

GEOTRACES IC1 (BATS) contamination-prone trace element isotopes Cd, Fe, Pb, Zn, Cu, and Mo intercalibration

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Abstract

We report data on the isotopic composition of cadmium, copper, iron, lead, zinc, and molybdenum at the GEOTRACES IC1 BATS Atlantic intercalibration station. In general, the between lab and within-lab precisions are adequate to resolve global gradients and vertical gradients at this station for Cd, Fe, Pb, and Zn. Cd and Zn isotopes show clear variations in the upper water column and more subtle variations in the deep water; these variations are attributable, in part, to progressive mass fractionation of isotopes by Rayleigh distillation from biogenic uptake and/or adsorption. Fe isotope variability is attributed to heavier crustal dust and hydrothermal sources and light Fe from reducing sediments. Pb isotope variability results from temporal changes in anthropogenic source isotopic compositions and the relative contributions of U.S. and European Pb sources. Cu and Mo isotope variability is more subtle and close to analytical precision. Although the present situation is adequate for proceeding with GEOTRACES, it should be possible to improve the within-lab and between-lab precisions for some of these properties.

The stable isotope composition of radiogenic and natural elements provides a powerful tool for unraveling element sources and biogeochemical processes in the marine environment. Depending on the element, trace element isotope ratios can

(1) narrow possible sources of the element in a sample and/or (given a temporal history boundary condition) con-

strain the time the when the element departed the ocean surface (e.g., Pb, Nd),

(2) provide information on redox processes that the element is directly or indirectly involved in (e.g., Fe, Mo, Tl),

(3) indicate the extent of biological uptake and/or ocean mixing of the element (e.g., Cd, Zn).

However, these trace metals occur at picomolar to nanomolar concentrations, and precise stable isotope measurements require 100–1000 times more sample than required for concentration determination. To have a sufficiently high ion signal to overwhelm detector noise and accumulate sufficient replicate analyses for satisfactory statistics, fairly large samples

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are necessary, ranging from 0.5–10 L. Samples for some elements—including Zn, Fe, Pb, Cu, and Cd—are particularly difficult to collect without contamination by shipboard equipment and sampling devices, and the difficulty of keeping samples clean tends to scale with the size of the samples (e.g., it is harder to handle large samples as carefully as smaller samples, and larger samples will have higher acid blanks). As indicated by the SAFe GEOTRACES intercalibration data <<http://www.geotraces.org/science/intercalibration/322-standards-and-reference-materials>>, it is now possible to collect uncontaminated samples for these elements reliably using sampling devices ranging from 1–30 L. Thus, it is possible to include contamination-prone trace element isotopes (CPTEI) in the forthcoming GEOTRACES global survey. Hence, it is important to provide baseline stations and laboratory intercalibrations to enable development of globally consistent databases whose accuracy and precision are known.

In this effort, we report data for the CPTEI compositions at GEOTRACES Atlantic (BATS) IC1. Here, we include data for Fe, Cd, Cu, Pb, and Zn isotopes. Although not considered as highly contamination-prone, we also report data on Mo isotopes because they were obtained from the same samples, and the common lubricant, WD-40™ has high Mo concentrations and could contaminate sampling bottles.

Materials and procedures

Sampling procedures

US GEOTRACES IC1 research cruise on the R/V *Knorr* departed Norfolk, Virginia, 8 Jun 2011, and immediately steamed toward the Bermuda Atlantic Time Series (BATS) station near Bermuda, stopping only to test GO-Flo bottles and fill them with uncontaminated seawater to leach and condition them. The ship arrived at BATS 11 Jun 2008, working there until leg one of the cruise ended in St. Georges, Bermuda on 27 Jun 2008.

Two different sampling methods were used to collect samples for the CP-TEI intercalibration: an underway towed-fish near-surface pumped seawater system (provided by Ken Bruland's group and operated by Geoff Smith of UCSC) and the US GEOTRACES 24-sample 12-L trace element General Oceanics GO-Flo Rosette system deployed on a 8000 m-capable Kevlar cable and dedicated winch operated by Greg Cutter's ODU group, which is constructed and operated similarly to the CLIVAR system developed by Measures et al. (2008). Fish samples were pressure-filtered through 0.45 μm Osmonics cartridge filters and GO-Flo samples were filtered through 0.2 μm Pall Acropak capsule filters after brief acid-leaching and flushing with ~500 mL each sample.

Four different types of samples were collected using these methods:

(1) GEOTRACES Surface Isotope (GSI) sample: ~500 L near-surface (7 m) water was pumped from the UCSC towed fish through the filter into a ~500 L polyethylene tank (acid-leached and rinsed to a trace metal clean state by Geoff

Smith). The sample was acidified with 1 L purified 6M HCl (provided by the MIT laboratory and previously analyzed to ensure no significant blanks) and homogenized by recirculation. Tank filling and tank homogenization was done in the Moss Landing Marine Lab (MLML) clean van by Geoff Smith and individual sample bottling was done in the same clean van by Ed Boyle and Seth John.

(2) At the arrangement of individual investigators, smaller (0.5–10 L) individual samples of near-surface seawater were obtained during a limited steaming time in the vicinity of BATS (courtesy of Geoff Smith).

(3) GEOTRACES Deep Isotope (GDI) sample: ~250 L of 0.2 μm Pall Acropak capsule filtered deep water was collected by tripping all 24 GO-Flo bottles on the US GEOTRACES trace metal rosette at 2000 m. The sample was acidified with 0.5 L purified 6M HCl (provided by the UCSC laboratory and previously analyzed to ensure no significant blanks) and homogenized by recirculation. Tank filling from GOFlos and tank homogenization was done in the US MLML clean van by Geoff Smith and the individual sample bottling was done in the MLML clean van by Ed Boyle and Seth John.

(4) GEOTRACES Profile Isotope (GPRI) sample: An eight-point vertical profile (between 75–3500 m) was collected using 2–4 GO-Flos tripped at each depth, with individual samples directly drawn through 0.2 μm Pall Acropak capsule filters into sample containers. Filtration and individual bottling was done in the GEOTRACES clean van by Ed Boyle and Seth John. Samples were acidified immediately after bottling with 2 mL 6N HCl (MIT, 4 $\times$ vycor-distilled) per liter sample.

Sample containers—commonly some form of polyethylene with polypropylene caps—were provided by the individual laboratories involved in the intercalibration after those labs cleaned the containers to their individual specifications. Some of the samples reported here were subsampled after the cruise into individual lab-cleaned bottles from 4-L high-density polyethylene sample bottles prepared by the MIT lab. Although we anticipate that most of these spare samples have been exhausted by the time this article is published, the MIT lab is willing to receive inquiries on whether some of these samples are still available for future intercalibration, as some labs may yet return unused samples.

Analytical procedures

Samples were processed by individual laboratories according to their standard procedures. Although the details vary between labs, most of the methods involved sample concentration, elemental purification, and Inductively Coupled Plasma Magnetic Sector Mass Spectrometry [although one laboratory used Thermal Ionization Mass Spectrometry (TIMS) for Cd isotope analysis]. References to methods employed by the individual labs or brief descriptions are given below, sorted by element and lab. The level of detail varies between labs because some of their information has been already reported in recent publications that are referenced here.

Imperial College cadmium isotope methods

Cd isotope compositions were determined using a double spike technique in conjunction with isotopic analyses on a Nu Plasma MC-ICP-MS, as described in Xue et al. (2012). In brief, the seawater samples were first acidified, and then a ^{111}Cd - ^{113}Cd double spike was added. For samples with low Cd concentrations (GSI and GPRI samples from 75 m and 125 m depth), the preconcentration of Cd was first achieved by coprecipitation with $\text{Al}(\text{OH})_3$. Further purification of Cd used a column chromatography procedure modified from Ripperger and Rehkämper (2007). The isolation of Cd from the samples with higher Cd concentrations (GDI and GPRI samples from depths of 500 to 3500 m) was carried out by column chromatography only (Ripperger and Rehkämper, 2007). The purified Cd fractions were analyzed with a Nu Plasma MC-ICPMS instrument coupled with a DSN desolvating sample introduction system at the Imperial College MAGIC Laboratories, using techniques modified from Ripperger and Rehkämper (2007). All sample measurements were conducted relative to the JMC Cd Münster Cd isotope reference zero-epsilon reference material (Wombacher and Rehkämper, 2004). These results were renormalized here, relative to the new NIST 3108 Cd isotope standard (Table 1). To this end, the original epsilon values were corrected for the $+1.0 \text{ } \epsilon^{114}/^{110}\text{Cd}$ offset determined for NIST 3108 Cd relative to JMC Cd Münster (Xue et al. 2012, Abouchami et al. 2012).

University of Otago cadmium isotope methods

Cadmium isotopic measurements were carried out at the Center for Trace Element Analysis, University of Otago, on a Nu Plasma-HR MC-ICPMS with a ^{110}Cd - ^{111}Cd double spike for instrumental mass fractionation correction. Five replicate 1 L samples were acidified with HCl, and appropriate amounts of double spike were added to obtain a spike to sample Cd molar ratio of 4 (Gault-Ringold and Stirling 2012). A three-stage ion exchange column chemical separation procedure, adapted from Ripperger and Rehkämper (2007), was used to preconcentrate and separate Cd from the seawater matrix and isobaric interferences (Sn, Pd, In) across the Cd mass range. The purified Cd samples were redissolved in 0.1 M HNO_3 for analysis and introduced through a Nu Instruments DSN 100 desolvator fitted with a PFA 50 $\mu\text{L}/\text{min}$ nebulizer to the MC-ICPMS. Four of five samples were analyzed twice (Table 1). Following analysis, data were reduced offline at the cycle level based on the iterative methods reported in Siebert et al. (2001) to correct the measured $^{114}\text{Cd}/^{110}\text{Cd}$ ratios for both isobaric interferences and instrumental mass fractionation, assuming an exponential mass fractionation law. All of the data are reported as $\epsilon^{114}/^{110}\text{Cd}$ relative to NIST SRM 3108. A more detailed description of the analytical methods is provided in Gault-Ringold and Stirling (2012).

Max Planck Institute, Mainz, cadmium isotope methods

Cd isotopic composition and concentration were obtained by TIMS using a Cd double spike (^{106}Cd - ^{108}Cd) optimized using numerical methods for mass fractionation correction (Schmitt

et al. 2009). The odd-mass isotopes of cadmium, ^{111}Cd and ^{113}Cd , display mass-independent fractionation during thermal ionization, and were consequently explicitly avoided. The double spike was prepared and calibrated in 2006 against our in-house JMC Cd Plasma solution (Lot: 15922032), which was taken to have $^{110}\text{Cd}/^{112}\text{Cd} = 0.520089$ (Rosman et al. 1980) for internal normalization purposes. Further details regarding methods and choice of double spike can be found in Schmitt et al. (2009). Samples were weighed and spiked with an optimal amount of double spike and left to equilibrate for 24 h. A first batch of samples was processed in collaboration with the Bristol group using an aluminum hydroxide coprecipitation method in an attempt to extract simultaneously Cd and Zn, followed by column chromatographic separation of Cd and Zn. These attempts, along with one Fe hydroxide coprecipitation, were discontinued due to low Cd recovery, and the presence of isotopically abnormal Cd in the Zn spike, and vice versa. Note that the data presented here were obtained following chromatographic clean-up of the respective spikes. Thereafter, a new separation method was developed for Cd alone—described in detail in Abouchami et al. (2011)—and processed four additional GDI samples using the latter technique. Briefly, chemical separation and purification of the cadmium fraction of approximately 1-L seawater samples is performed in two steps. The first “column” consists of a FEP separation funnel reservoir containing 2 mL pre-cleaned BioRad AG1-X8 anion exchange resin in Cl^- form. The sample was acidified to $\text{pH} = 1$ by addition of high-purity 12N HCl (Baseline Seastar) and loaded into the FEP reservoir. The flow rate was restricted to 1 mL min, or less, by letting the effluent pass through a 10-mm section of 0.001 inch-bore PEEK tubing. After the sample had passed through, the resin was rinsed with 1N HCl to wash off residual salts; subsequently, Cd was eluted using 0.25N HNO_3 . This fraction was dried down and then converted into bromide form by evaporation with concentrated HBr. The secondary “clean-up” columns are home-made from 3/8 inch diameter 4:1 shrink-fit PFA, and filled with anion exchange resin (100 μL AG1- $\times$ 8 resin, 100–200 mesh). The Cd fraction was purified using HNO_3 -HBr mixtures, as has been described elsewhere (Schmitt et al., 2009). Blanks are around 15 pg cadmium for the entire procedure. Measurements of Cd isotopic compositions were performed by TIMS on a ThermoFisher Triton instrument using Re filaments and silica gel-phosphoric acid activator. Isotope dilution Cd concentrations were derived from the fractionation-corrected isotopic composition run. The data are reported relative to the NIST SRM-3108 Cd standard, which has been adopted by several laboratories as the “zero delta” isotope reference for cadmium (Abouchami et al. 2012). Our nominal absolute measured $^{110}\text{Cd}/^{112}\text{Cd}$ for NIST SRM-3108 (100-ng loads) using the double spike is 0.520121 with a long-term external reproducibility on $^{110}\text{Cd}/^{112}\text{Cd}$ of $\pm 8 \text{ ppm}$ ($0.04 \text{ } \epsilon\text{Cd}/\text{u}$). (2 SD, $n = 12$). For direct comparison with MC-ICP-MS data reported by the other labs, our $\epsilon^{112}/^{110}\text{Cd}$ data have been converted into $\epsilon^{114}/^{110}\text{Cd}$ (see Table 1).

ANU copper and iron isotope methods

Dissolved seawater Cu isotope analyses were made at The Australian National University. Sample volumes of up to 0.4 L were used to preconcentrate Cu using a solvent extraction technique. Briefly samples were buffered to a pH of 4.5 with clean ammonium acetate and then extracted following the addition of ammonium pyrrolidine di-thiocarbamate and chloroform. Once the aqueous and nonaqueous phases had separated, the chloroform phase was removed and acidified with nitric acid to back extract Cu into the aqueous phase (Thompson et al. in prep.). The extracted Cu was purified using anion-exchange with AGMP-1 resin, based on the technique of Borrok et al. (2007). Copper isotope measurements were made by MC-ICPMS (Neptune Plus, Thermo Scientific). Instrumental mass bias was corrected using the $^{62}\text{Ni}/^{60}\text{Ni}$ ratio of an internal Ni standard combined with standard bracketing. Copper isotope values are reported as permil, relative to the NIST SRM 976 Cu standard.

ANU Fe isotope of DFe samples were determined by MC-ICPMS following preconcentration and matrix separation. Sample volumes between 300 and 900 mL were buffered to a pH 4.5 with purified ammonium acetate buffer. Purified ammonium pyrrolidinedithiocarbamate (APDC) and sodium diethyldithiocarbamate (DDC) were added to each sample, which was then extracted twice by shaking following the addition of purified chloroform. The two chloroform extracts obtained were combined, acidified with nitric acid, shaken for 1 min. and then diluted with purified water. The average iron recovery for GEO-TRACES standards GSI (7 m) and GDI (2000 m) was 94% and based on dissolved iron concentrations presented by John and Adkins (2012). The overall instrumental error associated with standard-bracketed dissolved iron samples ranged between $\pm 0.04\text{‰}$ and $\pm 0.26\text{‰}$ (2s) with an average of ± 0.08 (2s, $n = 21$), and is based on the standard error obtained for each mass biased corrected $^{56}\text{Fe}/^{54}\text{Fe}$ ratio. The overall procedural blank for sample preconcentration and iron separation was $2.0 \pm 0.3\text{ ng}$ ($n = 4$). Sample concentrations typically ranged between 10 and $50\text{ }\mu\text{g L}^{-1}$ and were matched to standards within the same concentration range prior to analysis.

Caltech iron isotope methods

Fe was double batch-concentrated from H_2O_2 -spiked samples using cleaned Qiagen NTA-Superflo resin, eluted with pure acid, purified using small anion exchange columns, and analyzed in high resolution on a ThermoFinnigan Neptune MC-ICPMS. Detailed methods can be found in John and Adkins (2010).

WHOI iron isotope methods

Fe was preconcentrated from samples by running H_2O_2 -spiked seawater through cleaned Qiagen NTA-Superflo resin, eluted with pure acid, purified using anion exchange chromatography, and analyzed using medium resolution on a ThermoFinnigan Neptune MC-ICP-MS using spiked $^{62}\text{Ni}/^{60}\text{Ni}$ for mass fractionation correction. Further details are given in Rouxel and Auro (2010).

LEGOS iron isotope methods

The complete procedure is given in Lacan et al. (2008 and 2010). Briefly, the filtered sample, acidified to pH 1.75, is double spiked with ^{57}Fe - ^{58}Fe . $10\text{ }\mu\text{mol H}_2\text{O}_2$ per L seawater is added to the sample. The sample is then preconcentrated through an NTA column (Qiagen nitriloacetic acid superflow resin) and purified with an AG 1- $\times 4$ anion exchange column. The Fe isotopic composition is then measured with a ThermoFinnigan Neptune MC-ICPMS, using an ESI Apex-Q desolvator, a PFA microflow nebulizer ($75\text{ }\mu\text{L/min}$), an X skimmer cone, and a high resolution slit (mass bias is corrected by using the double spike).

MIT lead isotope methods

The MIT lab uses a modification of the method described by Reuer et al. (2003). Each 250-500 mL acidified sample is placed into a cleaned 1-L polyethylene separatory funnel. A minimum amount of vapor-distilled ammonia solution is added to the solution, just sufficient to produce an $\text{Mg}(\text{OH})_2$ precipitate that scavenges Pb nearly quantitatively. The precipitate is allowed to settle overnight and then drawn off into 50 mL polypropylene centrifuge tubes, centrifuged, and the supernatant siphoned off. The precipitate is dissolved in a minimum amount of 6M high-purity HCl, and then NH_3 addition is repeated to reprecipitate Pb with a smaller amount of $\text{Mg}(\text{OH})_2$. The precipitate is then dissolved in a minimum amount of high-purity 1.1M HBr (see paragraph below) and loaded onto Eichrom anion-exchange resin in small-volume fluorocarbon columns. Anion column blanks were typically less than 7 picograms.

One problem that emerged in this technique is that $\text{Mg}(\text{OH})_2$ efficiently scavenges $\text{Si}(\text{OH})_4$ from seawater samples (as we established by colorimetric analysis of seawater before and after precipitation). If the final $\text{Mg}(\text{OH})_2$ precipitate is dissolved in an insufficient volume of 1.1M HBr (even though the acid is sufficient to completely dissolve the precipitate), silica reprecipitates as a thick gel (verified as Si by electron probe analysis of the dried gel) that will not pass through the column, especially for high-Si deep water. If a sufficient volume of 1.1M HBr is used, silica supersaturation is low enough that the gel does not precipitate. Therefore empirical adjustments were made to the 1.1M HBr volume based on the size and expected Si concentration of the sample to eliminate this problem.

The resin is converted to Cl form by first passing through 2M HCl and then the Pb is eluted with 6M HCl. The purified concentrates are evaporated on a hotplate in a recirculating clean flow hood in a positive-pressure HEPA-filtered air lab. The concentrates are then dissolved in 0.2M HNO_3 immediately before analysis.

Pb isotope analysis is performed on a GV/Micromass IsoProbe MC-ICP-MS largely as described by Reuer et al. (2003), with Tl addition for first-order mass-fractionation correction ("β method") with a tailing correction established by measuring the monoisotopic ^{209}Bi spectrum at half-mass intervals. Final linear normalization to the NBS SRM 981 Pb isotope standard used the absolute ratios reported by Baker et al. (2004). In this work, that

method was slightly modified as follows: (1) the IsoProbe was operated in “soft extraction” mode using Al hexapole rods, (2) ^{204}Pb was measured on a Daly-style ion counting unit, with careful calibration of deadtime (50 nanoseconds) and ion-counting efficiency (ranging from 92% to 96% over 2 years, but constant within 0.1% over an hour), and (3) the counter efficiency initially was monitored by beginning-of-day and end-of day calibration measurements of NBS-981 and internal laboratory standards, although in the most recent period of our analyses, a calibrated in-lab standard (whose count rate was at the upper end of the range of samples but well below maximum allowed count rate) was measured every 5 samples to account for within-day counter efficiency variations.

UCSC Pb isotope methods

At UCSC, lead was concentrated and extracted from the seawater matrix using an off-line chelating resin extraction method. Briefly, before extraction, ~500 mL aliquots of the samples were adjusted to pH 4.5 using an ammonium acetate buffer. Samples were then passed over a 345 μL column loaded with Toyopearl AF-Chelate 650 M resin (Tosohaas), subsequently washed with a weak ammonium acetate buffer. ~1-2 mL extracts were eluted with 1.5 M HNO_3 (sub-boiling quartz distilled) into 15 mL LDPE bottles and capped until analysis.

Lead isotopic composition measurements (^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb) were performed on a Thermo Finnegan Element XR ICPMS using a secondary electron multiplier detector. Instrument deadtime was monitored for every session and corrected accordingly. Measured isotopic ratios were corrected for mass bias using thallium additions according to an exponential function ($^{205}\text{Tl}/^{203}\text{Tl} = 2.388$; Gallon et al. 2008). Counts of ^{204}Pb were corrected for isobaric interferences from ^{204}Hg by monitoring ^{202}Hg and assuming natural abundances of mercury isotopes ($^{204}\text{Hg}/^{202}\text{Hg} = 0.2298$). Isotopic ratios were subsequently normalized to NBS SRM 981 Pb isotope standards measured concurrently, using average literature ratios reported for double- and triple-spike measurements (Gallon et al. 2008).

Kyoto University molybdenum isotope methods

The procedure described by Nakagawa et al. (2008) was used for measurements. Briefly, Mo is concentrated on a resin column, eluted, and analyzed by MC-ICPMS. All Mo data were expressed relative to a Johnson-Matthey Mo standard. Mo isotopic analysis of the Johnson-Matthey standard gave $\delta^{98}\text{Mo}/^{95}\text{Mo}$ of -0.117 ± 0.009 (2 standard deviations) relative to the CPI (Amsterdam) Mo ICPMS standard that was used in Archer and Vance (2008).

University of Bristol zinc isotope methods

The Bristol lab used a modification of the method described in Bermin et al. (2006). The principal difference was that $\text{Al}(\text{OH})_3$ was added to the samples for coprecipitation of Zn. The Al solution was first precleaned on an anion column. The Zn was separated from the aluminum and other coprecipitated metals using the column procedure described by Archer and Vance (2004), with some minor modifications. Primarily, 1 M

HCl has been used instead of 7 M HCl to dissolve the precipitate and elute seawater matrix. Zn samples are analyzed by MC-ICP-MS using a double spike in order to correct for analytical mass discrimination. The specific ^{64}Zn - ^{67}Zn double spike used, and the data reduction procedure, is described in Bermin et al. (2006).

Assessments

In considering the following assessments and comments, it should be understood that this effort is the first-ever attempt at between-lab intercalibration for these trace element isotopes in seawater samples.

Cadmium isotopes

Cd concentration and Cd isotope data for GDI are reported by three labs, Imperial, Mainz, and Otago (Table 1, Fig. 1). In addition, Imperial has measured Cd and Cd isotopes for GSI and six GPRl profile samples. Cd concentrations agree well with previous data reported for this region (Bruland and Franks 1983; [1] Sakamoto-Arnold et al. 1987; Lee et al. 2011). Agreement on the isotopic composition of GDI is good with the Imperial numbers just slightly higher than the Mainz numbers according to their respective internal reproducibilities. Despite degraded precision at very low Cd concentrations, significant gradients are seen in the Imperial vertical profile; the precision is sufficient to document a clear enrichment of ^{114}Cd relative to ^{110}Cd as Cd concentrations decrease (Ripperger et al. 2007; Abouchami et al. 2012). This enrichment has been attributed by these authors to progressive Rayleigh fraction due to preferential uptake of the lighter isotopes during biological uptake.

Fe isotopes

$\delta^{56}\text{Fe}$ values of -0.5 to $+0.7$ have been reported for open-ocean seawater samples (this study; Lacan et al. 2010) and in the suboxic Santa Barbara Basin bottom waters reach values as low as -3.45‰ (John et al. 2012). This intercalibration therefore demonstrates that all labs can measure significant differences throughout the ocean, and the most precise labs can detect more subtle features (Table 2, Fig. 2).

Redox processes such as the input of reduced Fe from sediments are associated with large isotopic fractionations (on the order of -1 to -3 permil $\delta^{56}\text{Fe}$), that can be easily traced in seawater with current analytical precision (Rouxel and Auro 2010; John et al. 2012). Non-redox processes such as the nonreductive dissolved Fe release from particles, however, are typically associated with smaller isotopic fractionation (on the order of a few tenths of a permil) that require higher precision in order to be detected (Radic et al. 2011).

The samples used for the inter-calibration (GSI and GDI) have relatively high Fe concentrations (0.42 and 0.84 nmol/kg, respectively) compared with some parts of the ocean where dust supply is more limited. For example, Fe concentrations as low as 0.02 nM (20 times less than the present surface sample) have been documented in the eastern Atlantic Ocean (Sarthou et al 2003). Measuring Fe isotopes at such low con-

Table 1. Cd concentrations and isotope compositions for GEOTRACES intercalibration samples.

GDI, GSI, and GPrI											
Sample	Depth m	Imperial	Mainz	Otago	Imperial ϵ 114/110 Indiv.runs	Imperial ϵ 114/110 Average $\pm$ 2 s.e.	Mainz ϵ 114/110 Indiv.runs	Mainz ϵ 114/110 Average $\pm$ 2 s.e.	Otago ϵ 114/110 Indiv. Runs	Otago ϵ 114/110 Average $\pm$ 2 s.e.	
		[Cd] pmol/kg	[Cd] pmol/kg	[Cd] pmol/kg							
GSI	7	1.2			+22.1 $\pm$ 5.3 (20 kg sample)						
GDI	2000	270.6	nd	268.5	+5.1 $\pm$ 0.4	+4.9 $\pm$ 0.3	+4.0 $\pm$ 0.9*	+4.1 $\pm$ 0.4	+4.1 $\pm$ 0.8	+4.8 $\pm$ 0.5	
		272.1	nd	268.5	+5.0 $\pm$ 0.4	(n=3)	+3.5 $\pm$ 0.9*	(n=8)	+3.9 $\pm$ 1.2	(n=9)	
		270.8	254	274.3	+4.5 $\pm$ 0.4		+3.3 $\pm$ 1.0**	(for all	+4.7 $\pm$ 0.7		
			272	274.3	(0.9 kg samples)		+3.9 $\pm$ 0.8\$	methods)	+5.4 $\pm$ 1.0		
			266	275.2			+4.6 $\pm$ 0.5\$	+4.5 $\pm$ 0.4	+5.4 $\pm$ 0.6		
			274	274.6			+4.4 $\pm$ 0.4\$	(n=4)	+5.6 $\pm$ 0.7		
			277	274.5			+4.7 $\pm$ 0.3\$	(for im-	+5.2 $\pm$ 0.7		
			278	274.4			+4.3 $\pm$ 0.3\$	proved	+5.0 $\pm$ 0.7		
				274.4				method)	+3.6 $\pm$ 0.9		
			nd=not determined				(0.5-1.0 kg samples)		(1 liter samples)		
GPrI	75	2.2			+13.5 $\pm$ 5.3 (~9 kg sample)						
GPrI	125	1.7			+11.8 $\pm$ 5.3 (~8 kg sample)						
GPrI	500	138.4			+5.7 $\pm$ 0.6 (~0.9 kg sample)						
GPrI	1000	293.8			+5.6 $\pm$ 0.6 (~0.9 kg sample)						
GPrI	2500	293.1			+4.2 $\pm$ 0.6 (~0.9 kg sample)						
GPrI	3500	295.1			+4.5 $\pm$ 0.6 (~0.9 kg sample)						

nd = not determined

All ϵ Cd data referred to NIST SRM 3108 = 0.0.

Notes for Mainz analyses:

\$Al coprecipitation method using Cd and Zn double spikes on 0.5 L seawater.

**Fe coprecipitation method.

\$Following improved method of Abouchami et al. (2011)

Table 2. Fe isotope data for GEOTRACES IC1 samples.

Sample	Depth (m)	ANU $\delta^{56}\text{Fe}/^{54}\text{Fe}$	WHOI $\delta^{56}\text{Fe}/^{54}\text{Fe}$	Caltech $\delta^{56}\text{Fe}/^{54}\text{Fe}$	LEGOS $\delta^{56}\text{Fe}/^{54}\text{Fe}$	LEGOS [Fe] (nmol/kg)
GSI	7	0.32 $\pm$ 0.06 (2se)	+0.24 $\pm$ 0.10 (2se n=3)	+0.32 $\pm$ 0.06 (2se n=2)	+0.41 $\pm$ 0.04 (2se n=3)	0.42
GDI	2000	0.45 $\pm$ 0.13 (2se)	+0.42 $\pm$ 0.11 (2se n=3)	+0.55 $\pm$ 0.03 (2se n=5)	+0.52 $\pm$ 0.07 (2se n=2)	0.84
GPrI	75			+0.41 $\pm$ 0.06 (2se n=4)		
GPrI	125			+0.30 $\pm$ 0.06 (2se n=5)		
GPrI	250			+0.45 $\pm$ 0.05 (2se n=3)		
GPrI	500			+0.34 $\pm$ 0.05 (2se n=2)		
GPrI	1000			+0.35 $\pm$ 0.05 (2se n=2)		
GPrI	1500			+0.35 $\pm$ 0.05 (2se n=2)		
GPrI	2500			+0.71 $\pm$ 0.05 (2se n=2)		
4200m	4200			+0.35 $\pm$ 0.07 (2se n=1)		
(individual sample)						

All $\delta^{56}\text{Fe}/^{54}\text{Fe}$ data are per mill relative to IRMM-014

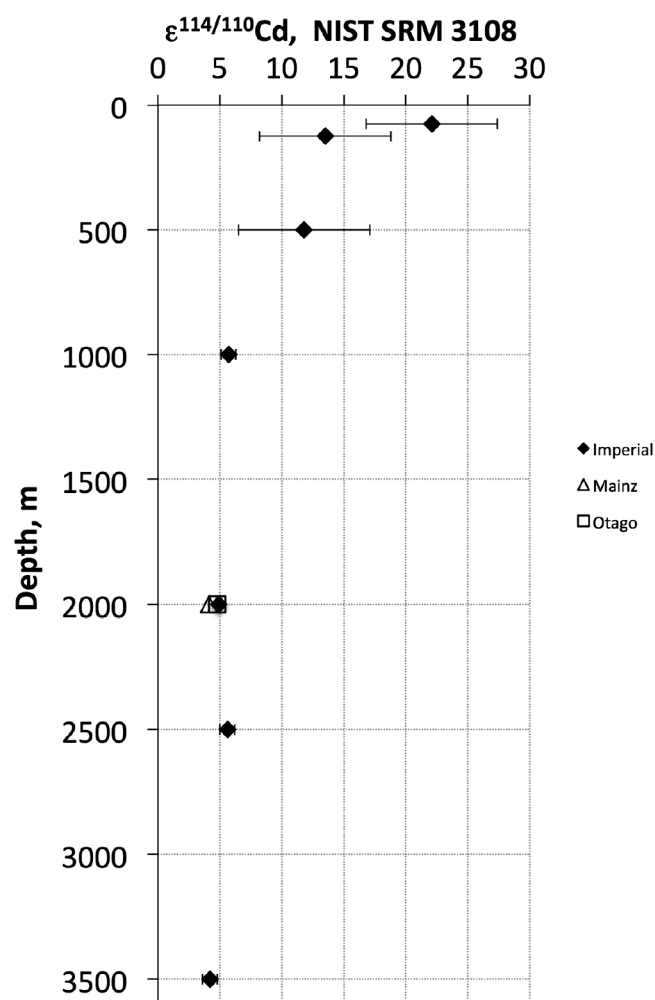


Fig. 1. Cadmium isotope profile from GEOTRACES IC1 (BATS, Atlantic) intercalibration. Where only a single analysis is available, 2 S.E. of the internal run statistics is plotted.

concentrations will obviously present a future challenge. The results presented here are not sufficient to evaluate the ability of the three participating labs to measure Fe isotopes in oceanic waters with low Fe concentration (<0.4 nM). The reader can refer to the publications of the participating labs to get more information on analytical precisions and water volumes required to perform measurements in seawaters with lower Fe concentrations (John and Adkins 2010; Lacan et al. 2008, 2010; Rouxel and Auro 2010).

Lead isotopes

Pb isotope data for GSI and GDI are reported by two labs, MIT and UCSC. Values reported by the two labs agree within ≤ 3 permil, ≤ 0.5 permil, and ≤ 11 permil for $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$, and $^{206}\text{Pb}/^{204}\text{Pb}$, respectively. In addition, for the GPrI profile, MIT has measured replicates of an additional five individual vertical samples (each taken independently through the entire analytical procedure) and three other pro-

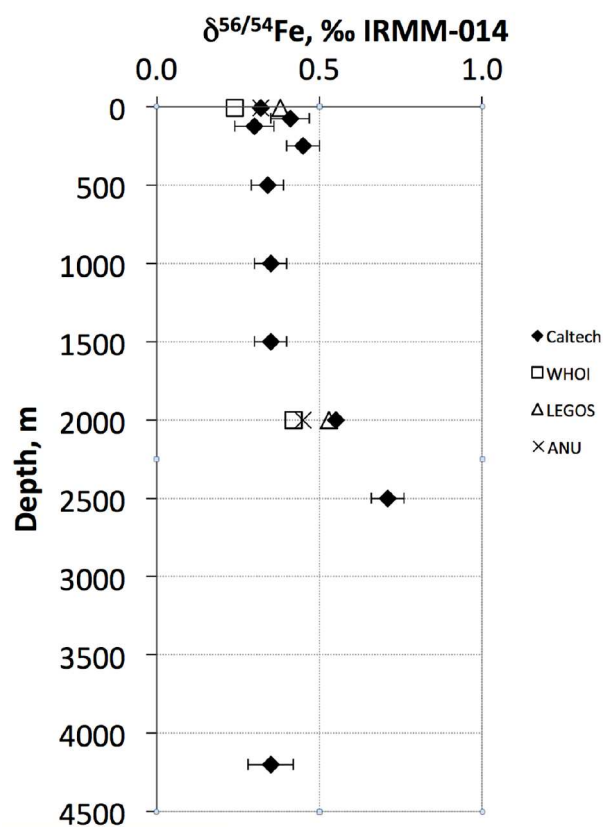


Fig. 2. Iron isotope profile from GEOTRACES IC1 (BATS, Atlantic) intercalibration. Where only a single lab reports data, 2 S.E. of the replicate analyses from that lab is plotted.

file depths with a single analysis (Table 3, Fig. 3). The present within-lab reproducibility is sufficient to resolve small vertical gradients of all three isotope ratios at this site (e.g., the two sigma pooled standard error for 10 samples with a total of 24 replicates in the MIT data are 1.4 permil for $^{206}\text{Pb}/^{207}\text{Pb}$, 0.2 permil for $^{208}\text{Pb}/^{207}\text{Pb}$; and 6 permil for $^{206}\text{Pb}/^{204}\text{Pb}$), and this precision is more than adequate to resolve global scale gradients (e.g., with $^{206}\text{Pb}/^{207}\text{Pb}$ reported as varying from ~ 1.16 to ~ 1.22 with a somewhat larger range likely as more data are obtained). The larger part of the variability is attributable to different Pb sources being used by different regions, for example Asian, Australian, and European lead aerosols differ from U.S. lead aerosols (e.g., see Bollhöfer and Rosman 2000, 2001) and the different relative contributions of these regions in space and time (e.g., Kelly et al., 2009).

Zinc isotopes

Zn concentration and Zn isotope data were reported for GSI, GDI, and GPrI by one lab (Bristol) (Table 4; Fig. 4). The Zn concentration data compare reasonably well with previous measurements near this site (Bruland and Franks 1983). The Zn isotope data are sufficiently replicable to show that the biggest variation in Zn isotopes exists in the upper waters. Samples from 75 m have the lightest Zn isotopes in the whole

Table 3. GEOTRACES IC1 Pb isotope data.

Sample	Depth	Pb (pmol/kg)	Individual analyses	Avg. $^{206}/^{207}\text{Pb} \pm 2 \text{ S.E.}$	Avg. $^{208}/^{207}\text{Pb} \pm 2 \text{ S.E.}$	Avg. $^{206}/^{204}\text{Pb} \pm 2 \text{ S.E.}$
GSI-MIT	7		(1.1746, 2.4449, 18.47) (1.1740, 2.4433, 18.38) (1.1745, 2.4459, 18.35) (1.1748, 2.4464, 18.37) (1.1746, 2.4469, 18.48*)	1.1745 $\pm$ 0.0003	2.4455 $\pm$ 0.0013	18.41 $\pm$ 0.05
GSI-UCSC	7		(1.1778, 2.4451, 18.46) (1.1771, 2.4484, 18.46)	1.1775 $\pm$ 0.0007	2.4467 $\pm$ 0.0033	18.46 $\pm$ 0.00
GDI-MIT	2000		(2 rep. analyses of single extraction) (1.1843, 2.4488) (1.1856, 2.4501, 18.83) (1.1820, 2.4484, 18.62) (1.1822, 2.4502, 18.76*)	1.1835 $\pm$ 0.0017	2.4494 $\pm$ 0.0009	18.74 $\pm$ 0.12
GDI-UCSC	2000		(1.1816, 2.4481, 18.54) (1.1810, 2.4499, 18.54) (1.1815, 2.4473, 18.52) (1.1818, 2.4512, 18.56)	1.1815 $\pm$ 0.0007	2.4491 $\pm$ 0.0035	18.48 $\pm$ 0.03
GPrI-MIT	75	19.2	(4 rep. analyses of single extraction) (1.1787, 2.4467, 18.44) (1.1785, 2.4476, 18.38) (1.1773, 2.4478, 18.40) (1.1780, 2.4489, 18.35)	1.1781 $\pm$ 0.0006	2.4478 $\pm$ 0.0009	18.39 $\pm$ 0.04
GPrI-MIT	125	19.9	(1.1770, 2.4486) (1.1766, 2.4485) (1.1774, 2.4487, 18.39)	1.1770 $\pm$ 0.0005	2.4486 $\pm$ 0.0001	18.39
GPrI-MIT	250	20.4	(1.1847, 2.4526, 18.52) (1.1850, 2.4532, 18.44)	1.1849 $\pm$ 0.0005	2.4529 $\pm$ 0.0006	18.48
GPrI-MIT	500	28.2	(1.1820, 2.4484, 18.53) (1.1823, 2.4476, 18.48)	1.1821 $\pm$ 0.0002	2.4480 $\pm$ 0.0008	18.51
GPrI-MIT	1000	31.6	(1.1864, 2.4537, 18.50) (1.1863, 2.4526, 18.52) (1.1850, 2.4524, 18.56*)	1.1862 $\pm$ 0.0003	2.4529 $\pm$ 0.0008	18.53 $\pm$ 0.04
GPrI-MIT	1500	41.5	(1.1848, 2.4524, 18.83*)	1.1848	2.4524	18.83
GPrI-MIT	2500	27.5	(1.1832, 2.4519, 18.51*)	1.1832	2.4519	18.51
GPrI-MIT	3500	13.9	(1.1847, 2.4534, 18.55*)	1.1847	2.4534	18.55

*for MIT 206/204 indicate improved bracketed counter efficiency correction as explained in text

Table 4. GEOTRACES IC1 Zn isotope data.

Sample	Depth (m)	[Zn], nmol/kg	Individual $\delta^{66/64}\text{Zn}(\text{‰})$	Average $\delta^{66/64}\text{Zn}(\text{‰}, \pm 2 \text{ S.E.})$
GSI	0	0.20, 0.22, 0.16, 0.34	+0.41, +0.23, +0.35, +0.32	+0.33 $\pm$ 0.08
GPrI	75	0.48, 0.50, 0.52	+0.14, -0.05, +0.06	+0.05 $\pm$ 0.13
GPrI	125	0.13	+0.22	+0.22
GPrI	500	0.68, 0.52	+0.31, +0.30	+0.31 $\pm$ 0.01
GPrI	1000	1.58, 1.61, 1.57	+0.60, +0.48, +0.51	+0.53 $\pm$ 0.07
GPrI	2000	2.24, 2.19, 2.20, 2.24, 2.21, 2.22	+0.41, +0.47, +0.47, +0.43, +0.45	+0.46 $\pm$ 0.03

all $\delta^{66/64}\text{Zn}$ isotope data relative to standard JMC-3-0749

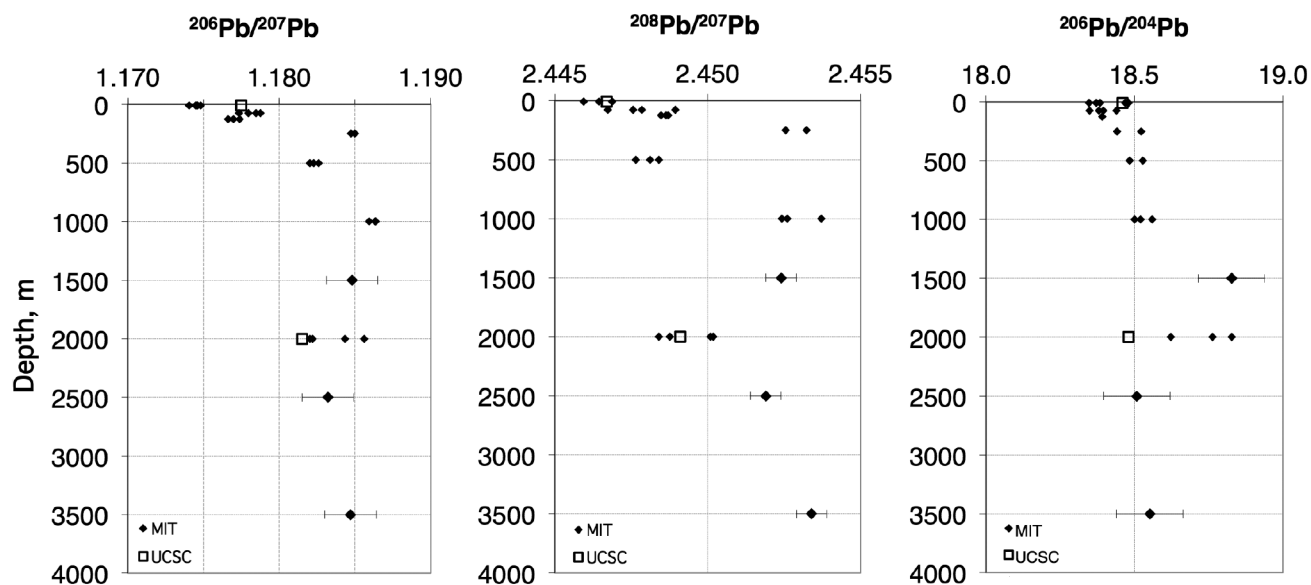


Fig. 3. Lead isotope profile from GEOTRACES IC1 (BATS, Atlantic) intercalibration. Where only a single analysis is available, 2 p.s.e. (pooled standard error) of the MIT data are plotted.

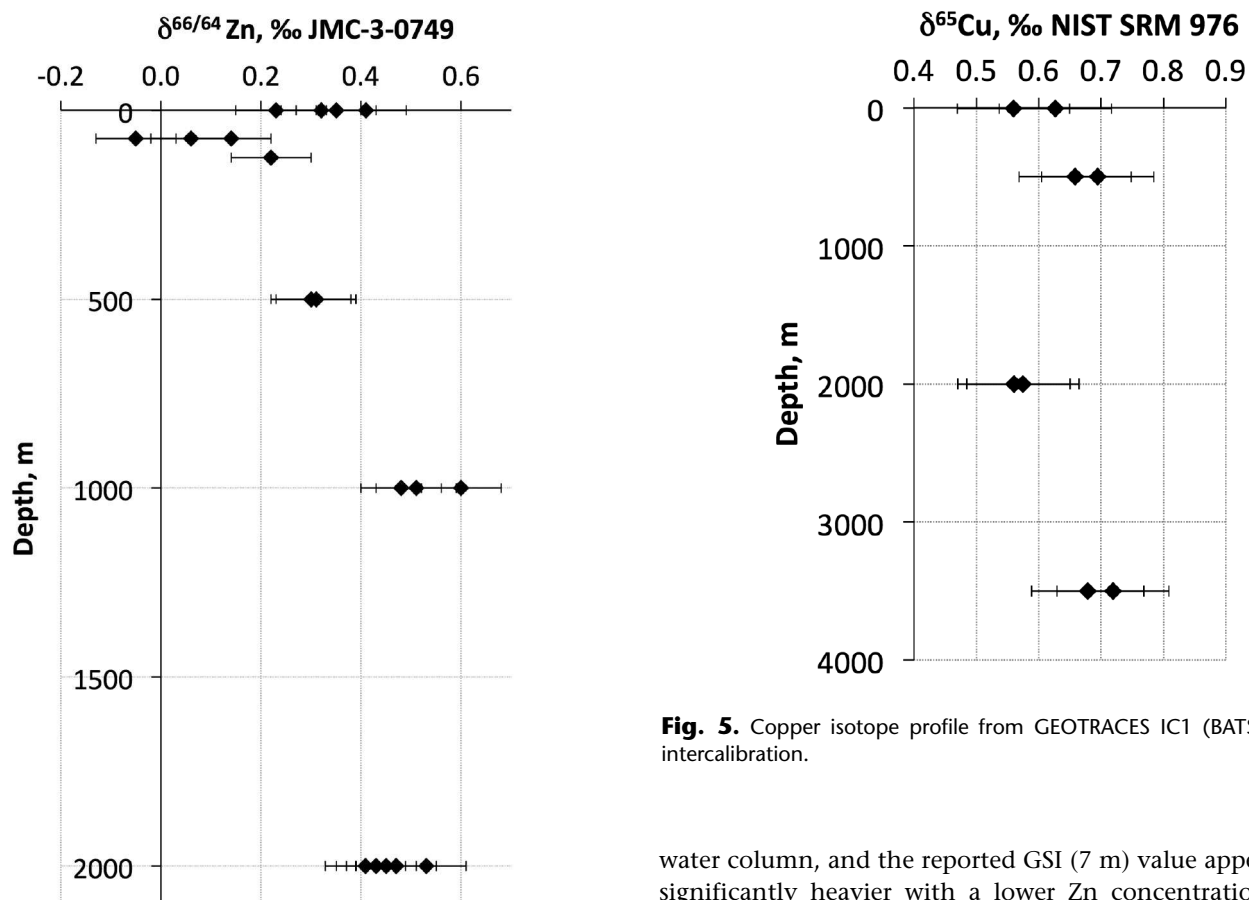


Fig. 4. Zinc isotope profile from GEOTRACES IC1 (BATS, Atlantic) intercalibration. Error bars are the reproducibility of Zn standard solution.

Fig. 5. Copper isotope profile from GEOTRACES IC1 (BATS, Atlantic) intercalibration.

water column, and the reported GSI (7 m) value appears to be significantly heavier with a lower Zn concentration. These may be attributable in part to isotope fractionation upon removal from solution by biogenic uptake and/or adsorption.

Table 5. Mo concentration and isotope data.

Sample	Depth, m	[Mo], nmol/kg	$\delta^{97/95}\text{Mo}$	Average $\delta^{97/95}\text{Mo} \pm 2 \text{ SE}$	$\delta^{98/95}\text{Mo}$	Average $\delta^{98/95}\text{Mo} \pm 2 \text{ SE}$
GSI	7	106,107	+1.70, +1.68	+1.69 $\pm$ 0.02	+2.52, +2.51	+2.51 $\pm$ 0.01
GDI	2000	104,104,103	+1.64, +1.68, +1.71	+1.67 $\pm$ 0.04	+2.47, +2.50, +2.50	+2.50 $\pm$ 0.03

All δMo data expressed relative to Johnson-Matthey Mo standard

Table 6. Copper isotope concentration and isotope data.

MIT bottle ID	ANU bottle ID	Depth (m)	[Cu] nM	$\delta^{65}\text{Cu}$	Error (2 SD)
GSI43/38	GT09-20	7	0.89	+0.63	0.09
GSI43/38	GT09-20	7	0.74	+0.56	0.09
GPrI24	GT09-09	500	0.93	+0.66	0.09
GPrI24	GT09-09	500	1.05	+0.69	0.09
GDI79/6	GT09-05	2000	1.22	+0.57	0.09
GDI79/6	GT09-05	2000	1.16	+0.56	0.09
GPrI 2	GT09-10	3500	1.39	+0.72	0.09
GPrI 2	GT09-10	3500	1.42	+0.68	0.09

Copper concentrations are indicative (not quantitative) values based on intensities relative to a bracketing standard.

Molybdenum isotopes

Mo concentration and isotope data were obtained by one lab (Kyoto University). Although Mo is not particularly contamination-prone, there are some shipboard contamination sources (e.g., the lubricant WD-40), and in any event, these samples were taken from GSI and GDI so the data should be reported in this compilation (Table 5). As expected for this conservative element with a residence time in excess of the ocean mixing time, there are no significant concentration or Mo isotope ratio differences. The vertical profiles of a full suite of stable Mo isotopes for the intercalibration station are reported elsewhere (Nakagawa et al. 2012).

Copper isotopes

Cu concentration and Cu isotope data were reported for GSI, GDI, and GPrI were reported by one lab (ANU) (Table 6; Fig. 5). Although there are hints of slight vertical differences, they are small and near measurement precision.

Discussion, comments, and recommendations

Cd isotopes

$\epsilon^{114}\text{Cd}/^{110}\text{Cd}$ values from +4 to almost +40 have been reported in the ocean (Ripperger et al. 2007; Abouchami et al. 2012). Depending on the concentration of Cd in the water, precisions of 0.5 to 1.5 $\epsilon^{114/110}\text{Cd}$ units can be attained in all but the lowest concentration samples, so global scale vertical and horizontal gradients can be resolved. The most extreme Cd isotope anomalies are seen at very low Cd concentrations; improved precision for these low level samples probably requires larger sample sizes and lower procedural blanks to move beyond the present state of the art.

Fe isotopes

$\delta^{56/54}\text{Fe}$ values of -0.8 to $+0.8$ have been reported for open-

ocean seawater samples, and in the suboxic Santa Barbara Basin bottom waters reach values as low as -3.45‰ (John and Adkins 2012, John et al. 2012). Fe isotope ratios are relatively vertically uniform at about $+0.3\text{‰}$ near Bermuda except for the 2000 and 2500 m samples, which increase to as high as 0.7‰ . John and Adkins (2012) have suggested that these heavier values may be due to an influence of hydrothermal Fe. The heavier values relative to the Santa Barbara Basin are attributed to “crustal” Fe released from terrestrial dust in the Atlantic as opposed to Fe released from reducing sediments (Welch et al. 2003; Waeles et al. 2007; Severmann et al. 2006; John and Adkins 2012, John et al. 2012). The intercalibration shows that all labs can see significant differences throughout the ocean, and the most precise labs can detect more subtle features.

Pb isotopes

Modern MC-ICP-MS multicollector mass spectrometers are capable of very high precision Pb isotope analyses. 2-sigma “internal” statistics on single-solution replicability during a single day of 100 ppm or better have been reported, so it should be possible and it would be desirable to work toward significant improvements for within-lab and between-lab precisions and accuracies, since those achieved within-sample 2-sigma standard errors are at least a factor of five better than actual subsample-to-subsample and lab-to-lab replicability.

Although the four lead isotopes lead to three independent isotope ratios that can provide unique information on sources, Pb isotope ratios tend to be correlated because of the geological extraction of Pb ores from not-quite-homogeneous global reservoirs. For example, in recent work at MIT, we find that the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio is correlated with the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio with a slope of about -1.2 with ~ 10 permil range of deviations of $^{208}\text{Pb}/^{206}\text{Pb}$ from the correlation. In order to take advantage of

the independent isotope ratios, the abundant isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) need to be measured with ratio two-sigma precisions better than 1 permil, and for useful between-lab comparisons, the inter-lab accuracy should be similar. Within-run standard errors show that MC-ICP-MS instruments are capable of very high precision Pb isotope measurement, but we must understand the reasons for longer-term variability of samples and independent standards within and between labs to achieve this potential.

Based on an observed seawater range (to date) for $^{206}\text{Pb}/^{207}\text{Pb}$ of about 60 permil (~ 1.16 to ~ 1.22), the intercalibration results are acceptable: they are adequate to show vertical gradients and between-profile gradients based on published values). Because modern ICPMS instrumentation is capable of very high precision analyses, it is both possible and desirable to work toward improvements in within-lab and between-lab calibrations, since the achieved within-sample 2-sigma standard errors are ~ 0.2 permil for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$, and ~ 2 permil for $^{206}\text{Pb}/^{204}\text{Pb}$, but the within-lab replication and between-lab differences are 0.1–3.5 permil for $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ and ~ 6 –12 permil for $^{206}\text{Pb}/^{204}\text{Pb}$. We recommend that NBS-981 standard be used in all analytical sessions for absolute calibrations of ion counters and Faraday cups. Because NBS-981 has an isotope composition that differs from the contamination Pb found in most laboratories, it is important to take stringent measures to avoid contamination of this standard. It would be helpful if another standard, either an internal lab standard (or perhaps even better a between-lab shared standard) that has an isotopic composition closer to laboratory blanks is used to assess the actual reproducibility of isotope ratio determinations from day to day (so slight contamination has little effect on the isotope ratio). We also recommend that some samples be analyzed independently in replicate so that the true precision across the entire analytical process can be evaluated.

Finally, we should note that mass-dependent (and even mass-independent) isotope fractionations of the order of 1 permil are being observed for other heavy elements (e.g., Hg, Bergquist and Blum 2007; Tl, Rehkamper et al. 2002; U, Weyer et al. 2008, Hiess et al. 2012). Because there is no way to correct Pb isotope ratios for isotope fractionation in the complex multi-source ocean environment, the utility of developing Pb isotope precision much better than 1 permil may be questionable, but we should certainly strive to attain a precision of at least 1 permil.

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