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# GEOTRACES - DATA-MODEL SYNERGY WORKSHOP

**Delmenhorst, September 6 - 8, 2007**

**Organizer:**

**Reiner Schlitzer**  
(Alfred Wegener Institute for Polar and Marine Research)  
**Email:** [reiner.schlitzer@awi.de](mailto:reiner.schlitzer@awi.de)  
**Phone:** +49 (0) 4831-1559

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**6 – 8 September 2007, Delmenhorst, Germany**

# **Workshop Report**

**Written by the workshop organizer and session chairs**

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## Table of Contents

Acknowledgements .....	4
Summary .....	5
Session Reports .....	6
1. Cycling of micronutrients – processes, transports, sources and sinks (M. Gehlen) .....	6
2. Potential of TEIs as recorders of ocean productivity and nutrient/carbon fluxes (N. Gruber) .....	8
3. Paleo-proxy development – separating the effects of circulation and particle dynamics (B. Anderson) .....	10
4. Data assimilation in the GEOTRACES context (O. Marchal) .....	15
5. Data and model resources for GEOTRACES (A. Oschlies) .....	17
Workshop Programme.....	18
Workshop Participants .....	21

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## Summary

In 2006, GEOTRACES published its Science Plan describing the scientific rationale behind the programme and listing a number of ambitious research goals. It was realized early on that most of these research goals could only be addressed successfully if the observational and modelling communities worked together in close cooperation. At the GEOTRACES SSC meeting in Dec 2006 it was therefore decided to organize in 2007 a Data-Model Synergy Workshop to bring these two communities together, to foster the exchange of ideas, and to provide a forum for constructive and fruitful discussions between the groups.

The specific workshop goals were

- To bring together GEOTRACES experimental geochemists and modellers.
- To initiate and foster collaboration between experimentalists and modellers.
- To discuss and evaluate promising modelling approaches for GEOTRACES and provide feedback for cruise planning.
- To discuss data sharing and data management procedures.

This workshop was held from September 6 to 8, 2007, at the Hanse Wissenschaftskolleg (HWK) in Delmenhorst, Germany. It was one of four workshops organized by GEOTRACES in 2007, the other three being dedicated to the development of observational plans in the three major basins of the world ocean. Forty-eight scientists from six countries participated in the workshop, and there was a good balance between experimentalists and modelers. The agenda consisted of five half-day sessions. The first four sessions covered major research themes of the GEOTRACES programme, while the fifth session was included to describe and highlight some of the most important data and model resources, likely to be used by GEOTRACES scientists.

All sessions were opened with two or three keynote presentations by leading scientists in the field, providing views from the experimental as well as modelling sides. The purpose of these presentations was two-fold: (1) to provide a status overview of the respective research area, and (2) to describe the major current research questions and unsolved problems. About one-third of the total workshop time was devoted to plenary discussions following the plenary talks. Additional poster sessions in the evenings allowed participants to present their own recent research and discuss new findings with colleagues.

The keynote presentations were excellent, and the discussions were lively and constructive. The results of the discussion rounds are documented in the session reports below. Electronic versions of most presentations are available via hyperlinks in the agenda below. Workshop participants generally found the meeting very interesting and stimulating. It was recommended to organize similar workshops bringing together the experimental and modelling geochemical communities on a regular basis. There was broad agreement that the next such workshop should be held in 2009.

Reiner Schlitzer  
October 2008

## Session Reports

### 1. Cycling of micronutrients – processes, transports, sources and sinks (M. Gehlen)

The discussion rapidly focused on the Fe geochemical cycle. Questions evolving around the cycles of Cd, Zn, etc. were not addressed, with the exception of a brief mention of the interaction between the cycles of Cu and Fe. The latter was quoted as a motivation not to lose sight of the other trace elements.

State-of-the-art numerical models of the ocean Fe cycle distinguish between different Fe pools (e.g. solid versus dissolved, free versus complexed). Not all of these fractions are bioavailable. Since a prime reason to include Fe in global biogeochemical models resides in its role as a micronutrient, emphasis is put on processes and reactions controlling the bioavailable Fe fraction. To the contrary, routine measurements of Fe are mostly reported as total dissolved Fe. It is thus possible that model output and data might not correspond. In this case, the observations might not allow model validation. There was a request from the modellers side for observations to include chemical speciation, along with a quantification of different Fe pools. While it is not impossible that this type of information will be collected during GEOTRACES cruises, it won't be part of a large-scale survey programme.

Very much along the same line, the modellers stressed the need for an improved process understanding/description. Process understanding can only be advanced through a combination of controlled lab experiments (e.g. reaction kinetics, identification of reaction pathways) and field observations (e.g. Fe speciation, ligand identification and quantification). While process studies are part of GEOTRACES, they are not its main focus.

Representatives of the observational community challenged the trend towards increasing complexity in biogeochemical models of the Fe cycle. The principal message was to “keep it simple”. Models are expected to be useful tools for first-order sensitivity studies. A model should, for example, allow verification of whether pelagic sediments are an important source of Fe or not. Despite their complexity, global ocean biogeochemical models are presently not well adapted to tackle this question. As a matter of fact, the vertical resolution increases with depth, resulting in a thick boundary layer. A flux from the sediment will be diluted in the large volume of the last box and not imprint the calculated profile. This limitation will also affect solute exchange across the sediment-water interface driven by flow-sediment interaction.

The discussion converged around the objectives of GEOTRACES with the following recommendations:

1. Modelling studies within GEOTRACES should make use of the large-scale (quality-controlled) data set to translate observed distributions into fluxes.
2. Proxies for external sources of micronutrients and trace elements have to be developed. The use of Al as a proxy for the atmospheric Fe source is an example of this approach.
3. Modelling studies should aim at disentangling the contribution of physics versus biology in controlling observed contributions.
4. Simple models should be developed to assess the first-order controls on global distributions, as well as the potential of trace elements as proxies for past environmental conditions (e.g. Cd/P).

5. Detailed process studies should be conducted in order to constrain Fe biogeochemical models of higher complexity. These models will in turn provide insight into the interplay among physical, chemical and biological processes in regulating global distributions.

The sensitivity of trace element and micronutrient cycles to global change was not addressed during the discussion.

The following questions were identified prior to the meeting:

To what extent can micronutrients such as Cd, Zn, and Fe be considered "Redfield Ratio" elements, and to what extent are the uptake and regeneration ratios dependent on physical, chemical, and biological conditions?

(2) Do anthropogenic modifications of the fluxes of elements such as Cd and Zn confound our ability to discern the natural ocean cycles for these elements?

(3) How well do we need to understand the oceanic cycles of elements such as Cd, Zn, and Ba in order to use them as paleoceanographic tracers?

(4) What is the contribution of sources such as sediments and hydrothermal vents to the cycle of micronutrients and to what extent is Fe released from continental margin sediments exported to the open ocean?

(5) In order to improve the representation of the Fe cycle in biogeochemical models:

- What processes control the deep water concentration of dissolved Fe or what is the respective importance of interaction of ligands versus coagulation?
- What role does coagulation play in the Fe cycle and how can the process be parameterized?
- Is there an iron limitation of heterotrophic production and how do elemental ratios change along the food chain?
- What are we using in the model and what are the appropriate field measurements? Can we better parameterize bFe and dFe in our models such that the modeled dFe better reflects measured dFe, without overestimating bFe?

(6) Specific input needed by modellers side:

- Extension of the data base: observations should include the speciation of micronutrients between different phases.
- Process studies targeting the kinetics of coagulation, dissolved iron ligand interactions, the stability of ligands.
- Measurements of elemental ratios along the food chain, as well as in export fluxes.

## 2. Potential of TEIs as recorders of ocean productivity and nutrient/carbon fluxes (N. Gruber)

The session on TEI of ocean productivity and nutrient cycling started with a presentation by Danny Sigman, who investigated how measurements of  $\delta^{15}\text{N}$  of  $\text{NO}_3$  can constrain rates and the distribution of marine  $\text{N}_2$ -fixation. On the basis of data obtained from a meridional transect south of the Bermuda Atlantic Time-series Station (BATS), he showed that a significant amount of the nitrate present in the thermocline of this region stems from "recently" fixed nitrogen (up to 50%). In order to convert this concentration into a fixation rate, he used results from an ocean general circulation model that permitted him to estimate how much  $\text{N}_2$ -fixation must occur in order to explain the vertical distribution of "recently" fixed N. It turns out that an areally integrated rate of  $28 \text{ Tg N yr}^{-1}$ , as estimated by Gruber and Sarmiento (1997) for the North Atlantic, would yield too much "recently" fixed nitrate, suggesting that that estimate is too high.

Christina deLaRocha followed by discussing how the isotopes of silicon can help to assess dissolved silicon (DSi) utilization by diatoms in the past. When diatoms take up DSi, they tend to fractionate with a mean value of about -1 to -1.5 per mil. When silicic acid is not used up entirely, the magnitude of DSi utilization (i.e. the ratio between supply and uptake) is directly related to the  $\delta^{30}\text{Si}$  of silicic acid, which can be reconstructed from the  $\delta^{30}\text{Si}$  of the Si in sedimentary opal. This approach is aided by the fact that the deep ocean distribution of  $\delta^{30}\text{Si}$  is relatively uniform (about 1 permil), so that the initial  $\delta^{30}\text{Si}$  value of the upwelled DSi should be generally known. However, there are many open issues that make past reconstructions challenging. Of particular concern are changes in the global mean value of  $\delta^{30}\text{Si}$  due to changes, for example, in the magnitude and  $\delta^{30}\text{Si}$  of river-derived DSi, or in the distribution of where Si is buried on the seafloor. In addition, local-to-regional scale variability in the  $\delta^{30}\text{Si}$  value of the upwelled DSi is not well known, yet needs to be taken into account. So far, only limited modeling has been undertaken (Wischmeyer et al., 2003; De La Rocha and Bickle, 2005) to assess the impact of such variations on paleoceanographic reconstructions of nutrient utilization (and, by extension, the strength of the biological pump) from  $\delta^{30}\text{Si}$ .

Andy Ridgwell presented a model that is optimally suited for undertaking fast computations, permitting extensive model parameter studies or long temporal integrations. This model, dubbed Genie, has already been used for the modeling of many TEIs, including Protactinium and Thorium ( $^{231}\text{Pa}/^{230}\text{Th}$ ) (e.g. based on the work of Siddall et al., 2006). The model has also been set up to assimilate observations, and is therefore well equipped to play a major role in the interpretations of the TEI measurements from the GEOTRACES program. The fast computations also come with a caveat in that the model's physical resolution is limited, so that many local and regional processes are not well resolved.

The isotopic pair Protactinium and Thorium was elaborated in more depth by Gideon Henderson, who showed the potential and limitations of this tracer to study past changes in the ocean's meridional overturning. In particular, he showed how the interpretation of this isotopic pair critically depends on the assumptions made about scavenging.

Finally, Yasuhiro Yamanaka showed first results from the modeling of the  $\delta^{15}\text{N}$  dynamics in the Sea of Okhotsk in comparison to recent observations. In particular, he was trying to understand why the  $^{15}\text{N}$  of POC increased in winter.

The ensuing discussion focused primarily on the question how models can help to define the optimal sampling strategy for GEOTRACES. In particular, it was debated whether models can be used to assess the spatio-temporal variability that one has to expect for different TEIs, and hence determine how often and when they should be sampled. The general consensus that emerged from the discussion is that this is generally not (yet) possible. The main reason is that our understanding of the processes that control the majority of TEIs is insufficient so that the model representation of these TEIs are currently useful for testing different hypotheses, but insufficient to be used for determining an optimal sampling scheme. The modeler's perspective was that GEOTRACES should really be viewed as an exploratory program for many TEIs and that it is very important to obtain a first global-scale view of the distribution of these tracers, from which much process information can be gleaned. Once such a first snapshot has been obtained and a better process understanding developed, models will have the ability to assist in devising optimal sampling strategies. Overall, the modelers felt very positive about the fruitful dialogue between the observational and modeling communities and encouraged the GEOTRACES SSC to continue this dialogue throughout the programme.

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### 3. Paleo-proxy development – separating the effects of circulation and particle dynamics (B. Anderson)

Various TEIs have been exploited to improve our understanding of ocean circulation, both in the modern ocean and through reconstruction of past conditions using paleo-proxies. The focus in this session was primarily on tracers of meridional overturning circulation (MOC), although the exchange of dissolved TEIs with continental margin sediments was also emphasized. Presentations and discussion during this session highlighted recent advances in this field, while also illuminating current challenges for both conceptual models and numerical models currently in use.

#### Overturning circulation of the Modern Ocean ( $^{230}\text{Th}$ )

First-order features of the distributions of certain TEIs are thought to be influenced by the MOC, so efforts are underway to model TEI distributions to provide quantitative constraints for the rate of overturning circulation. For example, in the modern ocean, concentrations of dissolved  $^{230}\text{Th}$  tend to increase with depth, reflecting the combined effects of uniform production throughout the water column by radioactive decay of dissolved  $^{234}\text{U}$  together with removal by reversible scavenging to sinking particles. In an ideal system where only these two processes are active, concentration profiles of dissolved  $^{230}\text{Th}$  are expected to increase linearly with depth. In many places, especially in the Pacific Ocean, observations agree with this expectation, at least to a first approximation. However, in recently ventilated deep waters of the North Atlantic Ocean, concentration profiles of dissolved  $^{230}\text{Th}$  increase linearly with depth only in the upper 1 to 2 km of the water column, below which the concentration of dissolved  $^{230}\text{Th}$  falls below that expected from the one-dimensional reversible scavenging model. Reduced concentrations of dissolved  $^{230}\text{Th}$  in deep waters are thought to reflect the recent incorporation of low- $^{230}\text{Th}$  surface waters during deepwater formation; that is during the initial phase of MOC.

Olivier Marchal described the application of an inverse model to observed  $^{230}\text{Th}$  distributions in the North Atlantic Ocean. When  $^{230}\text{Th}$  distributions are included in the model, the result is an increase in the estimated rate of MOC compared to a model that used salinity and temperature alone. Several simplifying assumptions are inherent in modeling  $^{230}\text{Th}$  this way, including assumptions about the uniformity of scavenging with depth, space and time. In addition, the model treats scavenging as an equilibrium process with very rapid kinetics. Other modeling efforts, described below, raised questions about this assumption, so an investigation of scavenging kinetics is recommended to be a part of the GEOTRACES effort.

Finally, the departure of dissolved  $^{230}\text{Th}$  concentration profiles from the expected linear trend could reflect enhanced scavenging of dissolved  $^{230}\text{Th}$  at the seabed. The strongest argument against this artifact is that similar features are not seen in most  $^{230}\text{Th}$  profiles from the Pacific Ocean. If bottom boundary scavenging were significant, then it would be expected to be as important in the Pacific as in the Atlantic Ocean. Unfortunately, most  $^{230}\text{Th}$  profiles from the Pacific Ocean either do not have good depth resolution near the bottom, or were obtained using unfiltered water samples (i.e., concentrations may be elevated due to the presence of high particle concentrations associated with near-bottom nepheloid layers). Thus, in addition to further work on spatial and temporal variability of scavenging kinetics, further work is needed to quantify source and sink terms at the seabed.

Overturning circulation of the ocean in the past ( $^{231}\text{Pa}/^{230}\text{Th}$ )

Like  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$  is produced uniformly throughout the ocean by radioactive decay of dissolved uranium ( $^{235}\text{U}$  in this case) at a constant initial  $^{231}\text{Pa}/^{230}\text{Th}$  activity ratio of 0.093. Like  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$  is also removed from seawater by scavenging onto sinking particles. However, scavenging of Pa is less intense than for Th, as reflected in the dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  activity ratios that generally fall in the range of 0.3 to 1.0. That is, the residence time of dissolved Pa in the ocean is much greater than for Th, and this allows for differential transport of the two tracers by MOC. The greatest potential effect occurs in the deep North Atlantic Ocean, where a survey of  $^{231}\text{Pa}/^{230}\text{Th}$  ratios in surface sediments led to the hypothesis that as much as half of the dissolved  $^{231}\text{Pa}$  produced in the North Atlantic water column is lost by advection to the South Atlantic and Southern oceans, rather than to local sediments by scavenging.

This principle has been invoked to explain down-core variability of  $^{231}\text{Pa}/^{230}\text{Th}$  ratios in North Atlantic sediments. For example, at sites where modern sediments have  $^{231}\text{Pa}/^{230}\text{Th}$  ratios of approximately 0.05 – 0.06, one finds much larger ratios (close to the production ratio) during times of extreme cold climate (Heinrich Events) during the last glacial period. This has been interpreted to indicate that Atlantic MOC came nearly to a stop during Heinrich events. Many modeling studies have investigated the response of Atlantic MOC to changes in freshwater flux to regions of deepwater formation, and the implications for climate change. More recently, models have been used to explore the sensitivity of sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios to variability of Atlantic MOC.

Perhaps the most serious factor complicating the use of sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios as a paleo-proxy for MOC is the very different affinities that Th and Pa have for adsorption to particles of different composition. Gideon Henderson reviewed historical data showing that particulate  $^{231}\text{Pa}/^{230}\text{Th}$  ratios or, more correctly, the fractionation of  $^{231}\text{Pa}$  from  $^{230}\text{Th}$  during scavenging by particles, is strongly dependent of particle composition. Here, the greatest effect is caused by the strong affinity of dissolved Pa for adsorption to amorphous silica (diatom tests, or biogenic opal, in this case). Therefore, it is becoming increasingly clear that down-core records of variability in  $^{231}\text{Pa}/^{230}\text{Th}$  can reflect changes in the diatom productivity as well as changes in MOC.

While potential artifacts associated with variable diatom productivity have been recognized for some time, Henderson also described two new problems that will complicate the use of sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios as a proxy for MOC. First, he used the layered water mass structure of the South Atlantic Ocean to show that sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios reflect changes in dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratios only within a layer about one km above bottom, rather than providing a measure of the integrated dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratio of the entire deep water column, as previously thought. This was illustrated using cores collected at different water depths on the margin of South America. The South Atlantic Ocean contains layers of water masses alternating between northern and southern origins. These water masses have distinctly different dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratios. Henderson found that sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios reflect the dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratio of the water immediately overlying the bottom (i.e., a layer a few hundred meters thick, although the exact thickness is not well constrained) rather than the integrated ratio for the entire deep water column. Thus, the rise in sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios seen in North Atlantic sediments during periods of extreme cold could reflect the intrusion of a thin layer of southern-source bottom water, carrying a high dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratio, rather than the shutdown of Atlantic MOC.

Henderson's second point is that dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratios reflect the history of a water mass as well as the local conditions at the study site. This was illustrated by measuring dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratios in the southern Indian Ocean, at a site where Antarctic Bottom Water (AABW) had recently emerged from a region of high diatom productivity in the Southern Ocean. In the southern Indian Ocean, low dissolved  $^{231}\text{Pa}/^{230}\text{Th}$  ratios of AABW are a relict of intense scavenging of dissolved Pa at an earlier time, when the water mass was passing under a region of intense diatom productivity.

Sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios clearly exhibit pronounced changes that are correlated with independent evidence for contemporary climate change. While these records may contain information about changes in MOC, there is growing evidence that variability of particle composition (especially that associated with diatom productivity) and other factors affect these records as well. A challenge for GEOTRACES is to determine whether or not models may still be successful in extracting meaningful information about past changes in MOC from records of sedimentary  $^{231}\text{Pa}/^{230}\text{Th}$  ratios if sufficient information can be gained through studies of the modern ocean to constrain fractionation factors, and their sensitivity to changes in particle composition.

Dissolved Nd isotopes: A proxy for MOC or for exchange with sediments?

The stable isotopic composition of dissolved Nd exhibits patterns of spatial variability that are governed by the age of rocks in the continental terrains surrounding each ocean basin. Consequently, dissolved Nd in deep waters of the North Pacific Ocean has a radiogenic isotopic composition, reflecting young volcanic rocks throughout the North Pacific rim. At the other extreme, dissolved Nd in deep waters of the North Atlantic Ocean has a non-radiogenic isotopic composition, reflecting old crustal ages of the surrounding terrain. Throughout much of the rest of the deep ocean, dissolved Nd has an isotopic composition that seems to reflect a mixture of the North Pacific and North Atlantic end members. This has led to the suggestion that the isotopic composition of Nd extracted from authigenic phases (i.e., formed from seawater) in sediments might be used to reconstruct past changes in the mixing ratio of water masses from different sources.

A down-core record of the isotopic composition of authigenic Nd recovered from South Atlantic sediments exhibits abrupt changes throughout the last glacial cycle that are correlated with independent measures of climate variability. This record has been interpreted to reflect climate-related changes in Atlantic MOC and its supply of non-radiogenic Nd to the South Atlantic water column, assuming that the isotopic composition of dissolved Nd serves as a conservative proxy of the mixing ratio of deep waters of North Atlantic and North Pacific Ocean. However, Thomas Arsouze summarized recent work showing that the global distributions of dissolved Nd concentration and of the isotopic composition of dissolved Nd cannot be reconciled if it is assumed that surface supply (rivers and dust) is the only significant source of dissolved Nd, and that this supply is balanced by scavenging and removal on sinking particles. Instead, it is necessary to invoke exchange of Nd between seawater and sediments at ocean margins to satisfy mass balance constraints for both total dissolved Nd and for its isotopic composition. While exchange with ocean margin sediments presents problems for the use of authigenic Nd isotopes as a proxy for ocean circulation, it opens the possibility for evaluating sources and sinks of other TEIs via exchange with ocean margin sediments. If future studies confirm the importance of boundary exchange, then Nd may become uniquely valuable as a tracer to help constrain the role of this process in the internal cycling of a wide range of TEIs.

This situation has stimulated an ongoing effort, involving both modeling and observations, to characterize the sources, sinks and internal cycling of Nd, including its exchange with ocean margin sediments. Experiments using models of intermediate complexity, with an assumption of equilibrium scavenging processes as the main removal mechanism (as for Th and Pa, see above), are starting to reproduce the global distribution of the isotopic composition of dissolved Nd. Arsouze illustrated this with results from the PISCES biogeochemical model coupled with the ORCA circulation model. However, he also noted that when the best estimate for the partition coefficient for Nd (i.e., ratio of particulate to dissolved Nd at chemical equilibrium) is included in the model, concentrations of dissolved Nd tend to be less than those observed, while concentrations of particulate Nd tend to be greater. The fit to observations by modeled distributions of dissolved Nd can be improved by tuning the scavenging parameters as well as the exchange with margin sediments. However, as pointed out by Andreas Oschlies during the discussion following Arsouze's talk, the system is then underdetermined, with so many potential sources and sinks that it is difficult to constrain any of them.

Akira Oka has also modeled the global distribution of rare earth elements (Nd and its neighbors in the periodic table) by including an equilibrium scavenging removal process in a GCM. In particular, he is investigating the sensitivity of Nd concentrations, and the shape of Nd concentration profiles, to variability in the partition coefficient for scavenging and removal. When parameters are tuned to reproduce observed Nd profiles in the Pacific Ocean, modeled concentrations of dissolved Nd in the Atlantic Ocean are too low, suggesting that a substantial unknown North Atlantic source of Nd may be required.

Jean-Claude Dutay used the coupled PISCES-ORCA model to simulate the behavior of dissolved and particulate  $^{231}\text{Pa}$  and  $^{230}\text{Th}$ . Using initial values for partition coefficients consistent with those reported in the literature, the model produced a global distribution of particulate  $^{231}\text{Pa}/^{230}\text{Th}$  ratios that is generally consistent with the global pattern observed in surface sediments. However, modeled concentrations of dissolved  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  are greater than those observed, while modeled concentrations of particulate  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  are much less. Gideon Henderson pointed out that other models exhibit similar biases (modeled concentrations of dissolved  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  exceed those observed) and this led to a general discussion of potential sources of this bias.

A number of potential problems with the current generation of models were identified. For example, scavenging may involve slow kinetics rather than the instantaneous equilibrium that is conventionally assumed. It is also possible that particle dynamics, such as aggregation and disaggregation, are more important than believed. Or, partition coefficients may be substantially different for large rapidly sinking particles, which carry most of the downward flux of particle mass, compared to small slowly sinking particles, which represent the bulk of the standing stock of particulate material in the ocean. An additional potential source of error is the assumption that atmospheric transport is the only significant source of lithogenic particles. This assumption is common to most models used to simulate TEI behavior, and the consequences of neglecting sources of lithogenic material at ocean margins should be investigated.

Parameterization of scavenging and removal is similar among the models discussed during this session, in that all involve the assumption of equilibrium adsorption (i.e., rapid scavenging kinetics). Further work to explore the implications of this assumption is warranted. In this context, however, it is interesting to note that using a common suite of parameters for scavenging and particle dynamics, the PISCES-ORCA model produces dissolved Nd

concentrations that are too low and dissolved  $^{230}\text{Th}$  concentrations that are too large, suggesting that some other factor may be missing from the models as well.

One of the founding principles of GEOTRACES is that one can learn more by studying a suite of TEIs together than from many studies of a single TEI in isolation. That principle applies here as well as anywhere in the realm of GEOTRACES. For example,  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  are removed by scavenging processes, as is Nd, while the distributions of all three tracers are influenced by the same ocean transport processes. Therefore, while a system may be underdetermined for a single tracer, modeling a suite of tracers where certain sources are known (e.g.,  $^{231}\text{Pa}$  and  $^{230}\text{Th}$ ) and certain processes affect all tracers equally (e.g., circulation) may lead to improved constraints for parameters of interest.

### Summary of Recommendations

1) Further work is needed to test assumptions in the current generation of models concerning particle dynamics and scavenging processes. This includes the need for more data about the size distribution of particles, sinking rates as a function of size, and the sensitivity of partition coefficients to variability of particle size, sinking rate, and composition. These parameters should be investigated during the GEOTRACES field program. Meanwhile, these sensitivities should be explored in future model experiments.

2) Simultaneous modeling of multiple TEIs can exploit the fact that certain TEIs have known sources, while many TEIs are influenced by common transport and removal processes. Therefore, estimates of surface sources and boundary exchange may be improved by modeling multiple TEIs. In addition to  $^{231}\text{Pa}$ ,  $^{230}\text{Th}$  and Nd discussed here, one could consider  $^{210}\text{Pb}$ ,  $^{10}\text{Be}$ , and non-radioactive TEIs whose distributions are not dominated by biological uptake (e.g., Al, Mn).

3) If the failure of the intermediate complexity models to reproduce observed concentrations of dissolved TEIs results from an invalid assumption about equilibrium scavenging, then this has implications for the approach of Marchal, as well, because he assumes rapid kinetics and equilibrium scavenging in his use of  $^{230}\text{Th}$  distributions to constrain Atlantic MOC. Future modeling of present-day MOC should consider the implications of slow scavenging kinetics and other factors mentioned above.

4) As the community continues to develop models for ocean biogeochemical cycles of particle-reactive TEIs, it would be useful to have a set of diagnostics of model performance that is agreed to by people working on this problem. Developing a common set of model diagnostics could be a topic covered in a future GEOTRACES modeling workshop.

#### **4. Data assimilation in the GEOTRACES context (O. Marchal)**

##### 1) Should we use models to guide sampling strategy for GEOTRACES?

The presentation at the workshop that provided the most direct example of the application of a model to design a sampling network was by Thomas Kaminski. In short, Thomas illustrated how different networks of stations of CO<sub>2</sub> measurements in the atmosphere can impact the uncertainty in estimates in CO<sub>2</sub> uptake. He also showed how varying uncertainties in these measurements can alter the uptake estimates.

Whereas the approach has clear benefits, it was also recognized that it assumes that the velocity (and diffusivity) field being employed to carry the tracer of interest (CO<sub>2</sub> in this case) is accurate enough for the purpose of sampling design. Whether ocean circulation models - be they forward or inverse (data-constrained) - have reached the point where they can effectively be used for a similar purpose is unclear.

What also makes it unclear whether models can be used to guide GEOTRACES sampling is that most of the tracers that are targeted by this program are poorly understood, that is both their spatial distribution and their behavior are poorly known (this state of affairs is actually a major motive of the program). Overall, it was felt that the current understanding in the distribution and behavior of the GEOTRACES tracers do not support the approach consisting in using models (forward or inverse) to guide the sampling in the frame of this program (the situation is very different than the much better constrained CO<sub>2</sub> problem illustrated by Thomas Kaminski).

##### 2) Should we use current knowledge about the ocean circulation in a more systematic and explicit way to guide GEOTRACES sampling?

During the meeting, a slide was presented that illustrates a tentative set of large-scale GEOTRACES transects in the Pacific basin. One of these lines was located right at the equator. This particular choice was at least partly motivated by the existence of the subsurface eastward flowing equatorial current. This line provides a striking example that knowledge about the ocean circulation is actually being employed to guide GEOTRACES sampling. What was less clear, however, is whether use of the current knowledge about the ocean circulation is systematic and explicit enough for guiding GEOTRACES sampling. An example of an ocean circulation estimate based on the quantitative combination of a numerical model and a variety of data was presented by Patrick Heimbach (ECCO program). Although this particular effort aims at providing a time-dependent estimate of the ocean circulation, the products of this analysis could be used to establish a climatology of the ocean circulation at the global scale. Participants discussed whether such a climatology could be used to help construct the network of stations visited during GEOTRACES.

##### 3) Should we use existing, relatively well-documented chemical tracer distributions to guide GEOTRACES sampling?

The idea was discussed, of using the distributions of relatively well-sampled chemical tracers to locate regions of strong chemical gradients in the ocean and hence to identify key sampling sites for GEOTRACES. One obvious example is provided by the distribution of dissolved

oxygen, which would allow one to identify regions with low subsurface O<sub>2</sub> concentrations and hence locations where redox-sensitive elements targeted by GEOTRACES could be sampled. It is likely that the information provided by the distributions of well-sampled chemical constituents is already being used to recommend sampling locations for GEOTRACES. But again, what was less clear is whether use of such distributions is systematic and explicit enough. One interesting problem was posed by one of the participants (Chris Measures): "Given knowledge about the horizontal gradients of [O<sub>2</sub>] in a given oceanic area, at which frequency (i.e., horizontal spacing between adjacent stations) should we sample a redox-sensitive tracer?" For example, should one opt for a constant spacing or for a variable spacing between stations? It is likely that the answer depends on the question being posed.

4) Should we opt for a "regular" station distribution (e.g., the WOCE model, with perpendicular transects) or an "irregular" station distribution (e.g., the TTO model, with zigzags)?

The case was made by one of the participants (Nicolas Gruber) that estimates of chemical inventories (in his case, inventory of anthropogenic CO<sub>2</sub>) may suffer from large uncertainties if they are based on a regular network of stations. That is, the estimation of the inventory of a chemical constituent within an oceanic volume may be delicate if no data are available within the volume but only at its lateral boundaries (consider, as an example, the problem of estimating a chemical inventory in a volume bounded by 2 zonal transects and 2 meridional transects). If one of the aim of GEOTRACES is to estimate chemical inventories, this consideration may need to be given due attention. One potential difficulty is that the station arrangement that would lead to precise inventory estimates (e.g., a relatively random distribution of stations) may not be the same as the station arrangement that would lead to precise flux estimates.

5) What should be the vertical sampling extent and frequency?

Whereas much of the discussion was about geographical coverage, much less has been said about whether one should sample tracers from the surface down to the seafloor and about the vertical spacing between samples. The issue of vertical sampling was partly motivated by data shown by one of the participants (Robert Anderson), which suggested that processes near the seafloor may influence the concentration of a chemical constituent way up in the water column. Several participants discussed whether models have the appropriate vertical resolution to address some of the biogeochemical processes targeted by GEOTRACES, in particular near the seafloor. In general, ocean circulation models have relatively high vertical resolution in the main pycnocline and lower resolution below. The coarse vertical resolution near the seafloor may not be adequate to study some of the processes targeted by GEOTRACES. It was considered, however, that the vertical grid of models could be accommodated to improve the representation of processes near the bottom. On the other hand, it was also mentioned that physical phenomena near the bottom (i.e., friction) are generally poorly represented in ocean circulation models.

## **5. Data and model resources for GEOTRACES (A. Oschlies)**

Data-related aspects discussed during this session included strategies for data availability and distribution (C. Measures, I. Robinson), and the use of a data assembly centre with a perspective of serving not only real data but also model output (C. Chandler). The model-related part of the session began with a presentation of a number of modelling tools available for GEOTRACES, ranging from fast Earth system models of intermediate complexity (A. Ridgwell) to eddy-resolving regional models (N. Gruber), and including computationally efficient off-line methods for passive tracer transport (S. Khatiwala), as well as global ocean syntheses of dynamically consistent hydrographic and transport fields (D. Stammer). While one goal of using high-resolution models is to represent the small-scale variability in tracer distributions and tracer gradients in a realistic manner and thereby make model-data comparison more straightforward, a second goal of such studies is to develop parameterisations of small-scale processes that cannot be included in coarser-resolution climate models (A. Oschlies). Initial attempts to estimate lateral mixing coefficients from high-resolution model results indicated, however, that different tracers may require different mixing coefficients when standard mixing parameterizations are employed.

## **Workshop Programme**

### **Thursday, September 6**

#### **1. Cycling of micronutrients – processes, transports, sources and sinks**

Chair: Marion Gehlen (LSCE)

09:00 – 09:15 Welcome, logistics, workshop objectives

09:15 – 10:00 Keynote 1: Ed Boyle (MIT)

[Cycling of Trace Micronutrients \(e.g., Fe, Zn, Cd\) in the Ocean: What We Know and What We Need to Know.](#)

10:00 – 10:45 Keynote 2: Olivier Aumont (IFREMER)

[Modelling micronutrients in the ocean: The case of Iron.](#)

10:45 – 11:15 Coffee Break

11:15 – 13:00 Discussion and short presentations

13:00 – 14:15 Lunch

#### **2. Potential of TEIs as recorders of ocean productivity and nutrient/carbon fluxes**

Chair: Nicolas Gruber (ETH)

14:15 – 14:45 Keynote 1: Danny Sigman (Princeton U)

[Nitrate isotopes as a constraint on the ocean's fixed N budget.](#)

14:45 – 15:15 Keynote 2: Christina de la Rocha (AWI)

[Understanding the distribution and behaviour of Si isotopes in the ocean](#)

15:15 – 15:45 Keynote 3: Andy Ridgwell (U Bristol)

[What can we learn by assimilating geochemical ocean data in computer models?](#)

15:45 – 16:15 Coffee Break

16:15 – 18:00 Discussion and short presentations

18:00 – 19:30 Dinner

19:30 – 21:00 Poster Session

## **Friday, September 7**

### **3. Paleo proxy development – separating the effects of circulation and particle dynamics**

Chair: Bob Anderson (LDEO)

09:00 – 09:40 Keynote 1: Gideon Henderson (Oxford U)

[The  \$^{231}\text{Pa}/^{230}\text{Th}\$  paleoproxy: How should we interpret the growing observational dataset?](#)

09:40 – 10:05 Keynote 2: Olivier Marchal (WHOI)

[An inverse method to combine radiochemical measurements and a circulation model: Application to the North Atlantic.](#)

10:05 – 10:30 Keynote 3: Thomas Arsouze (LSCE)

[Modelling the Nd cycle with a global circulation model.](#)

10:30 – 11:00 Coffee Break

11:00 – 12:45 Discussion and short presentations

12:45 – 14:15 Lunch

### **4. Data assimilation in the GEOTRACES context**

Chair: Olivier Marchal (WHOI)

14:15 – 15:00 Keynote 1: Patrick Heimbach (MIT)

The ECCO state estimation framework and its potential for GEOTRACES

15:00 – 15:45 Keynote 2: Thomas Kaminski (FastOpt, Hamburg)

[Quantitative design of observational networks](#)

15:45 – 16:15 Coffee Break

16:15 – 18:00 Discussion and short presentations

18:00 – 19:30 Dinner

19:30 – 21:00 Poster Session

## **Saturday, September 8**

### **5. Data and model resources for GEOTRACES**

Chair: Andreas Oschlies (IfM-GEOMAR)

#### **Data**

08:30 – 09:10 Chris Measures (U Hawaii)

Initial sampling plans for GEOTRACES in the Pacific and strategies for data availability and distribution within the GEOTRACES program.

09:10 – 09:40 Ian Robinson (NOC Southampton)

[Satellite data for GEOTRACES - Availability, potential and limitations.](#)

09:40 – 10:00 Cindy Chandler (WHOI)

[An Introduction to the Biological and Chemical Oceanography Data Management Office](#)

10:00 – 10:30 Coffee Break

#### **Models I**

10:30 – 10:50 Ernst Maier-Reimer (MPI Hamburg)

[Tracer simulations with HAMOCC and LSGor MPIOM](#)

10:50 – 11:10 Jean-Claude Dutay (LSCE)

Tracer simulations with PISCES and OPA/ORCA

11:10 – 11:35 Hiroyasu Hasumi (U Tokyo)

[An overview of global scale ocean modelling from low to high resolution](#)

11:35 – 12:00 Samar Khatiwala (LDEO)

Fast offline forward and adjoint modeling of ocean biogeochemical and paleoceanographic tracers using the transport matrix method

12:00 – 12:30 Detlef Stammer (IfM Hamburg)

[Global ocean syntheses in support of physical and bio-geochemical studies](#)

12:30 – 13:45 Lunch

#### **Models II**

13:45 – 14:10 Andy Ridgwell (U Bristol)

[Fast models of intermediate complexity as an analytical tool for GEOTRACES scientists](#)

14:10 – 14:30 Andreas Oschlies (IfM-GEOMAR)

[Regional high resolution models and why we need them within the GEOTRACES program](#)

14:30 – 15:00 Final discussion

15:00 End of workshop

## Workshop Participants

<p>Jess <i>Adkins</i>  California Institute of Technology  Division of Geological and Planetary  Sciences  MS-100-23  1200 E. California Blvd.  Pasadena, CA 91125, USA  Phone: +1 626 395-8550  E-mail: jess@gps.caltech.edu</p>	<p>Robert <i>Anderson</i>  Lamont-Doherty Earth Observatory  P.O. Box 1000  Palisades, NY 10964, USA  Phone: +1 845-365-8508  E-mail: boba@ldeo.columbia.edu</p>
<p>Thomas <i>Arsouze</i>  LSCE/CEA  Bat 712  Orme des merisiers  91191 Gif sur Yvette cedex, FRANCE  Phone: +33 5 61-33-30-03  E-mail: arsouze@cea.fr</p>	<p>Olivier <i>Aumont</i>  Centre IRD de Bretagne  BP 70  29280 Plouzané, FRANCE  Phone: +33 2 98-22-45-06  E-mail: olivier.aumont@ird.fr</p>
<p>Wolfgang <i>Barkmann</i>  University of Bremen  FB 2 - Meereschemie  Postfach 33 04 40  28334 Bremen, GERMANY  Phone:  E-mail: barkmann@uni-bremen.de</p>	<p>Ed <i>Boyle</i>  MIT  Department of Earth, Atmospheric, and  Planetary Sciences  E34-258, 77 Massachusetts Ave.  Cambridge, MA 02139, USA  Phone: +1 617 253-3388  E-mail: eaboyle@mit.edu</p>
<p>Cynthia <i>Chandler</i>  Woods Hole Oceanographic Institution  MS #43  Woods Hole, MA 02543, USA  Phone: +1 508 289-2765  E-mail: cchandler@whoi.edu</p>	<p>Giuseppe <i>Cortese</i>  Alfred Wegener Institute for Polar and Marine  Research  Am alten Hafen 26  27568 Bremerhaven, GERMANY  Phone: +49 (0)471 4831-1207  E-mail: giuseppe.cortese@awi.de</p>
<p>Peter <i>Croot</i>  IfM-Geomar  Marine Biogeochemie  Düsternbrooker Weg 20  24105 Kiel, GERMANY  Phone: +49 (0)431 600-4207  E-mail: pcroot@ifm-geomar.de</p>	<p>Christina <i>De La Rocha</i>  Alfred Wegener Institute for Polar and Marine  Research  Columbusstraße  27568 Bremerhaven, GERMANY  Phone: +49 (0)471 4831-1040  E-mail: christina.de.la.rocha@awi.de</p>

<p>Jean-Claude <b>Dutay</b>  LSCE - CEA Saclay  Orme des merisiers  91191 Gif sur Yvette, FRANCE  Phone: +33 1 69 08 31 12  E-mail: dutay@cea.fr</p>	<p>Russ <b>Flegal</b>  University of California, Santa Cruz  Environmental Toxicology  Santa Cruz, CA 95064, USA  Phone: +1 831 459-2093  E-mail: flegal@etox.ucsc.edu</p>
<p>Marion <b>Gehlen</b>  LSCE UMR CEA-CNRS-UVSQ CEN de  Saclay  L'Orme des Merisiers  Bât. 712  91191 Gif-sur-Yvette Cedex, FRANCE  Phone: +33 1 69 08 86 72  E-mail: marion.gehlen@cea.fr</p>	<p>Xavier <b>Giraud</b>  University of Bremen  Research Center Ocean Margins  P.O. Box 33 40 40  28334 Bremen, GERMANY  Phone: +49 (0)421 218-7187  E-mail: xgiraud@palmod.uni-bremen.de</p>
<p>Nicolas <b>Gruber</b>  ETH Zürich  Institute of Biogeochemistry and Pollutant  Dynamics  Environmental Physics  Universitätsstrasse 16  892 Zürich, SWITZERLAND  Phone:  E-mail: nicolas.gruber@env.ethz.ch</p>	<p>Hiroyasu <b>Hasumi</b>  The University of Tokyo  Center for Climate System Research  5-1-5 Kashiwanoha, Kashiwa  Chiba 277-8568, JAPAN  Phone: +81 4 7136-4407  E-mail: hasumi@ccsr.u-tokyo.ac.jp</p>
<p>Patrick <b>Heimbach</b>  MIT  Department of Earth, Atmospheric, and  Planetary Sciences  Room 54-1518, 77 Massachusetts Ave.  Cambridge, MA 02139, USA  Phone: +1 617 253-5259  E-mail: heimbach@mit.edu</p>	<p>Gideon <b>Henderson</b>  University of Oxford  Department of Earth Sciences  Parks Road  Oxford, OX1 3PR, U. K.  Phone: +44 1865 282123  E-mail: gideonh@earth.ox.ac.uk</p>
<p>Bruce <b>Howe</b>  University of Washington  Applied Physics Laboratory  1013 NE 40th St.  Seattle, WA 98105-6698, USA  Phone: +1 206 543-9141  E-mail: howe@apl.washington.edu</p>	<p>William J. <b>Jenkins</b>  Woods Hole Oceanographic Institution  MS#25, 360 Woods Hole Road  Woods Hole, MA 02543, USA  Phone: +1 508 289-2554  E-mail: wjenkins@whoi.edu</p>

<p>Thomas <b>Kaminski</b> FastOpt Schanzenstraße 36 20357 Hamburg, GERMANY Phone: +49 (0)40 48096347 E-mail: thomas.kaminski@FastOpt.com</p>	<p>Michael <b>Karcher</b> Alfred Wegener Institute for Polar and Marine Research Bussetraße 24 27570 Bremerhaven, GERMANY Phone: +49 (0)471 4831-1826 E-mail: Michael.karcher@awi.de</p>
<p>Samar <b>Khatiwala</b> Lamont-Doherty Earth Observatory Oceanography 204 Palisades, NY 10964, USA Phone: +1 845 365-8454 E-mail: spk@ldeo.columbia.edu</p>	<p>Martin <b>Losch</b> Alfred-Wegener-Institute for Polar and Marine Research Bussestraße 24 27570 Bremerhaven, GERMANY Phone: +49 (0)471 4831-1872 E-mail: martin.losch@awi.de</p>
<p>Ernst <b>Maier-Reimer</b> Max Planck Institute for Meteorology Bundesstraße 53 20146 Hamburg, GERMANY Phone: +49 (0)40 41173-233 E-mail: ernst.maier-reimer@zmaw.de</p>	<p>Olivier <b>Marchal</b> Woods Hole Oceanographic Institution Department of Geology and Geophysics MS#23 Woods Hole, MA 02543, USA Phone: +1 508 289-3374 E-mail: omarchal@whoi.edu</p>
<p>Chris <b>Measures</b> University of Hawaii Department of Oceanography 1000 Pope Road Honolulu, HI 96822, USA Phone: +1 808 956 8693 E-mail: chrism@soest.hawaii.edu</p>	<p>Akira <b>Oka</b> University of Tokyo Center for Climate System Research 5-1-5 Kashiwanoha, Kashiwa Chiba 277-8568, JAPAN Phone: +81 4 7136-4397 E-mail: akira@ccsr.u-tokyo.ac.jp</p>
<p>James <b>Orr</b> Marine Environmental Laboratories 4, Quai Antonie 1er 98000 Monaco, MONACO Phone: +377 9797-7229 E-mail: j.orr@iaea.org</p>	<p>Andreas <b>Oschlies</b> IfM-Geomar Düsternbrooker Weg 20 24105 Kiel, GERMANY Phone: +49 (0)431 600-1936 E-mail: aoschlies@ifm-geomar.de</p>

<p>Payal <b>Parekh</b>  University of Bern  Climate and Environmental Physics  Sidlerstrasse 5  301 Bern, SWITZERLAND  Phone: +41 31 631 4467  E-mail: parekh@climate.unibe.ch</p>	<p>André <b>Paul</b>  University of Bremen  Geosciences  P.O. Box 33 04 40  28334 Bremen, GERMANY  Phone: +49 (0)421 218-7189  E-mail: apau@palmod.uni-bremen.de</p>
<p>Yves <b>Plancherel</b>  Princeton University  Department of Geosciences  Guyot Hall  Princeton, NJ 08544, USA  Phone: +1 609 258-4665, -1311  E-mail: Yves@splash.princeton.edu</p>	<p>Christa <b>Pohl</b>  Baltic Sea Research Institute Warnemünde  Seestraße 15  18119 Warnemünde, GERMANY  Phone: +49 (0)381 5197-321  E-mail: christa.pohl@io-warnemuende.de</p>
<p>Andy <b>Ridgwell</b>  University of Bristol  School of Geographical Sciences  University Road  Bristol BS8 1SS, U. K.  Phone: +44 117 954 6858  E-mail: andy@seao2.org</p>	<p>Ian S. <b>Robinson</b>  University of Southampton  School of Ocean and Earth Science  National Oceanography Centre  European Way  Southampton SO14 3ZH, U. K.  Phone: +44 23 8059-3438  E-mail: ian.s.robinson@noc.soton.ac.uk</p>
<p>Keith <b>Rodgers</b>  Princeton University  AOS Program  300 Forrester Road, Sayre Hall  Princeton, NJ 98544-0710, USA  Phone:  E-mail: krodgers@princeton.edu</p>	<p>Mak <b>Saito</b>  Woods Hole Oceanographic Institution  Marine Chemistry and Geochemistry  Department  Woods Hole, MA 02543, USA  Phone: +1 508 289-2393  E-mail: mak@whoi.edu</p>
<p>Reiner <b>Schlitzer</b>  Alfred Wegener Institute for Polar and Marine  Research  Columbusstraße  27568 Bremerhaven, GERMANY  Phone: +49 (0)471 4831-1559  E-mail: reiner.schlitzer@awi.de</p>	<p>Birgit <b>Schneider</b>  LSCE UMR CEA CNRS UVSQ CEN de Saclay  L'Orme des Merisiers  Bât. 712  91191 Gif sur Yvette, FRANCE  Phone: +33 1 69 08 38 26  E-mail: birgit.schneider@lsce.ipsl.fr</p>

<p>Joachim <b>Segsneider</b>  Max Planck Institute for Meteorology  Bundesstraße 53  20146 Hamburg, GERMANY  Phone: +49 (0)40 41173-196  E-mail: joachim.segsneider@zmaw.de</p>	<p>Daniel <b>Sigman</b>  Princeton University  Department of Geosciences  Guyot Hall  Princeton, NJ 08544, USA  Phone: +1 609 258-2194  E-mail: sigman@princeton.edu</p>
<p>Yvette H. <b>Spitz</b>  Oregon State University  College of Oceanic and Atmospheric Science  COAS Admin Bldg 104  Corvallis, OR 97331, USA  Phone: +1 541 737-3227  E-mail: yvette@coas.oregonstate.edu</p>	<p>Detlef <b>Stammer</b>  University of Hamburg  Institute of Oceanography  Bundesstraße 53  20146 Hamburg, GERMANY  Phone: +49 (0)40 42838 5052  E-mail: detlef.stammer@zmaw.de</p>
<p>Christoph <b>Völker</b>  Alfred Wegener Institute for Polar and Marine  Research  Am Handelshafen 12  27515 Bremerhaven, GERMANY  Phone: +49 (0)471 4831-1848  E-mail: christoph.voelker@awi.de</p>	<p>Dieter <b>Wolf-Gladrow</b>  Alfred Wegener Institute for Polar and Marine  Research  Am Handelshafen 12  27570 Bremerhaven, GERMANY  Phone: +40 (0)471 4831-1824  E-mail: dieter.wolf-gladrow@awi.de</p>
<p>Yasuhiro <b>Yamanaka</b>  Hokkaido University  Faculty of Environmental Earth Science  N10W5  Sapporo, 060-0810, JAPAN  Phone: +81 11 706-2363  E-mail: galapen@ees.hokudai.ac.jp</p>	<p>Jing <b>Zhang</b>  University of Toyama  Graduate School of Science and Engineering for  Science  3190 Gofuku  Toyama, 9308555, JAPAN  Phone: +81 76 4456665  E-mail: jzhang@sci.u-toyama.ac.jp</p>



