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Lead and lead isotopes in the U.S. GEOTRACES East Pacific zonal transect (GEOTRACES GP16)



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ABSTRACT

Most of the lead (Pb) in today's ocean is from human activities, although natural sources contribute small amounts of Pb that are usually masked by massive anthropogenic emissions. In the U.S. GEOTRACES East Pacific Section (GP16), anthropogenic Pb is observed throughout the water column, and as seen elsewhere in the Pacific, Pb concentrations are highest in the upper hundreds of meters of the ocean and generally decrease with depth. Thermocline Pb concentrations are higher in the eastern portion of the section near the South American coast, decreasing with distance from the South American continent, as previously reported for redox sensitive trace elements (e.g., Mn). High precision Pb isotope ratios show that there has been a change over the past few decades in the source of Pb in the westernmost upper waters, shifting from an American-Australian type Pb intermixture to a Chinese-American-type Pb intermixture. Although it is known from the study of hydrothermal solutions and sediments that there is a large primary Pb flux from high temperature ridge crest hydrothermal springs, most of this Pb precipitates near the hydrothermal vents and very little escapes into the open water column. In fact, hydrothermal ferromanganese oxyhydroxides precipitated from the hot spring emissions strip anthropogenic Pb out of the water column, resulting in the lowest Pb concentrations ever observed in the ocean (a few tenths of a picomole/kg) in the high ³He-plume to the west of the East Pacific Rise.

Deeper waters have similarly low Pb concentrations, probably as a result of the sinking veil of hydrothermalsource ferromanganese oxyhydroxides. Core top sediments from this section and previous work show clear evidence of less-radiogenic Mid Ocean Ridge Basalt (MORB) Pb distinct from the crustal and anthropogenic Pb seen in non-ridge crest sediments, specifically, low values of $^{206}Pb/^{207}Pb$ (1.189), $^{208}Pb/^{207}Pb$ (2.449), and $^{206}Pb/^{204}Pb$ (18.42), compared to \sim 1.195, \sim 2.475, and \sim 18.75 respectively for the non- hydrothermal sediments. Near bottom dissolved (< 0.2 µm filter) water column Pb (with concentrations < 2 pmol kg⁻¹) at the ridge crest and in the near-downstream neutrally-buoyant hydrothermal plume show $^{206}Pb/^{207}Pb$ - $^{208}Pb/^{206}Pb$ trends that are lower than observed throughout the rest of the water column and fall within the mixing endmember isotope ratios of less radiogenic MORB and more radiogenic anthropogenic Pb sources. Thus there is a very small leakage (\sim 1%) of primary high temperature hydrothermal Pb into the water column. But at the westernmost station (36), which shows a diluted continuation of the ³He, manganese (Mn), and iron (Fe) plume from 2200 to 2700 m, the > 2200 m Pb isotope ratios deeper than 2000 m return to the non-hydrothermal ratios with no remaining detectable MORB.

1. Introduction

Anthropogenic lead (Pb) is the predominant source of Pb in the modern ocean as has been demonstrated since the pioneering work of Schaule and Patterson (1981) and by many publications by other authors in the past four decades (see review by Boyle et al., 2014). It is now known that anthropogenic Pb concentrations and inputs are much lower in the South Pacific (Flegal & Patterson, 1983; Flegal et al., 1984; Wu et al., 2010), but there still is relatively little published data on lead concentrations and isotopic compositions for either South America or

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the South Pacific. As a U.S. contribution to the international GEOTR-ACES program, samples from the complete water column were collected for Pb and Pb isotope analysis on a transect from Peru to Tahiti. Among the questions that these data can illuminate are: (1) What is the relative contribution of anthropogenic Pb sources from the South American continent and generally the western Pacific, and have they been changing during recent decades in response to changing patterns of industrial and automotive emissions? (2) How deeply has the anthropogenic Pb penetrated? (3) Are high-temperature submarine hydrothermal emanations a significant source of Pb to the bottom waters, or are the hydrothermal ferromanganese oxyhydroxide precipitates a sink of Pb from the ocean?

2. Methods

2.1. Cruise track and sampling

Samples were collected from GEOTRACES track GP16, referred to as the U.S. GEOTRACES East Pacific Zonal Transect (EPZT), that took place aboard the R/V Thomas G. Thompson (cruise TN 303, October-December 2013; chief scientists: James Moffett, Christopher German, and Greg Cutter). The cruise began in the upwelling region adjacent to Peru and ended on the edge of the South Pacific subtropical gyre about seven degrees north of Tahiti (Fig. 1). Thirty-six stations were then occupied at approximately even spacing across the basin alternating between full depth sampling of the water column and intermediate sampling to 1000 m. Full vertical profile stations during the two legs consisted of 36 depths, and shallow stations consisted of 12 depths. A surface towed fish was also deployed and a surface sample was taken for each station.

2.2. Trace metal sampling techniques

Three laboratories participated in this study: Ed Boyle's group (Massachusetts Institute of Technology, MIT), Ken Bruland's group (University of California Santa Cruz, UCSC-B), and Russ Flegal's group (University of California Santa Cruz, UCSC-F). The purpose of this collaboration was three-fold. First, the number of samples and rigor of the analyses were so large that no individual laboratory was poised to complete all of the measurements within a reasonable time. Second, there was a need to demonstrate the accuracy of those measurements through inter-laboratory intercalibrations, since it was anticipated that the lead concentration levels in surface waters would be among the lowest ever measured in the ocean. And third, there was an interest in expanding the number of individuals with demonstrated expertise in lead isotopic composition measurements in seawater. While Ken Bruland was one of the original leaders of GEOTRACES and actively involved in the GP16 cruise, he determined that Claire Till should be the only author from his group in this report.

Before the cruise, MIT 2 L HDPE bottles (Nalgene) lids and threads and exterior were soaked overnight in 2 M reagent grade HCl, then filled with 1 M reagent grade HCl, heated in an oven at 60 °C overnight, rotated top to bottom, heated for a second day, and rinsed 5 times with pure distilled water. The bottles were then filled with trace metal clean dilute HCl (0.01 M HCl) and again heated for two days in the oven, rotating top to bottom after the first day. These clean sample bottles were emptied, and double- bagged prior to rinsing and filling with filtered seawater.

UCSC-F samples were collected in 1 L LDPE bottle with HDPE caps (cleaned by submerging entire bottles into 2 M reagent grade HCl at room temperature for 4 weeks, rinsed 3 times with pure distilled water, then filled with trace metal clean dilute HCl for 3 weeks and shipped, triple bagged, with a few drops of acid inside). UCSC-B samples were collected in 500 mL LDPE bottles pre-cleaned as described in the GEOTRACES cookbook (www.GEOTRACES.org).

Samples were collected using the ODU GEOTRACES Carousel (Cutter and Bruland, 2012), and were filtered through 0.2 µm Acropak capsule filters in the GEOTRACES clean van. The carousel was used to collect samples from surface to near bottom waters, and an additional sample was collected from a surface towed "fish" at each station. Preconditioned, Teflon®-coated Go-Flo sampling bottles (General Oceanics, Miami, FL) of 12 L capacity were deployed on a polyurethane powder-coated aluminum rosette with titanium pylons and pressure housings (Sea- Bird Electronics, Inc., Bellevue, WA) attached to a Kevlar, non-



Fig. 1. Cruise track for GP16.



Fig. 2. Cruise track and Pb concentration data for the upper 1500 m and complete water column for the entire section.

metallic conducting cable. For more information regarding carousel deployment, please refer to the GEOTRACES Cookbook, located on the GEOTRACES Program website (www.GEOTRACES.org). After retrieval of the carousel, Go-Flo bottles were moved to the U.S. GEOTRACES Program class-100 trace metal clean van, and pressurized with HEPA filtered nitrogen (extracted from air) for sampling in accordance with published methods (Cutter and Bruland, 2012). The bottles were labeled with a sticker taken from the sampling GOFlo (allocated GEOT-RACES number). UCSC samples were acidified at sea. Upon return MIT, MIT samples were acidified by the addition of 8 mL of 6 M high purity HCl. Samples were kept at room temperature until analysis several months after acidification.

Surface towed fish samples were collected by suspending the towed fish off starboard with a boom, and sampled water at approximately 2 m depth using a Teflon[®] diaphragm pump following the GEOTRACES Program Cookbook sampling recommendations.

As part of the cooperative arrangement, three labs made Pb concentration analyses on a subset of the samples and two labs made Pb isotope ratio measurements on a subset of samples, with some overlap for intercalibration comparison. Pb concentration analyses were carried out separately by the Bruland (University of California Santa Cruz, UCSC-B), Flegal (UCSC-F), and Boyle (Massachusetts Institute of Technology, MIT) labs. UCSC-F focused on the surface and upper 1000 m, UCSC-B focused on the surface and eastern basin profiles, and MIT focused on the water column below 1000 m. Some samples were analyzed by all three groups for the sake of intercalibration (a subset of the surface water samples and station 1 was run by all three groups, and the entire station 36 profile was run by both UCSC-B and MIT and the upper 1000 m also run by UCSC-F. The upper 1000 m for stations 1-7, 9-12, and 14-15 were run by both UCSC-B and UCSC-F. MIT did the Pb and Pb isotope measurements from the upper 1000 m of the water column in most of the westernmost part of the transect.

In order to produce this manuscript, all of the Pb concentration

([Pb]) and Pb isotope data was combined into a composite file using an edited form of almost all of the data (excluding high outliers) from all of the labs. The exclusions involve "oceanographic inconsistency" most likely a result of contamination (e.g. a single high point falling off the surface or profile trends). These edited samples are indicated by data flag "3" in the supplementary file but are not plotted in our figures. Where multiple labs report data, the analyses are averaged. For the Pb isotope data, in view of the higher precision possible with multicollector ICP-MS, we used the MIT data preferentially in the composite file, although for the most part there were relatively few overlapping UCSC-F data. Except where noted, the composite data file is used for the figures in this paper.

For the case of the surface samples, most towed fish samples at hydrographic stations were measured for Pb concentrations by all three labs (but not the samples in-between the hydro stations, that were only analyzed by UCSC-F).

Because the UCSC-F Pb data trended toward lower concentrations, we did not include any of the samples from the in-between hydro stations as it would have introduced zig/zag noise that would obscure the overall picture. Instead, we chose to average the available results from all three labs for the full profile stations in the composite file.

2.3. MIT dissolved Pb concentration analysis methods

At MIT, samples were analyzed for [Pb] by ²⁰⁴Pb isotope dilution from NTA-pre-concentrated subsamples using a quadrupole inductively coupled mass spectrometer (Q ICP-MS) following a published 1.5 mL method (Lee et al., 2011). As it became obvious that many of the deep water samples contained far lower Pb concentrations than ever observed in the ocean, a second ²⁰⁴Pb isotope dilution method using 30 mL samples with Mg(OH)₂ coprecipitation followed by anion exchange purification using larger samples was used. Averaged blanks for the 1.5 mL method for a given day of analyses ranged from 4.3–7.0



Fig. 3. Surface (2-3 m) Pb concentrations and surface ²⁰⁶Pb/²⁰⁷Pb isotope ratio data (station by station).

(\pm 1.9 s.d.) pmol kg⁻¹ (10 analysis days). Averaged blanks for the 30 mL method for a given day of analyses ranged from 0.2–3.9 (\pm 0.9 s.d.) pmol kg⁻¹ (20 analysis days). More details are provided in the supplementary materials.

2.4. UCSC-F Pb dissolved concentration analysis methods

Samples were analyzed using the chelating resin flow-injection method described in Ndung'u et al. (2003). Briefly, seawater Pb was extracted using an automated pump manifold by Toyopearl AFChelate 650 M ion-exchange resin; 1.5 M HNO₃ eluted the Pb directly into a Thermo ELEMENT XR magnetic sector HR ICP-MS for analysis. The average blank (acidified MilliQ water) and precision ($3 \times$ the standard deviation of the blank) were consistent with previously published statistics for this method, 5.0 pmol kg⁻¹ and 3.8 pmol kg⁻¹, respectively (Zurbrick et al., 2013). Subsamples for SAFe S1 and D2 and GEOTRA-CES standards were consistent with the consensus values published on the GEOTRACES. website, http://www.geotraces.org/science/intercalibration/322-standards-andreference-materials.

2.5. UCSC-B Pb dissolved concentration analysis methods

Samples were analyzed using the method of Biller and Bruland

(2012) with modifications as described in Parker et al. (2016). Briefly, this involves offline pre- concentration of buffered seawater at pH of 6.0 +/- 0.2 on Nobias chelate PA1 resin, followed by analysis on the Thermo ElementXR Magnetic Sector Inductively Coupled Plasma Mass Spectrometer (ICP-MS) at the Institute of Marine Science at UCSC. Eight separate columns allowed pre-concentration of eight separate samples (or standards, blanks, etc.) at once. Column blanks (assessing column-to-column blank variability) and reagent blanks (a comparison between seawater ran normally and ran with twice the reagents) were tested at least once per ICP-MS run, and GEOTRACES reference samples were analyzed each run on the ICP-MS to confirm accuracy (see section 2.7, below, and the supplemental material.)

2.6. MIT dissolved Pb isotope analysis methods

Samples were analyzed on a Micromass IsoProbe multicollector ICP–MS with the use of an APEX/SPIRO desolvator and a 40 $\mu L/min$ Micromist glass nebulizer.

The multicollector ICPMS portion of the procedure is similar to a previously published protocol (Reuer et al., 2003 as modified by Boyle et al., 2012, using HBr/HCl anion exchange column chemistry based on Krogh, 1973 and Manhes et al., 1978). Due to relatively high dissolved silica concentrations in these samples, we could not use Mg(OH)₂



Fig. 4. Entire water column ²⁰⁶Pb/²⁰⁷Pb section.

coprecipitation because it concentrates the silica that precipitates as a gel in the concentrated sample preventing the subsequent anion exchange chemistry. Instead, Pb was preconcentrated from 400 to 2000 mL of acidified seawater by solid phase extraction onto Nobias Chelate PA1 resin (Sohrin et al., 2002).

MIT isotope ratio accuracy and precision: for samples near the upper range of the Pb signals shown for samples (~1 V), $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ can be reproduced to ~200 ppm. Low-level samples will be worse than that, but generally better than 1000 ppm in this data set. Due to the drift uncertainty in the Daly detector, $^{206}Pb/^{204}Pb$ for samples in the mid-to-upper range of sample concentrations will be at best reproducible to ~500 ppm and worse for low-level samples. Zurbrick et al., 2018) discuss the reproducibility the MIT lab obtains for duplicate analyses of multiple samples as a function of the Pb sample size.

2.7. UCSC Pb isotope analysis methods

Samples were analyzed using the method of Zurbrick et al. (2013). Briefly, 300 mL – 500 mL of Pb in was extracted onto Toyopearl AF-Chelate 650 M resin, and eluted with 1 mL of 1.5 M HNO₃. The extracts were analyzed with HR ICP-MS in counting mode. Isotope ratios were calibrated with concurrent measurements of National Institute of Standards and Technology (NIST) standard reference material 981 (common Pb). Typical precision (2 σ) associated with this method is 4800 ppm for ²⁰⁶Pb/²⁰⁷Pb, 6000 ppm for ²⁰⁸Pb/²⁰⁷Pb and 6300 ppm for ²⁰⁶Pb/²⁰⁴Pb (Zurbrick et al., 2013).

2.8. Intercalibration

In addition to the intercalibrations relative to SAFe or GEOTRACES quality control samples by each lab as reported in the previous section, some GP16 samples were collected and distributed to two or three labs. These included surface (\sim 3 m) samples from the towed fish that each lab received, and at some stations, replicate samples from the

individual GoFlo bottles. Where these were analyzed by two or three labs, an informal intercalibration showed that the interlab agreement was satisfactory. A more detailed comparison is given in the Supplementary Information file.

We also tried using samples for UCSC-F from the bottom of the upper 1000 m casts and MIT from the top of the \geq 1000 m casts. This form of intercalibration proved less useful than anticipated because of the relatively strong [Pb] gradient at this depth, so small offsets in sampling depths and variability between casts that were caused by internal waves leading to significant non-analytical differences.

2.9. MIT sediment Pb isotope analyses

Small "monocores" were collected with a corer deployed below the standard Niskin rosette. We were given small samples from the upper centimeter of each core. We extracted Pb using the Graney et al. (1995) 1.75 M HNO₃ - 3 M HCl 1 h. ultrasonic bath leach, that will extract all of the adsorbed and hydrogenous Pb and much of the Pb in poorly crystalline phases. The leached solutions were dried down, redissolved in 1.1 M HBr and purified by passage through an anion exchange column, as described by Lima et al. (2005). Quantification of the Pb isotope ratio for the purified solutions by IsoProbe multicollector ICPMS spectrometry was done in the same way as described in section 2.6 for dissolved Pb isotope analysis.

3. Results and discussion

3.1. East-West Gradients in the surface and upper ocean

The cruise track is shown in Fig. 1 and the Pb concentration data for the upper 1500 m and complete water column for the entire section are shown in Fig. 2 (see inset for cruise track). The surface (2-3 m) Pb concentration and surface ²⁰⁶Pb/²⁰⁷Pb isotope ratio data (station by station) appear in Fig. 3. The entire water column ²⁰⁶Pb/²⁰⁷Pb section is shown in Fig. 4. Individual Pb concentration profiles and ²⁰⁶Pb/²⁰⁷Pb



Fig. 5. Individual Pb concentration profiles.

isotope ratio profiles are shown in Figs. 5 and 6. All of the data with supporting oceanographic information is given in Supplementary Information. Maximum surface and upper thermocline Pb concentrations are seen near the South American coast (31 pmol kg⁻¹ in the entire data set, and 26 pmol kg⁻¹ at 200–250 m at stations 5 and 1), being slightly lower at stations immediately off the Peruvian coast. This distribution resembles some other properties (e.g. Mn, Resing et al., 2015), but probably results from slightly different processes (e.g., Pb predominantly anthropogenic transported from the South American

continent, Mn partially from partial solubilization of atmospherically transported dust and partially from reductive dissolution of manganese oxides from continental margin sediments). The Pb maximum persists as a feature deepening from ~200 to ~500 m going westwards out to 5800 km from the South American coast (approximately along the 26.25–26.50 kg m⁻³ neutral density surface for this cruise and the CFC11 ~ 1.2 pmol kg⁻¹ surface as seen in WOCE section P21 in 2001). This feature coincides with the water mass analysis of Peters et al. (2018) who note the deepening of Equatorial Subsurface Water (ESSW)



Fig. 5. (continued)

along this same depth trend. We attribute the high Pb to smelting and other high temperature industrial activities and natural volcanic activity in western South America. The Pb concentration gradient is complemented by a strong ²⁰⁶Pb/²⁰⁷Pb gradient from highest values of 1.183 in the surface water Pb concentration maximum (attributable to natural and recent anthropogenic South American Pb emissions) decreasing to 1.164–1.169 in the waters to the west of station 18 (attributable to Australian and Chinese Pb, emissions, see section 3.2).

Our attribution of natural volcanic and smelting Pb sources is based on measurements of kilotons of sulfur dioxide from Ecuadorean and Columbian volcanoes advected across those waters, and measurements of kilotons of sulfur dioxide from the La Oroya and Ilo copper smelters in Peru advected across those waters (Carn et al., 2007). Although we do not have comparable data for Pb concentrations and isotopic compositions of those volcanic and smelting aerosols, we surmise that the Pb concentrations of the latter are substantial because (1) sulfidic Pb and copper ores commonly occur together, (2) Pb and sulfuric acid are the principal atmospheric pollutants from copper smelters, and (3) La Oroya is infamous for its Pb pollution (Centers for Disease Control, 2005). Peru and Chile are also the world's largest copper producers, that release Pb as a by-product.

Moreover, the world's largest copper mine (Escondida) is located in northern Chile, just south of Peru; and volcanic emissions from a recent eruption of the Puyehue volcano in Chile were so extensive that they grounded air traffic across the Southern Hemisphere (NASA, 2011).

The other potentially important anthropogenic sources of Pb in the Eastern Tropical South Pacific are (1) aeolian inputs from the Mt. Isa copper and Pb mining and smelting operation in northeastern Australia, that the operators claim is not an environmental problem in Australia because those aerosols are advected across the South Pacific, and (2) remobilization of Pb from massive historic and contemporary forest fires in Patagonia (Odigie et al., 2015). Naeher et al. (2003) reported the Pb isotope ratios of 30 particulate air samples in and near Callao Peru from 1998. Although there is a wide spread in the sources ($^{206}Pb/^{207}Pb$ ranges from 1.12–1.21), most of them fall in the upper portion of that range with a median $^{206}Pb/^{207}Pb = 1.19$. Hence the higher $^{206}Pb/^{207}Pb$ values in the eastern seawater Pb maximum are consistent in terms of a dominant South American source.

Industrial Pb isotopic compositions from mining and smelting operations in that region contrast with those of historic emissions from the combustion of leaded gasoline in the area (Eichler et al., 2015). These include those of leaded gasoline $(^{206}\text{Pb}/^{207}\text{Pb} = 1.071-1.073)$ in Peru (Naeher et al., 2003), and those of urban aerosols in Puerto Natales $(^{206}\text{Pb}/^{207}\text{Pb} = 1.064)$, Punta Arenas $(^{206}\text{Pb}/^{207}\text{Pb} = 1.063-1.094)$, and Villas Rica $(^{206}\text{Pb}/^{207}\text{Pb} = 1.069)$ in southern Chile (Bollhöfer and Rosman, 2000). All are consistent with the isotopic composition of Pb



Fig. 6. ²⁰⁶Pb/²⁰⁷Pb isotope ratio profiles.

additives to gasolines from the Pb mines in Australia, that were extensively used throughout the Southern Hemisphere (Bollhöfer and Rosman, 2000). As a consequence of the predominance of those industrial inputs – from both historic emissions of leaded gasoline in the Southern Hemisphere and on-going mining and smelting operations in Broken Hill and Mount Isa in Australia – the isotopic composition of aerosols in Punta Arenas (206 Pb/ 207 Pb = 1.072 ± 0.008; 208 Pb/ 207 Pb = 2.342 ± 0.012) was recently selected as the endmember of contemporary industrial Pb emissions in the Southern Ocean and Antarctica (Ndungu et al., 2016). That assignment was based, in

part, on the recent review of sources of Pb in ice cores across Antarctica that attested to the probability of Australia and South America as possible source areas for Pb contamination in that polar region (McConnell et al., 2014).

The disparity between estimates of the predominant source(s) of industrial Pb in much of the Southern Hemisphere and those in EPZT surface waters is consistent with preliminary measurements of Pb isotopic compositions in surface waters collected off Peru (15°20'S; 75°45'W) three decades ago (Flegal, 1986). Then Pb concentrations in the nearshore waters were anomalously high (4–11 ng kg⁻¹) compared



Fig. 6. (continued)

to those in off shore waters (4 ng kg^{-1}). This data contrasted with the decrease of 210 Pb concentrations from 15 to 7.5 dpm 100 kg $^{-1}$ between those oceanic and nearshore waters, that was indicative of biological scavenging in the highly productive coastal waters off Peru. Moreover, Pb isotopic compositions in those surface waters (e.g., 206 Pb/ 207 Pb = 1.20–1.22) attested to inputs of industrial Pb from local sources (e.g., mining and smelting in Peru and Chile) and the Northern Hemisphere (e.g., Pb additives in gasolines produced in the United States. Along with the subsequent elimination of leaded gasoline emissions in the Northern Hemisphere, Pb isotopic compositions in the EPZT now appear to reflect a combination of aeolian Pb inputs from (1) mining and smelting operations in Peru, Bolivia and Chile and (2) fossil fuel (i.e., coal) combustion in Asia. The shift in sources of industrial Pb inputs to the EPZT since then is attributed to the decrease in Pb concentrations and shift in Pb isotopic compositions in those surface waters

Below the upper thermocline Pb concentration maximum, [Pb] decreases strongly with depth at most locations. This is to be expected given dominant Anthropocene atmospheric Pb sources and the great age of the underlying Pacific deep waters (Matsumoto, 2007). Wu et al. (2010) have argued that the Pb at great depth in the North Pacific is supplied by reversible scavenging of sinking particles of anthropogenic

Pb adsorbed by particles in the upper ocean and released in the deep ocean. We propose that a similar process occurs in the eastern South Pacific.

However, the deep water situation in the west is complicated by hydrothermal emissions of ferromanganese oxyhydroxides that remove anthropogenic Pb from the water column (to be discussed in section 3.3).

3.2. Pb isotope evidence for recent changes in Pb sources to central tropical Pacific waters

Fig. 7a shows high-precision MIT multicollector ICP-MS 208 Pb/ 206 Pb vs. 206 Pb/ 207 Pb data for the upper 1 km for stations in the western portion of the section (15, 26, and 35). There is an interesting bifurcation in the trendlines separating the uppermost waters (< 135-145 m) from the deeper waters. The upper waters must reflect the most recently deposited Pb and the deeper waters reflect Pb deposited in previous decades. Interestingly, the upper branch of the GP16 data coincides with the Pb isotope trend from surface waters collected from near Hawaii (HOT station, 22°45′N, 158°00′W) from 1997 to 2013 (Table 1, Fig. 7b), with the earliest samples from near Hawaii merging with the branch followed by the deeper GP16 samples. Flegal et al.



Fig. 7. (a), upper) ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb for the upper water column of the westernmost portion of the section (MIT multicollector data only). (b, lower). ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb for near-Hawaii (HOT) surface waters collected between 1997 and 2013 compared to the upper water column of the westernmost portion of the GA16 section.

(2013) proposed that Chinese Pb emissions dominate the most recent northern Pacific Pb aerosols as a result of the global phasing out of leaded gasoline with either high 206 Pb/ 207 Pb ratios (e.g., US Mississippi Valley Pb ores, 206 Pb/ 207 Pb > ~1.20, 208 Pb/ 206 Pb < ~2.10) or low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (e.g., Australian Broken Hill/Mt. Isa Pb ores, $^{206}\text{Pb}/^{207}\text{Pb}<\sim\!\!1.1,\,^{208}\text{Pb}/^{206}\text{Pb}>\sim\!\!2.2$). Chinese Pb emissions in the late 20th century fall on a higher ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb mixing line than that observed for North and South American-type and Australian-type isotope ratios. Taking into account the isotopic composition and emissions of various Chinese Pb sources, Chen et al. (2016) estimated that the average Chinese isotope composition of recent Chinese emissions is $^{206}\text{Pb}/^{207}\text{Pb}\approx 1.16$ and $^{208}\text{Pb}/^{206}\text{Pb}\approx 2.2$ (see Fig. 7b). The ETNP GP16 and recent HOT Pb isotope data for nearsurface seawater in the entire central tropical Pacific Ocean fall on the Chinese-dominated upper branch of the ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb relationship whereas the deeper and older Pb fall on the U.S.-type/ Australian-type lower branch of the ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb relationship. We attribute these differences in the central upper tropical Pacific to a shift during the past 1-2 decades from a dominant Australian-type / North and South American-type mixing line to a Chinesetype/North and South American-type relationship.

Interestingly, (Chen et al., 2016) showed that aerosols collected in Singapore from July 2011 to April 2012 fall on the far right hand extrapolation of the deep EPZT ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb trend during most of the year, but veer off to the higher ²⁰⁸Pb/²⁰⁶Pb side during the northeast monsoon, when the winds are blowing from China. Removal of anthropogenic Pb at and downstream of the Eastern Pacific Rise ridge crest is attributed to scavenging by hydrothermal ferromanganese oxyhydroxide precipitates.

3.3. Removal of anthropogenic Pb at and downstream of the eastern Pacific rise ridge crest by hydrothermal ferromanganese oxyhydroxide precipitates

One of the most striking geochemical features of the GP16 section is the δ^{3} He plume where hydrothermal emanations from the East Pacific Rise (EPR) ridge crest are carried downstream toward the west by a deep current (Lupton, 1998; Jenkins et al., 2018). Other chemical properties (e.g. Fe, Mn, Al: Resing et al., 2015, and Zn, Roshan et al., 2016; John et al., 2018) also show high concentration plumes whereas some other properties show deficiencies caused by scavenging by ferromanganese oxyhydroxide precipitates (e.g. ²³¹Pa, ²³⁰Th: Pavia et al., 2016).

It has been documented that primary hydrothermal emissions from sites such as 21°N on the East Pacific Rise have very high Pb concentrations (Chen et al., 1986) and that the Pb isotope ratios of ridge crest sediments precipitated from these emissions are the same as Mid-Ocean Ridge Basalt (MORB) - in contrast to the detrital Pb isotope ratios observed off the ridge crest (Dymond et al., 1973; German et al., 1997; Chen et al., 1986). So it might be expected that Pb would show a high-concentration plume downstream of the EPR ridge crest. Quite the contrary, Pb concentrations at the ridge crest and immediately downstream are extremely low, a few tenths of pmol kg⁻¹, challenging detection limits of our most sensitive analytical techniques. These Pb concentrations are in fact lower than have been observed anywhere in the ocean.

The GP16 evidence shows that despite the very high initial Pb concentrations in the high temperature hydrothermal vent fluids, seawater in the hydrothermal plume contains extremely low Pb concentrations. Low-Mg vent samples often include some admixture of high-Mg ambient seawater, so we use the Pb concentration of five low-Mg samples from 21°N EPR fluids, 0.19–0.32 µmol kg⁻¹ (Chen et al.,



²⁰⁸Pb/²⁰⁶Pb vs ²⁰⁶Pb/²⁰⁷Pb

Fig. 7. (continued)

Table 1

[Pb] and Pb isotope data from mixed layer samples from the ALOHA-HOT station near Hawaii. Station labels are HA and MOSEAN for samples collected from MITESS moored sample at ~40 m depth, HOT for samples collected at ~10 m with a MITESS ATE sampler.

Date	Station ID	Pb	²⁰⁶ Pb/ ²⁰⁷ Pb, 2 s.e.		²⁰⁸ Pb/ ²⁰⁷ Pb, 2 s.e.		²⁰⁶ Pb/ ²⁰⁴ Pb, 2 s.e.	
07/03/97	HA2 HA3	30.9. 33 3	1.1695	0.0002	2.4490 2.4485	0.0002	18.34 18.30	0.01
07/21/98	HA4	30.1	1.1744	0.0001	2.4464	0.0003	18.31	0.01
01/22/99	HA5	45.4	1.1729	0.0002	2.4463	0.0003	18.30	0.02
01/14/00	HA7		1.1652	0.0002	2.4447	0.0003	18.14	0.01
07/16/00	HA8		1.1657	0.0002	2.4455	0.0004	18.17	0.02
10/04/00	HA8		1.1649	0.0002	2.4452	0.0003		
08/29/02	HOT139	24.6	1.1664	0.0003	2.4458	0.0003		
01/18/03	HOT144	39.5	1.1670	0.0002	2.4458	0.0003	18.19	0.01
08/25/04	MOSEAN-1-A2	39.3	1.1660	0.0003	2.4455	0.0002	18.20	0.02
01/20/05	MOSEAN-2-A8	32.1	1.1656	0.0001	2.4459	0.0002	18.14	0.02
07/16/05	HOT171	34.0	1.1628	0.0002	2.4440	0.0004	18.18	0.01
08/08/06	HOT184	24.2	1.1728	0.0001	2.4472	0.0001	18.30	0.00
12/12/06	HOT176	26.7	1.1641	0.0002	2.4452	0.0002	18.18	0.01
07/07/07	HOT193	29.3	1.1646	0.0003	2.4477	0.0006	18.14	0.02
07/07/07	HOT193	29.3	1.1648	0.0002	2.4475	0.0001	18.17	0.01
12/20/07	HOT198	29.8	1.1651	0.0002	2.4473	0.0004	18.14	0.01
07/27/08	HOT203	31.3	1.1655	0.0001	2.4491	0.0005		
10/10/08	HOT205	31.4	1.1646	0.0001	2.4475	0.0002	18.29	0.01
07/19/11	HOT233	27.8	1.1646	0.0001	2.4478	0.0002	18.21	0.01
12/20/11	HOT238	31.1	1.1646	0.0001	2.4475	0.0003	18.20	0.01
07/15/12	HOE-Dylan5	32.1	1.1688	0.0002	2.4497	0.0004	18.26	0.01
12/03/12	HOT248	29.1	1.1654	0.0001	2.4472	0.0002	18.17	0.01
06/04/13	HOE/PhOR1	34.0	1.1646	0.0002	2.4474	0.0003	18.20	0.01



Fig. 8. Average Pb concentrations in the samples from 2200 to 2701 m (black – the depth range over which the δ^3 He maximum occurs) and 2701-3251 m (gray) by station number. Error bars are the two sigma standard error (2*s.d./ \sqrt{n}) of the mean.

Table 2

Monocore core top (upper 1 cm) Pb isotope ratios from Graney et al. (1995) leach. Note that the ridge crest station 18 seafloor was basalt with no sediment, so there is no data from that station.

EPZT Station#	²⁰⁶ Pb/ ²⁰⁷ Pb	2 s.e.	²⁰⁸ Pb/ ²⁰⁷ Pb	2 s.e.	²⁰⁶ Pb/ ²⁰⁴ Pb	2 s.e.
4	1.19733	0.00005	2.47343	0.00009	18.719	0.002
7	1.19882	0.00003	2.47594	0.00010	18.732	0.005
9	1.19817	0.00006	2.47505	0.00013	18.718	0.006
11	1.19781	0.00005	2.47425	0.00011	18.705	0.003
13	1.19535	0.00005	2.46986	0.00011	18.644	0.004
17	1.19599	0.00003	2.47087	0.00008	18.658	0.004
20	1.18887	0.00006	2.44918	0.00009	18.398	0.003
25	1.19092	0.00004	2.46031	0.00012	18.515	0.002
26	1.19222	0.00006	2.46318	0.00018	18.555	0.004
28	1.19452	0.00004	2.46630	0.00009	18.604	0.003
30	1.19630	0.00005	2.47010	0.00011	18.654	0.002
32	1.20035	0.00004	2.47636	0.00009	18.739	0.002
34	1.20007	0.00005	2.47567	0.00006	18.738	0.002
36	1.20037	0.00004	2.47531	0.00009	18.729	0.001

1986) to estimate Pb in EPR high-temperature fluids. The concentrations of Pb- scavenging ferromanganese oxyhydroxides precipitated near the plume are sufficiently high to remove almost all of the vent fluid Pb and then some, actually scavenging anthropogenic Pb from the ridge crest deep waters. This scavenging appears to continue some distance downstream of the ridge crest, as the lowest Pb concentrations are seen not at ridge crest station 18 but instead between stations 20-30, up to ~1500 km in the plume downstream of the ridge crest (Fig. 8). In fact, very low Pb concentrations are not only at the depth of the δ^3 He maximum (2394-2502 m; Jenkins et al. 2016), but often seen in the ~500 m below the depths where the δ^3 He maximum is seen. As has been reported for particulate and dissolved Fe chemistry for this section (Lam et al., 2018; Fitzsimmons et al., 2017), there is a distallytransported veil of sinking ferromanganese oxyhydroxide particles that are actively exchanging Fe with the dissolved phase as they sink. We believe that these sinking particles actively scavenge Pb as they sink resulting in the very low Pb deepwater concentrations downstream and below the depth of the ridge crest hydrothermal emanations.

Farther to the west, even comfortably within the deepwater δ^3 He plume, Pb concentrations increase to several pmol kg⁻¹. We propose that these higher Pb concentrations reflect mixing between the very low Pb plume waters with deep mid-Pacific waters containing higher levels of anthropogenic Pb brought to depth by reversible exchange with sinking particles containing high levels of anthropogenic Pb from the upper ocean.

To the east of the ridge crest (stations 13 and 15), very low Pb concentrations are seen in the deepest waters, even though this region is not downstream of the westward-flowing ridge crest ³He plume. However, relatively high ³He concentrations are seen in the eastern South Pacific at 2500 m depth (δ^{3} He > 27%, Lupton, 1998, Lupton and Jenkins, 2017, Jenkins et al., 2018), that presumably reflect the recirculation of waters that have passed over other ridge crests north or south of 15°S. And these waters (and below them as a result of the sinking veil of iron oxyhydroxide particles) are probably low because of the same scavenging mechanisms we see downstream of the westward-flowing ridge crest plume.

3.4. Dissolved and surface sediment Pb isotope evidence for a small leakage of MORB Pb into the EPR 3 He plume

The previous section documents that Pb in the EPR hydrothermal plume is dominated by overwhelming removal onto ferromanganese oxyhydroxides. In this section, we will show that despite this, there still is a very small contribution of MORB Pb into the plume.

The sediment surface Pb isotope ratios are listed in Table 2. Fig. 9 shows the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of the surface sediments for each station. Note the low ratios to the west of the ridge crest (stations 20, 25, and 26). Samples to the east and west of these are closer to typical crustal ratios ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.20$, $^{208}\text{Pb}/^{206}\text{Pb} \sim 2.07$). The station closest to the ridge crest has the lowest $^{206}\text{Pb}/^{207}\text{Pb}$ ratio – 1.1889 – that can be compared to the ratios furthest east (1.1954–1.1988) and furthest west (1.2001–1.2004). $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{204}$ Pb show similar near-ridge crest minima. This data reinforces previous Pb isotope data showing that near-ridge crest sediments have a MORB Pb isotope signature ($^{206}\text{Pb}/^{207}\text{Pb} \sim 1.19$, $^{208}\text{Pb}/^{206}\text{Pb} \sim 2.05$; Dymond et al., 1973, German et al., 1997, Chen et al., 1986).



Fig. 9. Pb isotope data for leaches from the surface sediment (top centimeter). Note that ridge crest station 18 seafloor was basalt, hence no sediment was collected.

Sun (1980) reports on eighteen ridge crest volcanic rocks from throughout the oceans, where ²⁰⁶Pb/²⁰⁷Pb ranges from 1.168–1.169, ²⁰⁸Pb/²⁰⁷Pb from 2.434 to 2.457, and ²⁰⁶Pb/²⁰⁴Pb from 18.100 to 18.588; his EPR sample closest to our transect showed ²⁰⁶Pb/²⁰⁷Pb of 1.175, ²⁰⁸Pb/²⁰⁷Pb of 2.436, and ²⁰⁶Pb/²⁰⁴Pb of 18.16, all somewhat lower than what we see in our near-ridge sediments. Also, Barrett et al. (1987) report 14 analyses of ridge crest sediments from ODP sites 599, 600, and 601 (near our transect) with an average ²⁰⁶Pb/²⁰⁷Pb of 1.189, ²⁰⁸Pb/²⁰⁷Pb of 2.445, and ²⁰⁶Pb/²⁰⁴Pb of 18.439 – all almost identical to what we see in our near-ridge sediments. Typically though, the MORB ²⁰⁶Pb/²⁰⁷Pb is lower than typical crustal Pb (e.g. Stacey and Kramers, 1975 suggest average crustal Pb isotopes of ²⁰⁶Pb/²⁰⁷Pb = 1.202, ²⁰⁸Pb/²⁰⁷Pb = 2.477, ²⁰⁶Pb/²⁰⁴Pb = 18.76 from their two-stage earth evolution model). Therefore coretop ridge-crest

sediments show lower 206 Pb/ 207 Pb than the dust-derived or hydrogeneous sediments off the ridge axis (as we see in our transect, Fig. 9).

Although the ridge plume Pb isotope measurements were challenging because of the very low concentrations (0.1–4.0 pmol kg⁻¹), and we cannot attain the same high analytical precision as for the sediments, the ²⁰⁸Pb/²⁰⁷Pb from ridge crest station 18 shows a clear shift toward low MORB values in the near bottom water (Fig. 10). ²⁰⁶Pb/²⁰⁴Pb shows a similar shift to lower ratios, but ²⁰⁶Pb/²⁰⁷Pb does not show a clear shift but is rather noisy. On a ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb plot (Fig. 11), the western plume samples with [Pb] < 2 pmol kg⁻¹ are shifted downwards from the trend of most of the nonplume data and the > 2000 m data from westernmost station 36. The plume data fall within a mixing envelope defined by the station 20 hydrothermal sediment data and the dominant mixing trendline of the



Fig. 10. $^{208}\text{Pb}/^{207}\text{Pb}$ data for ridge crest station 18. Note low $^{208}\text{Pb}/^{207}\text{Pb}$ near the bottom.

non-plume data. Hence we argue that despite the overarching scavenging of Pb by the ferromanganese oxyhydroxide precipitates, the low-Pb plume contains a small component (order 1%) of the original MORB Pb from high temperature ridge crest hydrothermal emanations. This finding is consistent with the ferromanganese crust data of van de Flierdt et al. (2004) who find MORB Pb was transported from the EPR to the Bauer Basin prior to 6.7 Ma.

4. Conclusions

We present Pb concentration and Pb isotope data from the Peru-Tahiti US GEOTRACES section GP16. Pb concentrations are highest (28–31 pmol kg⁻¹) in the upper ocean close to the South American coast and Pb isotope ratios of this higher concentration Pb (e.g. higher 206Pb/207Pb) are similar to the dominant South American ore Pb sources. In the upper km of the westernmost section, the shallow waters (< 135-145 m) fall on a different ²⁰⁸Pb/²⁰⁶Pb vs. ²⁰⁶Pb/²⁰⁷Pb trend than the deeper waters. This trend is the same as seen in near-surface waters near Hawaii from a time-series from 1997 to 2013. This finding supports the conclusion of Flegal et al. (2013) that Chinese Pb is the dominant recent source of Pb aerosols that are deposited into the North Pacific Ocean. We argue that this is also true for the Pb deposited in the past two decades in the central tropical South Pacific as well, because Chinese Pb has higher ²⁰⁸Pb/²⁰⁶Pb compared to the previously dominant Australian-type vs. American-type Pb isotope trendline. The Pb isotopic compositions in deeper South Pacific waters also appear to reflect older Pb depositions which fit the Australian-American trendline.

Ferromanganese oxyhydroxide precipitates from the ridge-crest hydrothermal emanations scavenge most of the Pb from the primary high- temperature fluids as well as much of the anthropogenic Pb from the surrounding deep waters, resulting in the lowest-Pb waters ever observed. Despite such dominant scavenging, the triple isotope Pb



208Pb/206Pb vs 206Pb/207Pb

Fig. 11. MIT Pb concentration and 208 Pb/ 206 Pb data vs. 206 Pb/ 207 Pb for all of the samples analyzed from the GP16 section compared to the sediment leach from near-ridge crest station 20 and the deep samples (> 2000 m) from westernmost station 36.

isotope data indicate that there is a small component of MORB hydrothermal Pb in the < 2 pmol kg⁻¹ hydrothermal plume waters.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

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