Supplementary Information to:

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

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Table S1. Column chemistry procedures using AG1-X8 resin for the purification of Pb separated from seawater for isotope composition (IC) and isotope dilution (ID) measurements by MC-ICP-MS.

Purpose	Pb IC chemistry 200 µL AG1-X8 (100–200 mesh)	Pb ID chemistry 20 µL AG1-X8 (100–200 mesh)
Clean resin	3 × 3 mL 0.1 M HNO_3	3 × 1 mL 0.1 M HNO_3
Equilibrate resin	2 × 0.1 mL 2 M HBr (+ 0.01 M HF)[a]	2 × 0.1 mL 0.5 M HBr + 0.2 M HNO_3
Load sample	~5 mL 2 M HBr (+ 0.01 M HF)[a]	2 mL 0.5 M HBr + 0.2 M HNO_3
Elute matrix	2 × 0.1 mL 2 M HBr (+ 0.01 M HF)[a]	2 × 0.3 mL 0.5 M HBr + 0.2 M HNO_3
	2 × 0.5 mL 0.2 M HBr + 0.5 M HNO_3	
	0.2 mL 0.03 M HBr + 0.5 M HNO_3	
Elute Pb	3 mL 0.03 M HBr + 0.5 M HNO_3	1 mL 0.03 M HBr + 0.5 M HNO_3

[a] During the first stage of Pb IC chemistry, the solutions used to equilibrate the resin, load the sample and initiate the elution of the matrix contained a HBr + HF mixture. These steps for the second stage of Pb IC chemistry employed HBr with no HF.

Table S2. Instrumental parameters for the Nu Plasma II MC-ICP-MS used for Pb isotope measurements.

Nu Plasma II MC-ICP-MS

RF Power	1300 W
Acceleration potential	6000 V
Ar coolant gas flow	13 L min^{-1}
Ar auxiliary gas flow	1 L min^{-1}
Expansion chamber vacuum	~0.75 mbar
Analyser vacuum	~2 × 10^{-9} mbar
Faraday cup resistors	10^{11} Ω, 10^{12} Ω
Sensitivity for Pb	~1500 V (μg/mL)$^{-1}$

Nu Instrument DSN-100 desolvating nebulizer system

Spray chamber temperature	110°C
Desolvator temperature	160°C
Argon sweep gas	~3.4 to 5 L min^{-1}
Nebuliser pressure	~60 psi
Sample uptake rate	~140 μL min^{-1}

Table S3. Lead isotope data for NIST SRM 981 measured in this study using either a ^{207}Pb–^{204}Pb double-spike or Tl-normalization for the correction of instrumental mass fractionation. Literature data for NIST SRM 981 Pb acquired by TIMS or MC-ICP-MS and Pb poly-spikes are shown for comparison.

Standard/ Reference	Pb (Tl) (ng) [a]	n [b]	Mass bias correction	^{206}Pb/^{204}Pb ± 2SD [c]	^{207}Pb/^{204}Pb ± 2SD [c]	^{208}Pb/^{204}Pb ± 2SD [c]	^{206}Pb/^{207}Pb ± 2SD [c]	^{208}Pb/^{207}Pb ± 2SD [c]
SRM 981 Pb - SRM 997 Tl	1 (3)	54	^{207}Pb-^{204}Pb DS	16.927 ± 17	15.486 ± 18	36.688 ± 50	1.0931 ± 03	2.3691 ± 05
			± 2SD rel. (ppm) [c]	1020	1190	1360	280	220
			± 2SE rel. (ppm) [d]	260	290	340	70	70
			Tl-normalization	16.935 ± 09	15.497 ± 08	36.723 ± 19	1.0928 ± 03	2.3697 ± 05
			± 2SD rel. (ppm) [c]	550	490	520	250	200
			± 2SE rel. (ppm) [d]	210	220	220	40	30
SRM 981 Pb - SRM 997 Tl	7 (21)	30	^{207}Pb-^{204}Pb DS	16.9332 ± 57	15.4915 ± 71	36.6995 ± 206	1.0931 ± 01	2.3690 ± 03
			± 2SD rel. (ppm) [c]	340	460	560	140	140
			± 2SE rel. (ppm) [d]	80	100	120	25	30
			Tl-normalization	16.9383 ± 23	15.4984 ± 23	36.7211 ± 52	1.0929 ± 01	2.3694 ± 02
			± 2SD rel. (ppm) [c]	140	150	140	55	100
			± 2SE rel. (ppm) [d]	60	70	90	10	20
Paul et al., (2015) and Bridgestock (2015)[1,2] (TIMS)	2	59	^{207}Pb-^{204}Pb DS	16.941 ± 20	15.495 ± 15	36.713 ± 39	1.0934 ± 02	2.3695 ± 03
			± 2SD rel. (ppm) [c]	950	1000	1070	190	130
			± 2SE rel. (ppm) [d]	400	420	440	60	50
Galer and Abouchami (1998)[3] (TIMS)	10	60	^{207}Pb-^{206}Pb-^{204}Pb TS	16.9405 ± 15	15.4963 ± 16	36.7219 ± 44	1.0932	2.3697
			± 2SD rel. (ppm) [c]	90	100	120		
Literature average [e] (TIMS, MC-ICP-MS)			Poly-spike	16.9410 ± 11	15.4983 ± 29	36.7221 ± 69	1.0931 ± 03	2.3694 ± 04
			± 2SD rel. (ppm) [c]	60	190	190	230	150

[a] Approximate mass of Pb used for a single Pb isotope measurement. [b] Number of analyses. [c] 2 x standard deviation (2SD) calculated from *n* analyses to characterize the long-term reproducibility of the NIST SRM 981 Pb measurements, with the relative 2SD (ppm) provided below. [d] 2 x standard relative error (2SE) of the mean based on results for the individual measurement cycles to characterize the within-run reproducibility. [e] An average of recently published poly-spike NIST SRM 981 Pb data obtained by updating the values provided by Taylor et al., (2015)[4] with recent studies from Paul et al., (2015),[1] Bridgestock (2015),[2] Klaver et al., (2016)[5] and Fukami et al., (2017).[6] For Fukami et al., (2017), the TIMS procedure with most replicate NIST SRM 981 Pb analyses (*n* = 15) was used to update the poly-spike reference values (for more details, see text and Figure 1a and b).

Table S4. Lead isotope compositions and concentrations determined for in-house quality control materials following different Pb separation 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) [d]	Meas. Pb (ng) [e]	Yield (mean) % [f]	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					
± 2SE run (ppm) [c]				120	140	160	40	30					
	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					
± 2SE rel. (ppm) [c]				110	120	130	30	30					
	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 ± 06	1.1833 ± 00	2.4455 ± 01					
± 2SE run (ppm) [c]				~130	~160	~190	~40	~40					
	co-precipt.	TI	2	18.535 ± 02	15.662 ± 02	38.304 ± 06	1.1835 ± 00	2.4458 ± 01					
				18.530 ± 02	15.661 ± 03	38.301 ± 06	1.1833 ± 00	2.4457 ± 01					
± 2SE rel. (ppm) [c]				~120	~130	~150	~30	~30					
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					
± 2SE rel. (ppm) [c]				70	70	80	20	20					
	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					
± 2SE rel. (ppm) [c]				70	70	80	20	20					
	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					
± 2SE rel. (ppm) [c]				200	240	280	60	60					
	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					
± 2SE rel. (ppm) [c]				150	150	150	20	20					
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					
± 2SE rel. (ppm) [c]				70	80	100	20	20					
	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					
± 2SE rel. (ppm) [c]				70	70	80	20	20					
	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					
± 2SE rel. (ppm) [c]				180	210	260	60	50					
	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					
± 2SE rel. (ppm) [c]				150	150	160	20	20					

[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; for samples with $n \leq 3$, the individual data are provided and the error corresponds to 2 x standard error (2SE) of the mean based on individual results during measurement cycles (i.e., within-run reproducibility). [c] The relative 2SE (ppm) of the mean based on the average 2SE of individual results during measurement cycles. [d] Volume of individual sample aliquots used for Pb isotope analyses. [e] Mean mass of Pb in individual unspiked sample aliquots used for isotopic analyses. [f] Yield obtained for Pb extraction following separation and purification from seawater.

Table S5. Lead isotope compositions and concentrations determined for GEOTRACES intercalibration samples following different Pb separation and mass bias correction procedures.

Sample	Pb separation	Mass bias corr.	n-IC [a]	206Pb/204Pb ± 2SD [b]	207Pb/204Pb ± 2SD [b]	208Pb/204Pb ± 2SD [b]	206Pb/207Pb ± 2SD [b]	208Pb/207Pb ± 2SD [b]	Sample size (L) [d]	Meas. Pb (ng) [e]	Yield (mean) % [f]	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	TI	1	18.482 ± 01	15.634 ± 01	38.303 ± 03	1.1822 ± 00	2.4500 ± 01					
TIMS[1,2]	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					
± 2SE rel. (ppm) [c]				~190	~200	~210	~30	~30					
Consensus [g]													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	TI	1	18.365 ± 02	15.634 ± 02	37.261 ± 04	1.1746 ± 00	2.4472 ± 01					
TIMS[1,2]	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					
± 2SE run (ppm) [c]				~160	~170	~180	~30	~30					
Consensus [g]													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					
± 2SE rel. (ppm) [c]				110	120	140	30	30					
	Nobias	TI	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					
± 2SE rel. (ppm) [c]				100	110	120	20	20					
	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					
± 2SE rel. (ppm) [c]				230	260	290	50	50					
	co-precipt.	TI	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					
± 2SE rel. (ppm) [c]				180	190	190	20	20					
TIMS[7]	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					
± 2SE rel. (ppm) [c]				150	150	160	30	20					
Consensus [g]													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; for samples with $n \leq 3$, the individual data are provided and the error corresponds to 2 x standard error (2SE) of the mean based on individual results during measurement cycles (i.e., within-run reproducibility). [c] The relative 2SE (ppm) of the mean based on the average 2SE of individual results during measurement cycles. [d] Volume of individual sample aliquots used for Pb isotope analyses. [e] Mean mass of Pb in individual unspiked sample aliquots used for isotopic analyses. [f] Yield obtained for Pb extraction following separation and purification from seawater. [g] Consensus values for Pb concentrations were obtained from GEOTRACES programme (www.geotraces.org/standards-and-reference-materials). For the 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.

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