COST Action ES0801:
The ocean chemistry of bioactive trace elements and paleoclimate proxies

2nd GEOTRACES Data-Model Synergy Workshop

December 7-10, 2009

Ecole Normale supérieure
rue d'ULM, Paris
France

Workshop Report

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G Henderson, R Anderson, M Siddall, M Frank, T Arsouze, B landing, M Boye,
R Schlitzer, F Lacan, B Reynolds

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1) *Summary*

The GEOTRACES program has been launched to study the physical, chemical and biological processes that control the fate of trace elements in the ocean. These research goals are addressed by both observational and modelling activities. In 2007, a first data-model synergy workshop took place in Delmenhorst, Germany in order to foster the collaboration between observational and modelling communities. Considering the success of such meetings, it was decided to organize regularly these kind of meetings. The second Data model synergy workshop took place in Paris in December 2010, at the Ecole Normale Supérieure, rue d'ULM. Around sixty scientists have participated to the workshop with an equilibrated proportion between the two communities. The meeting has lasts four days, and organized with six sessions:

S1: Observation and modelling of particle concentration
S2: Observation and Modelling particle reactive tracers, Th and Pa
S3: Observation and Modelling particle reactive tracers – part 2 Nd isotopes and boundary exchange
S4: Cycling of micronutrients – The Fe cycle
S5: Inverse modelling
S6: Stable isotope modelling (N, C, Si, etc)

The schedule was planned to leave sufficient time for the discussion in each session. This report provides a brief summary of the presentations and the discussions. The fruitful discussions during the workshop have another time revealed the usefulness of these events for reinforcing links between the scientists involved in the GEOTRACES program. Moreover, selected invited speakers working on observation and modelling of particle concentration (session 1) provided the opportunity to create some closer links with people more specifically working on carbon cycle.

We acknowledge GEOTRACES program, European COST Action ES0801 and INSU France for funding the workshop.

2) Agenda

Monday 7, afternoon

13h30 : welcome (J-C Dutay)

13h35: introduction to the goals of the meeting and the GEOTRACES program (RF Anderson)

S1: Observation and modelling of particle concentration:
Chair: Christoph Heinze
Rapporteur: Francois Lacan

13h50 H. Loisel, N. Sohne, L. Duforet, D. Dessailly, L. Boop, and O. Aumont : Analyse of the temporal variability of the space retrieved particulate organic carbon over the global ocean.

14h10 Lars Stemmann; Particle transformation in the mesopelagic layers of the oceans. What can we learn by using imaging systems.

14h30 Kriest, I., Oschlies, A., Khatiwala, S.: Parameterisation of Remineralisation Length Scales in Large-scale Models of Marine Biogeochemistry

14h50 M. Shigemitsu, Yamanaka, Y., Watanabe, Y. W., Okada, N. Kriest, I., Oschlies, A., Maeda, N., Noriki, S. Seasonal characteristics of the carbon isotope biogeochemistry of settling particles in the western subarctic Pacific: a model study

15h10 Break

15h40 C Heinze, T Ilyina: The potential of radionuclides for detecting the impact of ocean acidification on marine particle fluxes

16h00 A Burke, O Marchal , L Bradtmiller, J McManus, R François : Application of an Inverse Method to Interpret ^{231}Pa/^{230}Th Observations from Marine Sediments

16h20 A Okubo, H Obata, T Gamo: ^{230}Th distributions in the Pacific Ocean: effect of bottom scavenging

16h40 Discussion

Tuesday 8, morning

S2: Observation and Modelling particle reactive tracers, Th and Pa

Chair: Bob Anderson

Rapporteur: Mark Siddall

9h00 R Anderson , M Fleisher: What can we learn from ^{231}Pa/^{230}Th ratios?

9h20 S. Tyldesley , M. Siddall, S Mueller , A Ridgwell : Co-response of Pa/Th and export production during freshwater experiments

9h40 Luo, R. Francois, S. Allen: Sediment ^{231}Pa/^{230}Th as a recorder of the rate of the Atlantic meridional overturning circulation: Insights from a 2-D model

10h00 M Roy Barman: Modelling the effect of boundary scavenging on Thorium and Protactinium profiles in the ocean

10h20 T. Arsouze, S. Khatiwala, R. F. Anderson : The importance of lithogenic particles for scavenging ^{231}Pa and ^{230}Th from the entire ocean

10h40 break

11h00 S. A. Müller , G. Henderson , M. Siddall, N. R. Edwards: 231Pa and 230Th in the GENIE Earth system model: Exploring the combined effect of changes in circulation and biological export production on sedimentary 231Pa/230Th ratios

11h20 S. Marchandise, M. Roy-Barman, E. Robin, S. Ayrault and C. Colin: Distribution and isotopic signature of Thorium and REE-bearing phases in marine sediments

11h40 A. Radic, F. Lacan and C. Jeandel: Iron isotopes in seawater: a new tracer for the oceanic iron cycle ?

12h00 Discussion

Tuesday 8, afternoon

S3: Observation and Modelling particle reactive tracers – part 2 Nd isotopes and boundary exchange

Chair: Martin Frank

Rapporteur: Thomas Arsouze

14h00 T Arsouze: an overview on Nd modelling

14h20 Jeandel C. Peucker-Ehrenbrink B. , Godderis Y. , Lacan F, Arsouze T: Impact of ocean margin processes on dissolved Si, Ca and Mg inputs to the ocean

14h40 O. Aumont, A. Tagliabue, L. Bopp, and T. Gorgues: Sediment mobilization: revisiting the iron hypothesis

15h00 Johannes Rempfer, Fortunat Joos and Thomas Stocker: Modelling the neodymium cycle using the Bern3d model

15h20 M. Grenier, C. Jeandel, F. Durand, F. Lacan : Original study of the Equatorial Pacific Ocean fertilization based on a lagrangian simulation of the circulation coupled to Nd isotopic composition and Rare Earth Element concentration data

15h40 break

16h00 F Lacan, M Labatut : Trace element concentrations of the suspended particles in the Southern Ocean (Bonus/GoodHope transect)

16h20 A Oka, H Hasumi, H Obata,T Gamo, Y Yamanaka: Simulation of rare earth elements (REEs) with an ocean general circulation model

16h40 Cogez et al: Limitations of Neodymium isotopes modelling with Global Circulation Models

17h00 Discussion

Wednesday 9, morning

S4: cycling of micronutrient – The Fe cycle
Chair: Bill Landing
Rapporteur: Marie Boye

9h30 J.-M. Lee, E.A. Boyle, R.F. Zhang, J. Fitzsimmons, T. Ito: Distribution of dissolved Fe and Cu in the Bermuda Time-Series Station and the Tropical North Atlantic Ocean.
9h50 F. Chever, E. Bucciarelli, G. Sarthou, S. Speich, M. Arhan, P. Penven, A. Tagliabue: Dissolved iron concentrations in the Atlantic sector of the Southern Ocean, along a transect from the subtropical domain to the Weddell Sea Gyre
10h10 M Boye: The organic complexation in modeling the oceanic iron cycling
10h30 break
10h50 E Boyle and W Jenkins: Hydrothermal Iron in the Deep Western South Pacific
11h10 A Tagliabue, L Bopp, J-C Dutay, A R. Bowie, F Chever, P Jean-Baptiste, E Bucciarelli, D Lannuzel, T Remenyi, G Sarthou, O Aumont, M Gehlen , C Jeandel: On the importance of hydrothermalism to the oceanic dissolved iron inventory
11h30 M Jin, C Deal,S Elliott, E Hunke et al: Modeling of the influences of sea ice cover and sea ice ecosystem on iron cycle

Wednesday 9: afternoon

S4: CONTINUED: cycling of micronutrient – The Fe cycle

14h00 T Gorgues, C Menkes, O Aumont, J Murray, L Slemons: The iron phases, a crucial factor for the biomass variability in the Pacific HNLC region?
14h20 W landing, C Measures: The Trace Metals Component of the CLIVAR/Repeat Hydrography (CO2) project
14h40 Celine Gallon, A. Russell Flegal: Silver in the North Pacific Ocean: potential as a tracer of anthropogenic inputs

S5: Inverse modelling and others
Chair: Reiner Schiltzer
Rapporteur : J-C Dutay

16h00 W. J. Jenkins and A.C. Naveira Garabato: Constraining the oceanic budgets and fluxes of primordial helium-3
16h20 P Jean-Baptiste, J-C Dutay, P Peylin : Constraint on oceanic hydrothermal ^{3}He from inverse modeling.
16h00 Break
16h20 discussion

Thursday 10: morning

S6: Stable isotope modelling (N, C, Si, etc)

Chair: Gideon Henderson
Rapporteur : Ben Reynolds

9h00 B C. Reynolds, B Bourdon: Understanding the global marine □^{30}Si distribution

9h20 G F. de Souza, B C. Reynolds, J F. Rudge, B Bourdon : Modelling nutrient-type cycling and mass-dependent isotope fractionation using a simple 1D model: Silicon as an example

9h40 C Somes and A Schmittner: Modeling the Global Distribution of Nitrogen Isotopes in the Ocean

10h00 A de Brauwere, F Fripiat, A-J Cavagna, D Cardinal, M Elskens : Modelling Si isotopic compositions and fluxes in the Southern Ocean with a box model

10h20 Break

10h40 G Wang: Using Short-Lived Radium Isotopes to Study Transport Processes in South China Sea

11h00 Nives Ogrinc :The use of geotracers in the costal marine studies (the Gulf of Trieste, N Adriatic)

11h20 K Rodgers, S Mikaloff-Fletcher, Claudie Beaulieu, D Bianchi, E Galbraith, A Gnanadesikan, T Naegler, J Sarmiento, R Slater: Atmospheric radiocarbon as a tracer of large-scale Southern Ocean wind variations over the period 950-1950

11h40 Discussion

13h00 Workshop closes

3) Session reports

Monday 7, afternoon

Introduction by Bob Anderson

Bob Anderson invites all of the participants to the workshop to be provocative. He emphasizes the importance of trace metals and paleo-application issues for this workshop (illustrated by the limitation of nitrogen fixation by Fe, and by the contradictory interpretations of Nd and Pa-Th records of past THC, respectively).
He encourages the participants to challenge the way we think and to make new partnerships.

S1: Observation and modelling of particle concentration.

Chair: Christoph Heinze. Rapporteur: Francois Lacan

You will find below: first a brief summary of the questions for each talk, then a summary of the session discussion.

13h50 H. Loisel, N. Sohne, L. Duforet, D. Dessailly, L. Boop, and O. Aumont : Analyse of the temporal variability of the space retrieved particulate organic carbon over the global ocean.

- Schlitzer : how do you derive the data from the satellite ? Answer : Chla: ratio of 2 length scale and POC, scattering and a empirical relationship.
- Jeandel: the 10 year POC variation observed in the west Pac may be related to freshening
- Marchal: We could maybe use the length scale of the variability from the Satellite data to see if geotraces sampling scheme complies with such length scale.

14h10 Lars Stemmann; Particle transformation in the mesopelagic layers of the oceans. What can we learn by using imaging systems.

14h30 Kriest, I., Oschlies, A., Khatiwala, S.: Parameterisation of Remineralisation Length Scales in Large-scale Models of Marine Biogeochemistry

- It is reminded that particle traps collect particles that may originate from a significant distance.
- Marchal: when comparing biogeochemical models, one has to consider the fact that the dynamical models may differ. Kriest answers that she used a single velocity field with the different biogeochemical models.
- Frank: Could you estimate an impact of the particles on the dissolved. Kriest: yes, see for instance the phosphate distributions.

14h50 M. Shigemitsu, Yamanaka, Y., Watanabe, Y. W., Okada, N. Kriest, I., Oschlies, A., Maeda, N., Noriki, S. Seasonal characteristics of the carbon isotope biogeochemistry of settling particles in the western subarctic Pacific: a model study

- Does the model conserve heat? If it is not the case, it could explain why it is not closed for the isotopes.
- M. Frank: why no seasonality in the remineralized organic matter. Schlitzer answers that the surface carbon reservoir is always far from totally depleted so that no seasonality is expected.

15h40 C Heinze, T Ilyina: The potential of radionuclides for detecting the impact of ocean acidification on marine particle fluxes

- M. Frank suggests that the above mentioned application may be difficult given the short residence time of Pa and Th. Response: you can look locally (with even larger signal). Suggestion: go back to some locations 10 years after a first visit.
- B. Anderson: What is the sensitivity of different organisms? It might be useful to define regions where the species are sensitive (Aragonite) and where you suspect a big change.
- M. Roy Barman says that there is a location (BATS) where we already have 2 measurements 10 years apart.

16h00 A Burke, O Marchal , L Bradtmiller, J McManus, R François : Application of an Inverse Method to Interpret 231Pa/230Th Observations from Marine Sediments

-Jeandel suggest that the data that are too positive compared to the model may be due to opal. Marchal: remember that we take into account a big uncertainty (including particle reactivity).
-Frank: can you change your model so that the Scholten data becomes ok? Olivier: the discrepancies may be the result of local circulation.
-Siddall: Since you didn't parameterize different affinities for different particle types does that mean that circulation dominates? Olivier: I can not say that.
-Anderson: could mixing explain the southern ocean data. Olivier: Mixing is not understood enough.

16h20 A Okubo, H Obata, T Gamo: ^{230}Th distributions in the Pacific Ocean: effect of bottom scavenging

- Frank: would you expect also dissolved ^{232}Th to be depleted at the bottom? Jeandel says she agrees.
- Roy Barman is surprised by the very high diffusion coefficients.

DISCUSSION:

Schlitzer: about Siddall’s question to Marchal (above): Are the details of particle reactivity not critical to explain the data? Marchal: In order to conclude that the data and model were in agreement, we had to consider a large uncertainty that includes the particle reactivity. And I would be happy to include the detailed reactivity and then lower the error (epsilon).
Siddall to Marchal: given your other modelling experience, would you say that it is 50% 50% (particles/circulation)? Olivier: it depends where you are. You can compute the dominant term in each box in a forward model.
- Question to Marchal: Could inflow from the Indian Ocean explain the Sholten data?
- Question to Marchal: the data plotted against latitude and longitude looked almost uniform. Marchal: they were depth integrated. Therefore difficult to compare with the final plot (normalize anomalies)
- Anderson to MARCHAL: recommendation for sampling? depth resolution? Marchal: No major recommendation. A south Atlantic from west to east (both sides of the basin) would be good (but I think it is planned already)

Jeandel to Loisel : what kind of data do you need to better constrain your POC estimations from satellite: Size distribution, (also below 60µm), from the list? (laser). Loisel: Measurement of POC, carbonate and total SPM. DOC would be nice.
Stemmann: the mineral part of small particle. it is more difficult for larger particle, because they are not well sampled. Porosity is also important. Loisel: with polarization you can discriminate carbonate from not carbonate. But you need someone on board.

Kriest to the community: do you have a detailed measurement of the K_d for different particle types and class. Landing: every particle is coated with organic matter, so it should be all the same. Anderson: Yes, we measured systematic differences. Roy Barman: there are a few data, but we are not at the stage where we can define something firmly. Heinze: we define K_d as a function of particle mass. Details are not very well established. Marchal (about the relation of K_d with the particle concentration): This is because of the margin. If you only consider open ocean, you get a cloud.

Heinze about the remineralization length scale. Remineralization rate and sinking velocity. In a model they balance each other. How to discriminate the impact of one versus the other? To Kriest: Is it time to refine the remineralization modelling? If you add Th, Pa, Al, etc.. then you have more variables and you can separate the parameters. Schlitzler: the particle people and the PaTh people have a factor of 50 difference (lower for Pa and Th) for particle sinking velocity. Marchal: Collections in sediment traps are the fast sinking particles. They constitute the flux... [here we had the traditional discussion about BIG verus SMALL particles, fluxes and stocks].... Marchal says it is a spectrum. Roy Barman: there is no inconsistency: you look at two ends of the size spectrum.
Anderson: there have been studies about 234 and 228Th for aggregation and disaggregation. The error bars were too large. Is there a way to better use these data? Marchal: the problem is the mixing. I don't think it will add a lot. MRB: the error bars have been reduced. Marchal: above 1000m it is the same regardless of where you are in the Atlantic. The theory of reversible scavenging is working for the upper layer, but does not at depth. Lohan: Could the competition of other reactive element (iron?) favor the desorption of Th at depth. Siddall: the deep water masses have integrated characteristics; at the surface they are pristine. Marchal: yes things go quicker at the surface (even 1D no circulation).

Siddal for Steemann: what is the difference between the trap and the video? Is the difference between both "neutrally buoyant"? Steemann: We found that only in the Atlantic. And yes we saw very large particles that did not sink, or almost not. We think that we found traces of the same particles at roughly the same place months apart.

Tuesday 8, morning

Session 2: Observation and Modelling particle reactive tracers, Th and Pa

Chair: Bob Anderson
Rapporteur: Mark Siddall

9h00 R Anderson , M Fleisher: What can we learn from ^{231}Pa/^{230}Th ratios?

9h20 S. Tyldesley , M. Siddall, S Mueller , A Ridgwell : Co-response of Pa/Th and export production during freshwater experiments

9h40 Luo, R. Francois, S. Allen: Sediment ^{231}Pa/^{230}Th as a recorder of the rate of the Atlantic meridional overturning circulation: Insights from a 2-D model

10h00 M Roy Barman: Modelling the effect of boundary scavenging on Thorium and Protactinium profiles in the ocean

10h20 T. Arsouze, S. Khatiwala, R. F. Anderson : The importance of lithogenic particles for scavenging ^{231}Pa and ^{230}Th from the entire ocean

10h40 break

11h00 S. A. Müller , G. Henderson , M. Siddall, N. R. Edwards: 231Pa and 230Th in the GENIE Earth system model: Exploring the combined effect of changes in circulation and biological export production on sedimentary 231Pa/230Th ratios

11h20 S. Marchandise, M. Roy-Barman, E. Robin, S. Ayrault and C. Colin: Distribution and isotopic signature of Thorium and REE-bearing phases in marine sediments

11h40 A. Radic, F. Lacan and C. Jeandel: Iron isotopes in seawater: a new tracer for the oceanic iron cycle ?

12h00 Discussion

Summary

This session consisted of discussion of the state-of-the-art of our understanding of the cycling of reactive elements in the ocean. Th and Pa dominated the presentations, though iron was also presented in the same context.

Discussion following the presentations focused on two main themes: whether to follow a uniform sampling pattern when making GEOTRACES transects or whether to focus on specific interfaces and; appropriate model complexity for GEOTRACES problems.

Presentations

Pa/Th ratios as a circulation/productivity proxy

Bob Anderson asserted that Pa/Th is not a circulation tracer in much of the world ocean and questioned whether it is sensitive to circulation changes in the North Atlantic, rather Pa/Th effectively tracks biological (especially diatom) productivity. Modelling studies presented by Mark Siddall, Simon Müller and Luo asserted that Pa/Th is affected by circulation in the north Atlantic, but with a strong caveat – biological productivity has a strong, co-varying impact alongside circulation on north Atlantic Pa/Th, masking a simple relationship between Pa/Th and circulation at any one sight.

Effects on ocean margins

Observational studies presented by Matthieu Roy-Barman and modelling studies presented by Thomas Arsouze suggested the importance of understanding the effect of ocean margins on Pa/Th ratios. Matthieu Roy-Barman showed increasing offsets between observed Th and Pa profiles and a simple 1D vertical scavenging model for profiles closer to the ocean margin. Thomas Arsouze presented new results considering scavenging by lithogenic particles derived from the ocean margins (as opposed to aeolian dust). The broad conclusion of the two talks was that Pa and Th processes at the ocean margin need to be studied in more detail.

Other applications

Marchandise presented preliminary results on the distribution and isotopic signature of ^{232}Th and Nd bearing phases in marine sediments in the Mediterranean. Monazite, zircon and florencite can explain most of the ^{232}Th and Nd in the sediments. Francois Lacan presented new results concerning the distrubution of iron isotopes in the Southern Ocean and Equatorial Pacific. In brief: i) Iron isotopic ratios tended to me more negative in the south and more positive in the north; ii) Iron in the Equatorial Pacific was found to have an origin in Papua New Guinea and; iii) biological uptake may favour lighter isotopes in at least some locations.

Discussion

Uniformly sampled transects vs strategic sampling at interfaces

This discussion was driven largely by the presentations which focused on a number of unknowns with respect to particle reactive tracers. For example the extent to which nepheloid layers need to be better understood, the effect of release from the margins and the nature of particle interaction in the water column. These questions require new process studies and strategic observations. The opposing argument is that we need an even data coverage to avoid sampling bias and facilitate modelling efforts on larger-scale patterns in isotope distributions. No clear dominant consensus emerged either but strong arguments were put in both cases and a mix of the two approaches, with specific process-orientated and transect cruises was an emerging view.

Appropriate model complexity

The issue of appropriate model complexity was brought up. After some discussion consensus emerged around the need for a model hierarchy and the use of the appropriate complexity for a given question. In brief:

- One-dimensional process models are a useful starting point for interaction with observational workers, presenting hypotheses which are testable in broader 3D models.

- Simple global models reach steady state quickly and are adept at understanding tracers with long residence times at the global scale.

- Better resolved ocean models are needed to study finer-scale details such as eddy mixing and the interaction of boundary currents with isotope exchange at the margin.

Tuesday 8, afternoon

S3: Observation and Modeling of particle reactive tracers – part 2 Nd isotopes and boundary exchange.

Chair: Martin Frank
Rapporteur: Thomas Arsouze

14h00 T Arsouze: An overview on Nd modelling

After the talk, the question to define standard model comparison tools has been raised. This includes both the kind of data to be used and the type of graphics to validate a model output.

14h20 Jeandel C. Peucker-Ehrenbrink B. , Godderis Y. , Lacan F, Arsouze T: Impact of ocean margin processes on dissolved Si, Ca and Mg inputs to the ocean

Extension of the research on boundary exchange to other elements: possibly up to 90 % of the oceanic Fe is derived from boundary exchange but for the horizontal and vertical distribution seawater, the speciation is crucial.

14h40 O. Aumont, A. Tagliabue, L. Bopp, and T. Gorgues: Sediment mobilization: revisiting the iron hypothesis

Hypothesis: During periods of lower sea level the particulate input goes up. This indirectly results a quantitative importance of sedimentary inputs for CO2 drawdown.

15h00 Johannes Rempfer, Fortunat Joos and Thomas Stocker: Modelling the neodymium cycle using the Bern3d model

Implementation of Nd Cycle in the Bern3D model of intermediate complexity. This development is performed to allow long simulation (thousand of years) for paleo studies.

15h20 M. Grenier, C. Jeandel, F. Durand, F. Lacan : Original study of the Equatorial Pacific Ocean fertilization based on a lagrangian simulation of the circulation coupled to Nd isotopic composition and Rare Earth Element concentration data

The use of lagrangian model for the interpretation of Nd oceanic distribution is presented for measurements in the equatorial pacific.

16h00 F Lacan, M Labatut : Trace element concentrations of the suspended particles in the Southern Ocean (Bonus/GoodHope transect)

Several remarks emphasized the beneficial effects of a multi-proxy approach, as in this study where four different tracers lead to the same conclusion.

16h20 A Oka, H Hasumi, H Obata,T Gamo, Y Yamanaka: Simulation of rare earth elements (REEs) with an ocean general circulation model

Reversible scavenging with different partition coefficients can explain concentration profiles of both LREE and HREE. Suggestions to do this kind of work, and constrain partition coefficients for all elements. HREE profiles are more similar to nutrients.

16h40 Cogez et al: Limitations of Neodymium isotopes modelling with Global Circulation Models

A remark has been made to emphasize data vs. model plots for comparison, rather than sections or maps with data superimposed with the same color code.

17h00 Discussion

Although the talks mainly focused on Nd modeling, the discussion first focused on iron modeling and on model complexity (both dynamical and biogeochemical).
It turns out that the weak agreement obtained for iron modeling results when compared to the data is mainly due to the poor knowledge of ligands and the colloidal behavior in the ocean. Ligand concentrations are assumed to be constant in models, and any attempt to parameterize them in a more realistic way gives even worse results.

This raised the question of what is the priority between improving dynamical and biogeochemical models. Of course: “Both” was the answer! However, it was emphasized that the increasing complexity in biogeochemical models will increase the degrees of freedom, which can’t be well constrained considering our current knowledge of the processes in the water column, in particular in relation to ligands and colloidal phases.

Conclusions raised by recent Nd modeling work has focused on the necessity to study the processes controlling the inputs from different sources (particularly along the continental margins) and in the water column (reversible scavenging). The study of processes along the margins is of primary importance if we want to constrain the boundary source for the Nd cycle, and later on apply this element as a proxy for the sources and their input terms (similar to ^{3}He for hydrothermal inputs). In this way, Nd has a potential to provide information on the behavior of more complex elements such as Fe (or even Mg, Si or Ca, as stated in the talk by Jeandel et al. in the session). This will also enable a better understanding of why two elements such as Nd and ^{232}Th have so different vertical profiles (Nd concentrations increase with depth, whereas the Th concentration essentially remains constant vertically) while they respond to the same processes (boundary sources and reversible scavenging).

Also, one important outcome of the Nd isotope studies is an improved understanding of and better constraints on the behavior of the elements in relation with particles. That concerns particles in the water column (actually constraining the variability of reversible scavenging of different elements with different particle types), but also at the sediment/seawater interface. In particular, we need to focus, for both modeling and in-situ studies, on places where particles are abundant, such as margins and the bottom (nepheloid) boundary layer.

Wednesday 9

Session 4 : Cycling of micronutrient- the Fe cycle, and other trace metals

Chair : Bill Landing
Rapporteur : Marie Boye

9h30 J.-M. Lee, E.A. Boyle, R.F. Zhang, J. Fitzsimmons, T. Ito: Distribution of dissolved Fe and Cu in the Bermuda Time-Series Station and the Tropical North Atlantic Ocean.
9h50 F. Chever, E. Bucciarelli, G. Sarthou, S. Speich, M. Arhan, P. Penven, A. Tagliabue: Dissolved iron concentrations in the Atlantic sector of the Southern Ocean, along a transect from the subtropical domain to the Weddell Sea Gyre
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11h30 M Jin, C Deal,S Elliott, E Hunke et al: Modeling of the influences of sea ice cover and sea ice ecosystem on iron cycle
14h00 T Gorgues, C Menkes, O Aumont, J Murray, L Slemons: The iron phases, a crucial factor for the biomass variability in the Pacific HNLC region?
16h20 W landing, C Measures: The Trace Metals Component of the CLIVAR/Repeat Hydrography (CO2) project
16h40 Celine Gallon, A. Russell Flegal: Silver in the North Pacific Ocean: potential as a tracer of anthropogenic inputs

Summary of presentations:

Iron is among the key-trace metals selected in the GEOTRACES Science Plan due to its potential to limit the ocean productivity and its influences on the global carbon cycle.

The *internal cycle of Fe within the global ocean* is described by combining a nutrient-like cycling like that of major nutrient nitrate, with additional removal by a scavenging term. Iron is recycled from organic detritus less efficiently than nitrate, thus intermediate and deep waters have Fe/nitrate ratios below the stoichiometric uptake ratio for marine phytoplankton. Paradigms indeed merge when compiling the dissolved Fe distributions in the oceans [Boye; Boyle and Jenkins], particularly the absence of a deep ocean fractionation between the North Atlantic and the North Pacific in spite of DFe distributing like a nutrient at depth and being particle reactive. One very significant factor to reconcile the expectations with the observations is the organic complexation of Fe. Compilation of the organic Fe-binding ligands available in the global ocean shows a loss term of the dissolved organic iron in the deep oceans, potentially driven by the aggregation and settling of colloidal Fe complexes [Boye].

The internal processes of DFe cycle include its *interactions with particles* that act to scavenge DFe from the upper ocean and to release it in deeper waters by remineralisation and possibly by desorption, similar to Th isotopes. The internal cycle of Fe hence interacts with *external sources* of Fe into the ocean when the particles are not biogenic or when biogenic particles incorporate the external signal. The origins of particulate Fe and the potential for the interactions between the dissolved and particulate Fe-pools were inferred by regional surveys and models. It shows that the decomposition of sinking biogenic detritus enriched with Fe due to high surface concentrations contributed by African dust is the likely source of DFe in the oxygen minimum intermediate waters of the Tropical North Atlantic, as opposed to a sedimentary source above the west African margin and advection into the ocean interior [Lee et al.]. Deposition of South Africa dust to the Indian surface waters followed by the dissolution and the westward advection of the atmospheric signal may significantly account for the high surface DFe concentrations observed in the subtropical domain of the south-eastern Atlantic [Chever et al.].

Particulate TEI/Ti ratios provide evidence for particle scavenging and regeneration of TEIs such as Al, Mn and Fe. The ratio of PFe:PTi is near the crustal ratio in surface waters and in the oxygen minimum zone under the Saharan dust plume in the sub-tropical North Atlantic. This presents a significant and unresolved challenge to our understanding of the marine biogeochemical cycling of Fe [Landing and Measures].

Lithogenic particles originated from the Papua New-Guinea margin advected by the Pacific Equatorial Under-Current sustain high Fe concentrations in western EUC mainly in the particulate phase, but also contribute to scavenge dissolved iron along the eastward flow of the EUC [Gorgues et al.]. Shelf sedimentary inputs and possibly river discharges rather than atmospheric deposition are major source of iron to the sea-ices of the Bering Sea, which in turn supply iron by seasonal melting that sustain large ice-edge phytoplankton blooms [Jin et al.].

The anthropogenic inputs of particles can be identified by silver as it was successfully achieved to trace the emissions of coal combustion to the North Pacific [Gallon and Flegal].

External sources of Fe include input from "inside the planet" by *hydrothermal vents* at mid-ocean ridges. This source has often been assumed negligible for the global Fe budget keeping with the precipitation of Fe near the ridge crest. However recent issues resting on field observations [Boyle and Jenkins] and on model [Tagliabue et al.] both indicate that hydrothermal vents are significant source of DFe to the deep ocean. Anomalies in the ^{3}He/^{4}He isotopes ratio can be used for the detection and parametrisation of hydrothermal Fe sources [Boyle and Jenkins; Tagliabue et al.].

Discussion: Conclusions/future challenges on Fe cycling

i) Scavenging/interactions with particles:
Colloidal Fe complexes and its interactions with particles (aggregation and settling, adsorption onto particles, redissolution…) may be critical for iron distribution in the deep ocean. More field data and process studies of soluble and colloids Fe and ligands are requested from experimentalists to examine the distribution and dynamics of the small-size Fe-fractions. Modelers have to adequately parametrize the organic Fe ligands cycle in the oceans, and to consider the dynamics and speciation of Fe colloids in Global Model of Fe cycling.

The lithogenic particles may act both ways to supply dissolved Fe as well as to scavenge it. There is a need for more particulate Fe data, better constraints of remineralisation and scavenging rates of the particles and for understanding the underlying processes taken into account the size-spectrum of the particles, both for the observations and models. Th isotopes may help in constraining the scavenging/remineralization terms of Fe by particles and colloids in seawaters.

ii) External sources (aeolian input, continental margins, hydrothermal vents)
Process studies show the iron chemistry and solubility in aerosols and rainwater, although the question remains of how atmospheric Fe solubilises across the sea-surface micro-layer. Trace metals other than Fe can be used as tracers of lithogenic Fe inputs (such Ti, Al, Mn) and anthropogenic source (Ag).

The relative importance of the external sources to ocean Fe inventory may better relate with time-scales rather than with their relative intensities. The geographical extension of external Fe sources to the interior ocean is strongly linked with the ocean and/or atmospheric circulation. Hydrothermalism can buffer the oceanic DFe inventory at millennial timescales against shorter-term variability in other external sources such as dust deposition. There it is a need for observations in the hydrothermal plumes and for revision of models of marine Fe cycle to introduce the hydrothermal Fe inputs and transportation, and the timescales of distinct external Fe sources. Using He isotopes to trace and quantify the hydrothermal Fe input to the deep ocean may be problematic since current circulation models do not produce good model fits with the existing He-3 data.

S5: Inverse modelling and others

Chair: Reiner Schiltzer
Rapporteur : J-C Dutay

15h20 W. J. Jenkins and A.C. Naveira Garabato: Constraining the oceanic budgets and fluxes of primordial helium-3

15h40 P Jean-Baptiste, J-C Dutay, P Peylin : Constraint on oceanic hydrothermal ^{3}He from inverse modeling.

Summary

The budget and rate of injection of hydrothermal helium-3 was discussed in these presentations. The ^{3}He budget in the Pacific was estimated from observations and the rate of injection in this basin (630 mol/yr) was discussed in regard of the divergence inferred between the Drake passage and Australia (290±160mol/yr) (Jenkins and Garabato). A constraint on the global rate of injection was presented using an inverse method, using a bayesian inversion of a compilation of all GEOSECS and WOCE data (Jean-Baptiste et al).

Discussion

The rate of injection of hydrothermal 3He is of great interest since it can be used for evaluating the hydrothermal source of other non conservative tracers (Iron) in the ocean (see session 4). The discussion has raised the uncertainties associated to the rate of mantle helium injection. It was mentioned that the mismatch between the “a priori” rate of injection in the Pacific and the divergence in the Austral Ocean, could be attributed to air-ocean degassing in the Pacific Ocean (Eq. upwelling). Results from the global inversion suggest a minimum value of 800 mol/yr for the rate of helium-3 injection. It is performed with a coarse resolution ocean general circulation model (NEMO, 2°x2°), that tends to generate too slow deep ocean circulation. However this study does not reject the widely used hypothesis of a global rate of injection of 1000 mol/yr.

Thursday 10: morning

S6: Stable isotope modelling (N, C, Si, etc)

Chair: Gideon Henderson

Rapporteur : Ben Reynolds

9h00 B C. Reynolds, B Bourdon: Understanding the global marine δ^{30}Si distribution
Simple Multi-box models, able to model the observed Si isotope distribution that are not captured by a published GCM. Potential due to poor parameterization of the Southern Ocean

9h20 G F. de Souza, B C. Reynolds, J F. Rudge, B Bourdon : Modelling nutrient-type cycling and mass-dependent isotope fractionation using a simple 1D model: Silicon as an example
Advection Diffusion Reaction models of thermocline mixing, may enable observationalists to estimate stable isotope fractionation factors, with an example given for Cd isotopes.

9h40 C Somes and A Schmittner: Modeling the Global Distribution of Nitrogen Isotopes in the Ocean
OGCM of δ^{15}N distribution: Overconsumption of N in OMZ, suggests underestimate of N fixation, and sedimentary dentrification. Fe limitation on diazotrophs required. Submitted manuscript available soon from csomes@coas.oregonstate.edu.

10h00 A de Brauwere, F Fripiat, A-J Cavagna, D Cardinal, M Elskens : Modelling Si isotopic compositions and fluxes in the Southern Ocean with a box model
Dynamic steady-state model for Si uptake in KEOPS plateau, with Si supply in summer. Now being modeled, and parameter optimization ongoing.

10h40 G Wang: (title change) ^{223}R and ^{224}Ra in the South China Sea, preliminary data from the CHOICE-C cruise.
Niskin sampling from 80 stations with 23 profiles. Decreasing ^{223}R and ^{224}Ra away from coast, cannot be modeled with simple Advection Diffusion Reaction (radioactive decay) equations, due to highly variable boundary inputs. Called for help in modeling the 3D structure and rates of movement.

11h00 Nives Ogrinc :The use of geotracers in the costal marine studies (the Gulf of Trieste, N Adriatic)

Carbon and nitrogen isotope composition of POM during mucilage event, which caused change in $\delta^{15}N_{PN}$, with low $\varepsilon = 0.7‰$, possible impact of N fixation. Mercury pollution important in this area and monitored of MERCYMS cruises: 0.2 ng/L in Mediterranean. Hg stable isotopes measured, and can distinguish between natural and pollution sources.

11h20 K Rodgers, S Mikaloff-Fletcher, Claudie Beaulieu, D Bianchi, E Galbraith, A Gnanadesikan, T Naegler, J Sarmiento, R Slater: Atmospheric radiocarbon as a tracer of large-scale Southern Ocean wind variations over the period 950-1950

How perturbation of the wind speed can affect inter- hemispheric $\Delta^{14}C$ via the Southern Ocean mixing (driven by wind stress and more importantly by wind speed, i.e. gas exchange rates). Potentially wind speeds can help account for multi-decadal-to-centennial variations in climate.

11h40 Discussion

- Are the low resolution OGCMs problematic in modeling of Geotraces chemical tracers? Do we need eddy resolving models, at 0.5° resolution? Eddy resolving does have a large impact on the deep-water ventilation in the Southern Ocean, but they can't get the global ocean dynamics right (according to Christoph Heinze). Thery may be little point in having high resolution physical oceanographic models, without good parameterization of particulate fluxes. Increasing resolution may be important for modeling CFCs inputs, but the question remains for other parameters which are tuned. Some physical models now have mode water forming from subtropical cells, rather than the Southern Ocean as assumed in geochemical models (but isn't this a problem for geochemical models or tracers like Si* or N*)
- Is there is need for a simple model required for observationalists to "play" with? Would be a great teaching tool, but can't replace the required interaction between modelers and observationalists. There can be problem if things are too simple and are then misused (Reiner Schlitzer).
- The suitability of localized models rather than OGCMs to understand coastal processes? For dissolved nutrients these may be easily applicable, but models can be easily transferable. The problem is often the need for degrees of resolution, requiring unstructured grids/mess (mesh?) models with different numeric's (not finite difference). ROMs may be most easily applied.
- Are novel stable isotopes suitable to determine sources? Need to have only a few processes acting within well constrained systems in order to interpret results. The isotope compositions can be used to define the processes or mass-transfer, or potentially anthropogenic contamination if highly fractionated at source.
- Encouragement of simple models to understand processes, but problems with temporal variations expected in areas with strong seasonality like the Southern Ocean.
- Potential themes for the next meeting….Coupling of elements.

4) Abstracts

Session 1: Observation and modelling of particle concentration.

Title: Analyse of the temporal variability of the space retrieved particulate organic carbon over the global ocean.

Authors: H. Loisel, N. Sohne, L. Duforet, D. Dessailly, L. Boop, and O. Aumont.

Knowledge of the spatio-temporal variability of the particulate organic carbon, POC, in the surface ocean is essential to understand the ocean ecology and biogeochemistry, including particle dynamics and carbon cycling. Here we present the seasonal and inter-annual evolution of POC over the global ocean as retrieved from the remote sensing reflectance recorded by the SeaWiFS sensor from January 1998 to December 2007. This algorithm is based on the inversion of the particulate backscattering coefficient of suspended marine particles, b_{bp}. Until now, POC estimates from space have been restricted to the surface layer (Stramski et al., 1999; Loisel et al., 2002). An empirical algorithm is developed to derive the POC content integrated over the euphotic layer from the near surface POC concentration. Based on this approach the standing stock of POC are 39.2 10^{13} and 118.8 10^{13} g over the first penetration depth (surface) and the euphotic depth, respectively. The temporal evolution of POC is reported in oceanic regions characterized by different physical forcing and biogeochemical conditions. Finally, the origin of the temporal evolution of POC is analyzed by the mean of numerical simulations performed with a coupled physical-biogeochemical model (NEMO-PISCES). This model is able to separate the respective contribution of the carbon to chlorophyll ratio, small and large phytoplankton cells, and detritus (non-living particles), in the POC temporal variability. Comparison between POC-PISCES and POC-SeaWiFS are then provided and discussed.

Title Particle transformation in the mesopelagic layers of the oceans. What can we learn by using imaging systems

Authors: Lars Stemmann

It is surprising that despite early warnings from ecologists, studies of the biological pump have remained biogeochemically-oriented, focusing on ecologically inappropriate temporal and spatial scales and overlooking the role(s) played by organisms and their interactions. Major international initiatives are now trying to link ecological and biogeochemical processes (e.g. IMBER) and calibrating paleoproxies (GEOTRACES), using a classical approach. I will discuss how to relate models to the observed biological complexity and will present a new integrated approach, using original methodologies (observations with imaging systems and modeling), to address the particle transformation from the surface to the mesopelagic layers of the ocean.

Title: Parameterisation of Remineralisation Length Scales in Large-scale Models of Marine Biogeochemistry

Authors: Kriest, I. (IFM-GEOMAR), Oschlies, A. (IFM-GEOMAR, Kiel, Germany), Khatiwala, S. (LDEO, Columbia University, New York, USA)

Sinking and remineralisation of particulate organic matter in large-scale models of marine biogeochemistry is often parameterised as an instantaneous distribution of export production, or via explicit similation of detritus, characterised by a constant or vertically increasing sinking speed. Here we review several representations of sinking (remineralisation) commonly used in large scale models with respect to their intrinsic assumptions.
While simulated sedimentation fluxes are difficult to constrain directly, on long time scales the parameterisation of sedimentation, in conjunction with physics, will impact the distribution of simulated tracers such as nutrients, oxygen, or PO. We examine the effect of various export and sedimentation parameterisations on long-term tracer profiles by comparing output from different biogeochemical models coupled to a global offline tracer-transport model to observed tracers.
We further contrast the sensitivity of the models to changes in remineralisation scale with the sensitivity to changes in other parameters or model structure.

Title: Seasonal characteristics of the carbon isotope biogeochemistry of settling particles in the western subarctic Pacific: a model study

Authors: Shigemitsu, M., Yamanaka, Y., Watanabe, Y. W., Okada, N. (Faculty of Environmental Earth Science, Hokkaido University, Sapporo, Japan, 060-0810)
Kriest, I., Oschlies, A. (IFM-GEOMAR)
Maeda, N. (The General Environmental Technos Co., Ltd)
Noriki, S. (Graduate School of Environmental Science, Hokkaido University)

We used moored time-series sediment traps to collect settling particles at station KNOT (44°N, 155°E; trap depth 770 m) in the western subarctic Pacific (WSAP) from October 1999 to May 2006. Particulate organic carbon content (POC) and isotope ratios ($\square^{13}C_{POC}$) were measured in the samples collected. The general pattern of variation in $\square^{13}C_{POC}$ results showed lower values during the spring bloom periods, higher values during summer, and summer-to-spring decrease with maximum in winter. To interpret the processes controlling such variations quantitatively, we developed a one-dimensional ecosystem model that included carbon isotopes. In this model, we considered the isotope effects by photosynthesis, degradation of POC, precipitation of calcite and gas exchange. This model was validated with an observed data set and successfully reproduced the seasonal variations of $\square^{13}C_{POC}$. In simulations, the lower $\square^{13}C_{POC}$ during the spring bloom periods was caused mainly by the phytoplankton assimilation of aqueous CO_2 ($CO_{2(aq)}$) with the lowest $\square^{13}C$ of the year and the largest isotope effects due to the lowest growth rates of phytoplankton and the highest concentration of $CO_{2(aq)}$ of the year. The higher $\square^{13}C_{POC}$ in summer was mainly due to the change of photosynthesis isotope effects between the early and late spring bloom periods. The change was determined by the differences in phytoplankton growth rate and $CO_{2(aq)}$ concentration between the periods. The summer-to-spring decrease of $\square^{13}C_{POC}$ with maximum in winter mainly reflected the transition of phytoplankton species with different isotope effects during photosynthesis. The transition was mainly induced by the change of grazing pressure on phytoplankton by copepods with seasonal vertical migration. From these results, we suggest that the observations of $\square^{13}C_{POC}$ increase from spring to summer may indicate the difference in large phytoplankton growth rates between the early and late spring bloom periods, and the observed change of $\square^{13}C_{POC}$ values during summer to spring may record the transition of phytoplankton species induced by the downward vertical migration of copepods in the seasons of this region.

Title: The potential of radionuclides for detecting the impact of ocean acidification on marine particle fluxes

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Abstract : Ocean acidification may lead to significant changes in biological particle production in the ocean surface layer and hence respective changes in marine particle fluxes through the water column. Detection of large-scale changes in biocalcification through alkalinity measurements will presumably not be possible before 2030 and then only in areas of significant baseline values of $CaCO_3$ export production (Iliyna et al., 2009). Particle reactive radionuclides such as ^{230}Th and ^{231}Pa have the potential to indicate changes in marine particle fluxes given the primary carrier phase to which these particles attach is identified. We carry out model experiments with the biogeochemical ocean general circulation model HAMOCC (cf. Heinze et al., 2006; Heinze et al., in press) where we change the biogenic production of marine particles relative to a control run. An earlier pilot study indicated that ^{230}Th indeed can record a decrease in marine $CaCO_3$ fluxes. The intriguing feature is the integration of particle flux changes over depth, rendering increasing dissolved ^{230}Th changes with depth over time. We ask whether appropriately designed time series of radionuclide measurements could serve as a useful monitoring tool for changes in marine particle fluxes. Potentially such an observing system of regularly re-occupied measurement stations for radionuclides could be realized through GEOTRACES.

References:

Heinze, C., M. Gehlen, and C. Land, 2006, On the potential of ^{230}Th, ^{231}Pa, and ^{10}Be for marine rain ratio determinations - a modeling study. *Global Biogeochemical Cycles, 20, GB2018, doi:10.1029/2005GB002595.*

Heinze, C., I. Kriest, and E. Maier-Reimer, Age offsets among different biogenic and lithogenic components of sediment cores revealed by numerical modeling, *Paleoceanography*, in press.

Ilyina, T., R.E. Zeebe, E. Maier-Reimer, and C. Heinze, 2009, Early detection of ocean acidification effects on marine calcification, *Global Biogeochemical Cycles*, 23, GB1008, doi:10.1029/2008GB003278.

Title: Application of an Inverse Method to Interpret ^{231}Pa/^{230}Th Observations from Marine Sediments

Authors: Andrea Burke (1), Olivier Marchal (1), Louisa Bradtmiller (2), Jerry McManus (3), Roger François (4)

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(3) Department of Earth & Environmental Sciences, Lamont-Doherty Earth Observatory
(4) Earth & Ocean Sciences, University of British Columbia

Records of ^{231}Pa/^{230}Th from Atlantic sediments have been interpreted in terms of changes in ocean circulation during the geologic past. Such interpretations should be tested with due regard to the uncertainties in the ^{231}Pa/^{230}Th data (e.g., limited data coverage) and in our current understanding of the behavior of both nuclides in the ocean (e.g., particle scavenging). Here an inverse method is used to evaluate the information contained in ^{231}Pa/^{230}Th compilations for the Holocene, Last Glacial Maximum (LGM), and Heinrich Event 1 (H1). First, an estimate of the abyssal circulation in the modern Atlantic is obtained by combining hydrographic observations with dynamical constraints. Second, water column ^{231}Pa and then sediment ^{231}Pa/^{230}Th are combined with an advection-scavenging model to determine their (in)consistency with the modern circulation. We find that conservative assumptions about the uncertainties in water column ^{231}Pa data and the model are needed to bring these data into consistency with the modern circulation. Using such assumptions, the majority of sediment ^{231}Pa/^{230}Th data for the Holocene, LGM, or H1 appear compatible with the modern circulation. Whereas a bias in our data analysis cannot be excluded, it is concluded that the current uncertainties involved in the analysis

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Title: ^{230}Th distributions in the Pacific Ocean: effect of bottom scavenging

Authors : Ayako Okubo, Hajime Obata, Toshitaka Gamo,

Marine Inorganic Chemistry Division, Ocean Research Institute, University of Tokyo,

Total ^{230}Th and dissolved ^{232}Th distributions were determined for mid-latitudes of the North Pacific Ocean.

We first reported the depletion of total ^{230}Th compared with a reversible scavenging model prediction in the deep layers of mid-latitude of the North Pacific Ocean. Regarding stratified vertical profiles of density and dissolved oxygen below 2500 m, the depletion of total ^{230}Th could not be attributed to the advection. We presented a bottom scavenging model in which ^{230}Th in bottom water was depleted by the bottom scavenging effect and ^{230}Th-depleted bottom water was vertically mixed with eddy diffusion. Our observation shows that ^{230}Th is scavenged within each basin, which indicates that certainty of constant flux proxy method with ^{230}Th is robust in the study area.

The stations with smaller particle fluxes have more marked ^{230}Th depletion. In regions with large particle flux, removal of Th by bottom scavenging and diffusion might not affect the distribution of ^{230}Th within its short residence time in seawater. Conversely, in small particle flux regions, bottom scavenging and diffusion might markedly affect the removal of Th, which implies that the bottom scavenging might also affect the distributions of many other elements, which have less particle-reactivity than Th.

The accordance between ^{232}Th scavenging flux and aerial ^{232}Th flux indicates that lateral ^{232}Th transport is negligible in this study area.

Session 2: Observation and Modelling particle reactive tracers, Th and Pa

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Title: Title: What can we learn from ^{231}Pa/^{230}Th ratios?

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^{231}Pa/^{230}Th ratios in modern ocean sediments depart in systematic ways from the production ratio of 0.093 (activity ratio). Although there are exceptions, ratios in ocean margin sediments tend to be greater than 0.093 while ratios in open ocean sediments tend to be less. When first discovered, these findings supported the hypothesis of boundary scavenging, and led to the view that high fluxes of particles near ocean margins led to the preferential scavenging there of dissolved ^{231}Pa. These findings were extended to suggest that sedimentary ^{231}Pa/^{230}Th ratios could serve as a paleoproductivity proxy, given that most particles responsible for scavenging in the open-ocean environment are of biogenic origin. This view was supported by sediment trap studies showing that particulate ^{231}Pa/^{230}Th ratios increase with mean annual particle flux. However, it was later learned that within the suite of sediment trap samples used, mean annual particle flux was highly correlated with the opal content of the particles. This and a growing body of other evidence led to a revised view that sedimentary ^{231}Pa/^{230}Th ratios reflect primarily the abundance and flux of particulate biogenic opal (diatom productivity).

At about the same time it was suggested that sedimentary ^{231}Pa/^{230}Th ratios in North Atlantic sediments provide a kinematic tracer of past changes in the ventilation rate of North Atlantic Deep Water. This view was based on the theory that dissolved ^{231}Pa/^{230}Th ratios in newly formed deep waters should increase with water mass age due to the longer mean residence time of dissolved Pa in seawater compared to Th.

Here we will show that the spatial and temporal pattern of ^{231}Pa/^{230}Th ratios in North Atlantic sediments is better correlated with diatom productivity than with water mass age. Furthermore, we will show that there is surprisingly little variability in the dissolved ^{231}Pa/^{230}Th ratio of deep water along the path of the Great Ocean Conveyor, from the North Atlantic to the North Pacific, apparently violating the principle that dissolved ^{231}Pa/^{230}Th ratios should increase with water mass age.

Both modeling studies and field sampling within the GEOTRACES field program should be designed to address two questions: 1) What controls the broad range of ^{231}Pa/^{230}Th ratios in marine sediments? And 2) Can we learn something about rates of lateral mixing from the small range of spatial variability in the dissolved ^{231}Pa/^{230}Th ratio in deep waters?

Title: Co-response of Pa/Th and export production during freshwater experiments.

Authors: Sally Tyldesley (1), Mark Siddall* (1), Simon Mueller (2), Andy Ridgwell (1)

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*presenting

Data suggest covariation of Pa/Th with changes in export production during D-O stadial events. We investigate this suggestion using a coupled biological, circulation and Pa/Th model in the GENIE intermediate complexity model. We find that export production and sedimentary Pa/Th vary in a complex three-dimensional pattern during freshwater experiments intended to represent D-O stadials. We show that the coincidence of changes in export production and Pa/Th during such events is to be expected and conclude that changes in export production are not necessarily the cause of changes in sedimentary Pa/Th even if they are co-registered in the same core. Rather changes in export production and Pa/Th are likely linked to the same ultimate cause (freshwater forcing)

Title: Sediment ^{231}Pa/^{230}Th as a recorder of the rate of the Atlantic meridional overturning circulation: Insights from a 2-D model

Authors:Y. Luo, R. Francois and S. Allen

Ocean thermohaline circulation plays an important role in regulating climate and thus rapid changes in the strength and geometry of the Atlantic Meridional Overturning Circulation (AMOC) have been invoked to explain the abrupt climate variations that have punctuated the last ice age and deglaciation (Clark et al, 2002). The ^{231}Pa/^{230}Th ratio of Atlantic sediments is one of the several kinematic tracers which can be used to investigate the ocean circulation (Lynch-Stieglitz et al., 2007). Because both ^{231}Pa and ^{230}Th have uniform production rates in the water column from U isotope decay and ^{231}Pa has a relatively longer resident time than ^{230}Th in sea water, the overturning circulation effectively exports ^{231}Pa from the Atlantic into the Southern Ocean, while most of the ^{230}Th remains in Atlantic sediments. As a result, faster overturning is deduced from lower Atlantic sedimentary ^{231}Pa/^{230}Th, while higher ^{231}Pa/^{230}Th indicates slower overturning (Gherardi et al., 2009). However the application of this simple principle is complicated by the scavenging process because the composition of settling particles can decide the residence time of ^{231}Pa in seawater and recent modeling by Dutay et al. (2009) even suggest reasonable ^{231}Pa and ^{230}Th concentration profile output is difficult to obtain using a reversible scavenging model with appropriate partition coefficients. Also, Thomas et al. (2006) argue that sedimentary ^{231}Pa/^{230}Th may only record overturning occurring in the 1000m of water overlying the analyzed sediment and shallower overturning cannot be recorded in deep sediment using a 1-D scavenging model. In order to answer these questions and testify the ability of Pa/Th as a proxy for the strength of the overturning circulation, we have developed this 2-D scavenging-circulation model. We have examined the factors that may affect the distribution of ^{231}Pa/^{230}Th in Atlantic sediments and future sampling and modeling strategies are also advised using the output of our model.

Title: Modelling the effect of boundary scavenging on Thorium and Protactinium profiles in the ocean

Authors: M. Roy-Barman (LSCE/IPSL)

The "boundary scavenging" box model is a cornerstone of our understanding of the particle-reactive radionuclide fluxes between the open ocean and the ocean margins. However, it does not describe the radionuclide profiles in the water column. Here, I present the transport-reaction equations for radionuclides transported vertically by reversible scavenging on settling particles and laterally by horizontal currents between the margin and the open ocean. Analytical solutions of these equations are compared with existing data. In the Pacific Ocean, the model produces "almost" linear ^{230}Th profiles (as observed in the data) despite lateral transport. However, omitting lateral transport biased the ^{230}Th based particle flux estimates by as much as 50%. ^{231}Pa profiles are well reproduced in the whole water column of the Pacific Margin and from the surface down to 3000 m in the Pacific subtropical gyre. Enhanced bottom scavenging or inflow of ^{231}Pa-poor equatorial water may account for the model-data discrepancy below 3000 m. The lithogenic ^{232}Th is modelled using the same transport parameters as ^{230}Th but a different source function. The main source of ^{232}Th scavenged in the open Pacific is advection from the ocean margin, whereas a net flux of ^{230}Th produced in the open Pacific is advected and scavenged at the margin, illustrating boundary exchange. In the Arctic Ocean, the model reproduces ^{230}Th measured profiles that the uni-dimensional scavenging model or the scavenging-ventilation model failed to explain. Moreover, if lateral transport is ignored, the ^{230}Th based particle settling speed may by underestimated by a factor 4 at the Arctic Ocean margin. The very low scavenging rate in the open Arctic Ocean combined with the enhanced scavenging at the margin accounts for the lack of high ^{231}Pa/^{230}Th ratio in arctic sediments.

Title: The importance of lithogenic particles for scavenging ^{231}Pa and ^{230}Th from the entire ocean

Authors: T. Arsouze[a], S. Khatiwala[a], R. F. Anderson[a]

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^{231}Pa and ^{230}Th are particle-reactive radionuclide that are rapidly removed from the water column and buried toward the sediment via reversible scavenging process. Continental erosion supplies important amount of lithogenic material on the continental margin regions (e.g. over the continental slopes) leading to lithogenic particles concentration and fluxes roughly two orders of magnitude higher than in central ocean gyres, where the lithogenic material largely derives from dust sources. Although the margin area may be relatively small, the high fluxes do extend to fairly great depth out over the continental slope, where lateral mixing can supply significant fraction of both dissolved ^{231}Pa and ^{230}Th from the open ocean. It is therefore important to constrain the role of these lithogenic particles for scavenging ^{231}Pa and ^{230}Th from the entire ocean.

In this study, we use the Transport Matrix Method to simulate the ^{231}Pa and ^{230}Th distribution in the NEMO ocean global circulation model. A reversible scavenging model is parameterized to simulate dissolved/particulate interactions between different particle pools. Radioactive decay of uranium isotopes is the source for both isotopes to the ocean, while scavenging acts as a sink. Focusing on the oceanic margins, we test the influence of abundance and flux of lithogenic material on scavenging efficiency, and ultimately on ^{231}Pa and ^{230}Th global distribution.

Title: 231Pa and 230Th in the GENIE Earth system model: Exploring the combined effect of changes in circulation and biological export production on sedimentary 231Pa/230Th ratios

Authors: S. A. Müller (1), G. Henderson (2), M. Siddall (3), N. R. Edwards (1)

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(2) Department of Earth Sciences, University of Oxford, Oxford,
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(3) Department of Earth Sciences, University of Bristol, Bristol,
United Kingdom

We present 3-dimensional modelling results of sedimentary 231Pa/230^{Th} ratios simulated with an intermediate-complexity Earth system model (GENIE) complemented with an equilibrium-scavenging model for the 230Th and 231Pa isotopes. We analyse results from a large ensemble of simulations featuring a wide variety of circulation states produced with the climate model components of GENIE through sampling ofcirculation- and climate-controlling parameters and further constrained to restrict simulated biological export production within an estimated range of permissible variability for glacial and interglacial conditions. Based on this ensemble of simulations we statistically examine the direct dependence of spatial sedimentary 231Pa/230Th patterns on variations in circulation state as well as on circulation-induced changes in the strength and spatial pattern of export production.

Title: Distribution and isotopic signature of Thorium and REE-bearing phases in marine sediments

Authors: S. Marchandise[1], M. Roy-Barman[1], E. Robin[1], S. Ayrault[1] and C. Colin [2]
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One of the goals of the GEOTRACES international program is to determine the phases carrying the particle-reactive tracers like Thorium (Th) and Neodymium (Nd). We study the Th and Nd-rich phases in marine sediments from the Mediterranean Sea (DYFAMED site) in order to: (1) constrain the nature of the phases carrying Th isotopes (^{232}Th which is a "lithogenic" tracer but also, potentially, in situ produced $^{230}Th_{ex}$) and (2) determine the nature of the phases involved in the Boundary Exchange which is a key feature of the Nd cycle in the ocean.

We combine mineral separation, systematic survey and quantitative analysis by scanning electron microscopy (SEM), and isotopic analysis by Thermal Ionization Mass Spectrometer (TIMS) on the Th-REE rich phases. We have identified phases of clearly lithogenic origin such as zircon $ZrSiO_4$, xenotime YPO_4, monazite (REE, Th)PO_4, allanite $(REE,Y)_2(Al,Fe_3)_3(SiO4)_3(OH)_6$ but also florencite $(REE)Al_3(PO_4)_3(OH)_6$, a mineral of possible authigenic origin. The two main ^{232}Th carrying phases are monazite and zircon. The average U/Th ratio in zircon is quite high (0.6 g/g) but this ratio is very heterogeneous according to the crystal and probably depends on its origin. The monazite grains have a low U/Th ratio (~ 0.15 g/g), which is consistent (assuming secular equilibrium between ^{238}U and ^{230}Th) with the low ^{230}Th/^{232}Th ratio (~ 2.7×10^{-6} mol/mol) measured by TIMS on a monazite-rich fraction, significantly below the crustal average ($4\text{-}5\times10^{-6}$). These preliminary results help to understand the large variability of the U/Th ratio in marine particles collected in sediment traps moored in the Mediterranean Sea and to better evaluate the $^{230}\text{Th}_{xs}$ in these samples. It also provides clear indications on the ^{232}Th bearing phases; a question recently raised in the framework of the discussion of the phases carrying ^{230}Th in sediment traps. The analysis of Th and Nd isotopes in other phases is underway.

Title: Iron isotopes in seawater: a new tracer for the oceanic iron cycle ?

Authors: A. Radic, F. Lacan and C. Jeandel.

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The measurement of the isotopic composition of the iron dissolved in seawater is now feasible down to concentrations of 0.1nmol/L (Lacan et al. 2008). This allows its determination in most of the ocean, including most parts of HNCL areas. This tracer has the potential to trace the iron sources to the ocean and/or its internal cycle (biological uptake, redox processes ...).
We will present the first dissolved iron isotope data in HNLC areas, the southern Ocean (KEOPS cruise 2005 and Bonus-GoodHope cruise 2008) and the Equatorial Pacific (EUCFe cruise 2006). The data span a large range of isotopic values, from δ^{56}Fe = -0.7‰ to more than 1.0‰. These results will be discussed in terms of iron sources and internal cycle.

Session 3 : Observation and Modeling of particle reactive tracers – part 2 Nd isotopes and boundary exchange.

Title: Impact of ocean margin processes on dissolved Si, Ca and Mg inputs to the ocean.

Authors: Jeandel C. (1), Peucker-Ehrenbrink B. (1, 2), Godderis Y. (3), Lacan F.(1) and Arsouze T.(1)

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The observed neodymium (Nd) isotope distribution in the oceans can be reconciled with input fluxes from the continents if ~ 3% of the continental sediments deposited on the margins dissolve. Here we evaluate the significance of this margin process on the marine budgets of the more soluble elements silicon (Si), calcium (Ca) and magnesium (Mg). Premised on the assumption of 3% congruent dissolution, the annual fluxes of these elements are estimated at 1.5-4.7 Tmol Si, 0.3-1.1 Tmol Ca and 0.4-1.1 Tmol Mg. These input fluxes represent 30-94%, 2.5-9 % and 6.5-18 % of the dissolved river fluxes of Si, Ca and Mg, respectively. Fluxes of this magnitude could significantly shorten the residence time of Si in seawater, provide revised source/sink assessments for the marine M isotope budget, and impact the uptake of atmospheric CO_2 and thus climate on geological time scales.

Title: Sediment mobilization: revisiting the iron hypothesis

Authors : O. Aumont, A. Tagliabue, L. Bopp, and T. Gorgues

Iron is supplied to the ocean by four external sources: dust deposition, sediment remobilization, river discharge and hydrothermal vents. The first of these sources, i.e. dust deposition, has received by far the largest attention and it has long been considered as the only important source of iron to the ocean. However, both observations and modeling studies suggest that the other sources may play a significant role and, particularly regarding sediment remobilization, may be as important as dust. Unfortunately, very little is known about the magnitude or temporal and spatial variability of this source. In this study, we use a global ocean biogeochemical model, NEMO-PISCES, to improve our knowledge regarding the sedimentary input of iron to the open ocean. We propose different parameterizations of this source and use available iron data as well as chlorophyll data to evaluate their relevance. Then, in a second step, we examine the impact of this source on the air-sea CO2 fluxes. In particular, the model results suggest that sediment remobilization of iron may have a significant impact on atmospheric pCO2, comparable, or even greater, in magnitude to the impact of dust deposition. One consequence of this finding is that,during the Last Glacial Maximum (LGM), the iron supply from the sediments was probably considerably less thatn today, since the extent of the continental shelves was much smaller. Such reduction results, in our model, in an increase in atmospheric pCO2 which may completely cancel out the decrease due to increased dust deposition. Thus, according to our model, the iron hypothesis does not appear to be a good candidate to explain a significant part of the lower atmospheric PCO2 during the LGM.

Title: Modelling the neodymium cycle using the Bern3d model

Authors: Johannes Rempfer, Fortunat Joos and Thomas Stocker

Neodymium isotopic composition (e_{Nd}) is a promising tracer of water masses and variations of e_{Nd} in sediment records are explained in terms of variations in ocean circulation by various authors (e.g. Rutberg et al., 2000, Pahnke et al., 2008). e_{Nd} usually is expressed as e_{Nd} = ([^{143}Nd] / [^{144}Nd] / 0.512638 – 1) * 10^4, where 0.512638 corresponds to the “bulk Earth" value. It is considered a quasi-conservative tracer as it is not affected by remineralisation processes. In contrast, concentration of neodymium [Nd] shows nutrient-like behaviour in the ocean. With regard to the sources of Nd, it seems obvious that e_{Nd} of seawater is derived from the continents and delivered to the ocean through weathering and erosion and finally by particle-seawater interaction. However, how water masses precisely acquire their observed isotopic composition is still under debate (Lynch-Stieglitz, 2003).

So far, a few modelling studies have been conducted to investigate sources and sinks of Nd. Tachikawa et al. (2003), using the PANDORA box model, reported that riverine and atmospheric sources are insufficient to explain the magnitude and variability of observed values of e_{Nd} and [Nd], and therefore proposed continental margins as additional sources. Arsouze et al. (2007) used a restoring approach to model modern e_{Nd} of seawater in an OGCM. By considering continental margins as a single source they were able to reproduce the global pattern of e_{Nd} reasonably. However, the model had some deficiencies e.g. in adequately reproducing surface values. Intending to explain the "neodymium paradox", Siddall et al. (2008) were the first who simulated [^{143}Nd], [^{144}Nd] and e_{Nd} simultaneously. They included a reversible scavenging model into an OGCM using prescribed particle fields and Nd isotope concentrations at the surface and concluded that reversible scavenging is an important component in the cycling of Nd.

Usage and modelling of Nd, in particular with regard to paleoceanographic applications, requires a thorough understanding of the sources and sinks. Therefore, an important next step is the combination of the different approaches to get a more comprehensive representation of the Nd cycle within a model. We include Nd isotope concentrations [^{143}Nd] and [^{144}Nd] into the Bern3d ocean model of intermediate complexity and consider fluxes across the sediment-water interface as well as riverine and dust-associated input as sources of Nd. To represent internal cycling we include a reversible scavenging model as described by Siddall et al. (2008). In a first step export fluxes of carbonate ($CaCO_3$), organic matter (POM), and opal are prescribed at the ocean surface (Siddall et al., 2008) as are dust fluxes across the sea surface (Luo et al., 2003). However, after having tuned the model to modern observations, we plan to calculate export fluxes of POM, $CaCO_3$, and opal using a fully prognostic formulation (Tschumi et al., 2008). Using the cost-efficient Bern3d-model allows us to easily set up a variety of model runs in order to investigate the influence of the different parametrisations (e.g., of reversible scavenging, of fluxes) on the basin-scale patterns of [Nd] and e_{Nd}. This permits carefully tuning of the parametrisations of the model in order to simulate observations.

Results indicate the model to be able to reasonably reconstruct modern observations of [Nd] and e_{Nd}. However, some shortcomings are observed in the surface Atlantic, possibly indicating a missing source of Nd in this region. Model simulations yield an estimate of the magnitude of these fluxes.

Title: Original study of the Equatorial Pacific Ocean fertilization based on a lagrangian simulation of the circulation coupled to Nd isotopic composition and Rare Earth Element concentration data

Authors : M. Grenier[1], C. Jeandel[1], F. Durand[2], F. Lacan[1]

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The Equatorial Pacific Ocean thermocline is mostly fed and fertilized by the Equatorial UnderCurrent (EUC), which is carrying thermocline waters originating from the Southwest Tropical Pacific Ocean. Circulation in the Coral, Solomon and Bismark Seas is particularly complex, mostly due to the topography that concentrate the broad currents into narrow and swift jets. Here we used the lagrangian tool ARIANE (www.univ-brest.fr/lpo/ariane/), that integrates ouputs of a ¼° global OGCM, allowing us to reconstruct pathways of “virtual tracers”. Seasonal and interanual variations of this complex circulation have been investigated. The numerical results are confronted to in situ observations of lithogenic tracers, Nd isotopic composition (IC) and REEs concentration in the same area and at locations considered by the model. ARIANE simulations show that in situ stations in the Coral Sea and in the Bismark Sea are connected by the thermocline currents, which flow from the southernmost station towards the northern ones. The Solomon Sea station seems to be on a different streamline. Using the simulated transports allowed us to refine the rates of input of the lithogenic tracers into the EUC. New Nd IC and REE data obtained in the Coral Sea confirm the occurrence of lithogenic element supplies and scavenging in Coral and Bismark Seas, initially suggested by Lacan and Jeandel (2001) and Cros (2008), although these authors used a very rough approach of the circulation. Furthermore, lithogenic supplies appear to occur between South-Eastern Pacific and the Coral Sea. We also noticed a progressive enrichment in the Coral Sea, then in the Bismark Sea. These results stand in contrast with past interpretations which located most of enrichments in the Bismark Sea. These conclusions drawn for thermocline waters bound to the EUC also hold for surface and intermediate waters. This work underlines that associating virtual and real tracer analysis could be a good track for the future of the data-model synergy in GEOTRACES.

Title: Trace element concentrations of the suspended particles in the Southern Ocean (Bonus/GoodHope transect)

Authors : Francois Lacan and Marie Labatut
LEGOS (CNRS/UPS/IRD/CNES), Observatoire Midi Pyrénées, F-31400, Toulouse, France

Advances of Inductively Coupled Plasma Mass Spectrometry (ICPMS) performances, coupled with large volume samples, allow the determination of a large number of trace element concentrations in oceanic suspended particles. We will present a new dataset from 5 full depth stations in the Southern Ocean south of South Africa (Bonus/GoodHope cruise). The dataset includes concentrations for lithogenic tracers such as Al, Ti, Th and Cs ; tracers of dissolved/particles interactions such as Rare Earth Elements ; tracers of remineralisation such as Ba ; and also a number of transition metals (although some of these metal data need to be validated since the samples were taken with Niskin bottles) such as Cr, Co, Ni, Cu, Ag and Cd.

Title: Simulation of rare earth elements (REEs) with an ocean general circulation model.

Authors: Akira Oka(1), Hiroyasu Hasumi(1), Hajime Obata(2),
Toshitaka Gamo(2), and Yasuhiro Yamanaka(3)

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Observed vertical profiles of rare earth elements (REEs) in the North Pacific Ocean show a systematic change from lighter to heavier REEs.
Their source and sink consist of external fluxes coming from the surface and bottom of the ocean and internal recycling within the ocean.
In order to evaluate the role of each source and sink in controlling the vertical profiles of REEs, we conduct numerical simulations of REEs by using an ocean general circulation model.
These simulations demonstrate that the shape of their vertical profiles is not directly related to the external sources from river runoff, atmospheric dust deposition, and coastal regions but is sensitive to the internal recycling processes within the ocean.
Nutrient-like treatment where REEs are removed at the surface and released in the deep ocean is suitable for simulating the vertical profiles of lighter REEsbut not for heavier REEs.
When the irreversible scavenging is taken into consideration as a sink term and particle dissolution as a source term, the vertical profiles of heavier REEs can be reproduced but those of lighter REEs cannot.
The observed difference in the vertical profiles among REEs can be reproduced only when the reversible scavenging process is incorporated into the model.
Only the reversible scavenging process accounts for the observed vertical profiles of different REEs in comprehensive manner.

Title: Limitations of Neodymium isotopes modelling with General Circulation Models

Authors: Antoine Cogez[1], Carl Wunsch[2], Gael Forget[2], Laure Meynadier[1], Claude Allègre[1]

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Neodymium isotopes are a powerfull tracer of past ocean circulation and continental erosion. Their use is based on the isotopic heterogeneity between different ocean basins and on the fact that they are not fractionated by chemical or biological processes during their transport in rivers and oceans. A robust interpretation of palaeo ε_{Nd} data however requieres understanding of the balances (sources, sinks...) and processes that affect Nd. To this end existing data are used with different techniques to enhance our understanding of the marine Nd cycle. Simulations were performed with an offline version of the MIT GCM to calculate ε_{Nd} fields in the interior ocean. The boundary conditions were optimized on the basis of all data in the interior ocean, using a quadratic programming method. Different types of boundary conditions were tested, first at the entire surface, second at the surface near the coast only, and third at the mouth of the 34 main world rivers. We neglected the concentration variations in the ocean, so that ε_{Nd} has been considered as a conservative tracer. Our approach is very similar to the one of Jones et al. (2008), the only difference being the way of estimating the surface boundary conditions, yet the results are sensibly different. Jones et al. obtained relatively large misfits in the deep Pacific, that they explained by the need for a radiogenic source in the deep Pacific ocean, which could be the particulate exchange of Nd between seawater and sediments of passive margins (Tachikawa et al., 2003 ; Lacan and Jeandel, 2005 ; Arsouze et al., 2007). In contrast, no evidence was found here for a missing source in the deep Pacific ocean. Comparison of the different simulations shows that the results are greatly dependant on the boundary conditions and on the way of estimating them. With high resolution models, the sparcity and noise of Nd data (especially in the Pacific ocean) are major problems, and lead to unreliable results. Additionally approximations commonly introduced while writing the equations governing the flow and mixing introduce an other source of uncertainty that is difficult to estimate. Finally, the question is raised of whether the use of Nd with high resolution models is not premature, given the sparse data base.

Session 4: ***Cycling of micronutrient- the Fe cycle, and other trace metals***

Title: Distribution of dissolved Fe and Cu in the Bermuda Time-Series Station and the Tropical North Atlantic Ocean.

Authors: J.-M. Lee[1], E.A. BOYLE[1], R.F. ZHANG[1], J. FITZSIMMONS[1], AND T. ITO[2]

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One of the questions posed on trace element cycle in the ocean is the processes controlling the distribution of dissolved trace elements and their interaction with particulates. We present the results of dissolved Fe and Cu analysis from two cruises in the Bermuda Time-Series Station (BATS) and the tropical North Atlantic, which have implications on these issues.

Total dissolved Fe and Cu concentrations were measured in BATS station (2008 June GEOTRACES intercalibration cruise). As seen previously, Fe data shows low values below the seasonal mixed layer increasing to a maximum in deep waters. The Cu concentrations were low at the surface and increased almost linearly at depths below 500 m despite multiple water mass changes. This depth linearity feature of Cu was reported in other ocean regions such as North Pacific and has been explained by the result of mixing of low Cu surface seawater with high Cu deep seawater and removal by scavenging. The linear feature is also observed in many Th-230 and Pa-231 profiles. In this study, we suggest the possibility that the Cu profile is maintained by similar processes that control Th and Pa in the ocean; that is, a relatively uniform supply of Cu from decomposing organic particles combined with a rapid exchange of dissolved Cu with sinking particulate Cu. Based on this hypothesis, a simple 1-D steady-state model was constructed. The dissolved Cu profile observed in N. Atlantic and N. Pacific could be reproduced with this model although uncertainties of reaction rate constants are large and sensitive to the fraction of particulate Cu that is exchangeable with dissolved Cu pool.

Total dissolved Fe data was collected from tropical north Atlantic (TNAtl) where high iron levels (>1 nmol/kg) were observed by Bergquist and Boyle (2006, GBC 20 GB1015) and Measures et al. (2008, GBC 22 GB1005). Although iron is expected to be high in oxygen minimum waters because of the decomposition of sinking biological debris, these high iron levels are nearly a factor of three higher than would be expected from typical Fe:C ratios of marine organic matter. Two possibilities for these high Fe levels seem possible: (1) Fe may escape from reducing continental margin sediments on the African margin and diffuse/advect into the ocean interior, or (2) Fe:C ratios of biological debris in the TNAtl may be higher than elsewhere because of the supply of iron from North African dust transport into the surface waters. In 46 TNAtl surface samples from this cruise and two others, 70% of the Fe concentrations range from 0.4-0.8 nM, with 5 lower (min 0.12nM) and 7 higher (max 1.30nM). At 500m, Fe concentrations vary over a narrow range from 0.54nM in the northwest to 1.43nM in the northeast; Fe is correlated with AOU implying an C:Fe ratio of about 10^5. This ratio is about a factor of three lower than the ratio inferred from the northeast Pacific water column. Although there is somewhat of an east to west decreasing Fe concentration at 500m, the spatial distribution does not appear consistent with a northwest African sedimentary source. We conclude that the high levels of Fe in the TNAtl oxygen minimum are created by decomposition of biological debris that is enriched in iron because of high surface concentrations contributed by African dust. This finding has implications for modeling C uptake as a consequence of aeolian Fe supply; the most effective C uptake would occur at the places where surface Fe concentration is very low.

Title: Dissolved iron concentrations in the Atlantic sector of the Southern Ocean, along a transect from the subtropical domain to the Weddell Sea Gyre

Authors: F. Chever[1], E. Bucciarelli[1], G. Sarthou[1], S. Speich[2], M. Arhan[2], P. Penven[2], A. Tagliabue[3,4]

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Distribution of dissolved iron (DFe, 0.2 µm filtered) were investigated during the BONUS-GoodHope cruise in the Atlantic sector of the Southern Ocean (34°S/17°E – 57°S/0°), in February-March 2008. A decrease in the DFe concentrations was observed from the north (subtropical waters) to the south of the section (Weddell Sea Gyre). Continental margin and dust input might be the main sources of Fe in the subtropical domain. To better assess the impact of the atmospheric source in this domain, we used a regional oceanic model based on ROMS (SAfE, Southern African Experiments, Penven et al., 2006) and forced by two different atmospheric dust products. While ROMS-Safe is a high-resolution model suitable to represent the complex physics of the region, it does not include any DFe loss terms (such as biotic uptake and precipitation/scavenging) and should therefore be seen as providing the maximum potential impact of dust. To better assess our estimates when DFe losses are accounted for we also used results of the global ocean biogeochemistry model PISCES when dust DFe sources were eliminated, which is lower resolution, but provides an estimate as to the overall importance of different DFe sources when the iron cycle is accounted for (Tagliabue et al., 2009). The NCAR dust product (Mahowald et al., 2006) was first used and presents a large Patagonian dust source. The INCA dust product (Aumont et al., 2008) which takes into account the southern Africa as an important dust source, was then used. Enrichment by atmospheric dust inputs from Southern Africa, followed by lateral advection could thus be tested. For ROMS-SAfE a Fe content of 3.5 % (Desboeufs et al., 2005) and a solubility of 10 % (Duce and Tindale, 1991) were applied. The impact of atmospheric dust deposition over a four month summer period was then assessed at our subtropical stations (L1, S1, and L2) taking into account the regional oceanic circulation. The experiments with the NCAR dust product (large Patagonian source) showed that at the three stations, dust deposition coming from Patagonia has the potential to be a significant source of DFe (~0.6 nmol L^{-1}). PISCES results suggest that up to 0.2 nmol L^{-1} of DFe was maintained by dust deposition. The experiments with the INCA dust product (less Patagonian input) showed that at our most northern stations (L1 and S1), the enrichment was of 0.3 nmol L^{-1}, or 0.1 nmol L^{-1} from PISCES. Importantly, our ROMS-SAfE results revealed that this increase was mainly controlled by the advection of Indian Ocean waters. At L2 station, there was no significant advection of Indian Ocean waters (increase in DFe < 0.05 nmol L^{-1} for both ROMS-SAfE and PISCES), suggesting that only direct dust deposition coming from Patagonia is likely to increase DFe in surface waters at this station. Overall, it appears that dust deposition from Patagonia has the potential to be a significant source of DFe in subtropical waters (0.3 to 0.6 nmol L^{-1}). If dust deposition from Patagonia is overestimated (cf. Wagener et al., 2008), then deposition from Africa appears to play a smaller role (0.1 to 0.3 nmol L^{-1}) at the northern edge of our transect. PISCES results also suggest that continental margin DFe sources could also contribute up to 0.3 nmol L^{-1} at L1 and 0.1 nmol L^{-1} at L2, highlighting the need for more information on these sources.

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Title: The organic complexation in modeling the oceanic iron cycling

Authors: Marie Boye

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There is now compelling evidences to demonstrate that dissolved iron is principally complexed by organic ligands in oceanic waters. The organic complexation is a central factor in the oceanic iron cycling playing a key role in iron solubility and geochemistry, as well as in selective iron bioavailability. Despite this role the speciation and the cycling of the organic ligands are still poorly understood. The chemistry of iron, especially its organic complexation, is also poorly represented in models of the oceanic iron cycle. An overview of the distribution of the organic iron-ligands available in the global ocean will be presented. It will be used to propose some parametrizations and key issues to improve the modeling of the iron cycling.

Title: Hydrothermal Iron in the Deep Western South Pacific

Authors: Edward Boyle and William Jenkins

Although iron plays an important role as a limiting nutrient for ocean biogeochemical cycles, the difficulty of proper sampling and analysis of this contamination-prone trace element has severely limited data on the oceanic distribution of this element. E.g.: the most extensive recent compilation of data on Fe in the ocean (Braucher and Moore, 2007) does not contain a single measurement below 1000m in the entire South Pacific. Although iron regenerated from sinking biological debris (including iron originally released from atmospheric mineral aerosols as well as upwelled Fe) is generally thought to be the major source of Fe to the deep ocean, other sources have also been suggested as significant, such as iron from reducing continental margin sediments (Elrod et al., 2004). And although it has been known for decades that large quantities of iron are supplied to ocean ridge-crest sediments by hydrothermal activity, it has often been assumed that this iron precipitates near the ridge crest; there has been only one report suggesting that hydrothermal vents are a significant source of Fe for the deep water column at great distances (Wu, Oc. Sci. abstr. 2006). In this presentation, we show the first deep water Fe data from the eastern South Pacific Ocean and demonstrate that hydrothermal vents are a significant source of dissolved Fe to the deep ocean, by analogy to primordial He-3. Our samples were collected on cruise KM0703 of the R/V Kilo Moana (Station 19, 20°S 170°W) in April 2007. The similarity of the iron profile to He-3/He-4 is striking, as is its dissimilarity to the nutrient profiles. <0.4 µm Fe vs. excess ^3 He shows a linear relationship with a slope of 9.0×10^5 mol Fe/mol ^3 He. Our data indicate that <1% of the primary hydrothermal iron survives as "dissolved" iron in the water column at basin scale. Because this small percentage is sensitive to environmental conditions, the contribution from this source may be larger or smaller in the past or future. If all of this hydrothermal iron reached the ocean surface, it would be capable of supplying 30% of the Fe requirement for global ocean primary productivity. Scavenging onto falling particles will reduce this fraction before it reaches the surface, so the actual contribution to primary production may be ~10%.

Title: On the importance of hydrothermalism to the oceanic dissolved iron inventory

Authors : Alessandro Tagliabue, Laurent Bopp, Jean-Claude Dutay, Andrew R. Bowie,
Fanny Chever, Philippe Jean-Baptiste, Eva Bucciarelli, Delphine Lannuzel,
Tomas Remenyi, Géraldine Sarthou, Olivier Aumont, Marion Gehlen and
Catherine Jeandel

Iron limits phytoplankton growth and the biological carbon pump in large areas of the world's oceans, including the climatically important Southern Ocean. Studies attempting to address how changes in iron supply impact the global carbon cycle rely on global models of ocean circulation and biogeochemistry that typically include dust and continental margins as their predominant iron sources. However, recent observational studies have highlighted the potential importance of an additional iron source from deep-ocean hydrothermalism. In light of this, our prior understanding of the oceanic iron cycle must be re-evaluated. Here we show that hydrothermal iron sources are important in governing the oceanic iron inventory and reproducing dissolved iron observations in a global model. Helium isotopes and iron data are compiled to parameterise the hydrothermal source of dissolved iron using prior observational studies as additional constraints. Importantly, new deep-ocean GEOTRACES datasets from two distinct Southern Ocean basins are used to statistically evaluate model results. Hydrothermalism can increase the biological carbon pump by 20-30% in the Southern Ocean and the impact of variability in the assumed hydrothermal flux is non-linear. Additional deep ocean dFe data collected during GEOTRACES will further assist us in better representing this source of dFe in ocean models. We suggest a revised model of the marine iron cycle, particularly for the iron-limited Southern Ocean, with a role for different iron sources over distinct timescales. Due to its relative constancy at millennial timescales, hydrothermalism can "buffer" the oceanic dissolved iron inventory against shorter-term variability in other sources, such as dust deposition.

Title: Modeling of the influences of sea ice cover and sea ice ecosystem on iron cycle

Authors: Meibing Jin, Clara Deal (IARC/UAF),
Scott Elliott, Elizabeth Hunke, Mat Maltrud and Nicole Jeffery (LANL)

Sea ice cover can hold atmospheric dust inputs to ocean until ice melt, but the sea ice effect can be more than a delay of the dust input. Observations in the Bering Sea supports hypothesis that the sea ice formed in iron-rich shelf regions may be an important nutrient

contributor to the ice-edge phytoplankton blooms by releasing iron to iron-limited shelf break and basin areas during ice-melting. To test the hypothesis and investigate the influence of sea ice melt-induced iron on the total primary production in the Bering Sea, sensitivity studies are conducted using a coupled sea ice-ocean ecosystem models and physical models POP-CICE (Parallel Ocean Program- Los Alamos Sea Ice Model) that are developed for global biogeochemical cycles studies. Preliminary results will be presented.

Title: The iron phases, a crucial factor for the biomass variability in the Pacific HNLC region?
Authors: Thomas Gorgues, Christophe Menkes, Olivier Aumont, James Murray, Lia Slemons

The eastern equatorial Pacific biomass has been shown to respond to an iron limitation partly explaining the High Nutrient Low Chlorophyll condition found at this location. Lately, several studies based on model outputs and data have focused on the source of this bioavailable iron. Modeling studies have shown that dissolved iron located north of Papua New-Guinea is potentially advected to the eastern Pacific despite high scavenging. The location of the iron source in the western Pacific is confirmed by data based studies. However they also showed that most of the iron north of Papua New-Guinea are in the particulate phase. This result may have a significant impact on the iron advection by the Equatorial UnderCurrent and its bioavailability when arrived in the Eastern Equatorial Pacific. This work aims, through state of the art biogeochemical simulations, to document the potential advection and bioavailability of particulate iron when compared to previously published results of dissolved iron fate.

Title: Modeling Atmospheric Dust Deposition Using Oceanic Surface Water Dissolved Al
Authors: B Landing C. I. Measures, Dept of Oceanography, University of Hawaii.

Atmospheric deposition of mineral dust to the surface ocean and its partial dissolution is believed to be an important route by which reactive trace elements are delivered to the surface waters of the remote ocean. This is particularly relevant for the case of the micronutrient Fe since large regions of the high latitude and equatorial Pacific are thought to have their biological productivity limited by the availability of dissolved Fe. Since the efficiency of the biological carbon pump is an important component of the global carbon cycle, it is vital that the spatial and temporal addition of dissolved Fe to the surface ocean be incorporated accurately into global models that seek to replicate the carbon cycle. This is a complex problem however since not only are the parameters that control the fractional solubility of the Fe within mineral aerosols not well understood, the spatial and temporal pattern of mineral dust deposition is also poorly represented in global models.

The concentration of dissolved Al in the surface waters of the ocean has been used as a surrogate to estimate mineral dust deposition to the remote ocean with results showing reasonable agreement over three orders of magnitude of measured depositions where these data are available.

The CLIVAR/CO_2 Repeat Hydrography Program over the last 6 years has provided an opportunity to construct a global overview of dissolved Al in the surface waters of large areas of the ocean and thus has allowed the construction of a map of estimated mineral dust deposition. While in general much of the data is within the error bounds of the data-based estimates of the GESAMP model as reported in Duce et al., 1991, there are large discrepancies in some regions, particularly in the NW Pacific Ocean, where both the Duce et al., and many subsequent models overestimate dust deposition by an order of magnitude or more. Given that this is one of the regions that is Fe-limited the failure of models in this region implies there may be shortcomings in the parameterisations of the models. Global data sets such as those derived from the CLIVAR program, and those that will be produced from the GEOTRACES program will help modelers investigate regional problems such as these and improve parameterisations.

Title: Silver in the North Pacific Ocean: potential as a tracer of anthropogenic inputs

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Dramatic increases in coal combustion in Asia over the last three decades have induced the transport of substantial atmospheric emissions over the North Pacific Ocean, where they can potentially alter trace element biogeochemical cycles in oceanic surface waters and North America. These perturbations have recently been evidenced by measurements of elevated silver, which is a geochemical marker of coal combustion, in surface waters of the North Pacific, where this metal now appears to be the most contaminated trace element, relative to its natural concentration. However measurements there have been few and far between since they were first made over two decades ago. We partially fill this void by presenting vertical profiles of silver concentration (HR-ICPMS) measured in archived samples from the VERTEX VII (Vertical Transport and Exchange) cruise (1989), which covered a North South transect extending to the Alaska Gyre, as well as in new samples from the GoA (Gulf of Alaska) cruise (2007) collected in the Alaska Gyre and from the GEOTRACES cruise (2009) in the Central North Pacific.

Our results confirm that within the water column, silver exhibits a nutrient type behavior, as was previously observed in other oceanic waters. In intermediate depth waters, concentrations in all the profiles are higher than those measured in the southern hemisphere and North East Pacific in the early 1980s, and in the range of those reported more recently in the Western and Central North Pacific. In the Alaska Gyre, water samples collected 20 years apart present comparable silver concentrations. Measurements from this study also confirm that silver is significantly correlated with dissolved silica, with plots of Ag versus Si showing a concave shape typical of Pacific waters, suggesting that the biogeochemical cycles of these two elements are linked.

Session 5: inverse modelling

Title: Constraining the oceanic budgets and fluxes of primordial helium-3
Authors: W. J. Jenkins and A.C. Naveira Garabato

Abstract: The observed distribution of helium-3 in the deep ocean is of interest both from the viewpoint of constraining ocean circulation, and as an important diagnostic of terrestrial degassing. It is also a valuable tracer of hydrothermal input that is both conservative (away from volcanic centers and bomb-tritium decay) and sensitive over orders of magnitude in dilution. We use a combination of WOCE and CLIVAR sections to estimate the transports and flux divergences of primordial (non-atmospheric) helium-3 at a variety of locations in the ocean (especially in, but not restricted to the Pacific and Southern Oceans) and relate them to estimates of volcanic helium-3 input. We use these estimates to provide constraints on upwelling rates as well as the supply of abyssal nutrients to the surface of the Southern Ocean.

Title: Constraint on oceanic hydrothermal ^{3}He from inverse modeling

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Natural ^{3}He originating from mantle degassing represents a widely used tracer for deep ocean circulation. The enriched ^{3}He signal (700%) is injected in the ocean along the ridges axis by hydrothermal processes and is next transported in the ocean by the deep circulation. This tracer has been extensively measured during the GEOSECS and WOCE programs and now offers a satisfactory global oceanic cover. It has also been used to evaluate different Global Ocean models' circulation during the OCMIP2 project (Ocean Carbon Model Intercomparison Project). However its interest is limited by the knowledge of its source function. In model simulations, the ^{3}He source is set proportional to the ridge spreading rates, with a global rate of injection of 1000 mol/yr. We have attempted to constrain this source function using inverse modeling. We have used the NEMO ocean general circulation model and run basis source function for different source regions. A compilation of ^{3}He data (WOCE and GEOSECS) has been performed, and used to constraint the intensity of the source for each region. The inverse model is using a Bayesian approach that was previously developed for atmospheric carbon studies. We have then investigated the two hypotheses that are prescribed to build the source function: the global intensity, and the proportionality to the ridges spreading rates.

Session 6: Stable isotope modelling (N, C, Si, etc)

Title: **Understanding the global marine** δ^{30}Si distribution

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Similarly to C and N, Si is an important macro-nutrient in the oceans that undergoes mass-fractionation during biological uptake by diatoms. The silicon isotopic composition of opal sediments can be used as a proxy for past nutrient utilization by phytoplankton (De La Rocha et al., 1998; Brzezinski et al., 2002), to estimate paleo-productivity, given estimated rates of ocean circulation. Interpretations of this Si utilization proxy are limited by our understanding of the marine Si isotope distribution (which must be measured), and the effect that hydrographic changes would impose on this distribution (which must be modeled).

Observations show significant Si isotopic variations (expressed as δ^{30}Si) of silicic acid between deep-water masses, with higher δ^{30}Si values in the Atlantic than in the Pacific. These stable Si isotope variations are similar to the variations in more extensively studied δ^{13}C, but in stark contrast with the absence of δ^{15}N variations in deep-water (Sigman et al., 2000). Furthermore, a GCM model (HAMOCC4) of the Si cycle failed to predict any variations in deep-water δ^{30}Si values (Wischmeyer et al., 2003), which would imply the parameterization of the Si cycle used was incorrect. We thus need to establish if the observed δ^{30}Si values are compatible with our understanding of the marine Si cycle, in terms of the magnitude of fluxes and the fractionation process involved.

Here we address whether the observed δ^{30}Si variations are compatible with a basic understanding of the marine Si cycle, using simplified multi-box models of the global oceans (e.g. Pandora). Utilizing MATLAB coding of two different multi-box models, the δ^{30}Si distribution was calculated using variable published estimates of regional opal export fluxes. Using estimated Si fluxes, these simple box models do indeed predict the observed 0.3‰ difference between Atlantic and Pacific deepwater δ^{30}Si values. Thus, the observed δ^{30}Si distribution is compatible with estimates of the fluxes and mass-fractionation in the marine Si cycle.

In order to address why the GCM model failed to predict the δ^{30}Si distribution in deep-waters, we must understand what mechanisms drive the δ^{30}Si difference between the Atlantic and Pacific deep-waters, which may have been missing in the GCM model. The δ^{30}Si difference between deep-waters results from (i) overturning waters in the North Atlantic having a high dissolved δ^{30}Si composition and (ii) the dissolution of opal with low δ^{30}Si values in the deep-waters around the Southern Ocean which feeds into the Pacific. Probably the GCM model failed to generate any deep-water δ^{30}Si variations due to poor parameterization of the overturning fluxes in these two key high-latitude areas.

Future models should be able to predict the effects that hydrographic changes have on the Si isotope distribution for the interpretation of the Si isotope proxy, and enable quantification of the paleo-productivity from the degree of nutrient utilization.

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Title: Modelling nutrient-type cycling and mass-dependent isotope fractionation using a simple 1D model: Silicon as an example

Authors: Gregory F. de Souza[1], Ben C. Reynolds[1], John F. Rudge[2,1], Bernard Bourdon[1]

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Novel analytical techniques are permitting the development of new isotopic tracers for studying the upper ocean. However, the full potential of these tracers cannot be exploited without a firm grasp on the processes governing their distribution in the ocean. Our understanding of these mechanisms can be furthered by combining observational data from the modern ocean with models that include simple process parameterisations, allowing the influence of individual processes to be systematically assessed.

We model the low-latitude oceanic thermocline as a steady-state, one-dimensional (vertical) system. While fundamentally similar to advection-diffusion-reaction models applied to oceanographic problems since the 1960s (*1, 2*), the use of a finite difference code facilitates solution of the advection-diffusion-reaction equations with *variable* coefficients. This allows the incorporation of oceanographic features such as, for example, the suppression of vertical mixing in the pronounced pycnocline below the base of the low-latitude mixed layer. Furthermore, the model traces multiple isotopes of the element under study, so that mass-dependent stable isotope fractionation by chemical or biological processes can be modelled.

When modelling the behaviour of the nutrient silicon (Si), we prescribe the concentration and isotopic composition of the source of dissolved Si (i.e. the waters at the base of the thermocline). At suitable rates of Si consumption by phytoplankton in the mixed layer, the concentration of Si in the mixed layer drops to a prescribed critical value (i.e. the steady-state value observed in the low-latitude oligotrophic surface ocean). Given these constraints and the isotopic fractionation associated with uptake of Si by phytoplankton (diatoms), the model reproduces the major features of the observed Si concentration profile as well as the Si isotopic composition in the mixed layer and the export flux of Si. Model results also highlight the importance of vertical mixing and indicate one possibility of reconciling differences between field and laboratory estimations of the magnitude of Si isotope fractionation during utilisation by phytoplankton.

The versatility of the model facilitates adaptation to other elements, such as Cd and Zn, that are strongly cycled (and isotopically fractionated) by biogeochemical processes in the surface ocean, and may thus prove to be a useful tool for observationalists, allowing a fuller exploitation of the explanatory potential of new concentration and isotopic composition data without the need for extensive computational infrastructure. The one-dimensional nature of the model is both a limitation and an advantage, since it can help identify processes that must work either in other dimensions (e.g. current systems) or on other scales (e.g. basin-scale mixing).

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Title: Modeling the Global Distribution of Nitrogen Isotopes in the Ocean

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Bioavailable (fixed) nitrogen is one of the major nutrients required for algal phytoplankton growth and photosynthesis. The global fixed nitrogen inventory regulates the efficiency of the biological pump, which transports CO2 from the surface ocean and atmosphere to the deep ocean via the sinking of organic matter and hence influences climate. The main sources and sinks of oceanic fixed nitrogen are nitrogen fixation and denitrification. Denitrification occurs in subsurface waters and sediments at low dissolved oxygen concentrations (<5□M). The dissolved oxygen concentration of seawater depends on (a) its supply by temperature dependent solubility and air-sea gas exchange at the surface and transport to the subsurface by the ocean circulation, and (b) its removal through the remineralization of organic matter. Hence, oxygen concentrations and denitrification are sensitive to changes in climate, ocean circulation and productivity. Nitrogen fixers are a special class of phytoplankton that is able to convert dissolved N_2 gas into its biomass when fixed nitrogen is not available. They have an ecological advantage over fixed nitrogen assimilating algae in seawater with low N:P ratios but have relatively high iron demands. This advantage in low N:P seawater couples nitrogen fixation to denitrification, whereas iron limitation loosens this coupling somewhat. Nitrogen isotopes are fractionated during denitrification, nitrogen assimilation and excretion and are also influenced by nitrogen fixation. Therefore, nitrogen isotopes are valuable indicators of changes in the nitrogen cycle. We have constructed the first global 3-dimensional model of nitrogen isotopes in the ocean and compiled a global data set of □$^{15}NO_3$ observations. We show that it is important to include both sedimentary denitrification and iron limitation of nitrogen fixers in order to simulate the observed present day distribution realistically. Sensitivity experiments show that fractionation during nitrate assimilation, water column denitrification, as well as the input of light atmospheric nitrogen through nitrogen fixation are all important in explaining the global patterns of nitrogen isotopes, whereas processes within the food web such as excretion are unimportant. The effect of water column denitrification is restricted spatially to denitrification regions. Remaining challenges to model nitrogen isotopes are related to the simulation of suboxic zones, dissovled organic matter and the iron cycle. The model will be used to better understand past changes in the nitrogen cycle as recorded in ocean sediments.

Title: Modelling Si isotopic compositions and fluxes in the Southern Ocean with a box model

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The estimation of the silicon mass balance in the ocean from direct measurements (Si uptake-dissolution rates) is plagued by their strong temporal and spatial variability. Additional tracers with different sensitivities to physical and biological processes would be of great complementary use. The isotopic composition of silicon (δ^{30}Si) is a promising proxy to overcome both spatial and temporal variabilities since it integrates longer timescales compared to direct measurements and is able to trace back the Si sources. $Si(OH)_4$ uptake by diatoms, taking preferentially light Si-isotopes (De La Rocha et al., 1997), leaves a clear imprint on the isotopic compositions of both $Si(OH)_4$ and biogenic silica. Mixing and dissolution act differently on Si-isotopic composition allowing to discern these processes by mass and isotopic balance (Demarest et al., 2009; Fripiat et al., submitted).

The modelling approach developed for instantaneous biogenic silica production and dissolution rates (using ^{30}Si enrichment incubations) also exploits mass and isotopic balances (Elskens et al., 2007). This suggests that a similar tool could be used with natural isotopic compositions to quantify seasonal silicon fluxes (uptake, mixing, dissolution). This kind of analysis would be especially interesting in the Southern Ocean where globally the most extensive $Si(OH)_4$ concentration gradient is observed, both in surface and deep waters. Meridional transects in the Southern Ocean show that the different water masses exhibit contrasted δ^{30}Si and dissolved silicon concentration.

A multi-box model is being developed, based on mass and isotopic balance principles. The model represents a number of neighbouring zones each consisting of two boxes, corresponding to dissolved $Si(OH)_4$ and biosilica. Mass can be exchanged between the boxes by the processes of uptake (production of biosilica), dissolution and transport (both vertical and lateral). The magnitude of these fluxes is unknown a priori and the aim is to estimate them from the available observations of $Si(OH)_4$ and biosilica and their isotopic composition using an inverse approach. This would allow a fully data-based assessment of which processes are significant (at a given study area and period).

A number of choices regarding the equation formulation and used observations are worth discussing. For instance, the delta formulation for isotopic compositions seems inappropriate to constrain the model parameters. Furthermore, it is our intent to make the equations as generic as possible, such that the model (i.e. the number of boxes and considered processes) can be easily adapted for different applications. The sensitivity of a first model version to the different processes is being investigated, using the available Southern Ocean data set (Varela et al., 2004; Cardinal et al., 2005; Fripiat et al., submitted; Cavagna et al., submitted). Application to reconstruct temporal (e.g., EIFEX) and spatial (e.g., KEOPS) variations of Si fluxes in the mixed layer taking into account Southern Ocean's circulation is foreseen.

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Title: Using Short-Lived Radium Isotopes to Study Transport Processes in South China Sea

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Naturally occurring radium isotopes have served the oceanographic communities as tracers of submarine groundwater discharge and coastal mixing processes. As an attempt to study the transport processes, including eddy diffusion, advection, and potential upwelling, in the coastal ocean, South China Sea, using short-lived Ra isotopes (^{223}Ra, ^{224}Ra), seawater was collected in July and August of 2009. The next step would be setting up mass-balance equations for Ra and solve for transport parameters from Ra distributions. In specific, horizontally, a one-dimensional mass-balance equation will be set up for Ra, considering eddy diffusion and advection. Vertically, a similar mass-balance equation will be set up considering eddy diffusion and upwelling. This is the first time of using short-lived Ra isotopes to study transport processes in South China Sea and the suitability of the tracer method and the mathematical methods will be tested.

Title: The use of geotracers in the costal marine studies (the Gulf of Trieste, N Adriatic)

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Two different recent studies on the use of geotracers in the coastal marine environment in the Gulf of Trieste will be presented.

The stable carbon and nitrogen isotopes of particulate organic matter (POM) were studied in a period of mucilage appearance (2004) and without mucilage formation (2003), underscore the importance of the biogeochemical properties of the water column in spring (April-June) since great differences between data measured in 2003 and 2004 were observed. The significant correlation between $\delta^{15}N_{PN}$ values and nitrate concentrations in 2004 implies intense nitrate assimilation in the presence of higher nitrate concentration. This suggests nitrate as the key nutrient in the »new primary production«, later producing macroaggregates with a mean $\delta^{13}C$ and $\delta^{15}N$ values of -19‰ and 5‰, respectively. A low fractionation factor ε, <1‰, lower than that reported in other marine and lacustrine systems, was found probably to be a consequence of distinct phytoplankton species, i.e. several classes of autotrophic nanoflagellates, and specific growth conditions present in the Gulf of Trieste.

Special attention was given to provide pre-industrial background levels of heavy metals for the Gulf of Trieste, particularly for Hg. Sedimentary records of this geochemical tracer were compared with the records of 500 years of ore extraction in order to reconstruct the Hg depositional history, determine the accumulation rate and calculate the cumulative metal inventory. The Hg historical trend is well correlated with extraction activity at the Idrija mine, thus allowing indicative sedimentation rate estimation and tentative assessment of the rate of Hg accumulation in bottom sediments (from 1.77 to 31.5 mg m^{-2} y^{-1} at the surface) that is from one to two orders of magnitude higher than the Po river's, the main freshwater supply of sediments in the Adriatic sea. In addition the first results on the use of stable isotopes of Hg as distinct tracers of the contamination source will be outlight.

Title: Title: Atmospheric radiocarbon as a tracer of large-scale Southern Ocean wind variations over the period 950-1950

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ABSTRACT:

An ocean general circulation model (OGCM) has been used in conjunction with an atmospheric transport model (ATM) to argue that changes in the winds over the Southern Ocean can drive first-order changes in the delta-14C of atmospheric CO2.
In particular, the models reveal that only relatively modest perturbations to the winds over Southern Ocean can drive significant perturbations in the interhemispheric gradient in atmospheric delta-14C over decadal to centennial timescales.
Change-point analysis reveals that there may have been a number of significant transitions in the strength of the winds over the Southern Ocean over the last 1000 years.
In contrast to what is found with Northern Hemisphere climate variability over the last 1000 years, the transition between the Medieval Warm Period and the Little Ice Age in the Southern Hemisphere is not a singularly large change in the mean state.
The model results are considered within the context of the available atmospheric delta-c14 proxies and direct measurements.

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