Evaluation of optimized procedures for high-precision Pb isotope analyses of seawater by MC-ICP-MS

Alex Griffiths[1, *], Hollie Packman[1], Yee-Lap Leung[1], Barry J. Coles[1], Katharina Kreissig[1], Susan H. Little[2], Tina van de Flierdt[1], Mark Rehkämper[1]

[1] Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ

[2] Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT

* Corresponding author (a.griffiths15@imperial.ac.uk)

ABSTRACT

The application of Pb isotopes to marine geochemistry is currently hindered by challenges associated with the analysis of Pb isotopes in seawater. The current study evaluates the performance of MC-ICP-MS measurements of seawater Pb isotope compositions following Pb separation by either solid-phase extraction with Nobias Chelate PA-1 resin or co-precipitation with $Mg(OH)_2$, and using either a Pb double-spike or external normalization to Tl for mass bias correction. The four analytical combinations achieve results of similar quality when measuring 1–7 ng of seawater Pb, with reproducibilities (2SD) of 100–1200 ppm for $^{206}Pb/^{207}Pb$, $^{208}Pb/^{207}Pb$ and 300–1700 ppm for ratios involving the minor ^{204}Pb isotope. All four procedures enable significantly improved sample throughout compared to an established TIMS double-spike method and produce unbiased seawater Pb isotope compositions with similar or improved precision. Nobias extraction is preferable to co-precipitation due to its greater analytical throughput and suitability for analyses of large seawater samples with high $Si(OH)_4$ contents. The most accurate Pb isotope data are produced following Nobias extraction and double-spike correction as such analyses are least susceptible to matrix effects. However, Nobias extraction with Tl-normalization constitutes an attractive alternative as, unlike the double-spike procedure, only a single mass spectrometric measurement is required, which improves analytical throughput and optimizes Pb consumption for analysis. Despite the advantages of solid-phase extraction, co-precipitation represents a useful Pb separation technique for samples with low to moderate Si contents as it is inexpensive, simple to implement and the data are only marginally less accurate, especially when combined with a Pb double-spike for mass bias correction.

Over the last century, emissions from anthropogenic activities have significantly perturbed the lead (Pb) inventory of the modern ocean.[1,2] Stable naturally-occurring Pb isotopes, which encompass radiogenic ^{208}Pb, ^{207}Pb, and ^{206}Pb as well as non-radiogenic ^{204}Pb, have been employed as isotopic tracers to understand the spatio-temporal variability of these emissions to the surface ocean and the processes controlling the transfer of pollutant Pb to the deep ocean.[3–5] In addition, Pb isotopes have also been used to constrain various oceanic processes such surface currents, mesoscale eddies, and the ventilation timescales and pathways of deep ocean water masses.[6–8] Despite the successful application of Pb isotopes to marine geochemistry, advances in the field currently remain limited due to the significant challenges associated with the determination of seawater Pb isotope compositions. The complex and highly saline seawater matrix with ~3.5% of total dissolved solids, coupled with generally low Pb seawater concentrations (global mean 10 pmol kg^{-1})[9] and the high risk of Pb contamination during sampling and laboratory handling, render Pb isotope analyses of seawater a daunting analytical task. A particular challenge is thereby the initial extraction of Pb from seawater volumes that are large enough, typically exceeding 100 mL, so that sufficient Pb is available for isotopic analysis without introducing undue contamination. In addition, the limitations of existing methods and instruments hinder routine acquisition of Pb isotope data with a between-aliquot precision (2SD) better than about ± 1000 ppm, the analytical benchmark for resolving differences in marine Pb isotope compositions,[10] whilst maintaining reasonable sample throughput. Current practice and recent developments in sample preparation and analysis of seawater Pb isotope compositions are reviewed in the following as a backdrop to the state-of-the-art methods that are introduced and evaluated in this paper.

Pb extraction from seawater. Since the late 1990s, $Mg(OH)_2$ co-precipitation has provided a simple and effective procedure for the extraction of Pb from seawater prior to isotopic analysis.[11] The method takes advantage of natural Mg^{2+} in seawater, which, after increasing pH, precipitates as $Mg(OH)_2$ and removes Pb from solution by co-precipitation. The major advantage of this approach is the low blank contamination (0.01–0.12 pmol kg^{-1})[5,10,12] compared to traditional organic solvent (28 pmol kg^{-1})[13,14] and solid-phase (14–48 pmol kg^{-1})[15–17] extraction techniques, whilst simultaneously maintaining high extraction efficiencies of > 90% for Pb.[5,10,12]

The application of $Mg(OH)_2$ co-precipitation is relatively straightforward with seawater volumes of up to about 100 mL, but this restricts the precision of Pb isotope analyses (particularly for samples with low Pb concentrations and measurements of ratios encompassing ^{204}Pb) due to the limited Pb available for measurement.[7,10,12,18] Larger seawater volumes of up to 2 L have been processed to achieve more precise Pb isotope data,[19] but this comes with analytical challenges. In detail, the processing of larger seawater volumes is significantly more time-consuming as the precipitate takes longer to form. The extraction efficiencies are, furthermore, significantly lower with Pb yields of only about 40–60% for 1 to 2 L volumes because the fine suspended $Mg(OH)_2$ particles with adsorbed Pb are more difficult to separate efficiently from the seawater supernatant whilst maintaining low blank levels. Critically, the application of the co-precipitation technique is severely hindered by seawater samples with $Si(OH)_4$ contents exceeding about 75 μmol L^{-1}, such as waters found in the deep Southern and Pacific Oceans. In this case, the prolonged precipitation period associated with larger sample volumes allows the $Mg(OH)_2$ precipitates to accumulate hydrated silica. If the $Mg(OH)_2$ precipitate is too silica-rich, complete dissolution of the precipitate for further Pb purification by anion-exchange chromatography is difficult to achieve, even when minor hydrofluoric acid is present to improve solubility, and re-precipitation of a thick $Si(OH)_4$ gel can occur during the chromatographic procedure.[10,18,19] As such, $Mg(OH)_2$ co-precipitation is unsuitable as a Pb extraction method for larger volume seawater samples with higher Si contents.

In recent years, the commercial availability of a new generation of chelating resins has shifted the focus of research to an initial solid-phase extraction of Pb from seawater that employs either columns[20–25] or a batch procedure.[26,27] For Pb isotope analysis, columns with Toyopearl Chelate-650 or Nobias Chelate PA-1 resins are able to provide rapid, efficient (with Pb yields exceeding 90%) and relatively low blank (0.1–1.3 and 0.3 ± 0.2 pmol kg^{-1}, respectively) extraction procedures, which can be used to process larger volumes of seawater.[22,25]

Pb isotope measurements. The majority of published seawater Pb isotope data have been acquired by ICP-source mass spectrometry, including quadrupole inductively coupled plasma mass spectrometry (ICP-QMS), high resolution ICP-MS and, most recently, multiple collector ICP-MS (MC-ICP-MS).[10,22,25,28] Compared to the traditional use of thermal ionization mass spectrometry (TIMS) for high precision Pb isotope analyses in geo- and cosmochemistry, the use of ICP-source mass spectrometry provides distinct advantages including simplified sample preparation, much faster analyses and hence improved analytical throughput. However, due to instrumental limitations, ICP-source instruments other than MC-ICP-MS are unable to compete with the levels of accuracy that are achievable with Pb isotope analyses by TIMS. In part, this reflects the inferior Pb transmission efficiency (the ratio of ions detected by the collector to sample mass consumed in the analysis) of ICP-source instruments (0.5–3.5%) compared to TIMS (2–10%).[29–31]

A further factor that potentially limits the acquisition of high-precision Pb isotope data for seawater are the methods employed to correct for the instrumental mass discrimination incurred during analyses. The most robust Pb isotope measurements by TIMS employ the double-spike technique for this purpose, a methodology used by Paul et al. (2015) to produce the most precise seawater Pb isotope data available to date.[19] In contrast, Pb isotope analyses by ICP-source mass spectrometry typically employ either standard-sample bracketing or external normalization to admixed thallium (Tl) to correct for mass bias effects. Whilst the latter technique is preferable and has been successfully employed in numerous geochemical studies, it is also prone to analytical artefacts if too much sample matrix contaminates the purified Pb.[32] The double-spike technique is hence considered as the most robust method of mass bias correction for Pb isotope measurements. This technique, however, is relatively untested for MC-ICP-MS Pb isotope analyses and requires the measurement of both unspiked and spiked sample aliquots. In comparison to Tl-normalization, the double-spike correction therefore increases the analytical effort and the amount of Pb consumed for a single sample analysis.

In the context of these past developments in Pb isotope analysis, the aim of the present study was to test different combinations of optimized Pb extraction and mass bias correction procedures for seawater Pb isotope measurements, and to evaluate the methods based on their ability to provide precise and unbiased seawater Pb isotope data on a routine basis whilst decreasing the required analytical effort to improve overall sample throughput.

EXPERIMENTAL SECTION

Seawater samples. The performance of the methods was assessed using six filtered, acidified (pH ~2) and homogenized seawater samples that were available in quantities sufficient for multiple analyses of 0.1 to 2 L aliquots. The samples encompass an in-house quality control Southern Ocean surface water sample (SO-145),[33] and two separate Solent surface seawater samples (SSW-5 and SSW-9),[34] as well as the three GEOTRACES intercalibration samples GSP (Pacific Ocean surface water) and GSI and GDI (Atlantic Ocean surface and deep waters, respectively).[10] Together, these samples cover a range of marine biogeochemical regimes and the highly variable Pb concentrations from ~5 to 350 pmol kg^{-1} record nearly pristine environments with minimal anthropogenic Pb to those with significant Pb inputs from local pollution sources (Tables 1, 2).

Reagents and materials. All procedures were carried out in an ISO Class 6 clean room, where samples were handled in ISO Class 4 laminar flow benches during critical steps. Purified water with a resistivity ≥18.2 MΩ cm from a Milli-Q system was used throughout (Merk Millipore). Concentrated HNO_3 (15.8 M) and HBr (8.5 M) were obtained as analytical reagent grade acids from VWR and Fisher Scientific, respectively, while concentrated AristAR HF (28 M) was purchased from VWR. All acids were purified by sub-boiling distillation (HBr was double-distilled) using either a Savillex DST-1000 acid purification system or a quartz distillation unit. Also purchased from Fisher Scientific were concentrated Optima H_2O_2 (10 M), concentrated Optima acetic acid (17 M; HAc), Optima aqueous NH_3 (11 M; aq-NH_3) and reagent grade aq-NH_3 (18.1 M). The latter was purified by cold vapor phase equilibration prior to use. A 5 M NH_4Ac solution was prepared from Optima HAc and Optima aq-NH_3 and purified prior to use by extraction with Nobias Chelate PA-1 resin, using the same procedure applied to the seawater samples. The Nobias Chelate PA-1 resin (hereafter termed Nobias resin) was manufactured by Hitachi High Technologies and purchased from VWR.

Pre-concentration of Pb by magnesium hydroxide co-precipitation. The separation of Pb from seawater by co-precipitation with $Mg(OH)_2$ follows the methods outlined by Paul et al. (2015).[19] Briefly, in order to obtain about 1–10 ng of Pb for isotopic measurement, 0.1–2 L seawater samples were transferred to 1 L pre-cleaned Teflon separating funnels and $Mg(OH)_2$ precipitation was affected by the addition of small volumes of distilled aq-NH_3: initially, 2–4 mL of reagent followed by increments of 0.5–1 mL every 3 hours. Once approximately 5 mL of $Mg(OH)_2$ slurry had formed, the precipitate was drained through the separating funnel, collected in 15 mL pre-cleaned Teflon centrifuge tubes, and centrifuged at 1300 rpm for 10 minutes so that the supernatant could be removed by decantation. The latter steps were repeated several times until all the precipitate was recovered from the funnel. The precipitate was washed with 5 mL water, centrifuged and finally dissolved directly in the tubes by addition of 5 mL 2 M HBr + 0.01 M HF, which is used for loading of the subsequent anion-exchange columns for Pb purification. Samples were then left uncapped overnight in the laminar flow hood to allow emanation of any gas bubbles that formed in the solutions.

Solid phase extraction of Pb using Nobias Chelate PA-1 resin. The method used here follows a batch-extraction technique that employs Nobias resin for pre-concentration of transition metals from seawater for subsequent isotopic analyses.[27] To obtain about 1–10 ng of Pb for isotopic measurements, 0.2–2 L seawater aliquots were transferred to Nalgene LDPE bottles and treated with 1 mL 0.01 M H_2O_2 per 1 L of seawater. After a 24-hour period, 2 mL of 5 M NH_4Ac solution per 1 L of seawater were added to the sample to act as a buffer and the sample pH was subsequently adjusted to 4.8 ± 0.2 by addition of purified aq-NH_3. After setting the pH, a filtration rig consisting of a Savillex Teflon filter unit and an acrylic vacuum chamber, was attached to a vacuum pump. A Whatman Nuclepore polycarbonate membrane (5 µm pore size; 47 mm diameter) was fitted to the filter unit and approximately 2.5 mL (∼0.78 g) of Nobias resin was added to the filter reservoir and cleaned by filtration of ~30 mL 3 M HNO_3 and ~200 mL water. The cleaned resin was then transferred to the seawater sample, and the bottled mixture placed in a plastic container fitted to a circular bench shaker to allow agitation at 200 rpm for two hours. The filtration apparatus was then used again to separate the resin from the seawater and subsequently elute the seawater Pb from the resin with ∼30 mL of 3 M HNO_3 into 60 mL Savillex Teflon beakers. After evaporation, the sample residues were treated with concentrated HNO_3 and concentrated H_2O_2 (9 + 1 µL mixture) at 140 °C for at least 2 hours, then dried again and refluxed with 1 mL 2 M HBr to convert Pb to bromide form. After drying, the samples were re-dissolved in 5 mL 2 M HBr + 0.01 M HF for loading of the anion-exchange columns.

Procedural blanks were determined for every analyzed batch of 10 seawater samples by processing 1 L of synthetic ‘Pb-free seawater’ through either analytical procedure, whereby the extraction with Nobias resin was carried out twice, to quantify the maximum blank contribution for a 2 L seawater sample. The ‘Pb-free seawater’ was produced by passing

1 L of the in-house SSW-5 seawater five times through the full Nobias resin extraction procedure for complete removal of Pb.

Purification of Pb by anion-exchange chromatography. The anion-exchange purification of Pb was slightly modified from an established procedure to improve Pb purity.[19] In detail, two stages of anion-exchange chromatography with 200 µL columns of Eichrom AG1-X8 (100–200 mesh size) resin were employed with dilute HBr + HNO_3 mixtures to first elute the remaining seawater matrix and then collect a purified Pb fraction for isotopic analysis. The complete elution sequence of the column chemistry is provided in the Supporting Information (Table S1).

MC-ICP-MS analyses of Pb isotope compositions. Both the double-spike technique and external normalization to Tl were employed and evaluated for instrumental mass bias correction of Pb isotope measurements by MC-ICP-MS. The acquisition of data for Pb double-spike analyses requires separate measurements of unspiked and double-spiked sample aliquots. Therefore, the purified Pb fractions from the column chemistry were divided into two unequal aliquots. Two-thirds of the solution remained unspiked while a ^{207}Pb-^{204}Pb double-spike solution with a total Pb concentration of 10 ng mL^{-1} and ^{207}Pb/^{204}Pb ≈ 1.03 was added to the remaining third.[19] The amount of ^{207}Pb-^{204}Pb double-spike was adjusted based on an estimated Pb content for the sample and assuming an extraction yield of ~80% to produce a mixture with a molar ratio of spike-derived (S) to natural (N) Pb close to the optimum value of S/N = 1.226.[35]

Following the addition of the double-spike, both the unspiked and double-spiked aliquots were doped with a solution of National Institute Standards and Technology (NIST) standard reference material (SRM) 997 Tl to obtain Pb/Tl ≈ 1/3.[36] The addition of Tl allows external normalization of both the unspiked and spiked Pb isotope measurements. Both aliquots were then dried and re-dissolved in 1 mL 0.1 M HNO_3 with refluxing to ensure full dissolution and sample-spike homogenization.

All Pb isotope measurements were performed on a Nu Plasma II MC-ICP-MS by static multicollection using a Faraday collector array with ^{205}Tl on the axial cup and ^{201}Hg, ^{202}Hg, ^{203}Tl, ^{204}Pb+^{204}Hg, ^{206}Pb, ^{207}Pb, ^{208}Pb on collectors L4, L3, L2, L1, H1, H2, H3, respectively. The pre-amplifiers of the Faraday collector were equipped with 10^{11} Ω resistors, except L1 and L4, which were both fitted with 10^{12} Ω resistors. The 10^{12} Ω resistors assisted in monitoring the low Hg levels (^{204}Hg/^{204}Pb ≈ 1 x 10^{-4}) introduced by the plasma gas and improving the precision of the ratios that encompass the minor ^{204}Pb isotope (henceforth ^{20x}Pb/^{204}Pb ratios, where x = 6, 7 and 8).

Samples were introduced into the MC-ICP-MS as 0.1 M HNO_3 solutions using a CETAC ASX-112FR autosampler and a Nu instruments DSN-100 desolvation system fitted with Micromist cross-flow nebulizers (uptake rate ~140 µL min^{-1}). The instrument parameters were optimized on a daily basis for maximum intensity of the ^{208}Pb signal, with typical settings summarized in the Supporting Information (Table S2). Over a 15-month period, the average instrumental sensitivity for Pb was ~1500 V (µg mL^{-1})$^{-1}$, measured using a 10^{11} Ω resistor, equivalent to a transmission efficiency of 1.4%.

The same data collection procedures were applied to both the analyses of the spiked and unspiked sample aliquots. The two measurements, however, were carried out during different measurement sessions using separate DSN-100 desolvators and autosampler wash stations to avoid carryover of Pb between analyses of natural and spiked Pb aliquots. The analytical procedure featured an initial sample transfer time (50 s), followed by automatic peak centering, measurement of the electronic backgrounds whilst the ion beam was deflected in the electrostatic analyzer (30 s) and data acquisition in a single block of 60 integration cycles of 5 s each. After each sample, the introduction system was washed for 120 s with 0.1 M HNO_3 before the next run was started.

For the analyses of natural Pb, a set of mixed NIST SRM 981 Pb – SRM 997 Tl solutions in 0.1 M HNO_3 with Pb concentrations of 1 to 10 ng mL^{-1} and Pb/Tl ≈ 1/3 were measured alongside samples for quality control and to calibrate the Tl-based mass bias correction. Similarly, the analyses of spiked sample aliquots were bracketed with runs of mixed Pb – SRM 997 Tl solutions with Pb/Tl ≈ 1/3, where the Pb was a mixture of NIST SRM 981 and the ^{207}Pb-^{204}Pb double-spike adjusted to the optimal S/N = 1.226.

Data Reduction. All data processing was conducted offline using a program developed in MATLAB.[37] The raw ion beam intensities for both the unspiked and double-spiked measurements were initially corrected by removing the electronic background. Instrumental mass discrimination for unspiked measurements was corrected by external normalization using the measured ^{205}Tl/^{203}Tl ratio, the exponential mass fractionation law and an empirically optimized ^{205}Tl/^{203}Tl reference ratio to provide the best overall fit for the ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb and ^{20x}Pb/^{204}Pb ratios relative to the NIST SRM

981 reference values.[38,39] The isobaric interference from ^{204}Hg on ^{204}Pb was subsequently corrected based on the known ratio of ^{204}Hg/^{202}Hg = 0.22923.[40] For the spiked measurements, Pb ratios were corrected using a constant Tl reference ratio (^{205}Tl/^{203}Tl = 2.3888)[41] as the accuracy of the correction had no significant effect on the subsequent double-spike data reduction.

Data from the spiked measurements were combined with the Tl-normalized Pb isotope ratios of the respective unspiked runs to iteratively solve a series of non-linear equations and compute the double-spike corrected Pb isotope ratios of the samples.[35] The MATLAB program processes the data on a cycle-by-cycle basis to provide accurate propagated uncertainties. The NIST SRM 981 Pb isotope ratios determined with the double-spike were normalized to the reference values and the corresponding correction factor applied to seawater sample measurements by multiplication on a session-by-session basis.[39] Blank corrections were not applied to the Pb isotope data as the small corrections, using either a mean or batch-specific blank isotope composition, did not improve the reproducibility of replicate seawater analyses.

Determination of Pb concentrations. The seawater Pb concentrations were determined by isotope dilution (ID) following previously published methods with the same ^{207}Pb-^{204}Pb double-spike that was employed for the isotope composition measurements.[10,19] Briefly, an appropriate volume of the ^{207}Pb-^{204}Pb double spike solution was added to ~50 mL seawater aliquots in polyethylene centrifuge tubes to achieve an optimal $S/N \approx 2.61$ for ID data reduction.[19] Samples were left to equilibrate for 10 days and then Pb was co-precipitated with $Mg(OH)_2$ by addition of ~150 µL purified aq-NH_3. Following centrifugation, the seawater supernatant was removed, and the precipitate was dissolved in a dilute HBr + HNO_3 mixture for Pb purification by anion-exchange chromatography using an established procedure that employs 20 µL AG1-X8 resin columns (Supporting Information Table S1).[19,42] The subsequent ID runs for the determination of Pb concentrations were carried out using the same instrumentation and procedures that were employed for the isotope composition analyses. Blank corrections were applied to all measured Pb concentrations based on the mean procedural blank value over a 15-month period ($\bar{x}$ = 21 pg; $4 < \text{Pb} < 38$ pg; n = 11).

RESULTS AND DISCUSSION

Pb concentration measurements by isotope dilution MC-ICP-MS. The Pb concentrations determined for in-house quality control and GEOTRACES intercalibration samples are provided in Tables 1 and 2, respectively. The results show that ID MC-ICP-MS following $Mg(OH)_2$ co-precipitation achieves between-aliquot reproducibilities (1SD) of 0.6 to 2.0 pmol kg^{-1} for seawater samples with Pb concentrations ranging between 5 and 350 pmol kg^{-1}, which is comparable to the precision obtained by the ID TIMS method.[19] Importantly, the ID MC-ICP-MS results for GEOTRACES intercalibration samples are in accord with the international consensus values (Table 2).

Pb separation by solid-phase extraction versus $Mg(OH)_2$ co-precipitation prior to isotopic analysis. When using Nobias resin for solid-phase extraction, the adjusted pH value of the seawater sample is critical for the separation of metals from the seawater matrix. Previous studies that applied Nobias resin for the extraction of multiple trace metals from seawater typically used a pH of 6.05 to 6.20.[20,21,27] Here, a lower value of pH = 4.8 was adopted for Pb with the following rationale: (i) Pb yields plateau at 95–100% above pH ≈ 3.5, whilst the yields of major seawater cations and other trace metals continue to increase at a higher pH;[20] (ii) the acidified seawater samples (pH ≈ 2) require the addition of less reagent to reach a pH of 4.8, instead of 6.05–6.20, which reduces contamination; and (iii) consistent adjustment up to pH = 4.8 is readily achieved with the aid of a NH_4Ac solution as a buffer at pH 4.8 (pKa of HAc).

Multiple aliquots of in-house quality control seawater samples were analyzed following both solid-phase extraction with Nobias resin and $Mg(OH)_2$ co-precipitation to compare the performance of the methods (Table 1). The mean blank for the complete analytical procedure when Nobias resin was employed is 100 pg ($38 < \mathrm{Pb} < 202$ pg; $n = 14$). When normalized to the processed seawater mass, the obtained blank of 0.4 pmol kg^{-1} ($0.1 < [\mathrm{Pb}] < 0.9$ pmol kg^{-1}; $n = 14$) is consistent with other solid-phase extraction procedures using Nobias (0.3 ± 0.2 pmol kg^{-1})[25] or Toyopearl (0.1–1.3 pmol kg^{-1})[22] resins. When $Mg(OH)_2$ co-precipitation was employed for Pb separation, the total procedural blank of the method was about four times lower at 27 pg ($10 < \mathrm{Pb} < 40$ pg; $n = 6$), in accord with previous blanks recorded for this method when processing similar seawater volumes.[19]

Solid-phase extraction of Pb with Nobias resin, however, demonstrates higher Pb yields for the seawater samples when compared to $Mg(OH)_2$ co-precipitation (Table 1). The mean Pb yields of about 80 to 95% for Nobias extraction and 65 to 80% for $Mg(OH)_2$ co-precipitation are consistent with other studies that employed similar procedures.[19–21,27] The highly variable extraction efficiencies determined for seawater SO-145 (63–121%) with Nobias resin reflect the larger relative uncertainty of the Pb concentration measurements due to the low Pb content of this sample (Table 1). The total blank contributions from sample preparation to the quantity of Pb analyzed for each sample were estimated based on mean procedural blanks and measured Pb yields for a given sample volume. Across all seawater samples, the calculated blank contributions from the solid-phase extraction procedure were consistently higher (1.3–6.5%) compared to those of $Mg(OH)_2$ co-precipitation (0.4–1.8%).

The impact of the two Pb extraction methods on the quality of the measured seawater Pb isotope data, in particular due to any incurred mass fractionation, variable Pb blanks or instrumental mass bias effects caused by residual sample matrix in the purified Pb fractions, is evaluated in the following section.

Table 1. Lead isotope compositions and concentrations determined for in-house quality control materials using different extraction and mass bias correction procedures.

Sample	Pb separation	Mass bias corr.	*n*-IC [a]	^{206}Pb/^{204}Pb ± 2SD [b]	^{207}Pb/^{204}Pb ± 2SD [b]	^{208}Pb/^{204}Pb ± 2SD [b]	^{206}Pb/^{207}Pb ± 2SD [b]	^{208}Pb/^{207}Pb ± 2SD [b]	Sample size (L) [c]	Meas. Pb (ng) [d]	Yield (mean) % [e]	*n*-ID [a]	[Pb] ± 1SD (pmol kg^{-1})
SO-145	Nobias	DS	7	18.521 ± 23	15.646 ± 08	38.257 ± 25	1.1837 ± 14	2.4452 ± 08	~2	1.5	63–121 (80)	5	7.0 ± 1.2
± 2SD rel. (ppm) [b]				1230	490	640	1210	320					
	Nobias	TI	7	18.525 ± 25	15.651 ± 10	38.275 ± 36	1.1836 ± 14	2.4455 ± 10					
± 2SD rel. (ppm) [b]				1330	610	930	1160	410					
	co-precipt.	DS	2	18.528 ± 02	15.652 ± 02	38.276 ± 07	1.1837 ± 00	2.4454 ± 01	~2	1.4	78–79 (79)		
				18.527 ± 03	15.657 ± 03	38.288 ± 07	1.1833 ± 00	2.4455 ± 01					
	co-precipt.	TI	2	18.535 ± 02	15.662 ± 02	38.304 ± 06	1.1835 ± 00	2.4458 ± 01					
				18.530 ± 02	15.661 ± 02	38.301 ± 06	1.1833 ± 00	2.4457 ± 01					
SSW-5	Nobias	DS	5	18.095 ± 04	15.608 ± 06	37.914 ± 17	1.1593 ± 02	2.4291 ± 03	~0.2	7.0	88–95 (92)	7	248.4 ± 2.0
± 2SD rel. (ppm) [b]				240	370	450	150	100					
	Nobias	TI	5	18.088 ± 05	15.600 ± 07	37.887 ± 21	1.1595 ± 02	2.4286 ± 03					
± 2SD rel. (ppm) [b]				300	420	540	160	120					
	co-precipt.	DS	7	18.097 ± 05	15.611 ± 04	37.919 ± 15	1.1592 ± 03	2.4290 ± 04	~0.2	4.0	63–80 (73)		
± 2SD rel. (ppm) [b]				270	280	410	240	170					
	co-precipt.	TI	7	18.087 ± 10	15.598 ± 10	37.876 ± 30	1.1596 ± 03	2.4283 ± 04					
± 2SD rel. (ppm) [b]				560	640	790	230	170					
SSW-9	Nobias	DS	8	17.914 ± 08	15.590 ± 08	37.819 ± 23	1.1491 ± 02	2.4259 ± 03	~0.2	7.4	69–95 (82)	4	352.9 ± 0.6
± 2SD rel. (ppm) [b]				450	530	600	170	120					
	Nobias	TI	8	17.915 ± 12	15.591 ± 15	37.821 ± 48	1.1491 ± 03	2.4259 ± 09					
± 2SD rel. (ppm) [b]				680	930	1280	290	360					
	co-precipt.	DS	5	17.914 ± 05	15.598 ± 09	37.842 ± 30	1.1486 ± 03	2.4260 ± 04	~0.2	6.9	61–70 (66)		
± 2SD rel. (ppm) [b]				250	560	800	280	180					
	co-precipt.	TI	5	17.904 ± 07	15.584 ± 12	37.796 ± 36	1.1489 ± 04	2.4253 ± 05					
± 2SD rel. (ppm) [b]				410	760	960	380	210					

[a] Number of individual sample aliquots analysed for Pb isotope compositions or Pb concentrations using the ID technique. [b] 2 x standard deviation (2SD) calculated from individual results for *n* sample aliquots analysed across several batches of measurements (i.e., long-term reproducibility) with the relative 2SD (ppm) provided below. Where $n \leq 3$, the individual data are reported and the error corresponds to the within-run 2 x standard error of the mean (2SE); for ^{206}Pb/^{207}Pb ratios of individual measurements, the 2SE is smaller than the quoted number of decimal places. [c] Volume of individual sample aliquots used for Pb isotope analyses. [d] Mean mass of Pb in individual unspiked sample aliquots used for isotopic analyses. [e] Yield obtained for Pb extraction following separation and purification from seawater.

Table 2. Lead isotope compositions and concentrations determined for GEOTRACES intercalibration samples using different extraction and mass bias correction procedures.

Sample	Pb separation	Mass bias corr.	*n*- IC [a]	^{206}Pb/^{204}Pb ± 2SD [b]	^{207}Pb/^{204}Pb ± 2SD [b]	^{208}Pb/^{204}Pb ± 2SD [b]	^{206}Pb/^{207}Pb ± 2SD [b]	^{208}Pb/^{207}Pb ± 2SD [b]	Sample size (L) [c]	Meas. Pb (ng) [d]	Yield (mean) % [e]	*n*- ID [a]	[Pb] ± 1SD (pmol kg^{-1})
GDI	Nobias	DS	1	18.477 ± 01	15.626 ± 01	38.278 ± 04	1.1824 ± 00	2.4496 ± 01	~1	5.2	86	1	42.4
	Nobias	Tl	1	18.482 ± 01	15.634 ± 01	38.303 ± 03	1.1822 ± 00	2.4500 ± 01					
TIMS[19, 43]	co-precipt.	DS	2	18.460 ± 04	15.620 ± 03	38.255 ± 08	1.1818 ± 00	2.4491 ± 01	~2	6.0	50–55	5	45.7 ± 2.6
				18.489 ± 03	15.627 ± 03	38.298 ± 08	1.1831 ± 01	2.4506 ± 01					
Consensus [f]													42.7 ± 1.5
GSI	Nobias	DS	1	18.365 ± 02	15.634 ± 02	38.260 ± 05	1.1746 ± 00	2.4472 ± 01	~1	3.1	87	1	25.8
	Nobias	Tl	1	18.365 ± 02	15.634 ± 02	37.261 ± 04	1.1746 ± 00	2.4472 ± 01					
TIMS[19, 43]	co-precipt.	DS	3	18.356 ± 03	15.631 ± 03	38.237 ± 06	1.1744 ± 00	2.4463 ± 01	~2	3.4	45–60	6	27.9 ± 1.2
				18.347 ± 04	15.633 ± 03	38.237 ± 09	1.1736 ± 00	2.4458 ± 01					
				18.373 ± 02	15.639 ± 02	38.263 ± 06	1.1748 ± 00	2.4467 ± 01					
Consensus [f]													28.6 ± 1.0
GSP	Nobias	DS	9	18.075 ± 10	15.604 ± 07	38.192 ± 23	1.1584 ± 03	2.4476 ± 06	~0.2–0.7	3.5	76–96 (90)	6	58.7 ± 0.8
± 2SD rel. (ppm) [b]				530	450	600	280	230					
	Nobias	Tl	9	18.069 ± 06	15.596 ± 07	38.167 ± 22	1.1586 ± 05	2.4472 ± 07					
± 2SD rel. (ppm) [b]				310	460	590	430	180					
	co-precipt.	DS	7	18.076 ± 07	15.605 ± 05	38.194 ± 09	1.1584 ± 03	2.4476 ± 04	~0.2–1.0	3.8	75–89 (81)		
± 2SD rel. (ppm) [b]				360	310	240	220	50					
	co-precipt.	Tl	7	18.075 ± 20	15.602 ± 21	38.187 ± 66	1.1584 ± 04	2.4475 ± 10					
± 2SD rel. (ppm) [b]				1080	1340	1720	330	390					
TIMS[49]	co-precipt.	DS	4	18.072 ± 07	15.601 ± 04	38.183 ± 10	1.1584 ± 01	2.4475 ± 03	~0.5–2.0	7.3	84–97 (91)	5	56.3 ± 1.7
± 2SD rel. (ppm) [b]				390	270	260	120	110					
Consensus [f]													60.5 ± 5.0

[a] Number of individual sample aliquots analysed for Pb isotope compositions or Pb concentrations using the ID technique. [b] 2 x standard deviation (2SD) calculated from individual results for *n* sample aliquots analysed across several batches of measurements (i.e., long-term reproducibility) with the relative 2SD (ppm) provided below. Where $n \leq 3$, the individual data are reported and the error corresponds to the within-run 2 x standard error of the mean (2SE); for ^{206}Pb/^{207}Pb ratios of individual measurements, the 2SE is smaller than the quoted number of decimal places. [c] Volume of individual sample aliquots used for Pb isotope analyses. [d] Mean mass of Pb in individual unspiked sample aliquots used for isotopic analyses. [e] Yield obtained for Pb extraction following separation and purification from seawater. [f] Consensus values for Pb concentrations obtained from the GEOTRACES programme (www.geotraces.org/standards-and-reference-materials). For intercalibration sample GSP, the concentration was converted from pmol L^{-1} to pmol kg^{-1} by assuming a seawater density of $\rho = 1025$ kg m^{-3}.

Pb isotope analysis by MC-ICP-MS. Lead isotope measurements by MC-ICP-MS with mass bias correction using either the double-spike method or external normalization to Tl were evaluated at relevant conditions, based on multiple analyses of both pure standard solutions and Pb isolated from seawater using both extraction procedures.

Double-spike corrected runs of 1 ng SRM 981 Pb exhibit between-run precisions (2SD) of 200 to 300 ppm for ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb and 1000–1400 ppm for ^{20x}Pb/^{204}Pb ratios. As expected, the double-spike results for 7 ng SRM 981 Pb runs are more precise by a factor of about x2 to x3, with 2SD values of about 150 ppm and 250 to 500 ppm for ^{206}Pb/^{207}Pb, ^{208}Pb/^{207}Pb and ^{20x}Pb/^{204}Pb ratios, respectively (Table S3, Supporting Information). This reproducibility is comparable to double-spike TIMS measurements that employed similar quantities of Pb for analysis (Table S3, Supporting Information).[19,43] In both cases, the new double-spike corrected Pb isotope data are furthermore consistent with reference values that were obtained using poly-spike techniques with MC-ICP-MS or TIMS (Figure 1a, b; Table S3, Supporting Information).[26–28,33,35,38–43]

The latter comparison is not relevant for the Tl-normalized SRM 981 results as these data are empirically optimized for each measurement session to best match the reference values. However, for similar amounts of Pb, the Tl-normalized runs are about 2x more precise than the double-spike data (Figure 1a, b; Table S3, Supporting Information), which most likely reflects (i) the propagation of measurement errors for the unspiked and spiked runs to produce the double-spike corrected results; and (ii) the complete lack of matrix effects during runs of pure standard solutions, as such effects are typically more detrimental to externally normalized sample data that rely on a second element (rather than a double-spike of the same element) for mass bias correction.

Compared to the analyses of SRM 981 Pb, the determination of seawater Pb isotope compositions is significantly more challenging for a given mass of Pb due to the impact of low but variable blank contributions, potential isotope fractionation during sample preparation and matrix effects that produce a greater range of instrumental mass discrimination during sample runs. Given the potential impact of sample preparation and mass bias correction on data quality, the seawater results are evaluated separately for the four distinct datasets that were produced in the study. In detail, these correspond to results produced using Nobias resin for Pb separation in conjunction with mass bias correction by either the double-spike approach or Tl-normalization (termed the Nobias-DS and Nobias-Tl methods, respectively) as well as data obtained following Pb extraction by $Mg(OH)_2$ co-precipitation with either the Pb double-spike or Tl-normalization employed for mass bias correction (co-precipitation-DS and co-precipitation-Tl, respectively; Tables 1, 2). Most results were obtained using 0.2 to 2 L seawater aliquots, depending on Pb concentration, which provided about 1 to 7 ng Pb for isotopic analysis following chemical separation and purification. Replicate Pb isotope data with more than five individual sample aliquots analyses are, however, only available for three (or two, in one case) in-house quality control materials and the GEOTRACES reference sample GSP. As such, the statistical evaluation of the data must be conducted with care, as single spurious results can have an apparent impact on data quality.

The datasets for the four distinct analytical procedures exhibit, to a first order, similar between-aliquot reproducibilities (2SD) of about 300 to 1500 ppm for all Pb isotope ratios when measuring 1 to 4 ng Pb, and 100 to 1000 ppm when 4 to 7 ng were consumed in a run (Tables 1, 2; for within-run reproducibilities, see Tables S3 and S4 in the Supporting Information). This is similar to, or better than, results obtained with the most precise available double-spike TIMS method for seawater analyses (Table 2).[19,43] Furthermore, a possible bias in any of the four distinct datasets was assessed based on the Pb isotope results that were obtained for the GEOTRACES intercalibration samples GDI, GSI and GSP, whereby only one aliquot was analyzed for the former two, as only limited sample volumes were available. Importantly, all data produced in this study are identical, within the quoted uncertainties, to the robust TIMS reference values (Table 2).[19,43,49]

These results demonstrate that all four combinations of Pb separation and mass bias correction techniques are able to provide unbiased high-precision Pb isotope data, even for seawater samples with Pb concentrations of less than 10 pmol kg^{-1}. This indicates that both the double-spike approach and external normalization to Tl provide an adequate correction of the instrumental mass bias whilst variable isotope fractionation or Pb blanks incurred during the different extraction procedures had only a very limited impact on the accuracy of the Pb isotope measurements. A more detailed assessment of the results, however, reveals small but significant differences in the datasets of the individual analytical procedures, which can be better understood when compared to the replicate runs of SRM 981 Pb.

A plot of the ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios generated by replicate measurements of SRM 981 define error ellipses that align with a mass fractionation trend, suggesting that the observed scatter primarily reflects limitations in the mass bias correction procedures (Figure 1a, b). Similarly, the Nobias-DS and Nobias-Tl analyses of multiple SSW-5 and SSW-9 aliquots, carried out with 4 to 7 ng Pb, yielded error ellipses that were also roughly aligned to the mass fractionation curve (Figure 1c, d). In contrast, the Nobias-DS and Nobias-Tl results obtained for multiple aliquots of SO-145 and GSP, with about 1 to 4 ng Pb consumed per analysis, display only a weak co-variation between ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb (demonstrated by the oblate nature of the uncertainty ellipses) that appears to be unrelated to mass fractionation (Figure 1e, f). The observation of scatter that is unrelated to variable mass fractionation indicates that other sources of error from analytical and instrumental limitations are dominant, such as amplifier noise at low signal-to-noise ratios, blank contributions and memory effects. Data obtained using the co-precipitation-Tl procedure for SSW-5, SSW-9 and GSP, however, all clearly align with the mass fractionation trend, most likely due to residual sample matrix present in the purified Pb fractions, which limits the performance of the mass bias correction.

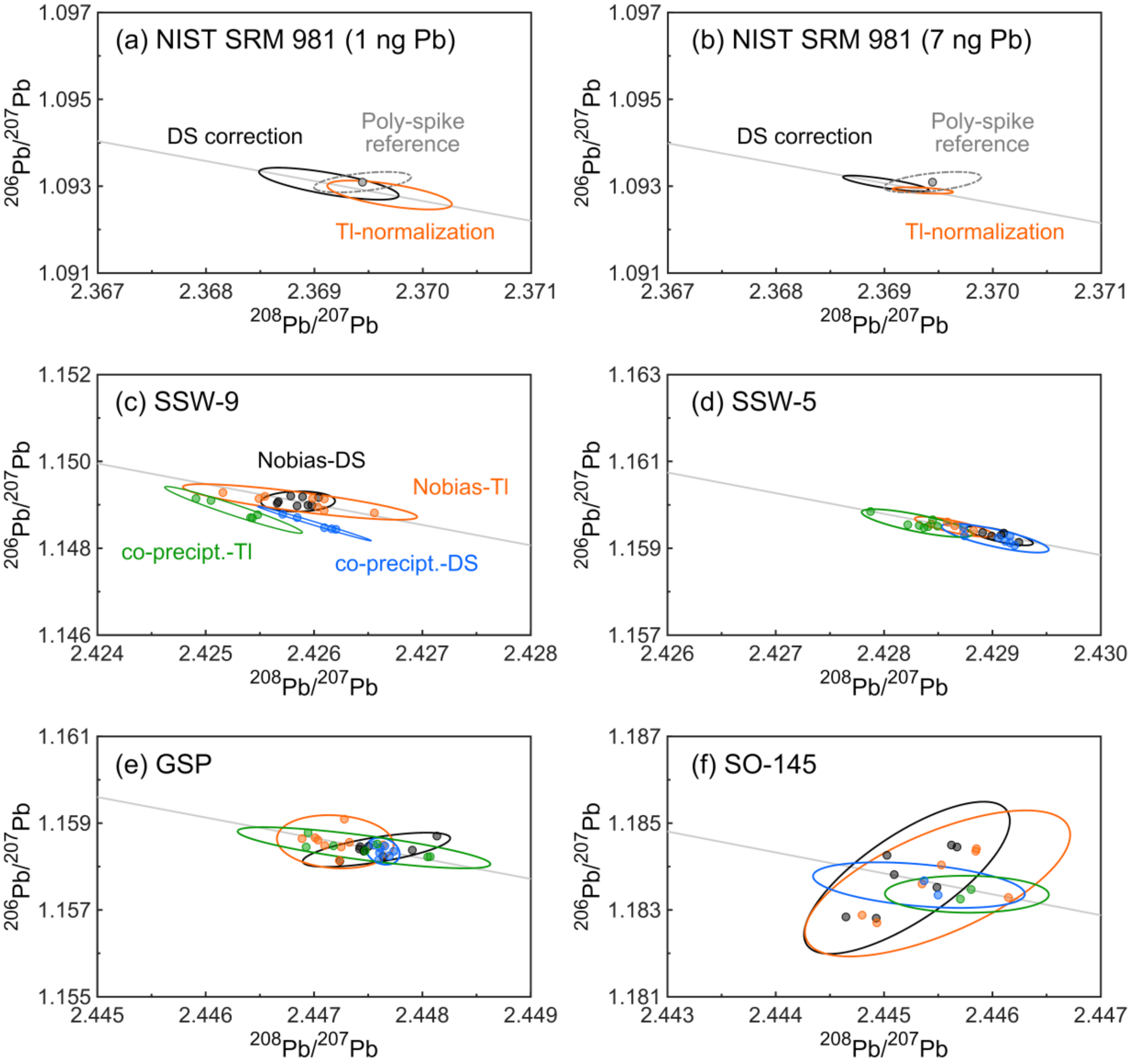

Figure 1. Plot of ^{206}Pb/^{207}Pb versus ^{208}Pb/^{207}Pb data and associated error ellipses obtained for (a, b) multiple measurements of NIST SRM 981 and (c–f) multiple aliquots of four seawater samples. No individual data are shown in Panels (a) and (b), only the error ellipses determined for multiple runs of 1 and 7 ng Pb during different measurements sessions, with solid black and orange ellipses representing double-spike correction and Tl-normalization, respectively. The grey circle represents the poly-spike NIST SRM 981 reference value (^{206}Pb/^{207}Pb = 1.0931 and ^{208}Pb/^{207}Pb = 2.3694; Table S3, Supplementary Information). For the seawater results of Panels (c–f), four datasets that correspond to distinct analytical procedures are shown (see text for details). For comparability, all six panels use the same x- and y-axis scaling, whilst the mass of seawater Pb used in a run decreases from Panel (c) to (f). The error ellipses represent the eigenvectors and eigenvalues (multiplied by the chi-squared factor to achieve a 95% confidence level) generated from co-variation regression analyses of the datasets. For the SO-145 sample of Panel (f), co-preciptation-DS and co-preciptation-Tl ellipses correspond to the combined 2SD within-run uncertainties of the two single runs that are available for this sample. The solid grey lines in all panels represent the exponential mass fractionation curves determined by using the mean ^{206}Pb/^{207}Pb and ^{208}Pb/^{207}Pb ratios of the Nobias-DS procedure as the unbiased Pb ratios.

Furthermore, a comparison of the double-spike results obtained using either Nobias resin or co-precipitation with the respective Tl-normalized data for samples that were analyzed multiple times ($n \geq 5$) reveals that the double-spike analyses typically have better reproducibilities and slightly smaller uncertainty ellipses than the Tl-normalized measurements (Table 1, Figure 1c–f). Even though sample numbers are limited, this difference appears to be particularly evident when co-precipitation is employed for Pb separation. This may indicate that $Mg(OH)_2$ co-precipitation is less effective than Nobias resin at separating Pb at high purity from the seawater matrix, which in turn increases the susceptibility of Tl-normalization to matrix effects during the MC-ICP-MS analyses.[32]

CONCLUSIONS

The performance of MC-ICP-MS analyses of seawater Pb isotope compositions was evaluated whereby two different methods were employed for both the initial Pb separation and the instrumental mass bias correction. The separation of Pb from seawater was carried out using either solid phase extraction with Nobias Chelate PA-1 resin or co-precipitation with $Mg(OH)_2$, whilst a ^{207}Pb-^{204}Pb double-spike and external normalization to admixed Tl were tested for mass bias correction.

The four distinct analytical procedures that result from the combination of these methods achieve, to a first order, results of similar quality. In detail, the seawater Pb isotope data demonstrate a between-aliquot reproducibility (2SD) of about 100 to 1000 ppm for all isotope ratios with 4 to 7 ng of seawater Pb, and 300 to 1500 ppm for 1 to 4 ng seawater Pb runs. As such, the methods enable high-precision seawater Pb isotope analyses that are similar to or better in precision than the best currently available seawater Pb isotope data from TIMS measurements with double-spike correction, even for samples with Pb concentrations as low as ~5 pmol kg^{-1}. Critically, all four tested procedures produced Pb isotope compositions for GEOTRACES seawater intercalibration samples that were identical to the published TIMS results. However, aside from establishing the accuracy of the methods, it is also important to factor in additional considerations in an evaluation of the analytical procedures. Notably, a key advantage of all four procedures is that the application of MC-ICP-MS significantly increases the sample throughput compared to TIMS analyses, as the individual runs are significantly shorter at about 6 min compared to about 55 min, and lengthy filament preparation and loading procedures are avoided.

The sample throughput of Pb isotope measurements is further enhanced if solid-phase extraction with Nobias resin rather than $Mg(OH)_2$ co-precipitation is employed for the separation of Pb from larger seawater volumes. In detail, the former method can readily improve analytical throughput by about a factor of x3 with the same overall effort. Moreover, Pb extraction with Nobias resin provides a much better separation from seawater $Si(OH)_4$, thus rendering this the more suitable method for the isolation of Pb from larger volumes of Si-rich samples, such as deep waters from the Southern and Pacific Ocean. In fact, the results of this study hint that the improved Pb separation achieved with the Nobias resin is associated with marginally more robust Pb isotope data as matrix effects are reduced, despite the elevated blank contributions. Similarly, seawater Pb isotope measurements that employ a double-spike rather than Tl-normalization for mass bias correction typically appear to be slightly more precise, as they are less susceptible to analytical artefacts generated by matrix effects.

As such, the results of the study indicate that the most accurate MC-ICP-MS analyses of seawater Pb isotope compositions are obtained using Nobias resin and the double-spike procedure. However, the combination of Pb separation with Nobias resin and Tl-normalization offers an attractive and only marginally less accurate alternative, provided that the mass bias correction is carefully calibrated for each analytical session. Notably, this approach requires only a single mass spectrometric measurement, whilst two runs are required for the double-spike procedure, which reduces the required effort, improves sample throughput, and allows more Pb to be analyzed in the single run. Furthermore, considering the large range in seawater Pb isotope compositions, with $^{206}Pb/^{207}Pb$ ratios varying by about 8% from 1.16 to 1.22, the slightly inferior accuracy has minimal impact on the utility of the results for research in marine geochemistry. Finally, the use of Tl-normalization circumvents the significant effort required to initially establish and validate the Pb double-spike methods in a laboratory.

A further consideration is that the Nobias resin employed in this study is a fairly expensive product that is currently not widely used and its application for Pb extraction from seawater thus requires non-standard equipment. In comparison, $Mg(OH)_2$ co-precipitation is relatively inexpensive and more straightforward in its application and, as a consequence, constitutes a useful alternative for Pb separation from seawater that is only marginally less accurate than the Nobias method, particularly when coupled with the double-spike approach for mass bias correction. Such analyses are, however, limited to seawater samples with low to moderate Si contents, when Pb purification by anion-exchange chromatography is not hindered by the formation of sparingly soluble silica precipitates.

SUPPORTING INFORMATION

The following Supporting Information is available as a PDF: the complete elution sequences of anion-exchange chromatography for Pb IC and ID procedures (Table S1); the typical settings used for MC-ICP-MS measurements (Table S2); the results obtained by MC-ICP-MS analyses of NIST SRM 981 Pb (Table S3); and the results of Tables 1 and 2 reproduced to include the within-run reproducibilities of the seawater quality control and reference materials (Tables S4 and S5).

AUTHOR INFORMATION

Corresponding Author

Alex Griffiths − MAGIC Group, Department of Earth Science & Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.; email: a.griffiths15@imperial.ac.uk

Authors

Hollie Packman − MAGIC Group, Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.

Yee-Lap Leung − MAGIC Group, Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.

Barry J. Coles − MAGIC Group, Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.

Katharina Kreissig − MAGIC Group, Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.

Susan H. Little − Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, U.K.

Tina van de Flierdt − MAGIC Group, Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.

Mark Rehkämper − MAGIC Group, Department of Earth Science and Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, U.K.

Notes

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