



U.S. GEOTRACES North Atlantic Cruise (2010-2011)

A Progress Report in 25 minutes or less...





Outline



- Introduction
- Overview of results so far
- Two vignettes





Outline



- Introduction
 - -An apology
 - -Program/cruise objectives
 - -Strategy & implementation
- Overview of results so far
- Two vignettes





An Apology



- I am presenting the hard work of many, many people
- I am not a card-carrying T-M chemist
 - any errors in presenting this are mine alone
- I have been given an impossible task
 - Too much to cover in too little time
 - Incomplete data sets (too early)
 - -No modeling/synthesis yet

This presentation + all slide contributions from P.I.s available on laptop in Foyer



Outline



- Introduction
 - -An apology
 - -Program/cruise objectives
 - -Strategy & implementation
- Overview of results so far
- Two vignettes







Program/Cruise Objectives

- To identify processes and quantify fluxes of key trace elements and isotopes (TEIs) in the ocean
 - That play a role in the global carbon cycle
 - That are diagnostic of biological, chemical, and geological marine processes
- To determine the global distributions of these TEIs (because very little is known)
 - Large-scale maps/inventories
 - Critical regions and boundaries/interfaces



Outline



- Introduction
 - -An apology
 - -Program/cruise objectives
 - -Strategy & implementation
- Overview of results so far
- Two vignettes





Strategy



- Global "mapping" and key "regions
 - Documenting water masses & biomes
 - Redox contrasts (e.g., Mauritanian OMZ)
 - Hydrothermal venting (e.g., TAG)
 - Ocean margins & interfaces
- Measure the key TEIs and their speciation
 - As a complete suite, all at the same time
 - Measure the ancillary properties/tracers
 - That give the rates and fluxes, all at the same time
 - A uniform, high quality, consistent data set
 - Including good hydrography, CTD, metadata



Implementation

- Multiple sampling systems:
 - Aerosol sampling
 - Underway TM-clean "fish"
 - T-M clean rosette (24 x 12L)
 - Hydrographic rosette (12 x 30L)
 - Particle pump-sampling















In Situ pumps – Particles & Diss. Radionuclides Paul Morris, Phoebe Lam, Dan Ohnemus, Stephanie Owens, Kuanbo Zhou, Steve Pike,

Paul Henderson, Matt Charette, Ken Buesseler, Billy Moore

- In situ pumps fitted dual flow filter heads and a Mn-sorption cartridge
- Niskin bottles collect ²²⁶Ra & ²³⁴Th samples to calibrate Mn-cartridge scavenging eff.
- Pump is a modified McLane pump. Modifications are patent pending (Lam & Morris)









Implementation

- 6 chemistry vans on deck
- Intensive use of lab space on the ship
 - Modified internal space (a lot of plastic partitioning)
- High degree of coordination between groups
- Organization of sample distribution







Outline



- Introduction
- Overview of results so far
 Some (really!) quick pictures
- Two vignettes





Organic complexation of dissolved Fe: Profiles from U.S. GEOTRACES North Atlantic section, Leg 1

Kristen N. Buck Preliminary Data Bermuda Institute of Ocean Sciences NSF Award OCE-0927453









* Ligands ([L₁], colored symbols) in excess of [Fe] at all depths

* Trends in [L₁] – [Fe] not simply reflecting [Fe]

BIOS



GEOTRACES 2010 Cruise Track 2010-11-09 23:45



* [L₁] vs [Fe] consistent with previous, maybe slightly higher [L₁]
* Strong (log K₁ > 11) Fe-binding ligands at all depths

BIOS

Dissolved total and labile Cobalt

Cobalt is the scarcest of metal micronutrients



A. Noble and M. Saito in prep

HOCEANOGRADHIC,



Dissolved total and labile Cobalt

0-400m for stations from both cruises excluding Line W

GT2010 and GT 2011



- 3. Despite removal of cobalt in intermediate and deep waters by scavenging:
 - A correlation with phosphate is found in shallow waters
 - The slope of which reflects the integrated ecological stoichiometry of cobalt by marine microbial processes



Dissolved total and labile Cobalt



A. Noble and M. Saito in prep



4000

5000 Stn 10 Stn 8 Stn 7

20°N

25°N

0.1

0.05

Data

ö o

.

30°N

Stn 5 Stn 3 Stn 1

35°N

Location map showing quasi-meridional section of GEOTRACES North Atlantic cruise Leg 1 (left), and interpolated sections of dissolved Fe (*dFe*, top right) and dissolved Fe(II) (*Fe-II*, bottom right).

Data: P. Sedwick, A. Bowie and B. Sosht.



4000 Stn 12

24°W

5000

Stn 11

22°W

Stn 10

20°W

0.1

0.05

0

Data View

Stn 9

18°W

Location map showing zonal section of GEOTRACES North Atlantic cruise Leg 1 (left) and corresponding interpolated sections of dissolved Fe (*dFe*, top right) and dissolved Fe(II) (*Fe-II*, bottom right).

Data: P. Sedwick, A. Bowie and B. Sosht.





Full water-column profile of dissolved Fe(II) showing relatively high concentrations in hydrothermal plume sampled over the Mid-Atlantic Ridge during Leg 2 of the GEOTRACES North Atlantic cruise.

Data: P. Sedwick, A. Bowie and B. Sosht.



Surface Total Dissolved Hg (pM)

Concentration of total dissolved Hg shows spatial trends:

Northern limb (2011) decreases from west to east.
CoFeMUG in subtropical South Atlantic was the same.
Southern limb (2010) very low in most locations, except where ITCZ or river plumes stray north.
Productivity + Trade winds/westerlies distinction?



Satellite salinity data for November 2011, from Aquarius (NASA).

Total Hg: Bio-active, Hybrid-type Profiles



Depleted at surface, with frequent mesopelagic maxima...biological scavenging.
NE Atlantic seems generally depleted compared to the rest of the basin, except in Mediterranean Overflow region.

•Dramatic peak at the TAG hydrothermal station...consistent with plume dilution of highly enriched vent fluids (ca. 1000 pM).



Elsie Sunderland and colleagues have documented a highly significant relationship between MMHg+DMHg (MeHg) and organic carbon remineralization rates (not AOU) within mesopelagic.

Implies dynamic

production/destruction...not just low oxygen is important...and limitation by carbon and/or other components.

Many N. Atlantic data off the line. Additional limitation? Different metabolism? Western Basin distinction?

all other stations virtually no DMHg

OCRR = ΔC_{org} /AGE = (R_{C:O}*AOU)/AGE (Feely et al., 2004)

Pacific and Indian Data courtesy of Elsie Sunderland, Harvard Sch. of Public Health Age data courtesy of Bill Smethie - LDEO



Chosen to quantify physics in order to quantify biogeochemical rates. Each tracer system has different/unique boundary conditions, time history, and space/time-scales.



Results from Smethie Lab







Distance (km)



Distance (km)

Dissolved Pb data from the US GEOTRACES North Atlantic Transect



MIT Pb data by Abigail Noble and Yolanda Echegoyen-Sanz

[Pb] sections (pmol/kg] are plotted west to east across the basin (above left) and eastern basin stations running south to north (above right). High Pb in intermediate waters remains from ventilation during previous decades when surface Pb concentrations were an order of magnitude higher than today. Surface and thermocline concentrations have decreased significantly relative to MIT profiles from the North Atlantic in 1989 and 1999 (see following figure). Station 16 sampled the TAG hydrothermal plume, and Pb appears to be scavenged within this oceanographic feature.

35°N

Temporal evolution of Pb in the western and eastern North Atlantic during the past 20-30 years



With the phasing out of leaded gasoline, the flux of Pb to the ocean's interior has decreased significantly over the last three decades. Stations that were previously occupied by our lab and others allow for a decadal "time-series" showing the gradual decrease in Pb concentrations in thermocline and intermediate waters from 1979 to 2011. See map on previous slide for locations of 2a, 2b, and 2c.

MIT Pb data by Boyle, Wu, Kayser, Echegoyen-Sanz, and Noble





Sigman group (D. Marconi, P. Rafter, A. Weigand)

The weak deep δ^{15} N increase to the west: NADW?



Sigman group (D. Marconi, P. Rafter, A. Weigand)



Sigman group (D. Marconi, P. Rafter, A. Weigand)
Iron Isotopes from (2010 Leg) Stations 9 and 10





Seth John and Tim Conway Marine Trace Element Lab, University of South Carolina

Several hypothesized features visible:

- 1. Dust input (+0.5-0.8 ‰)
- 2. Biological uptake of Fe
- 3. Deep sedimentary input of Fe

Cadmium Isotopes from (2010 Leg) Stations 9 and 10





Seth John and Tim Conway Marine Trace Element Lab, University of South Carolina

- Cd Isotope and concentration profiles reflect nutrient uptake and remineralization.
- Low concentration and high $\delta^{114}\text{Cd}$ at surface
- Deep water $\delta^{114}\text{Cd}$ stable at 0.3 0.4 %



Particle reactive isotopes

Differences in sorption between elements in the U-Th decay series highlights the particle and productivity dynamics in the water column, especially in hydrothermal plumes, bottom nepheloid layers and near boundaries.



Results from the ²³⁰Th-²³¹Pa-²³²Th group



Hayes, Anderson, Fleisher (LDEO); Robinson, Auro, Huang (WHOI); Cheng, Edwards (UMinn); Moran (URI)









New strategy to estimate trace element supply from aerosol deposition



Residence time of Th derived from ²³⁰Th/²³⁴U disequilibrium, Applied to dissolved ²³²Th gives <u>rate</u> of Th supply from dust.

(Hirose and Sugimura, 1987; Hsieh et al., 2011)

Paired Th isotopes to estimate soluble trace element supply by dust deposition:



Hayes, Anderson, Fleisher (LDEO); Robinson, Auro, Huang (WHOI); Cheng, Edwards (UMinn); Moran (URI)





Greatest Lateral Gradient Associated with Nepheloid Layer – Bottom Scavenging



Hayes, Anderson, Fleisher (LDEO); Robinson, Auro, Huang (WHOI); Cheng,, Edwards (UMinn); Moran (URI)

Basin-Wide, Size-Fractionated Particulate TEIs

Suspended (<51 μ m) and sinking (>51 μ m) concentrations for >20 pTEIs, in progress...



Phoebe J Lam particle group: Daniel Ohnemus, Maureen Auro

Fe_{xs} plumes in W. Basin, TAG, and near Mauritania



Fe_{xs} fully removes the strong benthic nepheloid signals in the deep western basin, indicating these layers are strongly terrestrial in nature. Strong Fe excesses (presumably from authigenic precipitation of Fe) are observed in particles at the TAG hydrothermal site and near reducing sediments at the Maruritanian coast. Weaker signals are found associated with Labrador seawater in the intermediate-depth west basin, and in the water column beneath the Saharan dust plume.

Phoebe J Lam particle group: Daniel Ohnemus, Maureen Auro



Particles (from pumps)

fraction susp POM [g/g]

fraction_susp_opal [g/g]

US-GT-NAT at the Ocean Carbon and Biogeochemistry meeting

<u>Contribution on ²¹⁰Po and ²¹⁰Pb activity in profiles from the GEOTRACES:</u> - Assessment of particles scavenging rate using ²¹⁰Po/²¹⁰Pb disequilibrium (soprtion+bioaccumulation processes) and ²¹⁰Pb/²²⁶Ra (sorption process only) - Assessment of POC export from surface ocean and biogenic particles regeneration in subsurface

Analysis of dissolved profiles

University of Delaware: T. Church, S. Rigaud

Analysis of small (<51 μm) particulate profiles + aerosols

Analysis of large (>51 μm) particulate profiles

Wayne State University: M. Baskaran

CUNY: G. Stewart, Y. Choi









Box model calculation



²¹⁰Pb atmospheric deposition

²¹⁰Pb activity in aerosols



 $\frac{\text{Total }^{210}\text{Pb deposition fluxes}}{F_{210Pb,T} = [^{210}Pb].v} \quad (v=1 \text{ cm.s}^{-1})$ $\frac{\text{Dissolved vs Particulate fluxes}}{F_{210Pb,D} = F_{210Pb,T} f_{Pb,s}}$ $F_{210Pb,P} = F_{210Pb,T} (1 - f_{Pb,s})$

*f*_{*Pb,s*} = 25% (*St1*) ; 2% (*St9*) [Shelley & Landing, Pers. Com.]



Measurements of biogenic particulate trace metals in the North Atlantic

Ben Twining Bigelow Laboratory for Ocean Sciences

Particulate metal stoichiometries in the upper water column



- Only a small percentage of many particulate metals are associated with phytoplankton.
- Bulk particulate P-normalized Fe, Mn and Ni are 10- to 20-fold above stoichiometries in ambient plankton (shown in green), even in the DCM. Co and Zn are comparable at DCM.
- See additional explanation in slide notes.

Ben Twining

Use of operational rinses to isolate biogenic fraction of particulate material



Ben Twining



Phytoplankton Fe quotas in different ocean basins

- Diatoms and Trichodesmium in the North Atlantic were extremely P-depleted (compare P-normalized to S-normalized Fe quotas)
- Diatoms have elevated Fe quotas in the North Atlantic, while picophytoplankton and nanoflagellates have similar Fe quotas in the North Atlantic and equatorial Pacific (is this due to different requirements or Fe storage abilities?)





Selected plots from Cutter Lab

2010 and 2011 US GEOTRACES North Atlantic Expeditions

Surface water nutrients (nmol/L) along 2010 and 2011 transects



NO2 [nM] @ DEPTH [M]=first

PO4 [nM] @ DEPTH [M]=first





G. Cutter, ODU



All surface water data along 2010-2011 transects







High resolution nutrients along N. African upwelling regime







Detailed behavior largely missed by conventional (4 h discrete) sampling. Elevated phosphate appears to correlate with lower temperature, an indicator of upwelled water.

G. Cutter, ODU



180°W

90°W

0°

90°E

180°E

300

0

2000

4000

Section Distance [km]

6000

8000

15

300

0

2000

4000

Section Distance [km]

6000

Combined 2010-2011 contoured nanomolar nutrient results

G. Cutter, ODU

8000

35.5

35

34.5



Compare to 2010-2011 contoured conventional nutrient results







Underway Surface Data: Abundances



Log (*nifH* DNA copies*L⁻¹) Log (*nifH* cDNA copies*L⁻¹)

Data from D361- UK GEOTRACES R. Langlois, J. LaRoche, T. Großkopf, E. Achterberg

Time-dependent fractional aerosol Fe solubility



Back trajectory simulations showing air mass provenance for three aerosol collections during the US GEOTRACES Atlantic cruises.

Instantaneous Leaches: leached in duplicate with same seawater as the extended leaches, and without replication using MQ (volume ~ 150 ml). Solubility was calculated

from the dissolved Fe in leachate and particulate Fe in unleached filters Extended Leaches: Leached in triplicate with homogenized freshly collected filtered seawater for ~ 24 hrs at a flow rate of 9.3 ml min⁻¹ (volume ~ 13 L). Solubility was calculated as the difference in particulate Fe from leached and unleached filters.

Time-dependent fractional aerosol Fe solubility



- The fraction of soluble aerosol Fe obtained with instantaneous MQ and sea water leaches was comparable and lower than the fraction obtained with the extended leaches.
- Free natural organic Fe-binding ligands were present in the leaching seawater and likely contributed to the enhanced Fe solubility in the extended leaches

Air mass provenance:

E = Europe, M = Maritime, S = Sahara, SMK = biomass smoke

Aguilar-Islas preliminary data








NUAA HYSPLIT WUDEL Backward trajectories ending at 1800 UTC 11 Nov 11











Total aerosol Al [ug/m2/d]









Total aerosol AI [ug/m2/d]



- (a) N. Atlantic GEOTRACES total Al deposition
- (b) Modeled N. Atlantic total Al deposition(Mahowald et al. 2009)



Outline



- Introduction
- Overview of results so far
- Two vignettes
 - -A slice of an oxygen minimum zone
 - -The TAG hydrothermal plume





The Mauritanian OMZ

Rates deduced by 2-D upwelling model calibrated by

- CFCs, SF₆, Pb, ³H-³He (ventilation, vertical/lateral diffusion)
- ¹⁴C, ³He (upwelling velocities via G.E.R. Δ balance)
- ²²⁸Th (remineralization), ²²⁸Ra (lateral diffusion) streamlines



228 Ra-derived vertical mixing – 1D Paul Morris, Matt charlette, Paul Henderson, Billy Moore ixing – 1D



- Diapycnal vertical mixing (K_v) calculated using a 1D steady-state diffusion model
- Vertical mixing increases as we move away from the coastline
- Data too sparse to perform the same calculation for horizontal mixing
- Questionable results higher than expected based on literature values
- Progress to a 2D modeling analysis

Paul Morris, Model Runs

- Physical Circulation, vertical & horizontal mixing
- Geochemical ²²⁸Ra supply ML, deep, & atmospheric



Paul Morris, Bill Perkins, Matt Charette – Modeled vs Obs.



DFe data from Uses, of tta & Randewined mixing



Utility of measuring mixing rates in parallel to other measurements Calculate vertical and horizontal mixing of DFe using ²²⁸Ra-derived mixing rate DFe gradient x K = DFe mixing rate

In Situ pumps – Particles & Diss. Radionuclides Paul Morris, Phoebe Lam, Dan Ohnemus, Stephanie Owens, Kuanbo Zhou, Steve Pike,

Paul Henderson, Matt Charette, Ken Buesseler, Billy Moore

- In situ pumps fitted dual flow filter heads and a Mn-sorption cartridge
- Niskin bottles collect ²²⁶Ra & ²³⁴Th samples to calibrate Mn-cartridge scavenging eff.
- Pump is a modified McLane pump. Modifications are patent pending (Lam & Morris)









Outline



- Introduction
- Overview of results so far
- Two vignettes
 - -A slice of an oxygen minimum zone
 - -The TAG hydrothermal plume



The TAG Hydrothermal Plume



Caveats:

Fe and ³He drawn on separate casts (Fe on multiple casts) Need to relate using CTDs with:

- (1) Neutral surface analysis
- (2) Thermal anomalies on T-S



Section Distance [km]

Global Fluxes and Rates

- ³He is stable & inert: a dilution tracer
 TE:³He relation diagnostic of loss/gain
- Global hydrothermal ³He flux is known – (~750 mol a⁻¹)
- Use TE:³He to infer TE hydrothermal flux
 - Western South Pacific^{*} Fe:³He ~ 10⁶ → 0.9 Gmol a⁻¹
 - South Atlantic^{**} Fe:³He \sim 70 x 10⁶ \rightarrow \sim 2 Gmol a⁻¹
 - North Atlantic???? Is chemistry different for slow spreading ridges?

TAG (N. Atl. M.A.R.) Fe:³He



- But ²²⁸Th says this is "fresh" Fe...
- Must look at flank relationship (d>2000m):



Need to do detailed OMPA to assess "non-local" ³He





Summary



- The first U.S. GEOTRACES transect a success*
- Wide range of properties (TEIs) measured
- Data sets emerging
 - Beautiful pictures
 - Clear process diagnostics (e.g., OMZ & TAG)
 - Completion and synthesis in progress
 - Modeling to follow

*Despite ship propulsion problems





Outline



- Introduction
- Overview of results so far
- Two vignettes
- Acknowledgements
 - -Bob, Gideon, and many others
 - -US-GNAZT co-conspirators
 - -Don Rice, NSF, & helpful reviewers
 - -The community at large



Paul Morris, Phorbe Lamps - Particles & Diss. Radionuclides

Henderson, Matt Charette, Ken Buesseler, Billy Moore



- In situ pumps fitted with dual flow filter holders and a Mn-sorption cartridge downstream of the filter holders
- 30L Niskin bottles collect ²²⁶Ra & ²³⁴Th samples to calibrate Mn-cartridge scavenging efficiency
- Pump is a modified McLane pump.
 Modifications are patent pending (Lam & Morris)
- Dual flow filter holders allow simultaneous particle collection on precombusted quartz fiber filters (QMA) and acid-leached polyethersulfone (Supor) filters. Both sides have a 51um prefilter for size fractionation

Suspended particulate matter concentration and composition

Phoebe J. Lam, Daniel C. Ohnemus, Maureen E. Auro, Stephanie Owens, Ken Buesseler

- Suspended particulate matter (SPM) *concentration* and *composition* are key parameters determining the scavenging removal of particle-reactive elements
- We measure the major chemical constituents of marine particles. SPM concentration is determined as their sum:



SPM = Σ(lithogenics, CaCO₃, opal, POM, oxyhydroxides)

- Lithogenic material dominates particle composition, especially under the Saharan plume (eg. Mauritanian coast) and in benthic nepheloid layers
 CaCO₃ is the next most abundant particle phase (20-60%)
- Opal varies by 10x from the coastal stations to the oligotrophic gyres, but is overall low (<20%)

4 "charismatic" particle features

Phoebe J. Lam, Daniel C. Ohnemus, Maureen E. Auro, Stephanie Owens, Ken Buesseler



- TAG hydrothermal plume: SPM is 3x above bkgd and composed of 60% FeOOH (typical FeOOH is 1%)
- Mauritanian nepheloid layer: SPM is 10x above bkgd, and is the only nepheloid layer enriched in FeOOH and MnOOH
- **BATS nepheloid layer**: SPM is also 10x above bkgd and enriched in lithogenics compared to the water column above, and extends *1000m* up from the ocean bottom
- Line W nepheloid layer is 500x (!) above background and is primarily lithogenic



 These samples provide a wide range of particle mass and composition to test hypotheses about particle control of scavenging