



FINAL REPORT
from the GEOTRACES workshop on
‘Stable isotopes of biologically important trace metals’

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1. Introduction

For most of the 20th century the paradigm for the open oceans was that productivity was limited by the macronutrients Si, N, and P. Major international programmes, such as GEOSECS and WOCE, mapped the global distribution of these nutrients and provided understanding of the processes involved in their cycling. Work in the 1980s and 1990s, however, discovered that a supply of Fe was as important for biological productivity as the availability of the macronutrients, and that other micronutrients (e.g., Zn, Co, Cd, Cu) were also required for many biological functions. This discovery has changed the paradigm and makes existing knowledge of macronutrient cycles quite insufficient if we wish to understand biogeochemical processes in the global ocean.

It might be expected that recognition of the importance of micronutrients for ocean ecosystems would be set in the context of a firm geochemical understanding of the oceanic cycles of these micronutrients. This is, however, not the case, and our knowledge of the oceanic distribution of micronutrients, and of the processes that control their marine cycles, remains rudimentary. Pioneering work has established the basic characteristics of marine micronutrient profiles, but the number of published data is still very limited.

The pressing need to understand micronutrient cycles is the primary motivation for the international GEOTRACES programme (www.geotraces.org). This programme seeks to do for the micronutrients what GEOSECS did for macronutrients in the 1970s, thereby advancing our understanding of chemical tracers that can be used to assess present and past oceanic processes. A fundamental principle of GEOSECS, and now of the GEOTRACES programme, is that measurements of a range of trace elements and isotopes (TEIs) on ocean sections which cross key marine chemical gradients, provide complementary information that cannot be derived from isolated studies of small subsets of tracers. The complex geographical and analytical efforts that are required for analyses of many TEIs in all ocean basins is a major undertaking that is beyond the scope of a single nation and is only possible with international co-operation.

A very exciting addition to the ‘key parameters’ measured on every GEOTRACES cruise, and which include the concentrations of the micronutrients Fe, Zn, Cd, Cu, is the recent effort to measure the stable isotopic compositions of these elements. These efforts are closely coupled to advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) as well as the development of refined analytical procedures such as double spike methodologies. By now, more than 20 laboratories worldwide are engaged in stable isotope measurements of micronutrient elements in marine samples. However, this community has never met at a dedicated conference to exchange analytical expertise, discuss new data, and formulate common challenges and targets.

2. Workshop Organisation and Goals

The idea to bring together the community of people working on stable isotopes of biologically important trace metals for a first workshop was generated in discussions between Mark Rehkämper, Tina van de Flierdt, Dominik Weiss (Imperial College London), Gideon Henderson (University of Oxford) and Hein de Baar (NIOZ). It was decided to focus the workshop on the stable isotopes of Zn,

Cd, and Fe, but to also encourage presentations on isotope systems of other micronutrient and contamination-prone elements (particularly Pb, but also including Hg and Cr).

An initial workshop invitation was distributed to individuals working in the field, and advertised through various email lists. More than 50 international scientists registered their interest, and after securing financial support from COST Action ES0801 and SCOR (Scientific Committee for Ocean Research), a final programme for the workshop was assembled (Appendix 1).

The workshop was held in the UK at the Department of Earth Science and Engineering of Imperial College London on 13-14 September 2012 and it was attended by 49 international participants from 12 different countries (Appendix 2).

3. Scientific Presentations

Over two days, 21 talks were given and 14 posters were on display highlighting exciting new data sets on direct seawater measurements, method developments, application of isotope proxies to understand the interface of seawater with marine biota, marine particulates, sediments, and aerosols, as well as intercalibration and modelling efforts.

A particular focus of the meeting was the presentation and discussion of new seawater isotope data for the elements Cd, Zn, Fe and Pb. The Cd and Zn talks. Presentations by C. Stirling, S. Galer, M. Rehkämper for Cd and D. Vance, J. de Jong, S. John for Zn demonstrated how the recent isotope results for seawater are starting to provide a better, more detailed understanding of how biological utilization and remineralisation of organic matter shape the marine distribution of these micronutrient elements. Whilst the seawater isotope data for Cd and Zn appear to show many similarities, there are also key differences, which indicate that distinct processes play an important role in the marine cycles of these two elements.

An important focus of the Fe isotope presentations (talks by T. Conway, F. Lacan, J. De Jong, O. Rouxel) was ongoing work to close the still large gaps in the current understanding of the isotope mass balance of iron in the oceans. Hence, significant efforts are being made to better constrain the Fe isotope compositions of the main sources and sinks of marine Fe and the effects of internal processes (such as biological utilization and isotopic exchange between dissolved and particulate Fe).

The two Pb isotope presentations (J. McAlister, E. Boyle) revealed the relatively large variability of seawater Pb isotope compositions and stressed that great care must be exercised during sampling to prevent contamination, for example from the use of unsuitable filtration membranes. It was also argued that the relatively large Pb isotope variations enable comparatively rapid analyses (albeit at limited precision) of surface water samples with volumes of less than 50 – 100 ml and this capability could be exploited with a dedicated sampling programme (shallow isosurface sampling for trace metals = SISTM; proposed by J. McAlister).

Another set of presentations explored Fe isotope variations in sediments and aerosols (W. Homokey, B. Srinivas) and discussed the application of Zn and Cr isotope analyses of sedimentary marine archives for research in paleoceanography (M. Andersen, H. Planquette, S. Dixon). The results highlighted the great potential of the isotopic methods to investigate past changes in marine conditions (such as nutrient utilisation and oxygenation) but also showed that care must be taken to ensure that the results are not biased by post-depositional alteration. A further presentation (by T. Horner) showed the results of an *in vivo* study, which investigated the physiological processes responsible for biological Cd isotope fractionation and suggested that the observed isotopic fractionation is not a consequence of Cd uptake or utilization within cells but due to sequestration within cell membranes. Additional workshop presentations (i) discussed the application and optimization of double spike protocols for precise stable isotope analyses (J. Klar, S. John), (ii) stressed the need for the marine stable isotope community to participate actively in the intercomparison program whilst offering a possibility to obtain new intercomparison samples in 2013 (H. de Baar) and (iii) documented the interest of the ocean modelling community to integrate novel stable isotope data into existing global or regional ocean models (J.-C. Dutay).

4. Summary of break out groups and follow up plan on identified challenges

Breakout groups were held on day 1 to facilitate a targeted discussion of element specific problems (Group 1: Cd & Zn, Group 2: Fe, Group 3: Pb) associated with sampling at sea, laboratory methods, standards, notation of data, and intercalibration. The breakout groups reported back to all participants later in the day and on the following day to discuss results/concerns, and a number of issues were identified for follow up actions in a concluding plenary session.

4.1. Cadmium and zinc isotopes in the marine environment

Standards (Cd and Zn isotopes):

- NIST SRM 308 has been adopted as primary reference material by all laboratories in the Cd isotope community
- JMC Lyon, which is used as reference material for Zn isotope measurements, will be depleted in the near future and a new reference material is needed

ACTION: Morten Andersen (University of Bristol) and Tim Conway (University of South Carolina) volunteered to coordinate the adoption of a new common standard material for everybody. Care should be taken to involve the hard rock community in this effort so that everybody uses the same new standard. Seth John (University of South Carolina) has a large volume of an additional secondary reference standard that he would be happy to distribute to the community.

Notation (Cd isotopes):

Currently papers on Cd isotopes use two different notations based on the preference of the individual groups ($^{114}\text{Cd}/^{110}\text{Cd}$ and $^{112}\text{Cd}/^{110}\text{Cd}$). Arguments have been made for the validity of both notations, but the larger GEOTRACES and marine geochemistry community would greatly benefit from settling on one ratio to use. A suggestion was made to at least report both notations in publications, but it would be more ideal to consent on one. Similarly, some groups currently use the delta notation, while others use the epsilon notation. While only different by a factor of 10, it would be easier for the wider community if agreement on one common notation could be reached.

Intercalibration (Cd and Zn isotopes):

A number of laboratories are not yet intercalibrated for Cd and Zn isotopes. SAFe standards are still available from Ken Bruland (UC Santa Cruz) for these isotopes for deep water intercalibration. It would be desirable to further intercalibrate on the more challenging surface waters, which however require large volumes of seawater. Furthermore, it was noted that an intercalibration for particulate samples would be beneficial as well. Again, the problem will be to collect particulate samples that are large enough to enable such an exercise.

ACTION: Hein de Baar (NIOZ) brought up the idea that a cruise planned for 2013 in the Mediterranean and Black Seas (GA04, http://www.bodc.ac.uk/geotraces/cruises/section_maps/atlantic_ocean/) could be used to collect the seawater and particulate samples required by the community. Funding is currently pending for this cruise, and Hein will keep everybody posted. If successful, a volunteer will be needed to coordinate this intercalibration exercise, potentially on relatively short notice, as the cruise is tentatively scheduled for May-June 2013 (e.g., bottles have to be ready by April 2013).

4.2. Iron Isotopes in the marine environment

Many of the issues identified for Cd and Zn isotopes are relevant for Fe isotopes as well and the detailed issues are briefly summarised below.

Standards:

- At the moment there exists uncertainty on how much of Fe isotope reference material IRMM-14 is still available. The group agreed that it would be beneficial to think about a new reference material in time.

ACTION: Robert Clough (University of Plymouth) volunteered to use his contacts to find out about the current status of supply for IRMM14.

Intercalibration:

The problem is that SAFe D2 is running out and that SAFe D1 is contaminated for Fe (but it is fine for Zn and Cd measurements). This means that there is not enough water left for expanding on the existing intercalibration effort to include all new laboratories that are currently measuring Fe isotopes. The group formulated that it would be desirable to collect two large

volume seawater samples with relatively high Fe concentrations (i.e., 1 nM) but different isotopic compositions (positive and negative), as well as one surface sample with a lower Fe concentration for intercalibration purposes. The suggestion was also made that a secondary standard should be distributed to all laboratories to compare the reproducibility of the mass spectrometric analyses between different laboratories – hence this would involve distributing a single sample of purified Fe that is ready for direct analysis. It was, however, noted that the distribution of a pre-concentrated seawater sample may not be feasible as different laboratories use different sample preparation procedures that are optimized for their own mass spectrometric data acquisition. A solution to this problem may be the distribution of a pure secondary standard material. Such a procedure was previously adopted by other intercalibration exercises (e.g., Nd – see van de Fliert and Pahnke, 2012, *Limnology and Oceanography Methods*).

As in the Zn & Cd discussion, it was brought up that different protocols for particle digestion should be tested. While intercalibration is an important aspect of this work, the first order issue is the identification of the best (most suitable) method and this has yet to be addressed. The most suitable methodology may furthermore vary depending on the scientific question that is to be answered.

ACTION: Large volume samples from the planned Mediterranean cruise (GA04) would be very welcome for intercalibration purposes (see details under 4.1.).

4.3. Lead Isotopes in the marine environment

The discussion in the Pb break-out group was centred on different issues than the other groups. In part this reflected the fact that there is a much longer history of Pb isotope analyses for samples from marine environments. However, there are still only very few groups that have taken on the challenge of measuring the isotope composition of contamination-prone Pb isotopic ratios in seawater samples and as a result there are currently only two intercalibrated laboratories. This lack of active laboratories represents a significant challenge to the GEOTRACES programme, as Pb isotopes are one of the key parameters that have to be measured as part of each cruise.

The group discussed in some detail the question whether future efforts should be devoted toward analysing more samples to provide a better resolution of geographical variations or toward improving the quality (precision) of the analytical data and ensuring the routine measurement of Pb isotope ratios that feature the minor ^{204}Pb isotope. The opinions were divided on this question, with arguments made in favour of both positions. If a precision about $\pm 1\%$ is deemed acceptable for $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$, this would enable relative simple and rapid measurements as only small samples volumes are needed, making the acquisition of high resolution ocean sections more feasible. It was furthermore questioned whether high-precision Pb isotope analyses are feasible on a routine basis and useful altogether given that (i) isotope fractionation may occur during chemical separation and purification of Pb from seawater, and that (ii) minor natural stable Pb isotope effects may be recorded in seawater. Lead isotope fractionations in the laboratory could be addressed through use of a ^{202}Pb - ^{205}Pb double

spike, but such a spike is currently only available in the Mainz laboratory. It was furthermore pointed out that precise analyses of $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios, which are currently targeted by some laboratories, may provide novel insights into Pb cycling in seawater and broaden the horizon for interpreting seawater Pb isotopic compositions.

Intercalibration:

- Only two laboratories participated in the intercalibration so far, but a small number of samples from the BATS and SAFE intercalibration exercise are still available from Ed Boyle (MIT) and Ken Bruland (UC Santa Cruz).
- Analyses of the first samples from cross-over stations give mixed results with respect to the agreement of Pb concentration data. These results therefore need to be looked at in more detail. In particular, problems were identified for Crossover Station E (UK GA10, D357 and French IPY4, Bonus Good Hope)

Bottle cleaning:

- Bottle cleaning and choice of bottle material remains a critical issue for contamination-prone elements

ACTION: Cheryl Zurbrick (UC Santa Cruz) volunteered to contact Geoffrey Smith and Ken Bruland to learn about the current status of bottle cleaning procedures and whether these are available to the general community.

Filtration:

- One ongoing point of discussion is whether seawater can be filtered at sea without introducing problematic levels of Pb contamination. It was mentioned that various tests were carried out on the intercalibration cruises to interrogate this issue, but it seems that only the US GEOTRACES community is currently aware of the results. In the past, Pb samples were mainly collected without filtration and this procedure was applied for by the UK and Dutch GEOTRACES cruises. However, on the first US cruise, the Pb samples were filtered with Acropak capsule filters, and on the French Bonus-Goodhope cruise Sartobran capsule filters were used.

ACTION: Jessica Fitzsimmons (MIT) agreed to look into and distribute the more detailed information on filtration results for Pb, which were presented at US GEOTRACES meetings. Tina van de Fliert (Imperial College London) agreed to assemble a 'Pb filter discussion' email list for people who are interested in following up the above discussion points. Tina also volunteered to contact Maeve Lohan to learn more about the results of filtration tests that were carried out on previous intercalibration cruises.

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