic coupling," include utilization of particulate organic matter (POM) and bioturbation by benthic fauna, decomposition and structural changes in deposited POM due to microbial activity, and effects of benthic boundary layer flow on chemical exchanges across the sediment-water interface. Below, I outline some of the important aspects of benthic-pelagic coupling that deserve attention if we are to truly understand our ocean's carbon cycle.

First, benthic fauna (i.e. macro- and megafauna) can impact the storage of carbon in the sediments through their feeding activities (benthic grazing and caching) and mixing of the upper sediments (bioturbation). Benthic grazing has proven to be an important factor in balancing the carbon budget in shallow ecosystems such as San Francisco Bay (Officer, 1982; O'Riordan, 1993). In the deep sea, where food input tends to be episodic or seasonal, there is evidence that some infaunal organisms "cache" food below the sediment-water interface (Jumars et al., 1990). Some organisms, for example maldanid polychaetes on the North Carolina slope (Levin et al., 1997), transfer organic matter below the redox boundary through storage of food in their burrows. Sediment-dwelling organisms also influence the mixing of organic and inorganic matter in the upper sediments through bioturbation. By keeping upper sediments well oxygenated, bioturbation has a direct impact on chemical transformations within the sediments. Bioturbation also may change sediment surface topography, and the pits and mounds created by benthic fauna can impact where particles are likely to collect on the seafloor (Yager et al., 1993). In the deep sea there is conflicting evidence for a response of benthic fauna (through increased growth rates or increased bioturbation) to episodic or seasonal inputs of POM (e.g. Gooday and Turley, 1990; Drazen et al., 1998). It will be important to incorporate benthic faunal studies in both OCTET and EDOCC.

Second, microbial activity can impact the chemical (and physical) degradation of POM reaching the seafloor. Although benthic fauna may consume particles reaching the seafloor or redistribute particles to different depths within the sediments, microbes ultimately impact the



composition of all POM as it sinks through the water column and accumulates on the seafloor. Microbes may contribute to structural changes in detrital aggregates on the seafloor; for example, microbial activity can change the "stickiness" and erodibility of detritus, making the material easier (or more difficult) to resuspend into the water column or mix into the sediments. Different kinds of microbes may affect the breakdown of organic (and inorganic) compounds in different ways. Studies of microbial transformations of organic matter, for example enzymes responsible for breakdown of carbohydrate polymers and lipids, should be an important component of OCTET and EDOCC. Studies of the response of the sediment microbial community to episodic food inputs through short- and long-term measurements of oxygen consumption (e.g. Smith et al., 1998) also should be important for EDOCC. In addition to the above studies, research on bacteria from reducing environments will be important for our understanding of deep-sea carbon cycling. For example, mat-forming bacteria, especially important in low oxygen/anoxic regions, may carpet the sediment surface, influencing chemical exchanges across the sediment-water interface (Pearson, 1999). Also, we should address the following question: does the sub-seafloor biosphere (e.g. the microbes associated with hydrothermal vents) contribute any significant fraction of "new" carbon to surrounding deep-sea sediments?

A third example for an aspect of benthic-pelagic coupling that needs to be examined is the impact of episodic, mass sedimentation of phytoplankton blooms on carbon cycling at the seafloor. Mass deposition of phytodetritus to the deep seafloor has been documented in many regions of the world ocean, including the northeast Atlantic (Billett et al., 1983), the northeast Pacific (Beaulieu and Smith, 1998), and the equatorial Pacific (Smith et al., 1996). I devote my own research to the study of phytodetrital "fluff" on the seafloor because I am intrigued at how fluff layers radically change the food resources for benthic fauna and (potentially) the fluxes of chemical compounds across the sediment-water interface. At the recent Ocean Sciences meeting, Martin and Sayles reported that sedimentary recycling of organic carbon was most rapid and variable when a fluff layer was carpeting the sediments at their Southern Ocean study site (1999). I consider a phytodetrital layer as an ephemeral sediment-water interface, lasting on the order of a week or more. This short time scale may be very important in systems such as the Southern Ocean or in other high latitude environments in which most of the annual export production reaches the seafloor in a short time span. Studies of the mass deposition of phytodetritus as POM can be conducted at both shallow and deep sites and will be important for OCTET and EDOCC. In particular for EDOCC, mass sedimentation events should be studied because they are intimately linked with phytoplankton ecology and likely affect the ecology of seafloor fauna and microbes.

In summary, the three main areas of research presented above will help us understand the importance of benthic-pelagic coupling in the ocean carbon cycle. I think that with more systematic sampling of the benthos, measuring fluxes at the same temporal resolution as we do in the water column, we will make great leaps in our ability to quantify the utilization and sequestration of carbon at the seafloor. There are very few time series of processes at the seafloor that we can compare to time series of production and sinking flux in the water column. The longest time series of deep-sea benthic carbon demand (7 years of seasonal sampling) found an imbalance between carbon demand and a decreasing carbon supply (Druffel and Robison, 1999; Smith and Kaufmann, 1999). Recently, at the Ocean Studies Board meeting for the development of a network of seafloor observatories (January 2000), I presented my personal vision for the use of seafloor observatories in ocean carbon cycle research. Perhaps with our increasing awareness of the importance of seafloor processes in affecting the fate of export

production and the increasing availability of technology for use in benthic work, we will, through OCTET and EDOCC, get a better handle on benthic-pelagic coupling in the ocean carbon cycle.

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## RiOMar - River-dominated Ocean Margins (Large rivers and associated shelf/slope environments)

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The importance of continental margins to global biogeochemical cycles has been the subject of several workshops in past decade:

Ocean Margins in GOFS. Report of the workshop on The Impact of Ocean Boundaries on the Interior Ocean. Chairman: G.A. Knauer. March 1987.

Ocean Margin Processes in Global Change. Report of the Dahlem Workshop (Editors: R.F.C. Mantoura, J.-M. Martin and R. Wollast) 1991.

The Dahlem Workshop Report (1991) suggested that “Globally representative and socially relevant ocean margin systems now need to be typologically identified and investigated by coordinated multidisciplinary teams...”. We believe that the best approach to understanding ocean margins is through interdisciplinary studies of representative margin ‘*classes*’. Arguably, the most important class of margins (in terms of oceanic influence and impact on man) is river-dominated margins (RIOMARs).

Although all these workshops stress the importance of large rivers and associated margin environments, none of the previous studies of the carbon cycle (transport and fate) in margin environments have been in river-dominated ocean margins. This is presently an active focus of the International JGOFS program

Large rivers are the primary interface between terrestrial and ocean environments. Major rivers play a disproportionately important role in transporting terrestrial materials to the ocean. Approximately 40% of the fresh water and particulate materials entering the ocean are transported by the ten largest rivers (Milliman, 1991).

The U.S. Carbon Cycle Science Plan (CCSP) stresses the importance of examining both the terrestrial and oceanic sinks for organic carbon; however, the connection between these two environments (i.e., river-dominated ocean margins) is not presently being addressed by planning initiatives. The central goal of RiOMar is to evaluate the role of river-dominated ocean margins in the global carbon cycle, and to better characterize the processes that govern the transport and fate of organic carbon in these environments. A workshop was held in November 1998 to assess the present state of knowledge regarding a broad spectrum of biogeochemical processes in RiOMar environments and their potential impact on the global carbon cycle. An initial overview of the workshop findings will be published in EOS Spring 2000.

### ***Why RiOMar? (the importance of RiOMars to the global carbon cycle)***

RiOMar environments undoubtedly represent the largest modern repository of particulate organic carbon. Approximately 80-85% of global *carbon burial* occurs in RiOMar environments (deltas and associated shelf / upper slope) during interglacial times (Berner, 1982; Hedges and Keil,

1995). High sedimentation rates in RiOMar environments may provide a *high-resolution record* of (a) changes within drainage basins over the past 200 years, as influenced by human activities (this represents a large portion of the terrestrial realm) and, (b) changes within the margin during the onset of the present interglacial (10-15 kyr bp). The insights that these sedimentary records can provide concerning organic carbon cycling during interglacial (and perhaps transitional glacial) times are indeed exciting.

RiOMars receive *large inputs* of terrestrial (allochthonous) organic carbon via rivers and marine (autochthonous) organic carbon resulting from high productivity rates---approximately 10 % of global production. Annually, the total organic carbon burial in marine sediments is less than one-third of the riverine organic carbon discharge---indicating that riverine organic matter is *rapidly mineralized*, (Hedges and Keil, 1995). Organic carbon *preservation* (allochthonous and autochthonous) may not be as complete as previously thought for RiOMar environments (Aller, 1998; Keil et al, 1997); the reason for this is unresolved.

The *storage* of terrestrial sediments in large river basins may be much more important than previously recognized (Stallard, 1998), and is directly affected by human influences. This organic carbon reservoir is directly connected, through RiOMar environments, to the ocean. One possible scenario is that RiOMar regions switch from serving as a *reactor/transformer* of organic matter during high sea-level stands to being a direct *conduit* for terrestrial organic matter input to the open ocean during low sea-level stands.

### Questions

There are many unanswered questions about organic carbon inputs, remineralization and transport in RiOMar environments. Most of the previous integrated studies of large rivers and adjacent margins (ex. AmasSeds) did not address fundamental biogeochemical questions related to carbon cycling, but did provide some very solid ground work from which a carbon cycle program can be launched.

A sampling of some scientific questions that RiOMar research can address are:

- Organic carbon storage/sequestration within the river system; how, where and for how long?
  - What is the age of POC/DOC/COC delivered by rivers to RiOMar environments?
- Are RiOMar environments net sources or sinks for organic carbon? (for annual, decadal, millennial time scales)
- Is the response of RiOMar regions to global change rapid compared to open ocean environments? If so how does this influence the global carbon cycle?
- How will the role of RiOMar environments (source or sink) change over time as a result of human activities?
- Terrestrial carbon sinks have been altered (created and destroyed).in the past by man
  - How has this influenced the dynamics of carbon storage within the river system and the amount/form that enters the ocean?

- How will climate variations (ex. El Nino) affect Carbon Cycling in RiOMar environments; the magnitude of their organic source or sink; rainfall rates in drainage basin; frequency of catastrophic floods.
- Large rivers are abundant sources of micronutrients; does this mean that micronutrients (ex. Fe) are not limiting? Is all Fe in RiOMar environments in an available form?

### **Strategy**

We suggest that a RiOMar initiative be carried out in two phases that are complimentary to the plan suggested in the CCSP:

#### (I) Intensive Phase

- As recommended in the CCSP (and followed by OCTET) initial phase should focus on continental/regional scale---North America.
  - Mississippi is one of the world's 10 largest rivers: Water and sediment discharge (7<sup>th</sup>), drainage basin size (2<sup>nd</sup>) ... (Milliman, 1991)
  - Approximately 40% of conterminous U.S. within drainage basin, part of Canada
  - Over 65% of the total suspended matter and dissolved solids transported from the conterminous U.S. to the ocean is carried by the Mississippi (Presley et al. 1980).
  - Logistics for a study of the Mississippi River system would be manageable and cost-effective compared to other global top ten rivers.
  - The Mississippi splits (~ 30% of its discharge) to form the Atchafalaya River which in its own right is a large world river. However, this split results in the same river entering two distinctly different RiOMar environments (shallow-muddy inner shelf and , deeper outer shelf) thereby extending the observation that could be made from one river system.
- After the initial process-oriented phase, it would be beneficial to continue with some measurements after initial phase (set up a Global River Observation Station similar to HOTS and BATS).

#### (II) Extensive Phase

- Study of selected global RiOMar environments; perhaps take advantage of sites used in other programs (e.g., MARGINS, International JGOFS study areas)
- Other major rivers chosen based on several factors (latitude, lithology, ...)
  - Papua New Guinea—same drainage basin with many types of RiOMars (MARGIN site)
  - MacKenzie—dominant source of particulate matter to the Arctic
  - Yangtze—Himalayan source, temperate river, broad shelf
  - Amazon or Zaire as large tropical RiOMar

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## Understanding The Controls Of Ecosystem Community Structure And Nutrient Availability On The Biological Pump.

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The fundamental goal of OCTET is to characterize physical, geochemical and biological controls governing the partitioning of carbon pools in the ocean. Although likely to be a prominent focus of EDOCC, the problem of how community structure and nutrient availability control processes of organic carbon partitioning and export also seems to be an essential element of OCTET.

The biological pump can be an important mechanism for the transfer of carbon from surface water to depth. The important processes associated with export include gravitational settling of particles, physical mixing of both sinking and non-sinking particles in the surface waters and vertical migration. Community structure and nutrient availability can play an important role in determining the partitioning of organic matter into sinking or non-sinking organic material. The importance of the biological pump in a given system is governed by mechanisms which control 1) the partitioning of organic matter between dissolved and particulate phases; 2) the production of sinking vs. suspended (recycled) particles and 3) the accumulation of DOM resistant to rapid remineralization.

Michaels and Silver (1988) and Peinert et al 1989 hypothesized that foodweb structure play an important role in determining the amount of organic carbon and associated nutrients which are either

exported from or recycled in the surface waters. In some systems the elevated POC flux can correspond to transient or episodic physical events (like eddies) which result in blooms of large phytoplankton cells that are quickly removed from the surface water by forming aggregates and sinking. Zooplankton community structure also can significantly affect export. For example, analysis of salp bloom dynamics over the BATS time series indicates fecal flux from salps can episodically constitute a large portion of the total sediment trap carbon flux (Steinberg et al., in prep.). In systems like the Ross Sea, the majority of organic carbon (80% of net community production) is partitioned as particulate organic carbon from the onset of Austral spring of which a significant fraction is exported from surface waters (Sweeney et al. in press). Hansell and Carlson (1998) have also demonstrated that the net community production of DOC varies considerably (10 – 70%) between oceanic systems.

In order for DOM to be a contributor to export the quality of the newly produced DOM must be resistant to microbial degradation for time scales long enough to be mixed out of the surface water. It has been hypothesized that community structure can affect the sequestration of dissolved organic matter. Legendre and Le Fevre (1995) and Toggweiler (1989) hypothesized that processing organic matter through a microbial food web resulted in the production of a refractory DOM pool. Williams (1995) hypothesized that nutrient availability may control stoichiometry of dissolved matter resulting in differential remineralization of DOM. In the Ross Sea the annually produced DOM pool has a C:N ratio close to 6 (Carlson et al. in press) and is remineralized on time scales of weeks to months whereas in the North Atlantic seasonally produced DOM exhibits a C:N ratio of 12 – 15 (Williams 1995) and may take longer to remineralize. Thingstad and Rassoulzadegan (1995) hypothesized that DOM build up in some systems may be due to the inability of microbes to take up DOM because of nutrient limitation i.e. “the malfunctioning microbial loop”.

What are the factors that control the partitioning of organic matter between dissolved and particulate pools? Does ecosystem structure control the production and lability of DOM or is the nutrient regime the ultimate control? Is remineralization of organic matter controlled by microbial community structure or does nutrient availability play a role in remineralization of DOM? The JGOFS program has helped us identify areas of the ocean where organic matter production, partitioning and export differ. Our ability to accurately model export from the euphotic zone and remineralization at depth will only come from a better understanding of how community structure and nutrient availability affect production, partitioning and export of organic matter. Understanding these mechanisms should be an important component of OCTET as well as EDOCC.

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This communication is in support of including the River-dominated Ocean Margins (RiOMar) initiative in the Carbon Cycle Science Plan (CCSP). I feel that establishment of RiOMar as a highly interactive but separate cohort of OCTET is both logical and scientifically compelling. It has become clear based on research by a wide variety of earth scientists that rivers and continental margins play a central and multifaceted role in linking the terrestrial and marine cycles of bioactive elements, and carbon in particular. Although we have recognized for decades that deltas and continental margin sediments account for >90% of all organic carbon burial, the great rate and extent to which discharged riverine organic matter is remineralized in these coastal zones has only been appreciated in the last few years. For example, we now recognize that roughly two-thirds of all fine particulate organic materials discharged by the Amazon River are lost from deltaic muds before they move far from the river mouth. If other rivers behave similarly, and there is growing evidence that they do, the organic carbon remineralization rate in these relatively restricted regions is on the order of  $0.1 \times 10^{15}$  gC per year, and hence comparable to the global burial rate of total organic carbon. What is so impressive about the Amazon system is that fine particulate organic matter discharged by the river is predominantly soil derived and already highly degraded. Whatever combination of processes is able to recycle these recalcitrant substrates so rapidly after they meet the ocean must be potent indeed. Although about half of all modern organic carbon burial is within deltas, these dynamic regions have been largely ignored.

One of the most fascinating aspects of river/margin interaction is that rivers provide a continuous integrated recording of terrestrial vegetation and climate that is uniquely recorded in continental margin sediments. Although the stored sedimentary information is multidimensional, the entrained organic compounds provide an unparalleled wealth of structural and isotopic information. These telltale patterns are first imprinted within soil profiles, where climatic conditions and local bedrock determine the types and amounts of vegetation and minerals that are formed. Erosion eventually translates this cumulative record to the river, through the floodplain, and into adjacent continental margin sediments. Since long-term preservation of any materials on eroding landscapes is rare, we must ironically turn to coastal marine sediments to understand the extremes of climatic history, which are typically most strongly expressed on land. RiOMar promises to strike to the heart of these key global cycling issues.



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## PANDORA (OCTET related portions)

### Productivity And Nutrient Dynamics and Ocean Reflux to the Atmosphere

#### **Bill Jenkins**

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#### **Rationale**

The ocean's response to, and participation in, climate change is a critical and poorly understood part of forecast and impact assessment models. The upper layer of the ocean plays a major regulatory role in atmospheric composition (including oxidation processes and aerosol loading) and forms the gateway for exchange of materials with the deepwater, the largest single component of the biosphere. The biogeochemical coupling of the ocean and atmosphere, mediated by the transfer, transport, and sequestration of gases and biologically important substances, occurs in a non-linear fashion over a broad range of time and space scales. The important processes occur on time-scales ranging from seconds (*e.g.*, photolytic reactions), through diel and seasonal (planktonic growth and species succession), to annual/decadal (nutrient regeneration and re-supply to the euphotic zone; ENSO events). The intimate entanglement of physical, chemical and biological processes provides us with a rich set of challenges that we must surmount to develop predictive skills for atmospheric chemistry, radiative budgets and climate models.

We have made considerable progress in developing skills for the basin-wide assessment of primary production, particularly with the use of satellite data, and through process-oriented programmes such as ACSOE, BOFS, and PRIME. However, there are a number of significant and worrisome gaps in our understanding of the linkages and controls in the system. These gaps occur principally on the regenerative side of the grand oceanic biogeochemical cycle, but are intimately linked to the generation, exchange and uptake of biogenic gases and biogeochemically important substances in the upper ocean.

#### **Programme Objectives**

The primary objective of the PANDORA programme is to advance our state of knowledge regarding the biogeochemical coupling of the ocean-atmosphere system in order to develop more realistic coupled ocean-atmospheric climate models. It is only in this manner that we will be able to make credible predictions of large-scale biogeochemical response to climate changes. Toward this basic end, we will embark on:

1. the characterisation, quantification and modelling of nutrient regeneration within the water column,
2. a determination of the mechanisms of nutrient speciation and reflux to the euphotic zone,
3. the quantification and modelling of the large-scale biogeochemical exchanges between the ocean and atmosphere (both air-sea gas exchange and dust inputs), and
4. improvement in the mechanistic modelling of climatically important biogenic gases and their fates in the upper ocean.

The primary objective of PANDORA is to develop a quantitative and functional understanding of these processes sufficient to provide rational and accurate parameterisation of biogeochemical processes in climate models. The major issues at the heart of the PANDORA programme include:

***Nutrient regeneration and speciation:*** These processes are not well characterised or understood in the open ocean. The regeneration of nutrients within the water column below the euphotic zone involves the microbial transformation of a range of biological materials in an extremely complex and poorly characterised environment. Material processing by bacterial assemblages depends on heterogeneous micro- and macro-environmental conditions that initiate in the upper water-column, are difficult to observe *in situ*, and impossible to replicate in the laboratory. Such processing occurs progressively as material evolves and moves vertically through the water column, through successive stages of particle aggregation and destruction. Elemental transformations are likely to occur at different rates for different elements, and through a variety of intermediate and transitory states (particulate, colloidal and soluble). Differential remineralisation in a highly stratified water column (characteristic of the North Atlantic) raises the potential for separation of life-forming elements (*e.g.*, phosphorus and nitrogen), and the interplay of regional differences in bio-stoichiometry on regulation of productivity, species succession and dominance, and the generation and exchange of biogenic gases.

Due in large part to early surveys and the WOCE programme, there exists a large database of dissolved inorganic nutrients (principally nitrite + nitrate, phosphate and silicate) for the world oceans. Recent advances in measurement techniques for dissolved organic materials (carbon, nitrogen and phosphorous) show that significant elemental pools exist in such states. The distributions and roles of such materials in the global carbon cycle are not at present well documented or understood, but it is clear that a complete understanding must be achieved for predictive biogeochemical climate models.

***The pathways and mechanisms of nutrient reflux to the euphotic zone:*** The quantitative supply of nutrients to the upper ocean has not been successfully identified and modelled, particularly in oligotrophic waters. Such processes are critical to the regional, long-term regulation of primary production, to mediating decade time-scale changes in biogeochemical response to climate forcing, and of sustaining ecosystem structure in the face of climate change. Estimates of nutrient fluxes based “traditional” mechanisms (*e.g.*, turbulent diffusive transport and Ekman convergence) are orders of magnitude too small to support observed levels of production in the oligotrophic subtropical gyres. Enhancement of new production *via* nutrient transport associated with “eddy heaving” has been recently proposed, but model calculations and observations appear to fall quantitatively short in broad areas of the subtropical gyres. There are reasons to suspect that such models do not at present encapsulate an adequate level of biogeochemical complexity, particularly at the smaller scales, to effectively simulate full system behaviour. Moreover, ecosystem response is likely sensitive to the temporal character of nutrient (and possibly senescent livestock) delivery. Adequate mechanistic and quantitative characterisation of these processes is critical to our ability to model oceanic biogeochemical behaviour in the face of climate change.

Consideration of tracer observations (carbon, isotopes, oxygen, nutrients and transient tracers) coupled with their disparate boundary conditions places powerful constraints on the magnitudes, mechanisms, and modes of these material transports, but at present there is no clear and mutually satisfactory explanation for the full set of observations. First order questions of how the individual tracers are linked (or decoupled) by near-surface oceanic processes remain unanswered. Such uncertainty underscores the fundamental inadequacy of our prognostic skills in biogeochemical forecasting.

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## A case for reconsidering deep sediment organic carbon sources in global oceanic budgets

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Deep subsurface sediment sources of organic carbon are currently considered to be unimportant in global budgets on short time scales (1 to 10 years). However, sources related to gas venting through the seafloor are potentially very important and need to be reconsidered. Several potential sources are: 1) direct injection of biogenic or thermogenic gas and oil through the seafloor, often through localized fractures and faults; 2) active oil or gas seepage accompanied by partial biodegradation which adds water soluble organic compounds to the water column; 3) active gas discharge which forces pore water dissolved organic carbon (DOC) into the overlying water column; 4) DOC contributed by biota associated with active seepage; and 5) direct venting of gas to the atmosphere in shallow continental shelf areas. Volumetrically, recent estimates of methane leakage from continental shelf areas ( $8.7 \times 10^{14}$  g/y, Hovland & Judd, 1992; 0.8 to  $4.8 \times 10^{13}$  g/yr, Hornafius et al, 1999, Table 1) and from oceanic gas hydrates (2 to  $8 \times 10^{14}$  g/yr, calculated from data in Whitaker, 1994) are equivalent to estimated total annual global methane fluxes to the atmosphere ( $5.4 \times 10^{14}$  g/yr, Cicerone & Oremland, 1988;  $5.1 \times 10^{14}$  g/yr, Khalil & Rasmussen, 1995) and to oceanic dissolved organic carbon (DOC) turnover ( $1 \times 10^{14}$  g/yr, Williams & Druffel, 1987) which are considered to be important.

Obtaining reliable estimates of this deep sediment carbon flux is difficult because gas venting through the seafloor is commonly spatially and temporally discontinuous and often occurs through highly localized small fractures and faults in the seafloor (Roberts and Carney, 1997). This heterogeneity may be responsible for inconsistencies between recent estimated fluxes for individual seeps (e.g. 0.1 to  $3.5 \times 10^{12}$  g/yr to the United Kingdom continental shelf and  $3.8$  to  $10 \times 10^{12}$  g/yr to the Gulf of Mexico; Table 1) which are equal to or greater than previously published global estimates ( $2 \times 10^{11}$  to  $3.4 \times 10^{12}$  g/yr, Hunt, 1996; Kvenvolden & Harbaugh, 1993) and are 10 to 100 times greater than carbon estimated to be derived from continental margins by compaction ( $2.5 \times 10^{10}$  g/yr; Elderfield et al 1990). Highly localized seeps can represent large volumes

of hydrocarbons. For example, large methane bubbles (1m in diameter) venting through a fracture of about the same length in the Gulf of Mexico were calculated to represent  $>0.9 \times 10^8$  g/carbon/year, or one percent of the total continental margin compaction flux estimated by Elderfield et al., 1990 (Table 1, Whelan 2000).

A large body of circumstantial evidence, summarized in Whelan, 1997 & 2000, suggests that even recent seafloor gas flux figures in Table 1 may be substantially low:

i) Seepage to areas of the ocean floor where there is no active oil and gas production is almost always found accidentally; huge areas of the seafloor are unexplored. Even for known seeps, measurements of flow rates are rare. Oil and gas seepage into surface sediments is patchy, but very common beneath actively subsiding basins worldwide (Abrams, 1996). These include most of the world's major river deltas and continental slope areas. Widespread oil and gas seepage to the seafloor has been documented by geophysical, geological, biological, and satellite data (e.g. Hovland and Judd, 1988 & 1992; Judd, 1993; Hovland, et al. 1997; Collett, 1997; Abrams, 1996; Whelan, 1997; MacDonald, et al 1993 & 1996; MacDonald, 1999; Sassen, et al 1994).

ii) Worldwide, only about 1.7% of thermally generated oil and gas ever makes its way into a producible oil or gas reservoir; about 54 % of the remainder is lost through the ocean floor (Hunt, 1996).

iii) Large surface-sediment features called pockmarks, or craters, often 100m or more in diameter, occur over much of the ocean floor worldwide and are thought to be diagnostic of past fluid or gas flow (Hovland and Judd, 1988; 1992). Many are paved with carbonate derived from biodegraded petroleum or methane. Huge carbonate mounds, often 10's of meters high comprised of degraded biogenic methane, are observed in some areas of older or extinct seeps (Roberts, et al., 1989; Roberts & Carney, 1997; Hovland and Judd, 1992). One currently active Gulf of Mexico seep was shown by  $^{14}\text{C}$  and U/Th dating to have been on-going for about the last 1400 to 3200 years (Aharon, et al., 1997).

iv) Prolific biologic communities reminiscent of those surrounding hydrothermal vents are common and diagnostic of long-term-on-going seeps. However, very recent seeps show highly disturbed subsurface sediments and huge mud volcanoes which are devoid of biota (Roberts and Carney, 1997). Miocene forams were found in the crater of one of these; we estimate that the forams were vented vertically

from a subbottom depth of at least 15,000 ft (Kohl and Roberts, 1994; vertical depth to Miocene sediments estimated from unpublished seismic data of Cathles).

v) Chemosynthetic cycling of hydrocarbons has been documented in the Gulf of Mexico (Carney, 1994; LaRock et al, 1994; Sassen et al, 1994), in the California Margin (Hinrichs et al., 1999), and in the Santa Barbara Channel (Spies & DesMarais, 1983; Bauer et al, 1990) and appears to be widespread in many other gas and oil seepage areas worldwide (Hovland and Judd, 1988).

vi) Methane gas hydrates, a solid ice-like crystalline material formed from methane and water under high pressure and low temperature conditions typical of the deep ocean floor occur worldwide (Brooks et al, 1984 & 1986; Kvenvolden, 1993 & 1995; Kvenvolden et al., 1993; Collette, 1997) and constitute one of the largest carbon reservoirs on earth (DoE, 1999; Table 1). An upward steady state flux of gas may be required to maintain these oceanic gas hydrates over geologic time (Zatsepina & Buffett, 1997 & 1998)

vii) Dissolved organic carbon in the deep ocean has an average  $^{14}\text{C}$  age of about 4000-6000 years (Druffel et al., 1992). This old age is an enigma considering that the vast majority of DOC appears to be of marine origin, coming directly and/or indirectly from primary production in the euphotic zone (Meyers-Schulte and Hedges, 1986) and conservatively would be expected to give an age of about 200 years or less (Aluwihare et al, 1996). Preliminary evidence has been presented that upward seeping oil or gas, reworked by biota near the sediment water interface, or sediment pore waters pushed out of bottom sediments by upward fluxing gas, may be contributing to this old DOC pool (Whelan, et al 1998 & 2000).

Evidence for massive spatially heterogeneous and possibly episodic natural upward gas seepage to the ocean is not subtle, and requires further study of extent, rates, and magnitudes to define potentially important biogeochemical effects. This seepage could also be an important source of other oceanic elements and nutrients (e.g. iron, manganese, sulfur, and phosphorous).

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**Table 1: Global carbon reservoirs compared to estimated fluxes of petroleum to the seafloor**

<u>Carbon Reservoir</u>	<u>Amount (g)</u>	<u>Rate (g/yr)</u>	<u>Reference</u>
Reduced insoluble carbon in sedimentary rocks	$1.1 \times 10^{22}$		Hunt 1996, pp 19-21
World ocean DOC	$1.70 \times 10^{18}$		Druffel et al. 1992
Marine primary production		$5 \times 10^{16}$	Martin et al., 1987
Ocean DOC turnover		$1 \times 10^{14}$	Williams Druffel, 1987
Ocean margins, normal compaction		$2.5 \times 10^{10}$	Elderfield et al., 1990
<u>Gas Reservoirs</u>			
Annual global methane flux to atmosphere		$5.4 \times 10^{14}$	Cicerone & Oremland. 1988
Total Methane flux to atmosphere		$5.1 \times 10^{14}$	Khalil & Rasmussen, 1995
Hydrates (marine only)	$2-8 \times 10^{18}$	$2-8 \times 10^{14}$	Whitaker, 1994
Methane hydrates (oceans only)	$1.3 \times 10^{22}$ $>1 \times 10^{19}$		DOE, 1999 Kvenvolden, 1993
<u>Recent estimates of gas &amp; oil venting to ocean floor</u>			
Total methane seepage (offshore, Global continental shelf areas)		$1.8-4.8 \times 10^{13}$	Hornafius et al, 1999
Total global methane seepage from shallow (<200 m) water depths		$8.7 \times 10^{14}$	Hovland & Judd 1992
Methane venting from United Kingdom Continental shelf		$0.1-3.5 \times 10^{12}$	Judd, 1997
Natural gas venting to ARCO tents, 1982 (30 x30 m area)		$1.1 \times 10^{10}$	Rintoul, 1981
Natural gas venting, Coal Oil Point Santa Barbara Channel, Calif		$2.9 \times 10^{10}$	Hornafius et al, 1999
Methane venting, Dive site 2894, Gulf of Mexico, Aug 1999 (Through fracture in $1 \text{m}^2$ area)		$>0.9 \times 10^8$	Whelan et al. 2000
<u>oil</u> - Gulf of Mexico – surface oil slicks only		$0.76 \times 10^{11}$ to	MacDonald, 1996

(natural oil seeps)		$3.8 \times 10^{12}$	& unpublished
<u>oil</u> - Gulf of Mexico – total water column (all water depths)		$>10 \times 10^{12}$	Chevron, Deep Spills workshop, July 1999
Global flux methane (natural marine seeps)		$8 \times 10^{12}$ to $6.5 \times 10^{13}$	Hovland et al., 1993
<u>Older estimates:</u>			
Oil & gas lost at surface over last 100 million years	$4 \times 10^{19}$	$4 \times 10^{11}$	Hunt, 1996, p.597
Annual petroleum seepage (marine sources)		$0.2-3.4 \times 10^{12}$	Kvenvolden & Harbaugh, 1983; Hunt, 1996; Miller, 1992
Total natural seepage all geological sources		$1 \times 10^{13}$	Houghton et al., 1995