ANNUAL REPORT ON GEOTRACES ACTIVITIES IN THE UNITED STATES

June 1st, 2015 to April 30th, 2016

Principal activities of the U.S. GEOTRACES program include:

1. Preparing manuscripts from Pacific section (GP16),
2. Analyzing samples from the Arctic (GN01), and
3. Preparing to host a synthesis workshop.

Activities

North Atlantic: Papers from Atlantic section GA03 continue to be published (see Publications below). New data sets have been submitted for IDP2017.

Eastern Tropical Pacific: Approximately 65 investigators (scientists, post docs and students) participated in a data workshop for the Eastern Tropical South Pacific section (GP16) covered by U.S. GEOTRACES. The workshop was held 8-13 November 2015 at the University of Southern California – Wrigley Institute for Environmental Studies facility on Catalina Island. The workshop allowed investigators the opportunity to scrutinize each data set, comparing similarities and dissimilarities among the various tracers, with a view toward identifying information provided by each tracer about the principal processes (e.g., dust deposition) and environmental conditions (e.g., oxygen minimum zone, hydrothermal plume) that regulate the distributions of trace elements and their isotopes along the section. A more complete report on the workshop is included as an Appendix 2 to this report.

A number of oral and poster presentations of GP16 data were made at the 2016 Ocean Sciences meeting in New Orleans (21–26 February). Presentations from GP16 were distributed throughout all of the GEOTRACES-related sessions at the meeting, rather than in a single session devoted to the GP16 section.

Arctic Ocean: U.S. investigators participated in an international GEOTRACES study of the Arctic Ocean during the summer of 2015, sailing aboard the U.S. Coast Guard Cutter Healy (HLY1502, 9 August to 12 October, sailing out of and returning to Dutch Harbor, Alaska; Chief Scientist: David Kadko, Co-Chief Scientist: Bill Landing, Logistics Coordinator: Greg Cutter). The expedition included a northbound track through the Makarov Basin, reaching the North Pole on 7 September, followed by a southbound track through the Canada Basin (Figure 6).

Relatively thin ice allowed investigators to cover the entire cruise track, which was by no means certain before the ship sailed. Indeed, this expedition was the first occasion that a U.S. surface ship has reached the North Pole without an escort by another icebreaker, an indication of the changes in the Arctic ice as a consequence of recent global warming.

While on station at the North Pole the U.S. team was visited by the Polarstern, carrying the German GEOTRACES program from the opposite side of the Arctic Ocean under the leadership of Michiel Rutgers van der Loeff of the Alfred Wegener Institute in Bremerhaven.

GN01 was carried out in partnership with the CLIVAR Repeat Hydrography program under the leadership of Jim Swift of the Scripps Institution of Oceanography. By sharing their combined hydrographic data, sampling was carried out at a much greater spatial resolution than would have been possible if GEOTRACES had completed the expedition by itself. The expertise of the Repeat Hydrography team will be invaluable in providing a hydrographic framework to interpret the GEOTRACES trace element and isotope results.

Sampling of sea ice was also carried out on GN01. However, due to the relatively fragile ice conditions and related concerns about the safety of investigators working on the ice, only six of the ten planned ice stations were completed.

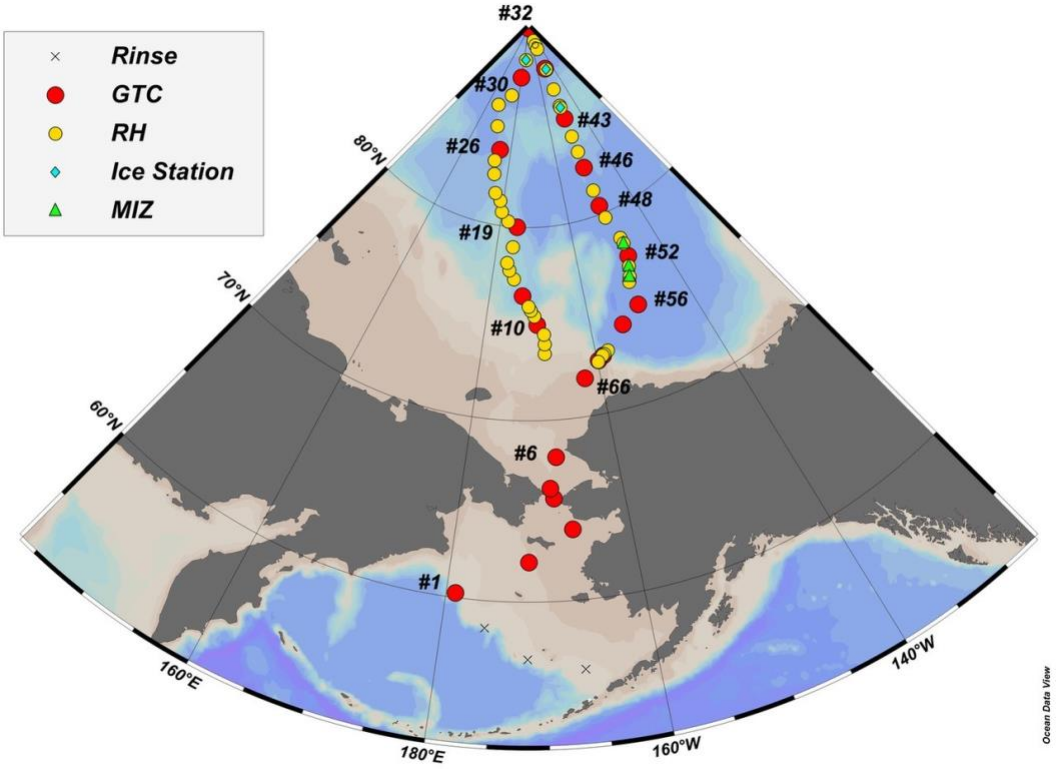

Figure 1. US GEOTRACES cruise track along GN01 (Healy 1502), heading north on the western, Makarov Basin leg, returning south along the eastern, Canada Basin leg. The legend indicates the various types of stations occupied: GTC refers to a full-depth GEOTRACES station; RH indicates a full depth Repeat Hydrography station, which involved a single hydrographic cast to sample the full water column for selected hydrographic parameters and circulation tracers; MIZ refers to stations in the marginal ice zone where sampling of the upper water column was conducted, and Ice Station indicates locations where sea ice and melt pond water were collected. Map compliments of Mariko Hatta, University of Hawaii.

Pacific Meridional Section: The U.S. GEOTRACES SSC has designated GP15 to be the next section to be carried out by the U.S. program, conditional on funding. A team led by Greg Cutter (Chief Scientist) as well as Phoebe Lam and Karen Casciotti (co-Chief Scientists) plans to submit a proposal to the U.S. NSF Chemical Oceanography program for its 15 August 2016 proposal deadline to secure ship time and cover major logistics costs (e.g., operation of the trace metal clean sampling system) of the expedition. If the plan is approved and funded, then individual U.S. investigators will submit proposals for research on specific TEIs and other

tracers for the NSF proposal deadline on 15 February 2017. Cruise dates have been requested to sail southbound from Alaska to Tahiti in period July – September 2018.

Although funding for GP15 is by no means guaranteed, the U.S. GEOTRACES community plans to meet in early October to refine the goals laid out in the U.S. GEOTRACES Pacific Plan (2008) and set scientific priorities for the section. The workshop will also allow individual investigators to coordinate their planned research for GP16 well in advance of the 15 February 2017 proposal deadline.

Town Hall: Working together with SCOR and the GEOTRACES IPO, US GEOTRACES cohosted a town hall at the 2016 Ocean Sciences meeting to inform the oceanographic community about plans for future data products and upcoming cruises, while also seeking feedback from the community to improve the next data product, scheduled for release in 2017.

New Funding

- A proposal to continue funding for the U.S. GEOTRACES project office at the Lamont-Doherty Earth Observatory was submitted to the US NSF in February 2015. The proposal was selected for funding and will cover project office expenses for three years. Funding is provided jointly by the Chemical Oceanography program and the Arctic Natural Sciences program at NSF.

Presentation of results

- A large number of presentations based on results from the GP16 section were made at the 2016 Ocean Sciences meeting dates New Orleans, USA, as described above.

U.S. GEOTRACES Meetings

- As described above, investigators involved in GP16 held a data workshop 8-13 November 2015.

Outreach Activities

Significant effort was invested in outreach for the U.S. Arctic GEOTRACES program under the leadership of Bill Landing, Florida State University, co-chief scientist of the expedition together with chief scientist David Kadko, Florida International University. Several ongoing cruise "blogs" were maintained as well as significant representation at home university web sites and the ship's shore-based website.

1. Bill Schmoker, the on-board PolarTREC science teacher, posted over 65 blogs (with descriptive text and photos) to the PolarTREC web site: www.polartrec.com/expeditions/us-arctic-geotraces/journals
2. Dr. Peter Morton's blog: http://SeaPeteRun.tumblr.com;
3. Dr. Katlin Bowman maintained a personal blog: http://hginthesea.wordpress.com; she was also invited to write for the Huffington Post: www.huffingtonpost.com/katlinbowman/
4. Alison Agather's blog: http://alisonsarcticadventure.wordpress.com

5. Laura Whitmore's blog: http://healy-polar-usm.tumblr.com
6. Dr. Jim Swift: http://ushydro.ucsd.edu/outreach
7. Andrew Margolin's blog: http://arctic-andy-usaos2015.blogspot.com; http://instagram.com/arctic_andy/; http://twitter.com/arctic_andy; http://rsmas.miami.edu/blog/
8. Dr. Tim Kenna's blog: TRACES of Change in the Arctic: http://blogs.ei.columbia.edu/tag/traces-of-change-in-the-arctic/
9. Dr. Dave Kadko, Florida International University news release: http://news.fiu.edu/2015/08/fiu-professor-to-lead-historic-arctic-research-expedition
10. Dr. Bill Landing's home web site: http://www.eoas.fsu.edu/
11. Dr. Ana Aguilar-Islas, University of Alaska Fairbanks news release: https://web.sfos.uaf.edu/wordpress/news/?p=1953
12. Healy cruise track: http://icefloe.net/uscgc-healy-track-map
13. Daily pictures from the aloft conning tower: http://icefloe.net/Aloftcon_Photos/index.php?album=2015

In addition, there were other outreach efforts:

14. Kawerak Conference: As part of the US Arctic GEOTRACES outreach effort, Dave Kadko, Bill Landing and Ana Aguilar-Islas put together a package for presentation at the Kawerak Conference (31 May – 4 June, 2015; Nome, Alaska USA). This was a meeting for rural Alaska natives and other rural Alaska residents. Ana Aguilar-Islas represented GEOTRACES at the meeting where she made a presentation for GEOTRACES, passed out a brochure, and was available for interviews and discussions with attendees. The local radio station did a story that was later picked up by Alaska Dispatch News. Links to those stories: http://www.knom.org/wp/blog/2015/06/05/over-50-arctic-researchers-on-coast-guardcutter-healy-preparing-north-pole-voyage/ http://www.adn.com/article/20150609/arctic-researchers-prepare-voyagenorth-pole-aboard-coast-guards-healy

15. U.S. GEOTRACES participated in a novel outreach project designed and coordinated by Dave Forcucci (US Coast Guard Marine Science Coordinator) to involve students and the public with an Arctic research cruise on Healy. GEOTRACES was a perfect match for the inaugural kick off of "Float your Boat". One thousand 8-inch-long cedar boats were commissioned (funded by GEOTRACES with 1,300 boats being the final number) from the Center for Wooden Boats (CWB.org) in Seattle, Washington, USA and distributed to school groups, scout troops, and science open-house events around the country. Students personalized their boats with bright colors and after returning to Seattle the boats were branded with floatboat.org and packed into the hold of Healy for journey to the North Pole. During the GEOTRACES cruise, four groups of boats were deployed on ice floes between 87.5° N and 80° N on the 150° W meridian, each with a small satellite buoy that was deployed by the University of Washington Applied Physics Lab to study ice movement. The iridium satellite-linked buoys provide an opportunistic chance for high-resolution, real-time tracking of the boats for at least the short term (1 year or so). After drifting with the Arctic ice, the boats will eventually be free of its grasp and float to a distant shore to be discovered and reported. This was documented by our on-board PolarTREC teacher, Bill Schmoker, on his PolarTREC web site blog:

https://www.polartrec.com/expeditions/us-arcticgeotraces/journals/2015-09-16. The "Float Your Boat" wooden boat project: http://www.floatboat.org/; and https://www.facebook.com/explorethearctic

16. The U.S. Coast Guard offered an oceanography course to its crew aboard the Healy for college credit. US GEOTRACES investigators Dave Kadko, Jim Swift, Chris Measures, Phoebe Lam, Bill Landing, Susan Becker and Greg Cutter contributed lectures to this program. Two students, Alyson Agather and Lauren Kipp also contributed lectures.

17. Science lectures were presented every Wednesday night during the expedition, geared to the Coast Guard crew. Numerous scientists and students contributed to this activity.

Outreach Activities after completion of the Arctic Expedition:

18. Katlin Bowman (University of California Santa Cruz) participated in a community event at Filson's San Francisco store where she discussed working in the Arctic Ocean. Filson is an outdoor clothing brand that highlights the stories of men and women that work outdoors. Her cruise photos were on display during the event and she gave an informal presentation about working in the Arctic and why GEOTRACES is studying the chemistry of the global ocean.

19. Jessica Fitzsimmons (Texas A&M University) prepared four scripts on Arctic Ocean climate change and oceanography for a monthly series of On the Ocean National Public Radio show, produced by Texas A&M Oceanography and radio station KAMU-FM: http://abcmgr.tamu.edu/ontheocean/

20. Both prior to and following the Arctic expedition Mariko Hatta (University of Hawaii) presented talks at the Mid-Pacific Institute (July and December 2015). She provided a pre-cruise lecture to ~150 students (6-10 years old) at Mid-Pacific Institute in order to introduce the GEOTRACES projects as well as the nation-wide project "Float Your Boat." This was followed up by a joint talk between Hatta and Chris Measures (University of Hawaii) showing results and interesting features of the cruise during a December, 2015 presentation. During the cruise, Hatta and Measures sent weekly emails with limited photographs to the teachers at the institute to update real-time cruse projects, life, and wild animal information. Their lectures aboard the Healy are mentioned above.

21. In January 2016 Hatta and Measures made a similar presentation to approximately 100 students, 15 – 18 years old, at the Honolulu Waldorf School.

22. During their institutional (SOEST) open house, 23-24 October 2015, shortly following the cruise, Hatta and Measures presented a 15 min movie made from the photo/movie clips during the cruise to share with students (6-15 years old) our latest knowledge and the highlights of the projects in the Arctic Ocean.

23. Greg Cutter (Old Dominion University, ODU), who was responsible for research logistics aboard the Healy, made several presentations following the expedition. In October 2015 he gave a presentation to the Society of Naval Architects and Marine

Engineers, Hampton Roads Section, entitled "US GEOTRACES Expedition to the North Pole." In February he presented "The Changing Arctic Ocean" at the ODU February Science Pub Nights, Wasserhund Brewery, Virginia Beach, Virginia USA. In April 2016 he presented "Arctic Ocean Adventures – A two-month expedition to the North Pole and back" to the Hampton Yacht Club membership, Hampton Virginia USA.

Publications (GEOTRACES, GEOTRACES Compliant and GEOTRACES-related)

During the past year US GEOTRACES investigators published a total of 21 peer-reviewed papers.

- Charette, M.A., Morris, P.J., Henderson, P.B., Moore, W.S., 2015. Radium isotope distributions during the US GEOTRACES North Atlantic cruises. Marine Chemistry, 177, Part 1, 184-195.
- Conway, T.M., John, S.G., Lacan, F., in press. Intercomparison of dissolved iron isotope profiles from reoccupation of three GEOTRACES stations in the Atlantic Ocean. Marine Chemistry.
- Fitzsimmons, J.N., Hayes, C.T., Al-Subiai, S.N., Zhang, R., Morton, P.L., Weisend, R.E., Ascani, F., Boyle, E.A., 2015. Daily to decadal variability of size-fractionated iron and iron-binding ligands at the Hawaii Ocean Time-series Station ALOHA. Geochimica et Cosmochimica Acta, 171, 303-324.
- Haskell II, W.Z., Kadko, D., Hammond, D.E., Knapp, A.N., Prokopenko, M.G., Berelson, W.M., Capone, D.G., 2015. Upwelling velocity and eddy diffusivity from 7Be measurements used to compare vertical nutrient flux to export POC flux in the Eastern Tropical South Pacific. Marine Chemistry, 168, 140-150.
- Hayes, C.T., Fitzsimmons, J.N., Boyle, E.A., McGee, D., Anderson, R.F., Weisend, R., Morton, P.L., 2015. Thorium isotopes tracing the iron cycle at the Hawaii Ocean Timeseries Station ALOHA. Geochimica et Cosmochimica Acta, 169, 1-16.
- Kadko, D., Landing, W.M., Shelley, R.U., 2015. A novel tracer technique to quantify the atmospheric flux of trace elements to remote ocean regions. Journal of Geophysical Research: Oceans, 120, 848-858.
- Kipp, L.E., Charette, M.A., Hammond, D.E., Moore, W.S., 2015. Hydrothermal vents: A previously unrecognized source of actinium-227 to the deep ocean. Marine Chemistry, 177, 583-590.
- Lee, J.-M., Boyle, E.A., Gamo, T., Obata, H., Norisuye, K., Echegoyen, Y., 2015. Impact of anthropogenic Pb and ocean circulation on the recent distribution of Pb isotopes in the Indian Ocean. Geochimica et Cosmochimica Acta, 170, 126-144.
- Lerner, P., Marchal, O., Lam, P.J., Anderson, R.F., Buesseler, K., Charette, M.A., Edwards, R.L., Hayes, C.T., Huang, K.-F., Lu, Y., Robinson, L.F., Solow, A., 2016. Testing models of thorium and particle cycling in the ocean using data from station GT1122 of the U.S. GEOTRACES North Atlantic section. Deep Sea Research Part I: Oceanographic Research Papers, 113, 57-79.

- Maiti, K., Charette, M.A., Buesseler, K.O., Zhou, K., Henderson, P., Moore, W.S., Morris, P., Kipp, L., 2015. Determination of particulate and dissolved 228Th in seawater using a delayed coincidence counter. Marine Chemistry, 177, Part 1, 196-202.
- Marconi, D., Alexandra Weigand, M., Rafter, P.A., McIlvin, M.R., Forbes, M., Casciotti, K.L., Sigman, D.M., 2015. Nitrate isotope distributions on the US GEOTRACES North Atlantic cross-basin section: Signals of polar nitrate sources and low latitude nitrogen cycling. Marine Chemistry, 177, Part 1, 143-156.
- Mawji, E., Schlitzer, R., Dodas, E.M., Abadie, C., Abouchami, W., Anderson, R.F., Baars, O., Bakker, K., Baskaran, M., Bates, N.R., Bluhm, K., Bowie, A., Bown, J., Boye, M., Boyle, E.A., Branellec, P., Bruland, K.W., Brzezinski, M.A., Bucciarelli, E., Buesseler, K., Butler, E., Cai, P., Cardinal, D., Casciotti, K., Chaves, J., Cheng, H., Chever, F., Church, T.M., Colman, A.S., Conway, T.M., Croot, P.L., Cutter, G.A., de Baar, H.J.W., de Souza, G.F., Dehairs, F., Deng, F., Dieu, H.T., Dulaquais, G., Echegoyen-Sanz, Y., Lawrence Edwards, R., Fahrbach, E., Fitzsimmons, J., Fleisher, M., Frank, M., Friedrich, J., Fripiat, F., Galer, S.J.G., Gamo, T., Solsona, E.G., Gerringa, L.J.A., Godoy, J.M., Gonzalez, S., Grossteffan, E., Hatta, M., Hayes, C.T., Heller, M.I., Henderson, G., Huang, K.-F., Jeandel, C., Jenkins, W.J., John, S., Kenna, T.C., Klunder, M., Kretschmer, S., Kumamoto, Y., Laan, P., Labatut, M., Lacan, F., Lam, P.J., Lannuzel, D., le Moigne, F., Lechtenfeld, O.J., Lohan, M.C., Lu, Y., Masqué, P., McClain, C.R., Measures, C., Middag, R., Moffett, J., Navidad, A., Nishioka, J., Noble, A., Obata, H., Ohnemus, D.C., Owens, S., Planchon, F., Pradoux, C., Puigcorbé, V., Quay, P., Radic, A., Rehkämper, M., Remenyi, T., Rijkenberg, M.J.A., Rintoul, S., Robinson, L.F., Roeske, T., Rosenberg, M., van der Loeff, M.R., Ryabenko, E., Saito, M.A., Roshan, S., Salt, L., Sarthou, G., Schauer, U., Scott, P., Sedwick, P.N., Sha, L., Shiller, A.M., Sigman, D.M., Smethie, W., Smith, G.J., Sohrin, Y., Speich, S., Stichel, T., Stutsman, J., Swift, J.H., Tagliabue, A., Thomas, A., Tsunogai, U., Twining, B.S., van Aken, H.M., van Heuven, S., van Ooijen, J., van Weerlee, E., Venchiarutti, C., Voelker, A.H.L., Wake, B., Warner, M.J., Woodward, E.M.S., Wu, J., Wyatt, N., Yoshikawa, H., Zheng, X.-Y., Xue, Z., Zieringer, M., Zimmer, L.A., 2015. The GEOTRACES Intermediate Data Product 2014. Marine Chemistry, 177 Part 1, 1 - 8.
- Middag, R., Séférian, R., Conway, T.M., John, S.G., Bruland, K.W., de Baar, H.J.W., 2015. Intercomparison of dissolved trace elements at the Bermuda Atlantic Time Series station. Marine Chemistry, 177, Part 3, 476-489.
- Ndungu, K., Zurbrick, C.M., Stammerjohn, S., Severmann, S., Sherrell, R.M., Flegal, A.R., 2016. Lead Sources to the Amundsen Sea, West Antarctica. Environ Sci Technol, DOI 10.1021/acs.est.1025b05151.
- Parker, C.E., Brown, M.T., Bruland, K.W., 2016. Scandium in the open ocean: A comparison with other group 3 trivalent metals. Geophysical Research Letters, DOI 10.1002/2016GL067827.
- Quay, P., Cullen, J., Landing, W., Morton, P., 2015. Processes controlling the distributions of Cd and PO4 in the ocean. Global Biogeochemical Cycles, 29, 830-841.
- Roshan, S., Wu, J., 2015a. Cadmium regeneration within the North Atlantic. Global Biogeochemical Cycles, 29, 2082-2094.
- Roshan, S., Wu, J., 2015b. The distribution of dissolved copper in the tropical-subtropical north Atlantic across the GEOTRACES GA03 transect. Marine Chemistry, 176, 189-198.

- Roshan, S., Wu, J., 2015c. Water mass mixing: The dominant control on the zinc distribution in the North Atlantic Ocean. Global Biogeochemical Cycles, 29, 1060-1074.
- Sherrell, R.M., Lagerström, M.E., Forsch, K.O., Stammerjohn, S.E., Yager, P.L., 2015. Dynamics of dissolved iron and other bioactive trace metals (Mn, Ni, Cu, Zn) in the Amundsen Sea Polynya, Antarctica. Elementa: Science of the Anthropocene, 3, 1-27.
- Twining, B.S., Rauschenberg, S., Morton, P.L., Vogt, S., 2015. Metal contents of phytoplankton and labile particulate material in the North Atlantic Ocean. Progress In Oceanography, 137, 261-283.

In addition, we have identified the following as a US GEOTRACES publication from 2014 that was missed in preparing our annual report last year.

- Kwon, E.Y., Kim, G., Primeau, F., Moore, W.S., Cho, H.-M., DeVries, T., Sarmiento, J.L., Charette, M.A., Cho, Y.-K., 2014. Global estimate of submarine groundwater discharge based on an observationally constrained radium isotope model. Geophysical Research Letters, 41, 8438–8444.

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APPENDIX – U.S. GEOTRACES

GP16 DATA WORKSHOP REPORT

Results of the GEOTRACES GP16 Synthesis Workshop held at the University of Southern California Wrigley Institute for Environmental Studies 8 - 13 November 2015.

An Informal Summary by James Moffett, University of Southern California, Co-chief Scientist

A synthesis workshop for the Eastern Tropical South Pacific Zonal Section (GEOTRACES GP16) was held Nov 8-13 at the USC Wrigley Institute for Environmental Studies on Catalina Island. Approximately 65 attendees represented all of the research groups who were funded to participate in the project. In addition, four modelers attended the workshop, plus an expert on continental weathering who studies the Andes. The meeting was scheduled like a Gordon Conference, with morning and evening sessions and including a break in the afternoon. The primary objectives of the meeting were to bring everyone up to speed with the latest results, and to identify important problems where small groups could work together to generate synthesis papers.

The first evening was devoted to characterizing the basic features of the section. Chris German gave an overview of the hydrography of GP16 with a contribution from Jim Swift. Brian Peters (graduate student at Stanford University) presented an OMPA water mass analysis of GP16 and Dan Ohnemus (Bigelow Laboratory) described an approach to assign a consistent value for the mixed layer depth over the section.

Each group gave 1 to 3 15-minute presentations. Monday's presentations focused on the western half of the section, particularly the hydrothermal plume, while Tuesday was focused on the eastern margin and OMZ. On Monday evening, four modelers (Tim De Vries, Keith Moore, Curtis Deutsch and Thomas Weber) described results specifically focused on GP16. Their contributions are included in the discussion below.

The remainder of the meeting focused on important observations and highlights, many of which were made by different groups with very different experimental approaches and a different suite of key parameters. Breakout groups were organized around these phenomena. Of primary importance were the two plumes that were featured on the cover of Nature in July 2015, associated with the report by Resing et al. Basic features of each plume were studied in breakouts, and they were compared in plenary. Iron in the hydrothermal plume (hereafter designated "HTP") was of great interest because of its persistence, and the linear relationship with dissolved Fe and ^{3}He. However, a closer inspection revealed that the particulate Fe maxima showed an increase with depth moving offshore (Sherrell and Lam groups). Results indicate that there may be a significant adsorption and desorption of Fe from these particles, leading to a net removal that may have significant implications for the fraction of Fe that ultimately makes it to surface waters. It was also shown that much of the dissolved Fe was actually colloidal – in the plume and elsewhere (Wu group, University of Miami). Comparison with the organic ligand data indicated that the colloidal fraction probably appears as a very strong Fe complex with no excess ligand. Indeed, in the high Fe environments such as these plumes, there did not appear to be any excess ligands. There was generally a feeling that the earlier paradigm of Fe speciation

and transport being determined by a strong ligand class (with Fe concentrations ultimately controlled by whatever is controlling the ligand) need significant revision. It was also apparent that Mn was controlled by very different processes, in spite of the cursory similarities of the plume. Particulate Mn sank more slowly (with respect to ^{3}He) and there was no colloidal component in the dissolved fraction (Wu group). Particulate Fe was predominantly Fe oxides, according to synchrotron data (Toner group, University of Minnesota). There are no Mn data yet from the Synchrotron, but it was assumed that particulate Mn is probably associated with free-living Mn oxidizing bacteria, which sink slowly. Participants strongly encouraged the Toner lab to pursue more synchrotron work on Mn with HTP particulate samples.

Comparison of Zn to Si suggests that there is a slight excess of Zn within the plume, suggesting the hydrothermal sources of zinc may lead to significant revisions of global Zn budgets. For other TEIs, including Th-230, the particles within the plume acted as important scavenging sinks (Anderson Group, Lamont-Doherty Earth Observatory).

Resing et al. (2015) argued that the HTP was significant because it is probably an important source of Fe to the Southern Ocean. This assertion was examined by the group. Dissolved Fe data determined by ICPMS, particularly at the core of the HTP, were ~25% lower than the shipboard Fe data reported by Resing et al (2015). Moreover, models presented at the workshop suggested that a smaller fraction of Fe makes its way to the Southern Ocean. Nevertheless, there was a consensus that the HTP is still a significant source of dissolved Fe to the plume.

The Eastern Boundary Plume (EBP) received less attention in Resing et al. (2015), but a lot of attention at the workshop. There were similarities and important differences in these two plumes. Fe concentrations were similar in both of these features and dissolved Fe was persistent, in spite the EBP being in highly oxygenated water (as was the HTP). This suggested chemical transformation into fairly non-reactive Fe(III) species. Speciation data indicated that the dissolved Fe was strongly complexed, but it may have been colloidal. Samples for colloids within the EBP were collected by the Wu group but were not analyzed at the time of the meeting. The plume was much deeper than the oxygen minimum zone and disconnected from the overlying Fe(II) plume extending westward off the shelf (Moffett group, University of Southern California).

Nevertheless, several aspects of the EBP chemistry suggest that the Fe in the EBP has undergone redox cycling. Firstly, there is the virtual absence of Al and Mn in the EBP. This is in stark contrast to the HTP, where Al and Mn are abundant. It is surprising given the crustal ratios of both elements to Fe. Fe redox cycling could decouple it from Mn and Al in a variety of ways if there are significant benthic transformations associated with the source. For example if Fe and Al are delivered to reducing margin sediments in sinking particles, Fe would be released as Fe(II) whilst Al remains. This would decouple the two elements even if Fe(II) were re-oxidized in the overlying waters. Mn could be decoupled from Fe as a result of its slow oxidation and exceedingly long residence time in the upper water column, where it is strongly correlated with Ra-228 (see below). Consistent with this mechanism is the very light delta Fe-56 signature of the EBP (John Group, University of Southern California) in contrast to the HTP which showed no fractionation. The isotopically light Fe indicates fractionation associated with partial reduction of Fe(III) to Fe(II).
The source of Fe in the EBP was not determined at the meeting. While dissolved Fe is very high on the Peruvian shelf, I argued that much of this Fe is retained on the shelf by redox 'trapping' (Vedamati et al (2015) and is not exported. Moreover, fluvial sources in Peru are small.

However, there are several large rivers in Ecuador that could be the source of this Fe. A northern source is consistent with the water mass associated with the core of the EBP – Pacific Deep Water. This was established in the water mass analysis performed by Brian Peters (Stanford) and presented at the start of the meeting. Josh West, a weathering expert from the University of Southern California who works on the Andes, gave a presentation making this case. Josh also pointed out that there is a strong volcanic signature in Ecuadorean source rocks very distinct from the Peruvian Andes. Neodymium isotope ratios are influenced by a volcanic source and might provide important insight when those data become available.

The oxygen minimum zone itself was characterized by high concentrations of Fe over the shelf, predominantly as Fe(II), and a plume of Fe extending west of the shelf/slope break that was composed of Fe(II) and Fe(III) and coincident with the secondary nitrite maximum. The feature was coincident with a maximum in iodide, which was presumably generated from the microbial reduction of iodate.

A major question is whether these features (and the secondary nitrite maximum itself) are generated from in situ processes or lateral advection from more reducing and biologically active regions on the shelf. Ra-228 isotopes provided important insight. Within the core of the oxygen minimum zone there was a strong correlation between Ra-228 and Fe(II) and iodide, suggesting that offshore transport may be more important than we had previously thought.

Curtis Deutsch (University of Washington) presented a high-resolution model of cross-shelf transport at the eastern end of the transect. His model revealed the importance of wind-driven eddies generated over the broad Peruvian shelf that transport materials offshore. Surprisingly, he was able to generate extensive westward transport of dissolved Fe offshore without invoking redox chemistry. However, his boundary conditions were not correct, in that he did not include the exceedingly high dissolved Fe concentrations we actually measured over the shelf. If he had done so, there would have been a massive offshore flux of Fe that is inconsistent with our observations. Instead, it appears that redox cycling traps much of the Fe on the shelf. But is there any direct evidence for internal redox cycling over the shelf and shelf/slope break? In fact, the cruise produced the best evidence yet for that process. The Lam group (University of California Santa Cruz) showed that much of the particulate Fe forming within shelf waters and the secondary nitrite maximum beyond the shelf-slope break was Fe oxide (specifically lepidocrocite). This is presumably produced by the abiotic oxidation of Fe(II) by nitrite, or the microbial oxidation by nitrate or nitrite. This was the first evidence for the occurrence of this process in the marine water column. It has important implications for the transport of Fe within this system, but also for the linkage of the Fe and nitrogen cycles in the evolution of early ocean chemistry.

Mark Altabet (University of Massachusetts, Dartmouth) posed an interesting question for the group. He pointed out that the Peruvian OMZ has a global significance for the nitrogen cycle. Could we make the case that the Peruvian OMZ has a global significance for metals? This question is still not settled. Redox dynamics and coastal physics within the OMZ are clearly important in supplying Fe to the interior of the eastern tropical Pacific, but this is a regional impact. The real question is whether the features of the massive EBP which is much deeper than the OMZ arise in whole or in part because of the presence of the OMZ and associated reducing sediments along the margin. If so, then the OMZ does indeed have a global impact. That is because the EBP is almost certainly an important source of Fe to the Southern Ocean, based on simulations performed by Tim DeVries (University of California Santa Barbara) using his

inverse model and presented at the workshop. Aside from the redox signature of the Fe isotopes, a compelling role for the OMZ is simply that such boundary plumes are rare elsewhere.

Plumes of Ra-228 extended far to the west from the Peruvian shelf and slope (Charette group, Woods Hole Oceanographic Institution). The most westward plume was in the surface waters and was strongly correlated with a strong maximum in dissolved Mn. This suggested that the strong surface Mn maximum in the eastern tropical Pacific arises from a boundary source, rather than atmospheric deposition within the interior of the basin. The absence of a surface Al maximum is consistent with this observation. Subsurface Ra-228 plumes were also observed extending west from the slope. The presence of such plumes at different depths reflects the complex interplay of eastward and westward flowing filaments within the OMZ. Interestingly, these subsurface Ra-228 plumes were coincident with local iodide, Fe and Fe(II) maxima, suggesting that at least some component of the novel redox chemistry within the OMZ arises from slope sediment processes.

Nitrogen and oxygen isotope measurements of nitrite suggest that there is an important oxidation pathway of nitrite within the OMZ (Casciotti group, Stanford University). It is not clear what the terminal electron acceptor might be in this process, in the absence of oxygen. Iodate is an obvious choice, and iodide accumulation (Cutter group, Old Dominion University) is consistent with this. But there is no direct evidence that this reaction is important.

Next Steps

The group agreed to publish a special issue with a target deadline of November 1. However, some groups will publish sooner in high profile journals. We collectively encouraged that. It was felt that the Resing et al. paper in Nature was an important step in elevating the profile of GEOTRACES.

My original goal had been to use the workshop to identify sub-groups who would work on synthesis topics. But I was a bit overly optimistic about getting to this point in the workshop. Nevertheless, I expect some collaboration will get spun up soon and hopefully the special issue will see some good synthesis papers. Here are some representative interactions I see developing (a bit more focused on me, but just because that is what I am most certain about).

1. I expect that Bruland's student, Claire Parker, will work with the Ra folks given the remarkable relationship between Ra-228 and Mn in the upper ocean west of Peru.
2. Dave Kadko and I are collaborating to use his ^{7}Be –derived upwelling rates over the shelf to estimate a shelf-wide oxidation flux of Fe(II) as anoxic waters outcrop into the mixed layer. We can compare this with German estimates of 'redox recycled Fe' from sediment trap data to see how much Fe(II) oxidation can be attributed to aerobic oxidation coupled with upwelling, or if we must invoke internal oxidation by nitrite and nitrate.
3. Curtis Deutsch's high-resolution model of eddy-driven transport across the shelf will lead to numerous collaborations, I expect. I want to collaborate with him on a redox-driven model of Fe transport across the shelf. I anticipate that the model will show that we must have a nonoxygen dependent Fe(II) oxidation pathway to account for the abrupt Fe gradients at the shelf-slope break. This collaboration will explicitly include the formation of particulate Fe oxides as an oxidation product, so Phoebe Lam will be

involved. I also recognized that Ra isotopes, especially Ra-228, might be very valuable in constraining his model. But the issue there is how to define the Ra-228 end-member on the shelf. We did not make as much progress there as I was hoping.

4. Greg Cutter and I will collaborate on a redox paper characterizing the redox potential of the OMZ. Our iodide and Fe(II) numbers were virtually identical.
5. I expect that Tim DeVries and Seth John will continue their collaboration on a global zinc scavenging model.
6. Bob Anderson is getting really engaged in atmospheric deposition processes these days, using Th-232 and Th-230. I expect that he will work closely with Cliff Buck and Ana Aguilar-Islas on atmospheric deposition at the eastern end of the transect. The paradox of high surface Mn and low surface Al is challenging our conventional approaches there.
7. I expect that the Wu group and Kristen Buck will work closely on Fe speciation in the HTP in order to determine what fraction of the 'ligand-bound' Fe is actually colloidal.

Role of Modelers in the Future

Tim DeVries, Curtis Deutsch and Keith Moore (University of California, Irvine) invested a lot of time and effort into their presentations, and presented model data that were highly relevant to two aspects of our program: explaining the features we observed and determining the fate of the two major plumes identified in the section. We all agreed that modelers need financial support soon.

Student Participation

Many of the presentations at the workshop were made by students. These included veterans of the cruise – Saeed Roshan (RSMAS), Claire Parker (UCSC), Nick Hawco (WHOI), Erin Black (WHOI), Dan Ohnemus (WHOI, now Bigelow) and Cheryl Zurbrick (UCSC – now MIT), as well as students who are now working on cruise-derived data, such as Molly Martin (RSMAS). They were important participants in breakout. Dan Ohnemus also did a good job leading the particle inter-comparison session.

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