Principles and Priorities of the U.S. GEOTRACES Intercalibration Initiative

Intercalibration is defined as – *The process, procedures, and activities used to ensure that the several laboratories engaged in a monitoring program can produce compatible data. When compatible data outputs are achieved and this situation is maintained, the laboratories can be said to be intercalibrated* (Taylor, 1987). Intercalibration therefore is an active process between laboratories that includes all steps from sampling to analyses, with the goal of achieving the same accurate results regardless of the method or lab.

OBJECTIVES:

To meet the objectives embodied in the definition above, the GEOTRACES Intercalibration Initiative will:

1) compare results obtained by different methods used to collect and analyze samples of seawater and of marine particulate material in determining concentrations and, in some cases, speciation of trace elements and their isotopes,

2) ensure that the methods used to collect and analyze samples are free of contamination and other artifacts (e.g., related to storage), and

3) identify factors that cause different methods to lead to differing results and, where differences are found, modify the methods as needed to ensure that different methods used in GEOTRACES provide internally consistent results that are as accurate and precise as possible.

The purpose of the GEOTRACES intercalibration initiative is to ensure that different methods used to measure a parameter give accurate, precise and internally consistent results; not necessarily to establish a single method for each parameter to be used by all investigators on all GEOTRACES cruises. Nevertheless, convergence on a single superior method would be a welcome contribution of the intercalibration process.

PRINCIPLES:

1) Intercalibration represents the highest priority of U.S. GEOTRACES during FY08. Ship time for the GEOTRACES intercalibration initiative, related infrastructure, and support for core activities were funded in FY07 through a proposal led by Greg Cutter, Old Dominion University (Co-PIs Ken Bruland, University of California, Santa Cruz and Rob Sherrell, Rutgers University). A copy of the proposal, and related information, may be downloaded from the GEOTRACES web site (www.geotraces.org; go to INTERCALIBRATION on the left side of the home page, and then select “documents”).

2) Proposals to the U.S. NSF Chemical Oceanography program requesting support for additional GEOTRACES Intercalibration activities are to be submitted by 15 August,

2007. This includes proposals requesting support solely for work aboard the second intercalibration cruise in 2009 (see below).

3) Proposals to the U.S. NSF will be evaluated for their relevance to GEOTRACES objectives, as well as for their Scientific Merit. Relevance will be evaluated based on the principles and priorities established in this document, as well as the objectives defined in the original intercalibration proposal by Cutter et al. Neither the US GEOTRACES SSC nor the intercalibration PIs will provide letters of endorsement for proposals. Instead, proposers are advised to establish the relevance of their proposal by reference to this document and to the proposal by Cutter et al. Proposal reviewers will be provided with copies of both documents and asked to assess the proposal's relevance to GEOTRACES intercalibration objectives. Proposal reviewers will be informed that the intercalibration team will make every reasonable effort to provide samples, and ship time where necessary, for proposed work that is judged to have high levels of merit and relevance.

4) It is anticipated that proposals will request support primarily for the collection and processing of samples at sea, the distribution of samples to participating investigators, and the analysis of samples collected to test sampling and storage artifacts. Most proposals will be organized by groups (see below), and in most cases it is anticipated that costs associated with analysis of the intercalibration samples to be distributed widely to members of the community will be covered by existing projects. Where this is not feasible, for example with labor-intensive analyses, it is preferred to have analytical fees to cover those expenses incorporated into group proposals rather than submitting a large number of small, single-investigator proposals.

5) Intercalibration team leaders (Cutter, Bruland, Sherrell) will provide participating investigators with 0.5-liter samples stored in acid-cleaned low-density polyethylene bottles, and with whole filters or filter subsamples for particulate intercalibration. Water will be filtered through 0.2 μm PCTE membrane filter cartridges (Osmonics) in polypropylene housings and acidified immediately after filling to pH 1.7 with 2 mL of 6 N quartz-distilled hydrochloric acid (Q-HCl). It is expected that 0.5-liter samples will be sufficient for intercalibration of most trace elements. Representative samples of particulate matter will be collected on several filters types, including but not limited to established quartz fiber and polycarbonate filters. Details for particulate procedures will be decided among funded investigators.

If alternative types of bottles (e.g., Teflon) or acidification is required, then participating investigators are asked to provide the intercalibration team with the necessary bottles (precleaned and ready to be filled), acids, and protocols for sample handling, archiving and shipping.

6) The methods used by the intercalibration team leaders may be inappropriate for certain trace elements of interest to GEOTRACES (e.g., Hg, Sn and Pb). The U.S. GEOTRACES Scientific Steering Committee recommends that special attention be afforded during the intercalibration effort to the development and testing of methods suitable for analyzing seawater samples for these elements.

7) Intercalibration of methods for certain trace elements, radionuclides, and stable isotopes will require either samples much larger than 0.5 liters, or special processing at sea. It is anticipated that groups of investigators involved with such analyses will coordinate their efforts and select a representative investigator who will participate in one or both intercalibration cruises, collect and process samples following protocols defined by each participating PI, and distribute samples to participating labs for analysis. The coordinating investigator(s) will also be responsible for synthesis of the findings, and for recommending steps to resolve any inconsistencies that may be discovered.

8) Intercalibration of methods for certain analyses, such as chemical speciation, require that samples be processed and/or analyzed at sea. Where possible, groups of investigators involved with such analyses will coordinate their efforts and select a representative investigator who will collect and process samples at sea following protocols defined by each participating investigator. In addition, berths will be reserved during the second intercalibration cruise for at-sea intercalibration of speciation methods, and for other at-sea analyses where processing cannot be delegated to a representative investigator.

9) Self-organized groups (see below) are led by investigators in the U.S. to facilitate support for organizing and implementing these intercalibration activities by the U.S. NSF. However, the intercalibration initiative is intended to be an international GEOTRACES activity, and scientists worldwide are encouraged to participate in the intercalibration initiative. Scientists who wish to participate should contact the leader of the relevant group(s), with cc to Greg Cutter (gcutter@odu.edu), to express their interest if they have not already done so.

10) GEOTRACES anticipates that approximately $2M will be available in FY 08 to fund proposals submitted to the U.S. NSF for intercalibration activities. Proposers should keep this number in mind, as well as the number of groups likely to be submitting proposals (see below), when developing their proposals and budgets.

11) Proposals to the U.S. NSF requesting support for this intercalibration effort should have a title that begins with "GEOTRACES" followed by a concise description of the nature of the intercalibration activity to be supported.

SAMPLING SYSTEMS:

1) Water: Intercalibration team leaders will collect water by:

a) Individual Teflon-coated GO-Flo bottles hung manually on a Kevlar wire, the standard method used for the past two decades, and

b) A newly designed trace metal-clean rosette system equipped with 12-liter GO-Flo bottles (the U.S. GEOTRACES system).

Other systems with proven records of contamination-free sampling are invited to participate in intercalibration, both as a test of the new GEOTRACES rosette system and

to ensure that results obtained with all systems that may be used during GEOTRACES cruises provide internally consistent results.

2) Particles: Intercalibration team leaders will obtain particulate material by filtering (47 mm diameter filters) water collected in GO-Flo bottles and by underway sampling systems. Certain objectives of the GEOTRACES program require larger amounts of particulate material than can be derived using these methods, thereby requiring the use of in situ filtration systems to collect sufficient amounts of particulate material.

In situ filtration systems with a proven record of sampling for particulate trace elements, radionuclides, and stable isotopes are invited to participate in the intercalibration, both to ensure that the in situ filtration systems give consistent results with bottle samples for major particulate constituents, and to ensure that different in situ filtration systems that may be used throughout the GEOTRACES program provide internally consistent results for trace elements and their isotopes.

SCHEDULE:

1) First cruise, June-July 2008, will emphasize comparison of different sampling systems for water and particulate matter, as well as sampling for trace elements and isotopes that require volumes substantially greater than 0.5 liters (e.g., certain radionuclides and stable isotopes).

2) Second cruise, mid 2009, will allocate time to test modifications of methods implemented in response to problems identified in the results from the first cruise, as well as methods for trace element speciation (including colloids).

PRIORITIES:

To summarize and reiterate points established above, each of the following activities have been afforded priority by the U.S. GEOTRACES Scientific Steering Committee to achieve the objectives of the Intercalibration initiative:

1. Proven sampling systems for the dissolved and particulate phases. The Intercalibration team will have the Kevlar hydrocable and 30L GO-Flos, and a near-surface pumping apparatus, but additional systems proven to take uncontaminated samples are needed to ensure that the GEOTRACES rosette system provides uncontaminated samples for key trace elements and isotopes.
Similarly, in situ pumping systems are needed to provide large volume particulate and dissolved (in conjunction with adsorption or chelating cartridges) samples.

2. On board determinations of contamination-prone analytes. The Intercalibration team will provide on board measurements of Fe and Zn, two contamination-prone trace elements. However, additional investigators are needed to evaluate whether the new GEOTRACES rosette system takes uncontaminated samples for key elements not covered by the team leaders (e.g., Pb, Pb isotopes, and Hg). In cases where

contamination is found, these investigators are expected to help modify methods and sampling systems, as necessary, to eliminate contamination.

3. Coordination and sample processing for GEOTRACES key trace elements and isotopes that are not amenable to the "standard" trace element sample size (0.5 L), bottle type (low density polyethylene), and acidification (pH< 1.8 with HCl) to be used on the Intercalibration Cruises. In many cases, this will include tests for sample storage artifacts, where time-zero samples must be processed at sea. This category includes, but is not limited to, radionuclides and stable isotopes.

4. Aerosols. Aerosols represents a key parameter listed in Table 2 of the GEOTRACES Science Plan that is not covered by the Intercalibration Team. A strategy to define the methods used to sample for aerosols aboard GEOTRACES cruises, and to analyze those samples, is needed.

5. Chemical speciation. Although not a parameter per se, chemical speciation, especially for iron, is a priority identified in the Science Plan. It is anticipated that tests of methods for chemical speciation will be emphasized during the second intercalibration cruise (Spring, 2009).

COORDINATORS

Coordinators of the self-organized GEOTRACES Intercalibration groups, and their Contact Information, are provided below. Persons interested in participating in one or more of these groups should contact the coordinator if they have not already done so:

1) Dissolved and particulate sampling systems, “core” trace elements – G. Cutter, K. Bruland, and R. Sherrell; gcutter@odu.edu
2) Si isotopes - Mark Brzezinski, brzezins@lifesci.ucsb.edu
3) N isotopes– Karen Casciotti, kcasciotti@whoi.edu
4) P (oxygen isotopes) – Albert Colman, colman@umbi.umd.edu
5) Hg – Carl Lamborg, clamborg@whoi.edu
6) Trace element stable isotopes – Ed Boyle, eaboyle@mit.edu
7) REE concentrations; Nd and Hf isotopes – Tina van de Flierdt, tina@ldeo.columbia.edu
8) Os isotopes - Bernhard Peucker-Ehrenbrink, behrenbrink@whoi.edu
9) ^{230}Th, ^{231}Pa, ^{10}Be - Bob Anderson, boba@ldeo.columbia.edu, and Brad Moran, moran@gso.uri.edu
10) Ra isotopes (and ^{227}Ac?) – Billy Moore, moore@geol.sc.edu
11) Pu isotopes and ^{137}Cs - Tim Kenna, tkenna@ldeo.columbia.edu
12) ^{210}Pb, ^{210}Po, and ^{7}Be – Mark Baskaran, ag4231@wayne.edu
13) Aerosols - Bill Landing, wlanding@fsu.edu
14) Fe (and other) speciation - Jim Moffett, jmoffett@usc.edu
15) Particulate ^{234}Th - Ken Buesseler, kbuesseler@whoi.edu