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High-precision measurements of seawater Pb isotope compositions by double spike thermal ionization mass spectrometry

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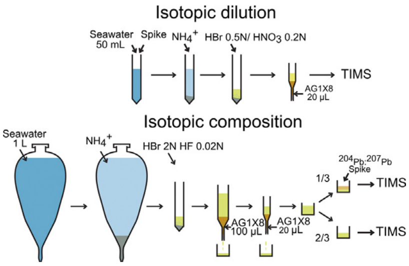
HIGHLIGHTS

- Precise and accurate determination of seawater Pb isotope compositions.
- Uncertainties (2sd) for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ are better than ±3‰.
- Analysis of a GEOTRACES depth profile from the South Atlantic Ocean.
- Pb isotopic compositions reflect the different water masses that were sampled.
- The $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ ratios display a correlation.

GRAPHICAL ABSTRACT



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ABSTRACT

A new method for the determination of seawater Pb isotope compositions and concentrations was developed, which combines and optimizes previously published protocols for the separation and isotopic analysis of this element. For isotopic analysis, the procedure involves initial separation of Pb from 1 to 2 L of seawater by co-precipitation with Mg hydroxide and further purification by a two stage anion exchange procedure. The Pb isotope measurements are subsequently carried out by thermal ionization mass spectrometry using a ^{207}Pb–^{204}Pb double spike for correction of instrumental mass fractionation. These methods are associated with a total procedural Pb blank of 28 ± 21 pg (1sd) and typical Pb recoveries of 40–60%. The Pb concentrations are determined by isotope dilution (ID) on 50 mL of seawater, using a simplified version of above methods. Analyses of multiple aliquots of six seawater samples yield a reproducibility of about ±1 to ±10% (1sd) for Pb concentrations of between 7 and 50 pmol/kg, where precision was primarily limited by the uncertainty of the blank correction (12 ± 4 pg; 1sd). For the Pb isotope analyses, typical reproducibilities (±2sd) of 700–1500 ppm and 1000–2000 ppm were achieved for $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, respectively. These results are superior to literature data that were obtained using plasma source mass spectrometry and they are at least a factor of five more precise for ratios involving the minor ^{204}Pb isotope. Both Pb concentration and isotope data, furthermore, show good agreement with published results for two seawater intercomparison samples of the GEOTRACES program. Finally, the new methods were applied to a seawater depth profile from the eastern South Atlantic. Both Pb contents and isotope compositions display a smooth evolution with depth, and no obvious outliers. Compared to previous Pb isotope data for seawater, the $^{206}Pb/^{204}Pb$ ratios are well correlated with $^{207}Pb/^{206}Pb$, underlining the significant improvement achieved in the measurement of the minor ^{204}Pb isotope.

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1. Introduction

Investigations that map the distribution of trace metals and their isotopes in seawater and which study their relationship to and potential impacts on global biogeochemical cycles in the oceans are an overarching goal of modern marine geochemistry and a key objective of the international GEOTRACES program [1]. The global scale impact of human activities on natural Pb budgets was established more than 40 years ago by Chow and co-workers [2–5] and massive inputs of anthropogenic Pb into the oceans were soon thereafter identified by Patterson and co-workers [6–8], based on the first accurate and precise Pb concentration measurements for seawater. Studies of the anthropogenic impact on marine Pb budgets were further advanced with the first successful Pb isotope analyses of seawater [6,9–13]. Whilst these early measurements were all carried out by TIMS (thermal ionization mass spectrometry), the majority of seawater Pb analyses since the 1990s have been conducted using various types of ICP-MS instrumentation. At present, the most precise Pb isotope analyses of seawater apply either single collector high resolution or multiple collector ICP-MS (HR-ICP-MS and MC-ICP-MS, respectively), most commonly following low-blank pre-concentration of the element by co-precipitation with $Mg(OH)_2$ [14,15].

These methodological advances are a consequence of the particular importance of seawater Pb isotope data to studies of environmental pollution and marine geochemistry. For example, analyses of corals yielded a seawater Pb isotope record for the North Atlantic over the last 220 years [12,15,16], which revealed significant isotopic variability through time, in accord with known changes in the extent and type of anthropogenic emissions. Similarly, Pb isotope data for the modern ocean are used to infer the distribution of Pb from different anthropogenic and natural sources in surface seawater [9,13,17,18] and to determine the lateral mixing and advection of subsurface water masses [19–23]. Shen and Boyle [12], furthermore, highlighted that temporal changes in the Pb content and isotope composition of different water masses can be applied to trace ventilation times.

In this paper, we present a new method for the accurate and precise determination of seawater Pb concentrations and isotope compositions. The methodology involves pre-concentration of Pb by $Mg(OH)_2$ co-precipitation [24] followed by ion exchange chromatography [25,26], and subsequent isotopic analyses by TIMS using a ^{204}Pb–^{207}Pb double spike to achieve precise control of instrumental mass fractionation [27,28]. The technique is validated by analyses of both in-house and international seawater reference materials and its utility demonstrated by data obtained for a GEOTRACES seawater depth profile from the South Atlantic Ocean.

A number of previous investigations [28–34] have shown that the application of Pb double or triple spikes enables Pb isotope measurements that are significantly more precise and accurate than conventional TIMS or MC-ICP-MS techniques and less susceptible to the analytical artifacts, which can be generated by instrumental mass bias effects. Our study is the first to apply the double spike methodology to seawater Pb isotope analyses. Using these techniques, we are not only able to analyze the commonly measured ratios $^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$ to high precision but $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ can also be determined to an uncertainty of better than about ±3‰. Only very scarce seawater data are available for the latter ratios due to the analytical challenges but measurements of non-radiogenic ^{204}Pb are deemed to be important to fully exploit the potential of the Pb isotope system.

2. Experimental

2.1. Samples

A gravimetric solution of the well-characterized NIST standard reference material SRM 981 Pb was employed for calibration of the Pb double spike and to evaluate the precision of the mass spectrometric methods. Four filtered seawater samples that were available in large quantities were utilized as in house reference materials to further assess reproducibility. These encompass a surface water sample (Atlantic – S) and three subsurface water samples, Atlantic – D1, Atlantic – D2 (both from 2000 m depth), and Weddell (400 m depth). These samples were not specifically collected for Pb isotope analyses, and potential contamination during sampling and initial handling hence renders them unsuitable for evaluation of accuracy or an assessment of water mass properties.

To enable a comparison of our results with literature data for assessment of accuracy, we analyzed the international seawater reference samples GSI and GDI. These were collected at water depths of 7 m and 2000 m, respectively, at the Bermuda Atlantic Ocean Time Series station (BATS) during the 2008 GEOTRACES intercalibration cruise on the R/V Knorr (KN193-6). The collection and handling of these samples employed materials and procedures that were specifically designed for the intercalibration of contamination-prone trace metals and isotopes [35].

The seawater for a Pb isotope and concentration depth profile was collected in the South Atlantic Ocean off the African coast at 36.46°S, 13.39°E in October 2010 during the eastern part of the GEOTRACES GA10 transect along 40°S on the R.R.S. Discovery (D357; 18 October–22 November 2010) [1]. This depth profile from station 3 encompasses 12 samples that cover the entire 4500 m of the water column at the sampling location. Station 3 serves as a 'cross over station', which means that it was sampled by three separate GEOTRACES cruises (UK GEOTRACES cruise D357 – this study; UK GEOTRACES cruise JC068 in 2011/2012; MD166 BONUS – GoodHope Cruise in 2008, Boye et al. [36]), thereby enabling a comparison of results for samples from a single location but that were collected at different times and analyzed using different methodologies. The samples from cruise D357 analyzed here were obtained with a titanium rosette deployed from plasma rope and equipped with trace metal clean sample bottles and supplemented by underway surface water sampling (2–3 m depth) using a towed 'fish' (Wyatt et al. [37]). All bottle handling was conducted in a clean container and each sample was transferred into two pre-cleaned 1 L LPDE bottles without filtration or acidification. About one year after collection and two weeks prior to analysis, the samples were acidified to pH 2 with 6 M HCl.

2.2. Reagents

Water with a resistivity of >18.2 MΩ cm from a Milli-Q water system was used throughout for reagent preparation and cleaning of labware. Purified concentrated HF (~28 M) and HBr (~8.5 M) were purchased from VWR as Optima (distilled) grade acids whilst concentrated (14.5 M) HNO_3 and 6 M HCl were prepared in-house by subboiling distillation of reagent grade acids in quartz stills. The Pb blanks of these acids were checked regularly and found to be consistently less than 2 pg/mL. The dilute mineral acids that were employed for the separation chemistry were freshly prepared for each batch of samples.

A purified aqueous solution of NH_3 was used to affect precipitation of $Mg(OH)_2$ from seawater and prepared by cold vapor phase equilibration of reagent grade 28% (w/w) aqueous NH_3 with Milli-Q water in a Savillex Teflon elbow. Approximately 2 volumes of 28% aqueous NH_3 were employed for each