Electronic Supplementary Information (ESI)

Evaluation of laser ablation double-focusing SC-ICPMS for "common" lead isotopic measurements in silicate glasses and minerals

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Calibration of the ion-counting detector

The voltage and the dead time of the discrete dynode secondary electron multiplier on the AttoM were calibrated to obtain precise and accurate Pb isotope ratios. The voltage was monitored regularly and adjusted to lie on the plateau, as necessary. The dead time was determined using the results for each of the three sessions of SRM981 in solution mode: 2014 (five days), 2015 (two days, immediately after the ES upgrade), and 2016 (three days). Prior to each of these sessions, any residual Pb was carefully eliminated from the sample introduction system by cleaning the cones and glassware (i.e., torch, bonnet, spray chamber, nebulizer, and elbow that connects the spray chamber to the torch), and replacing all of the expendable plastic tubing. This procedure was effective at minimizing any memory effects during the calibration of the ion-counting detector. For example, the average background (measured using a clean solution of 0.2M HNO_3) was ~330 cps of ^{208}Pb (n=76) with an approximate measured (i.e., not corrected for the instrumental mass bias) isotopic composition of $^{207}Pb/^{206}Pb$=0.895±0.009 and $^{208}Pb/^{206}Pb$=2.15±0.02 (both ±2SE), which is distinct from both the measured and "true" Pb isotope ratios of SRM981 (Fig. 1). It was not possible to measure the $^{20X}Pb/^{204}Pb$ ratios of the background because the signal intensity of ^{204}Pb was too low. This Pb background was insignificant (<0.3%) relative to the minimum signal intensity ($^{208}Pb>1.0\times10^5$ cps) for the measured Pb isotope ratios of SRM981 shown in Fig. 1. Analyses of SRM981 with a lower signal intensity (^{208}Pb down to ~2.5×10^4 cps) displayed Pb isotope ratios that trend toward the isotopic composition of the average background, and thus, are not reported.

For each session, the dead time of the ion-counting detector was determined by measuring the Pb isotope ratios of SRM981 in solution mode at the range of signal intensities shown in Fig. 1. The dead

time was set to eliminate any correlation between the signal intensity of ^{208}Pb and the ^{20X}Pb/^{206}Pb and ^{20X}Pb/^{204}Pb ratios. Initially, in 2014, the dead time was ~11 ns. It drifted to ~11.5 ns by 2015 (measured immediately after the ES upgrade). In 2016, after the last of the LA measurements were performed, the dead time was ~12 ns. The solution data from each session (Fig. 1) were corrected using these dead time values. The Pb isotope ratios for the reference materials measured by LA were collected between these measurements of the dead time. Data from the first (Oct. 2014 to Jul. 2015) and second (Dec. 2015 to Mar. 2016) series of LA sessions were corrected relative to dead times of 11 and 12 ns, respectively.

Evaluation of potential interferences other than ^{204}Hg

Spectral interferences on ^{202}Hg or the Pb isotopes (in addition to ^{204}Hg on ^{204}Pb) may potentially arise from singly charged molecules produced during LA of silicate glasses and minerals.[24,29] This is a particular concern for SRM610 or SRM612 because they have been doped with relatively high concentrations of nominally trace elements. Two of the potentially most significant molecular interferences[24] are ^{166,167,168}Er^{40}Ar on ^{206,207,208}Pb (respectively) and ^{186}W^{16}O on ^{202}Hg (which would affect the correction for ^{204}Hg on ^{204}Pb) because SRM610 and SRM612 are unusually rich in Er (~455 and ~38 ppm, respectively) and W (~440 and ~38 ppm, respectively).[47] The Er and W abundances of St. Gotthard adularia, Haer sanidine, and Inyo obsidian reference materials are unknown, but are expected to be relatively low (compared to SRM610). Except for GOR132-G (~25 ppm W) and ATHO-G (~9 ppm W), the other reference materials have ≤10 ppm Er and <1 ppm W (Jochum et al. 2006b).[34]

The signal intensity at mass 210 (potentially from ^{170}Er^{40}Ar, representing ~15% of Er) during LA in raster mode for both SRM610 (20 μm spot and ~5×10^5 cps of ^{208}Pb) and SRM612 (65 μm spot and ~4×10^5 cps of ^{208}Pb) was used to evaluate the presence or absence of ^{166,167,168}Er^{40}Ar on ^{206,207,208}Pb. In both cases, no peak was visible at mass 210 and the signal intensity (<30 cps) was indistinguishable from the high-mass tail of ^{209}Bi (Bi is present at relatively high concentration in both SRM610 and SRM612). Thus, we conclude that an interference of ^{166,167,168}Er^{40}Ar on ^{206,207,208}Pb is insignificant for SRM610, SRM612, and all of the other reference materials from Table 2.

The importance of a potential interference of $^{186}W^{16}O$ on ^{202}Hg is harder to evaluate because each of the $W^{16}O$ molecules overlaps with an isotope of Hg. The only two isotopes of Hg that are free of a potential WO interference are ^{201}Hg and ^{204}Hg, although the former may be impacted by an interference from $^{184}W^{16}OH$. One way to gauge the level of WO production is based on the measured ThO/Th ratio during LA of SRM610 and SRM612, which was ~0.06% (for both reference materials) for the raster analyses described above. If the WO/W ratio is assumed to be ~0.06%, the WO production (relative to the signal intensity of Pb during LA of SRM610 and SRM612 for these raster analyses) would give a $^{186}W^{16}O/^{208}Pb$ ratio of ~500 ppm (equivalent to ~200 cps at mass 202 that would be incorrectly attributed to ^{202}Hg). This would correspond to a significant overcorrection of the $^{20X}Pb/^{204}Pb$ ratios for the ^{204}Hg interference. For example, the $^{20X}Pb/^{204}Pb$ ratios of both reference materials (assuming $^{186}W^{16}O/^{208}Pb$=500 ppm) would be ~0.4% higher than the reference values based on the equation

$$(^{20X}Pb/^{204}Pb)_{WO} = 1/\{[1/(^{20X}Pb/^{204}Pb)_{NoWO}] + [0.2299 \times K_{20X}]\},$$

where $(^{20X}Pb/^{204}Pb)_{WO}$ and $(^{20X}Pb/^{204}Pb)_{NoWO}$ are the Pb isotope ratios (respectively) with and without a proper accounting for the potential $^{186}W^{16}O$ interference (the latter is equivalent to the $^{20X}Pb/^{204}Pb$ ratios in this study), and K_{20X} is the (assumed) constant WO production ratio, $^{186}W^{16}O/^{20X}Pb$.

However, two lines of evidence suggest that the K_{20X} value inferred from the measured ThO/Th ratio is a significant overestimate of the actual WO/W ratio. First, we measured the $^{201}Hg/^{202}Hg$ ratio during LA of SRM610 and SRM612 in raster mode (again, from the same experiments described above). Given the lack of a WO interference on ^{201}Hg, this ratio might be expected to be lower during LA of SRM610 and SRM612 compared to the gas blank due to the production of $^{186}W^{16}O$ on mass 202. The $^{201}Hg/^{202}Hg$ ratio during LA of SRM610 and SRM612 was indeed ~2-3% lower (0.434±0.003 and 0.438±0.004, ±2SE, respectively) than the $^{201}Hg/^{202}Hg$ ratio of the gas blank (~0.446), which is equivalent to a K_{208} value of <80 ppm. This would correspond to an overcorrection of the $^{20X}Pb/^{204}Pb$ ratios relative to the reference values of <0.06% (for both reference materials). Second, we compared the maximum difference between the signal intensity at mass 202 during all of the raster analyses of SRM610 (at 40-65 μm) and SRM612 (at 135 μm) and the associated gas blank at mass 202, which is thought to be exclusively ^{202}Hg. This difference (~40 to 1600 cps during this study based on the data presented in the ESI) provides an

estimate of the maximum proportion of the signal intensity at mass 202 that can be attributed to $^{186}W^{16}O$ (rather than ^{202}Hg) during LA of SRM610 and SRM612. Most of this difference (which decreased over the course of this study as the Hg background improved) likely results from Hg within the sample cell that is liberated during LA. Thus, the sessions with the lowest total signal intensity of ^{202}Hg provide the best estimate of the maximum possible signal intensity of $^{186}W^{16}O$ (~40 cps). Dividing ~40 cps of $^{186}W^{16}O$ by the signal intensity of ^{208}Pb for each analysis corresponds to K_{208} values of <30 ppm for SRM610 and <60 ppm for SRM612, and potential overcorrections of the $^{20X}Pb/^{204}Pb$ ratios relative to the reference values of <0.03% for SRM610 and <0.05% for SRM612. Thus, we conclude [consistent with the experience of Souders and Sylvester (2010)[24]] that any (uncorrected) $^{186}W^{16}O$ interference on ^{202}Hg is insignificant.

Summary of potential matrix effects and a comparison to literature data.

Jochum et al.[25,31-33] used SRM612 as the bracketing standard (and either its $^{205}Tl/^{203}Tl$ or Pb isotope ratios) to correct for mass bias on an Element II SC-ICPMS, a 193-nm or 213-nm Nd:YAG laser, an average of three spots for each analysis, and only measured the $^{20X}Pb/^{206}Pb$ ratios to a relatively high precision. This approach would tend to minimize a potential matrix effect (if it was similar in origin to the one we observed for the Fe-rich glasses) because it would be (1) most significant for $^{208}Pb/^{204}Pb$ due to the greater mass difference of this ratio (4 AMU) and (2) smaller in spot mode. On the other hand, we did not observe a matrix effect for SRM612 in spot mode (Fig. 7), which would (in principle) allow for similar, small offsets in the Pb isotope ratios of BCR-2G, GOR132-G, and T1-G (and possibly, KL2-G and ML3B-G) when SRM612 is used in spot mode as a bracketing standard instead of SRM610. BCR-2G and GOR132-G were analyzed only once (BCR-2G) or twice (GOR132-G) at ≥120 μm by Jochum et al.[31,32], so it is difficult to judge the accuracy of the $^{20X}Pb/^{206}Pb$ ratios for these reference materials (which range from ~0.1% lower to ~0.3% higher than the reference values from Supplementary Table S1). The $^{20X}Pb/^{206}Pb$ ratios of T1-G (n=14), KL2-G (n=23), and ML3B (n=14) were analyzed using both the 193-nm and 213-nm Nd:YAG lasers at relatively large (≥75 μm) spot sizes.[25,31-33] For each LA system, the average $^{208}Pb/^{206}Pb$ ratios matched the reference values from Supplementary Table S1 mostly within the ±2SE errors of <0.1% (based on the external reproducibility of the replicate analyses), whereas the average $^{207}Pb/^{206}Pb$ ratios of each reference material ranged up to ~0.2% higher than the reference

values (slightly outside the ±2SE errors in some cases). In addition, the $^{20X}Pb/^{206}Pb$ ratios of BCR-2G were analyzed by LA-MC-ICPMS (using a 193-nm excimer laser) relative to SRM612 as a bracketing standard (n=7) in spot mode[25]. Compared to the BCR-2G reference values in Supplementary Table S1, the average $^{208}Pb/^{206}Pb$ ratio was ~0.2% high (outside the ±2SE error of <0.1%) and the average $^{207}Pb/^{206}Pb$ ratio was ~0.1% low (within the ±2SE error of ~0.1%). All of these results are within or close to the ±2SE errors of the reference materials, but nevertheless allow for the possibility of a small matrix effect characterized by slightly elevated $^{20X}Pb/^{206}Pb$ ratios (when normalized to SRM612 in spot mode). Thus, the LA-ICPMS analyses of Jochum et al.[25,31-33] do not rule out a potential matrix effect on the Pb isotope ratios of up to 0.1%/AMU.

All of the other published Pb isotope ratios for BCR-2G, GOR132-G, T1-G, KL2-G, and ML3-B used LA-MC-ICPMS and include the $^{20X}Pb/^{204}Pb$ ratios. For simplicity, we mostly consider only the average $^{208}Pb/^{204}Pb$ ratio of each reference material because it is more likely to reveal a potential matrix effect. The Pb isotope ratios are compared to the reference values from Supplementary Table S1. Paul et al.[2,27] used spot mode (with a 193-nm excimer laser) and the $^{208}Pb/^{206}Pb$ ratio of SRM612 to correct the measured Pb isotope ratios of BCR-2G and KL2-G for mass bias. Paul et al. (2005)[27] obtained a precisely determined average $^{208}Pb/^{206}Pb$ ratio (2.0660±0.0002, ±2SE) for BCR-2G (n=70) that is ~0.15% higher than the reference value of 2.063. Their average $^{208}Pb/^{204}Pb$ ratio for BCR-2G (38.75±0.02, ±2SE) was also slightly (~0.08%) higher than the reference value of 38.72. Two additional analyses of BCR-2G by Paul et al. (2011)[2] gave an even higher average $^{208}Pb/^{204}Pb$ ratio of 38.84. The average $^{208}Pb/^{204}Pb$ ratio of KL2-G by Paul et al. (2005)[27] agreed with the reference value within the ±2SE error of ~0.3%, based on the external reproducibility of the 20 replicate analyses. Kent (2008)[18] analyzed BCR-2G in spot mode (using either a 213-nm Nd:YAG or 193-nm excimer laser) and obtained accurate results for the $^{208}Pb/^{204}Pb$ ratio (n=15) within the ±2SE error of ~0.1-0.2% (based on the external reproducibility of the replicate analyses), but did not state which reference material (SRM610 or SRM612) was used to correct for mass bias. Souders and Sylvester (2008)[29] used a 193-nm excimer laser in spot mode and the Pb isotope ratios of BCR-2G (a potentially matrix-matched reference material for the Fe-rich MPI-DING glasses) to correct their analyses of T1-G (n=11), KL2-G (n=6), and ML3B-G (n=6) for mass bias.

Both of these choices (spot mode and BCR-2G as the bracketing standard) would be expected to minimize the type of matrix effect that we observed on the SWIRL AttoM. Their results at the largest spot sizes (and thus, the highest signal intensity of ^{208}Pb) gave mostly accurate results for the ^{208}Pb/^{204}Pb ratios within the ±2SE errors of ~0.3-0.8% (based on the external reproducibility of the replicate analyses). The Pb isotope ratios for the reference materials analyzed by Chen et al. (2014)[26] with a 266-nm femtosecond laser cannot be used to evaluate the presence or absence of a matrix effect (with respect to our study) because their data were collected using Tl-doping to correct for mass bias. Finally, Zhang et al. (2015)[28] presented a large number of replicate Pb isotopic measurements for BCR-2G (n=50) and the Fe-rich MPI-DING glasses (n=26 to 62) using a 193-nm excimer laser in spot mode, which were corrected for mass bias relative to the Pb isotope ratios of SRM612. Their average ^{208}Pb/^{204}Pb ratio for GOR132-G was ~0.1% higher than the reference value, but all of the other reference materials (BCR-2G, T1-G, KL2-G, and ML3B-G) gave slightly low ^{208}Pb/^{204}Pb ratios (up to ~0.1% lower than the reference values). We conclude that none of these experiments, with the possible exception of the high-precision data from Zhang et al. (2015),[28] rule out the presence of a matrix effect on the Pb isotope ratios measured by LA-ICPMS in SSB mode (relative to SRM610 in raster and spot mode, and possibly, SRM612 in spot mode).

Supplementary Table S1
Reference materials

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	Pb $\mu g\ g^{-1}$	SiO_2 wt.%	FeO^{T}[a] wt.%	Material type	Locality
Synthetic glasses[b]:										
NIST SRM610 glass	17.05	15.52	36.99	2.169	0.9099	426	~72	tr.		
NIST SRM612 glass	17.10	15.52	37.02	2.165	0.9075	38.6	~72	tr.		
USGS glasses[c]:										
BCR-2G	18.77±0.00	15.63±0.00	38.72±0.01	2.063±0.000	0.8328±0.0002	~10	54.9	12.6	Basalt	Columbia River Basalt
BHVO-2G	18.77±0.03	15.59±0.01	38.27±0.00	2.039±0.003	0.8302±0.0008	~2	50.5	11.2	Basalt	Kilauea, Hawaii
Natural materials[d]:										
St. Gotthard	19.00±0.02	15.65±0.02	38.60±0.06	2.034±0.002	0.8237±0.0003	~130	n.d.	n.d.	Adularia	St. Gotthard, Switzerland
Inyo	19.13±0.02	15.67±0.02	38.91±0.06	2.034±0.002	0.8192±0.0003	~25	n.d.	n.d.	Obsidian glass	Inyo Craters, California
Haer	17.01±0.01	15.49±0.02	37.18±0.06	2.186±0.002	0.9105±0.0004	~4	n.d.	n.d.	Sanidine megacryst	Haer Volcano, Mongolia
MPI-DING glasses[e]:										
GOR132-G	19.25	15.72	38.71	2.011	0.8166	19.5	45.8	10.1	Komatiite	Gorgona Island
T1-G	18.73±0.01	15.68±0.01	38.97±0.01	2.081±0.000	0.8372±0.0000	11.6	58.6	6.5	Quartz diorite	Italian Alps
StHs6/80-G	18.90±0.00	15.61±0.00	38.52±0.01	2.038±0.001	0.8262±0.0002	10.3	63.8	4.4	Andesitic ash	Mount St. Helens
ATHO-G	18.38±0.00	15.48±0.00	38.11±0.00	2.073±0.001	0.8420±0.0003	5.7	75.8	3.2	Rhyolite	Iceland
KL2-G	19.03±0.01	15.63±0.00	38.52±0.01	2.024±0.000	0.8215±0.0002	2.1	50.4	10.7	Basalt	Kilauea, Hawaii
ML3B-G	18.72±0.02	15.60±0.02	38.45±0.05	2.054±0.002	0.8334±0.0007	1.4	51.0	11.0	Basalt	Mauna Loa, Hawaii

[a]Total iron expressed as FeO.

[b]The Pb isotope ratios for SRM610 and SRM612 were measured on purified Pb in solution mode by MC-ICPMS.[41] The ±2SE errors for the Pb isotope ratios (based on the external reproducibility of the replicate analyses) were negligible. The element concentrations are the NIST certificate values. These reference materials have only a trace (tr.) of iron.

[c]The Pb isotope ratios for BCR-2G and BHVO-2G were measured on purified Pb from whole and powdered fragments of each reference material (n=10 for BCR-2G and n=7 for BHVO-2G) in solution mode by MC-ICPMS.[46] The ±2SE errors for the Pb isotope ratios are based on the external reproducibility of the replicate analyses, excluding the three analyses of BHVO-2G with the highest in-run error. Errors of "0" are due to rounding. The element concentrations are the certificate values for the corresponding USGS powdered whole-rock reference material.

[d]The Pb isotope ratios for St. Gotthard, Inyo, and Haer were measured at the USGS SWIRL on purified Pb from mineral or glass chips by thermal ionization mass spectrometry (TIMS). The Pb isotope ratios were corrected for a negligible 20 pg Pb blank and adjusted for instrumental mass-dependent isotopic fractionation by 0.095%/AMU based on multiple analyses of SRM981 under the same run conditions. The ±2SD errors (~0.04%/AMU) are based on the long-term reproducibility of SRM981. The approximate Pb concentrations were measured on dissolved mineral or glass chips at the USGS SWIRL by quadrupole ICPMS. The major element abundances of these materials were not determined (n.d.).

[e]The Pb isotope ratios for the MPI-DING glasses were measured on purified Pb by TIMS or in solution mode by MC-ICPMS.[31] The errors for the Pb isotope ratios are based on either (1) the ±2SE external reproducibility of the replicate analyses (n>2 for KL2-G and ML3B-G) or (2) the difference in the Pb isotope ratios (n=2, for all except GOR132-G). Errors of "0" are due to rounding. GOR132-G was analyzed only once, and the in-run errors were negligible. The element concentrations are from Jochum et al.[31,34]

Supplementary Table S2

Pb isotope ratios of reference materials in raster and spot modes by LA-SC-ICPMS

	Raster analyses					Spot analyses				
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
	SRM612 (n=107), 135 μm					SRM612 (n=143), 135 μm				
Avg.	17.11	15.52	37.06	0.9074	2.167	17.09	15.51	37.00	0.9076	2.165
±2SD	0.05	0.04	0.13	0.0026	0.006	0.07	0.07	0.18	0.0034	0.008
%	0.31	0.26	0.34	0.29	0.27	0.38	0.46	0.49	0.37	0.37
±2SE	0.01	0.00	0.01	0.0003	0.001	0.01	0.01	0.02	0.0003	0.001
%	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.03	0.03
Ref. values	17.10	15.52	37.02	0.9075	2.165	17.10	15.52	37.02	0.9075	2.165
% Diff.	0.05	0.04	0.12	-0.01	0.08	-0.04	-0.05	-0.05	0.01	0.00
	BCR-2G (n=25), 135 μm					BCR-2G (n=70), 135 μm				
Avg.	18.78	15.63	38.83	0.8323	2.067	18.79	15.64	38.79	0.8325	2.065
±2SD	0.07	0.06	0.11	0.0026	0.006	0.13	0.11	0.28	0.0045	0.011
%	0.39	0.39	0.28	0.32	0.31	0.68	0.69	0.72	0.54	0.54
±2SE	0.01	0.01	0.02	0.0005	0.001	0.02	0.01	0.03	0.0005	0.001
%	0.08	0.08	0.06	0.06	0.06	0.08	0.08	0.09	0.06	0.06
Ref. values	18.77	15.63	38.72	0.8328	2.063	18.77	15.63	38.72	0.8328	2.063
% Diff.	0.08	0.03	0.27	-0.06	0.17	0.11	0.08	0.17	-0.03	0.07
	BHVO-2G (n=20), 135 μm					BHVO-2G (n=65), 135 μm				
Avg.	18.79	15.60	38.48	0.8305	2.049	18.75	15.56	38.36	0.8306	2.047
±2SD	0.15	0.16	0.33	0.0061	0.011	0.32	0.27	0.74	0.0090	0.028
%	0.80	1.0	0.86	0.74	0.54	1.7	1.7	1.9	1.1	1.4
±2SE	0.03	0.03	0.07	0.0014	0.002	0.04	0.03	0.09	0.0011	0.003
%	0.18	0.22	0.19	0.17	0.12	0.21	0.21	0.24	0.14	0.17
Ref. values	18.77	15.59	38.27	0.8302	2.039	18.77	15.59	38.27	0.8302	2.039
% Diff.	0.11	0.11	0.53	0.04	0.49	-0.15	-0.14	0.23	0.04	0.43
	St. Gotthard (n=37), 85-135 μm					St. Gotthard (n=29), 110-135 μm				
Avg.	19.00	15.65	38.61	0.8240	2.033	18.99	15.65	38.57	0.8242	2.031
±2SD	0.06	0.05	0.13	0.0023	0.006	0.06	0.06	0.16	0.0029	0.006
%	0.30	0.29	0.34	0.28	0.28	0.34	0.38	0.42	0.35	0.30
±2SE	0.01	0.01	0.02	0.0004	0.001	0.01	0.01	0.03	0.0005	0.001
%	0.05	0.05	0.06	0.05	0.05	0.06	0.07	0.08	0.07	0.06
Ref. values	19.00	15.65	38.60	0.8237	2.034	19.00	15.65	38.60	0.8237	2.034
% Diff.	0.01	0.04	0.04	0.03	-0.06	-0.03	0.02	-0.07	0.06	-0.14
	Inyo (n=26), 85-135 μm					Inyo (n=15), 135 μm				
Avg.	19.14	15.68	38.95	0.8189	2.035	19.13	15.66	38.89	0.8189	2.033
±2SD	0.09	0.05	0.15	0.0025	0.008	0.10	0.11	0.22	0.0037	0.009
%	0.48	0.34	0.39	0.30	0.41	0.54	0.69	0.57	0.45	0.45
±2SE	0.02	0.01	0.03	0.0005	0.002	0.03	0.03	0.06	0.0009	0.002
%	0.09	0.07	0.08	0.06	0.08	0.14	0.18	0.15	0.12	0.11
Ref. values	19.13	15.67	38.91	0.8192	2.034	19.13	15.67	38.91	0.8192	2.034
% Diff.	0.06	0.06	0.12	-0.03	0.04	0.00	-0.07	-0.04	-0.03	-0.04
	Haer (n=25), 135 μm					Haer (n=31), 135 μm				
Avg.	16.97	15.52	37.27	0.9144	2.196	16.97	15.50	37.30	0.9136	2.196
±2SD	0.14	0.19	0.40	0.0059	0.010	0.30	0.27	0.76	0.0112	0.025
%	0.84	1.2	1.1	0.65	0.46	1.8	1.7	2.0	1.2	1.1
±2SE	0.03	0.04	0.08	0.0012	0.002	0.05	0.05	0.14	0.0020	0.004
%	0.17	0.25	0.21	0.13	0.09	0.32	0.31	0.37	0.22	0.20
Ref. values	17.01	15.49	37.18	0.9105	2.186	17.01	15.49	37.18	0.9105	2.186
% Diff.	-0.19	0.21	0.22	0.43	0.46	-0.23	0.10	0.31	0.34	0.43

The individual analyses and associated metadata are presented in the ESI. The reference (ref.) values are from Supplementary Table S1. Errors of "0" are due to rounding.

Supplementary Table S3
Pb isotope ratios of MPI-DING reference materials in spot mode by LA-SC-ICPMS

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
	GOR132-G (n=40), 135 μm				
Avg.	19.27	15.74	38.78	0.8167	2.012
±2SD	0.10	0.09	0.24	0.0034	0.010
%	0.51	0.54	0.63	0.42	0.48
±2SE	0.02	0.01	0.04	0.0005	0.002
%	0.08	0.09	0.10	0.07	0.08
Ref. values	19.25	15.72	38.71	0.8166	2.011
% Diff.	0.09	0.11	0.18	0.02	0.05
	T1-G (n=40), 135 μm				
Avg.	18.75	15.69	39.03	0.8367	2.081
±2SD	0.12	0.10	0.28	0.0051	0.011
%	0.64	0.62	0.72	0.61	0.51
±2SE	0.02	0.02	0.04	0.0008	0.002
%	0.10	0.10	0.11	0.10	0.08
Ref. values	18.73	15.68	38.97	0.8372	2.081
% Diff.	0.13	0.04	0.14	-0.06	0.02
	StHs6/80-G (n=47), 135 μm				
Avg.	18.89	15.61	38.52	0.8262	2.039
±2SD	0.10	0.09	0.20	0.0047	0.011
%	0.55	0.60	0.52	0.57	0.55
±2SE	0.02	0.01	0.03	0.0007	0.002
%	0.08	0.09	0.08	0.08	0.08
Ref. values	18.90	15.61	38.52	0.8262	2.038
% Diff.	-0.07	-0.01	0.01	0.01	0.03
	ATHO-G (n=41), 135 μm				
Avg.	18.48	15.49	38.20	0.8380	2.066
±2SD	0.19	0.15	0.30	0.0067	0.015
%	1.1	0.98	0.79	0.80	0.73
±2SE	0.03	0.02	0.05	0.0010	0.002
%	0.16	0.15	0.12	0.13	0.11
Ref. values	18.38	15.48	38.11	0.8420	2.073
% Diff.	0.55	0.10	0.22	-0.48	-0.32
	KL2-G (n=42), 135 μm				
Avg.	19.03	15.63	38.52	0.8215	2.024
±2SD	0.23	0.21	0.48	0.0077	0.021
%	1.2	1.4	1.2	0.94	1.0
±2SE	0.03	0.03	0.07	0.0012	0.003
%	0.18	0.21	0.19	0.15	0.16
Ref. values	19.03	15.63	38.52	0.8215	2.024
% Diff.	-0.03	0.01	-0.01	0.00	0.01
	ML3B-G (n=40), 135 μm				
Avg.	18.70	15.61	38.40	0.8345	2.054
±2SD	0.37	0.35	0.80	0.0114	0.022
%	2.0	2.2	2.1	1.4	1.0
±2SE	0.06	0.06	0.13	0.0018	0.003
%	0.32	0.35	0.33	0.22	0.17
Ref. values	18.72	15.60	38.45	0.8334	2.054
% Diff.	-0.13	0.09	-0.14	0.13	-0.02

The individual analyses and associated metadata are presented in the ESI. The reference (ref.) values are from Supplementary Table S1.

Supplementary Table S4

Pb isotope ratios of the SRM612 and SRM610 reference materials in raster and spot modes by LA-SC-ICPMS

	Raster analyses					Spot analyses				
	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
	SRM612 (n=107), 135 μm					SRM612 (n=143), 135 μm				
Avg.	17.11	15.52	37.06	0.9074	2.167	17.09	15.51	37.00	0.9076	2.165
±2SD	0.05	0.04	0.13	0.0026	0.006	0.07	0.07	0.18	0.0034	0.008
%	0.31	0.26	0.34	0.29	0.27	0.38	0.46	0.49	0.37	0.37
±2SE	0.01	0.00	0.01	0.0003	0.001	0.01	0.01	0.02	0.0003	0.001
%	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	0.03	0.03
Ref. values	17.10	15.52	37.02	0.9075	2.165	17.10	15.52	37.02	0.9075	2.165
% Diff.	0.05	0.04	0.12	-0.01	0.08	-0.04	-0.05	-0.05	0.01	0.00
	SRM612 (n=4), 85 μm					SRM612 (n=20), 85 μm				
Avg.	17.11	15.53	37.08	0.9075	2.167	17.08	15.50	36.96	0.9075	2.165
±2SD	0.03	0.04	0.02	0.0020	0.005	0.10	0.09	0.20	0.0055	0.010
%	0.16	0.23	0.06	0.22	0.25	0.58	0.57	0.55	0.60	0.47
±2SE	0.01	0.02	0.01	0.0010	0.003	0.02	0.02	0.05	0.0012	0.002
%	0.08	0.11	0.03	0.11	0.13	0.13	0.13	0.12	0.13	0.11
Ref. values	17.10	15.52	37.02	0.9075	2.165	17.10	15.52	37.02	0.9075	2.165
% Diff.	0.08	0.09	0.15	0.00	0.07	-0.13	-0.11	-0.17	0.01	-0.02
	SRM612 (n=8), 65 μm									
Avg.	17.13	15.54	37.09	0.9075	2.166					
±2SD	0.04	0.04	0.10	0.0024	0.005					
%	0.21	0.25	0.26	0.26	0.25					
±2SE	0.01	0.01	0.03	0.0008	0.002					
%	0.07	0.09	0.09	0.09	0.09					
Ref. values	17.10	15.52	37.02	0.9075	2.165					
% Diff.	0.18	0.18	0.20	0.01	0.02					
	SRM612 (n=15), 50 μm					SRM612 (n=20), 50 μm				
Avg.	17.11	15.52	37.07	0.9068	2.167	17.10	15.51	36.97	0.9069	2.161
±2SD	0.09	0.06	0.15	0.0032	0.008	0.26	0.19	0.55	0.0108	0.021
%	0.52	0.38	0.41	0.36	0.39	1.5	1.2	1.5	1.2	0.99
±2sm	0.02	0.02	0.04	0.0008	0.002	0.06	0.04	0.12	0.0024	0.005
%	0.13	0.10	0.11	0.09	0.10	0.35	0.28	0.34	0.27	0.22
Ref. values	17.10	15.52	37.02	0.9075	2.165	17.10	15.52	37.02	0.9075	2.165
% Diff.	0.06	0.03	0.14	-0.07	0.10	0.00	-0.05	-0.15	-0.06	-0.17
	SRM612 (n=30), 40 μm					SRM612 (n=10), 40 μm				
Avg.	17.11	15.53	37.08	0.9072	2.167	17.09	15.53	36.99	0.9084	2.164
±2SD	0.07	0.07	0.20	0.0029	0.009	0.23	0.16	0.43	0.0117	0.023
%	0.39	0.42	0.53	0.32	0.42	1.4	1.1	1.2	1.3	1.1
±2SE	0.01	0.01	0.04	0.0005	0.002	0.07	0.05	0.14	0.0037	0.007
%	0.07	0.08	0.10	0.06	0.08	0.43	0.34	0.37	0.41	0.33
Ref. values	17.10	15.52	37.02	0.9075	2.165	17.10	15.52	37.02	0.9075	2.165
% Diff.	0.07	0.06	0.15	-0.03	0.10	-0.03	0.10	-0.09	0.10	-0.07
	SRM610 (n=19), 25 μm					SRM610 (n=15), 30 μm				
Avg.	17.05	15.52	36.96	0.9100	2.169	17.05	15.50	36.93	0.9098	2.167
±2SD	0.07	0.09	0.31	0.0041	0.012	0.13	0.15	0.29	0.0068	0.019
%	0.39	0.59	0.85	0.45	0.56	0.78	0.99	0.77	0.75	0.89
±2SE	0.02	0.02	0.07	0.0009	0.003	0.03	0.04	0.07	0.0018	0.005
%	0.09	0.14	0.19	0.10	0.13	0.20	0.25	0.20	0.19	0.23
Ref. values	17.05	15.52	36.99	0.9099	2.169	17.05	15.52	36.99	0.9099	2.169
% Diff.	-0.02	0.00	-0.08	0.01	-0.01	-0.03	-0.09	-0.15	0.00	-0.12
	SRM610 (n=39), 20 μm									
Avg.	17.00	15.46	36.77	0.9099	2.163					
±2SD	0.15	0.15	0.35	0.0093	0.029					
%	0.90	1.0	0.96	1.0	1.3					
±2SE	0.02	0.02	0.06	0.0015	0.005					
%	0.14	0.16	0.15	0.16	0.21					
Ref. values	17.05	15.52	36.99	0.9099	2.169					
% Diff.	-0.28	-0.32	-0.60	0.01	-0.28					
	SRM610 (n=141), 15 μm									
Avg.	17.01	15.47	36.78	0.9101	2.164					
±2SD	0.19	0.14	0.45	0.0126	0.030					
%	1.1	0.92	1.2	1.4	1.4					
±2SE	0.02	0.01	0.04	0.0011	0.003					
%	0.09	0.08	0.10	0.12	0.12					
Ref. values	17.05	15.52	36.99	0.9099	2.169					
% Diff.	-0.25	-0.31	-0.57	0.02	-0.24					

The individual analyses and associated metadata are presented in the ESI. The reference (ref.) values are from Supplementary Table S1. Errors of "0" are due to rounding.

Supplementary Table S5

Comparison of the average expected and achieved precision (±2SD) for the $^{20X}Pb/^{204}Pb$ ratios of the SRM612 and SRM610 reference materials in raster mode by LA-SC-ICPMS

	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	Avg. $^{20X}Pb/^{204}Pb$
SRM612 (n=107), 135 μm				
Expected (%)	0.07	0.07	0.07	0.07
Achieved (%)	0.31	0.26	0.34	0.30
Diff. (%)	0.23	0.19	0.27	0.23
Achieved/Expected	4.1	3.5	4.6	4.1
SRM612 (n=4), 85 μm				
Expected (%)	0.10	0.10	0.10	0.10
Achieved (%)	0.16	0.23	0.06	0.15
Diff. (%)	0.06	0.13	-0.04	0.05
Achieved/Expected	1.6	2.3	0.6	1.5
SRM612 (n=8), 65 μm				
Expected (%)	0.16	0.16	0.16	0.16
Achieved (%)	0.21	0.25	0.26	0.24
Diff. (%)	0.05	0.09	0.10	0.08
Achieved/Expected	1.3	1.5	1.6	1.5
SRM612 (n=15), 50 μm				
Expected (%)	0.19	0.19	0.19	0.19
Achieved (%)	0.52	0.38	0.41	0.44
Diff. (%)	0.33	0.19	0.23	0.25
Achieved/Expected	2.7	2.0	2.2	2.3
SRM612 (n=30), 40 μm				
Expected (%)	0.20	0.20	0.20	0.20
Achieved (%)	0.39	0.42	0.53	0.45
Diff. (%)	0.19	0.22	0.33	0.25
Achieved/Expected	1.9	2.1	2.6	2.2
SRM610 (n=19), 25 μm				
Expected (%)	0.10	0.11	0.10	0.10
Achieved (%)	0.39	0.59	0.85	0.61
Diff. (%)	0.28	0.49	0.74	0.50
Achieved/Expected	3.7	5.6	8.2	5.8
SRM610 (n=39), 20 μm				
Expected (%)	0.18	0.18	0.18	0.18
Achieved (%)	0.90	1.0	0.96	0.95
Diff. (%)	0.72	0.82	0.78	0.77
Achieved/Expected	5.0	5.5	5.4	5.3
SRM610 (n=141), 15 μm				
Expected (%)	0.18	0.18	0.18	0.18
Achieved (%)	1.1	0.92	1.2	1.1
Diff. (%)	0.94	0.74	1.1	0.91
Achieved/Expected	6.1	5.0	6.8	6.0

The expected precision of the $^{20X}Pb/^{204}Pb$ ratios is based on the counting statistics of each analysis from the ESI using the method of Currie (1968)[42]. The achieved precision of the $^{20X}Pb/^{204}Pb$ ratios is from Supplementary Table S4.