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Accuracy and long-term reproducibility of lead isotopic measurements by multiple-collector inductively coupled plasma mass spectrometry using an external method for correction of mass discrimination

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Abstract

The precision of isotopic measurements of Pb by thermal ionization mass spectrometry (TIMS) is limited by the fact that this element does not possess an invariant isotope ratio that can be used for the correction of mass fractionation by internal normalization. Multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) can overcome this limitation, because with plasma ionization, elements with overlapping mass ranges are thought to display identical mass discrimination. With respect to Pb, this can be exploited by the addition of Tl to the sample solutions; the mass discrimination factor obtained for Tl can then be used for the correction of the measured Pb isotope ratios. In this article we present the results of a detailed study that investigates the accuracy and precision of such an external correction technique for mass discrimination based upon the results of multiple analyses of a mixed standard solution of NIST SRM-981 Pb and SRM-997 Tl. Our data indicate that normalization of the Pb isotope ratios to the certified isotopic composition of SRM-997 Tl produces Pb isotopic results that are significantly lower than recently published reference values by TIMS. This systematic offset can be eliminated by renormalization of the Pb data to a different Tl isotopic composition to obtain an empirically determined mass discrimination factor for Pb that generates accurate results. It is furthermore shown that a linear law is least suited for the correction of mass discrimination, whereas a power or exponential law function provide significantly more accurate and precise results. In detail, it appears that a power law may provide the most appropriate correction procedure, because the corrected Pb isotope ratios display less residual correlations with mass discrimination compared to the exponentially corrected data. Using an exponential or power law correction our results, obtained over a period of over seven months, display a precision (2σ) of better than 60 parts per million (ppm) for ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb and of better than 350 ppm for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb. This represents a significant improvement compared to conventional TIMS techniques and demonstrates the potential of MC-ICPMS for routine, high-precision measurements of Pb isotopic compositions. (Int J Mass Spectrom 181 (1998) 123–133) © 1998 Elsevier Science B.V.

Keywords: Pb isotopes; Isotope ratio measurement; Inductively coupled plasma mass spectrometry; Mass discrimination; Multiple collector

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1. Introduction

The precise and accurate determination of Pb isotopic compositions by thermal ionization mass spectrometry (TIMS) is not straightforward because this element does not possess a naturally occurring invariant isotope ratio that can be used for correction of mass fractionation by internal normalization. Whereas the isotopic compositions of elements such as Sr or Nd can be measured with an external precision of better than 100 ppm, routine Pb analyses are generally characterized by a reproducibility that is at least a factor of 5 worse. With respect to these limitations, the relatively new technique of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) may be an efficient alternative for the routine determination of Pb isotopic compositions at high precision. The mass discrimination in the source of the MC-ICPMS is independent of time, the chemical properties of the analyte, and the admixing of other elements at normal operating conditions [1–4]. Using a solution containing a mixture of elements with overlapping mass ranges, the mass discrimination observed for an element of known isotopic composition can therefore be used to determine the unknown isotopic composition of the other element [2,4]. With respect to isotopic analyses of Pb, such an “external” correction method for mass discrimination can be utilized by admixing Tl to the sample solutions. By simultaneously monitoring the Pb and Tl isotopic compositions during the measurement, the Pb data can be accurately corrected for mass discrimination [2,5].

Whereas these advantages of MC-ICPMS have now been known for several years, there exists a lack of detailed isotopic studies that precisely evaluate the quality of such external normalization procedures for the correction of mass discrimination. Previous Pb isotopic studies by MC-ICPMS [2,5,6], for example, compared their results for NIST (National Institute for Standards and Technology) standard reference materials (SRM) with the certified isotopic data [7]. Geochemical studies, however, generally report Pb isotopic results relative to the recent reference values of Todt et al. for these SRM, which were obtained using a ^{202}Pb-^{205}Pb double spike technique [8,9]. The latter data therefore provide a significantly more precise reference frame for the evaluation of Pb isotope data obtained by MC-ICPMS.

During a recent study concerned with the development of analytical techniques for the determination of Tl isotopic compositions in geological materials by MC-ICPMS [10], we performed a large number of isotopic analyses on mixed Pb-Tl standard solutions. In this article, we discuss the Pb isotopic data obtained in these measurements and evaluate the precision of the results with respect to different correction procedures for mass discrimination. Furthermore, we present a detailed comparison of our isotopic data, and the MC-ICPMS data of two other laboratories [6,11], with the reference values of Todt et al. [9]. Thereby, we are able to identify normalization procedures that generate MC-ICPMS results that are comparable to the reference values and to assess the internal consistency of Pb isotope ratios measured by MC-ICPMS.

2. Experimental

2.1. Instrumentation and sample preparation

A VG Elemental Plasma 54 multiple-collector inductively coupled plasma mass spectrometer was used for all Pb isotopic measurements. The instrument at the University of Michigan and our general operating conditions have been described in detail in a number of recent publications [4,12,13]. The Plasma 54 produces flat topped, symmetrical peaks and is equipped with nine Faraday cups that permit the simultaneous measurement of all Pb and Tl ion beams for high precision isotope ratio measurements in the static mode. The amplifier boards of the collectors were calibrated on a daily basis using a 10 V reference signal. The detectors Low 4, Low 3, Low 2, Low 1, Axial, High 1, and High 2, were used to collect the ion currents corresponding to ^{202}Hg, ^{203}Tl, ^{204}Pb, ^{205}Tl, ^{206}Pb, ^{207}Pb, and ^{208}Pb, respectively.

Sample delivery was achieved using a CETAC Technologies MCN 6000 desolvating high-efficiency nebulizer in the free-flow mode (no pumping). With this system we routinely achieved total ion beam intensities corresponding to $> 4 \times 10^{-11}$ A for a 100 ng g^{-1} solution of Pb.

Concentrated stock solutions of NIST SRM-981 Pb and SRM-997 Tl in 2 mol l^{-1} HNO_3 had been previously prepared in our laboratory [10]. A mixed standard solution containing 150 ng g^{-1} SRM-981 Pb and 100 ng g^{-1} SRM-997 Tl was made up from these stock solutions by dilution with high-purity water.

2.2. Measurement procedure

Following ignition of the plasma and application of the accelerating voltage, the instrument was carefully tuned to maximize the signal intensities for Pb and Tl. Furthermore, we performed repeated peak scans to check that the collectors were properly aligned and to monitor the peak shapes in order to ensure proper instrumental operating conditions for isotope ratio measurements. Following an initial warm-up period of approximately 60–90 min the Plasma 54 was generally stable and ready for sample analysis.

To investigate the long-term reproducibility of Pb isotopic measurements by MC-ICPMS, we performed multiple analyses of a mixed NIST SRM-981 Pb–SRM-997 Tl standard solution over a period of several months. From February to November 1997, the mixed standard was analyzed a total of 32 times on 14 separate occasions. In each measurement the standard solution was analyzed for approximately 13 or 16 min, in order to obtain either 80 or 100 integrations in blocks of 20. For a typical sample solution flow rate of 40–45 μl min^{-1}, one analysis consumed approximately 80 or 100 ng of Pb, respectively.

Because of the presence of trace amounts of Hg in the plasma support gas, the measured ^{204}Pb ion beam was corrected for isobaric interference from ^{204}Hg. For this reason, we monitored ^{202}Hg, and applied a correction based upon a ^{204}Hg/^{202}Hg ratio of 0.2239 [14]. The magnitude of this correction, however, was quite small with ^{204}Hg generally contributing < 50 parts per million to the total ion beam at mass 204. Only occasionally did we observe ^{204}Hg/^{204}Pb$+^{204}$Hg ratios as high as ~200 ppm.

2.3. Correction for mass discrimination

An on-line correction of the measured Pb isotope ratios for mass discrimination was performed during the analyses relative to the certified isotopic composition of SRM-997 Tl using a power law function [15]. Upon completion of all analyses in November 1997, the dataset of corrected Pb isotope ratios was filtered using a 2σ test, and this removed one or two outliers from each set of isotopic ratios that lay beyond the mean $\pm 2\sigma$ range. Because the "raw" run data was only stored in the case of ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb, ^{208}Pb/^{207}Pb, and ^{205}Tl/^{203}Tl, all further renormalization experiments were performed with this filtered set of online corrected Pb isotopic data. For renormalization, the corrected mean Pb isotope ratio of each individual run was back-corrected to the original raw ratio using the mean uncorrected ^{205}Tl/^{203}Tl that was obtained for this particular analysis. A comparison of these calculated raw ratios with the measured uncorrected values for ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb, and ^{208}Pb/^{207}Pb demonstrated that the procedure did not introduce any significant numerical artefacts. For these ratios, the measured and back-corrected values for each run of our dataset agree with one another to within <10 ppm. The individual back-corrected results for each run were then renormalized as described below, and the new mean values were calculated as the average of the individual renormalized run data. For this secondary correction of mass discrimination using either a linear, power, or exponential law function, we utilized the mathematical expressions of Wasserburg et al. [16]. This is of importance because the simplified equations of Hart and Zindler [15] are not applicable to an exponential correction of Pb using Tl isotopic compositions.

3. Results and discussion

3.1. Accuracy

In Tables 1 and 2 we compare our new isotopic results for SRM-981 Pb with previously published values from the literature. Selected data are further

Table 1.
Comparison of Pb isotopic ratios for SRM-981 Pb determined in this study by MC-ICPMS using the certified isotopic composition of SRM-997 Tl for the correction of mass discrimination with previously published results from the literature

	^{208}Pb/^{206}Pb	^{207}Pb/^{206}Pb	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
Certified values [7]	2.1681 (8)	0.91464 (33)	16.937 (11)	15.491 (15)	36.721 (36)
Hamelin et al. (TIMS) [17]	*2.16747*	*0.914718*	16.9403 (54)	15.4956 (80)	36.7176 (215)
Todt et al. (TIMS) [9]	2.16701 (43)	0.914585 (132)	16.9356 (23)	15.4891 (30)	36.7006 (112)
Hirata (ICP-MS)[a] [6]	2.16469 (86)	0.914325 (28)	16.9271 (90)	*15.4769*	36.642 (20)
Belshaw et al. (ICP-MS)[b] [11]	*2.1661 (2)*	*0.91455 (6)*	*16.929 (7)*	*15.483*	*36.671*
This study:					
Power law correction to ^{205}Tl/^{203}Tl = 2.3871[c]	2.16522 (10)	0.914381 (47)	16.9277 (53)	15.4781 (47)	36.6519 (113)
Δ_{Ref}	−826	−223	−466	−710	−1327
Exponential correction to ^{205}Tl/^{203}Tl = 2.3871[c]	2.16589 (14)	0.914499 (49)	16.9295 (55)	15.4818 (51)	36.6671 (128)
Δ_{Ref}	−517	−94	−363	−473	−911

Analytical errors are given in parentheses and refer to the least significant digits. All errors are 2σ, except for the certified data where we quote the values given in the original certificate [7]. Δ_{Ref} is the relative deviation of a result from the reference value of Todt et al. [9] in parts per million. Results shown in italics were calculated from the data given in the original publication.

[a] Results obtained on a Plasma 54 MC-ICPMS using a power law correction relative to ^{205}Tl/^{203}Tl = 2.3871.

[b] Results obtained on a Nu-Plasma MC-ICPMS using an exponential correction that was back-calculated to obtain a normalization relative to ^{205}Tl/^{203}Tl = 2.3871. The original results were normalized to ^{205}Tl/^{203}Tl = 2.3875 (see Table 2).

[c] Certified isotopic composition of SRM-997 Tl [18].

shown in Fig. 1. As benchmark reference values we use the recent TIMS results of Todt et al. [9], obtained using a highly precise ^{202}Pb-^{205}Pb double spike technique. Also shown in Table 1 are the data from the original certificate of SRM-981 [7] and the TIMS values of Hamelin et al. [17], that are based upon the use of a ^{207}Pb-^{204}Pb double spike for fractionation correction. Our results are listed in several rows of Tables 1 and 2, where the measured Pb isotope data are corrected for mass discrimination relative to ^{205}Tl/^{203}Tl using different normalization procedures. Clearly, the intent of this study is not the determination of the absolute isotopic composition of SRM-981 (via a calibrated measurement), but to investigate if and how MC-ICPMS measurements of Pb isotopic composition with external normalization to Tl can reproduce the extremely precise Pb isotope data of Todt et al. [9], that are generally used as benchmark reference values in geochemical studies. Furthermore, the high-precision of the data provided by Todt et al. [9] also permits a detailed study of the internal consistency of the MC-ICPMS Pb data. This means that an adequate normalization for MC-ICPMS should be able to generate Pb isotope results that agree with the reference values for *all* Pb isotope ratios simultaneously. If good agreement can only be obtained for some, but not all of the ratios, this would indicate that an inadequate normalization procedure may be generating analytical artefacts. Thus, our aim is to investigate in detail the accuracy of MC-ICPMS data for “differential” measurements of Pb isotopic compositions.

Initially our Pb data, shown in Table 1, were corrected for mass discrimination using a power law technique relative to the certified SRM-997 Tl isotopic composition of ^{205}Tl/^{203}Tl = 2.3871 ± 10 (2 σ error) [18]. This value is based upon an “absolute” measurement of the Tl isotopic composition that was calibrated with the help of enriched isotopes and which thus should be considered reliable within the errors given. In addition, we also show our results renormalized to ^{205}Tl/^{203}Tl = 2.3871 using an exponential correction function (Table 1). A comparison of these data with the reference values of Todt et al. [9] demonstrates that our MC-ICPMS results are systematically lower by approximately 100–1300 ppm (Table 1 and open symbols in Fig. 1). It is also noteworthy that our values are significantly lower than the

Table 2

Comparison of Pb isotopic ratios for SRM-981 Pb determined in this study by MC-ICPMS using empirically optimized Pb bias factors for the correction of mass discrimination with previously published results from the literature

	^{208}Pb/^{206}Pb	^{207}Pb/^{206}Pb	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
Todt et al. (TIMS) [9]	2.16701 (43)	0.914585 (132)	16.9356 (23)	15.4891 (30)	36.7006 (112)
RSD (ppm)	99	72	70	97	153
Hirata (ICP-MS)[a] [6]	2.16636 (82)	0.914623 (37)	16.9311 (90)	*15.4856*	36.6800 (210)
RSD (ppm)	189	20	266		286
Belshaw et al. (ICP-MS)[b] [11]	2.1665 (2)	0.91463 (6)	16.932 (7)	*15.487*	*36.683*
RSD (ppm)	50	35	200		
This study:					
Power law correction to ^{205}Tl/^{203}Tl = 2.38854[c]	2.16652 (10)	0.914656 (47)	16.9379 (53)	15.4922 (47)	36.6961 (113)
RSD (ppm)	24	26	156	151	153
Δ_{Ref}	−225	+78	+135	+197	−122
Exponential correction to ^{205}Tl/^{203}Tl = 2.38808[c]	2.16677 (14)	0.914685 (49)	16.9364 (55)	15.4912 (51)	36.6969 (128)
RSD (ppm)	32	27	162	165	174
Δ_{Ref}	−112	+109	+45	+138	−99
Linear correction to ^{205}Tl/^{203}Tl = 2.38951[c]	2.16599 (65)	0.914597 (120)	16.9412 (46)	15.4942 (42)	36.6945 (139)
RSD (ppm)	150	66	136	136	189
Δ_{Ref}	−465	+13	+330	+328	−167

Analytical errors (2σ) are given in parentheses and refer to the least significant digits. RSD = 1σ relative standard deviation. Δ_{Ref} is the relative deviation of a result from the reference value of Todt et al. [9] in parts per million. Results shown in italics were calculated from the data given in the original publication.

[a] Results obtained on a Plasma 54 MC-ICPMS using a modified power law correction with external normalization to Tl (see text).

[b] Results obtained on a Nu-Plasma MC-ICPMS using an exponential correction with external normalization to ^{205}Tl/^{203}Tl = 2.3875.

[c] The Tl isotopic compositions were determined using a least squares technique and represent normalization values that minimize the differences between the corrected Pb data and the reference values of Todt et al. [9].

certified isotope ratios (which are based upon a calibrated “absolute” measurement of isotopic composition [7]) with respect to ^{208}Pb/^{206}Pb and ^{208}Pb/^{204}Pb. This indicates that our results are not only too low on a relative scale (in comparison to the benchmark data of Todt et al. [9]), but also inaccurate with respect to the true isotopic composition of NIST SRM-981 [7].

A similar discrepancy for MC-ICPMS Pb data, obtained using an external power law correction relative to the certified Tl isotopic composition, was also noted by Hirata [6] and this can be verified in Table 1. Belshaw et al. [11] recently made repeated measurements of SRM-981 Pb with external correction for mass discrimination relative to Tl using an exponential function. These analyses were performed on a Nu-Plasma mass spectrometer, a new, second-generation MC-ICPMS instrument. The results, shown in Table 1 after renormalization to ^{205}Tl/^{203}Tl = 2.3871 using an exponential function, are also systematically lower than the values of Todt et al. [9]. It is noteworthy, however, that our data are in excellent agreement with the MC-ICPMS result of other laboratories, if the same procedure is used for the correction of mass discrimination. The fact that two different instruments from three laboratories are able to produce very consistent Pb isotope ratios, further underlines the reliability of this relatively new mass spectrometric technique.

Additional isotopic measurements conducted by Hirata [6] for various elements suggest that the mass discrimination factors observed by MC-ICPMS are a linear function of mass for many elements, decreasing with increasing atomic weight. Use of the mass bias factor calculated for Tl to correct for the positive mass discrimination of Pb during isotopic analysis should therefore result in corrected Pb isotope ratios that are slightly too low, in agreement with our Pb results

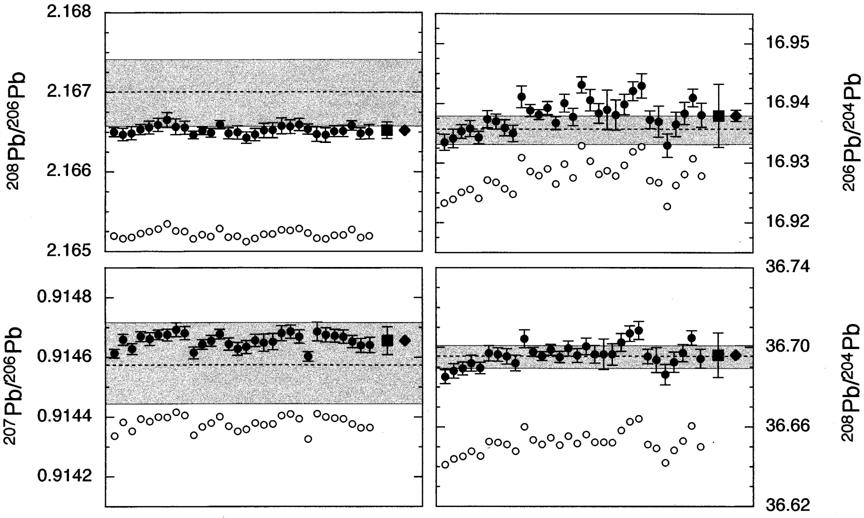

Fig. 1. Pb isotopic results obtained in this study by MC-ICPMS for SRM-981 Pb. The measured Pb isotope ratios were corrected for mass discrimination using a power law technique and external normalization to Tl. Small open circles: Pb data were corrected relative to ^{205}Tl/^{203}Tl = 2.3871. Small filled dots: correction of the Pb results relative to ^{205}Tl/^{203}Tl = 2.38854; the errors bars indicate the $2\sigma_{\text{mean}}$ run errors of the individual analyses that are generally 0.002–0.004% for ^{208}Pb/^{206}Pb, ^{207}Pb/^{206}Pb, and 0.006–0.015% for ^{206}Pb/^{204}Pb, ^{208}Pb/^{204}Pb. The large symbols with errors bars show the mean value of the MC-ICPMS data with 2σ and $2\sigma_{\text{mean}}$ uncertainties (squares and diamonds, respectively). The hatched lines and shaded fields mark the reference values of Todt et al. [9] with 2σ uncertainties

normalized to ^{205}Tl/^{203}Tl = 2.3871. To account for this effect Hirata [6] calculated the relationship between bias factor and atomic mass using the bias factors determined for Rb, Sr, Nd, Hf, Re, Tl, and Pb. Using the negative linear correlation thus obtained, the Pb bias factor was calculated from the mass discrimination of Tl and applied to the correction of the measured Pb isotope data. This procedure was termed a modified power law technique [6] by the author, but it is more similar to an exponential correction for mass discrimination, because the magnitude of the correction factor is inversely related to the atomic mass of the analyte [19]. Using this procedure, Hirata [6] obtained results for SRM-981 Pb that are, within error, identical to the, albeit relatively imprecise, certified reference values [7] (Table 2). This modified external correction technique has a variety of disadvantages, however, that hinder its routine application for isotopic analysis. First, it requires that the mass bias is determined for a number of elements to establish the relationship between bias factor and mass; second, this relationship appears to be valid only for certain elements, whereas others (e.g. Ru, Os) show strong deviations from the inferred linear relationship, such that it is unknown to what degree of accuracy the relative mass discrimination of two elements can be determined with such a procedure.

In this article we investigate a new empirical procedure to increase the accuracy of Pb isotopic measurements by MC-ICPMS that is significantly simpler in its application than the method of Hirata [6]. It is similar to the approach of Belshaw et al. [11], who normalized their Pb isotopic data to a value of ^{205}Tl/^{203}Tl = 2.3875 (rather than the certified Tl isotopic composition) using an exponential function, to obtain results that are identical, within error, to the certified reference values of SRM-981 Pb (Table 2). Our method is based upon the observation that the mass discrimination factors of Pb and Tl appear to show only negligible changes with respect to one another, over a time period of several months. The procedure involves renormalization of the uncorrected Pb isotope data with an empincally optimized ^{205}Tl/^{203}Tl isotope ratio. First, a least squares technique is used to identify which Tl isotopic composition, when used for external normalization, produces the best fit between the mean corrected Pb data and the reference values of Todt et al. [9]. This value is then used for the mass discrimination correction of the individual run results. We use the data of Todt et al. [9], rather than the certified isotopic composition of SRM-981 Pb in this context, because the former values provide a significantly more precise reference frame for the evaluation of the MC-ICPMS results and because most geochemical studies report Pb isotope ratios relative to these benchmarks.

The approach outlined above was applied to our dataset for SRM-981 Pb using linear, power and exponential law functions to correct for mass discrimination, in order to identify the most suitable correction technique for the present purpose. The results of these numerical experiments are shown in the lower part of Table 2 and in Fig. 1. Using a power law function and $^{205}\mathrm{Tl}/^{203}\mathrm{Tl} = 2.38854$, the differences between our results and the data of Todt et al. [9] for SRM-981 are reduced to $<$250 ppm for all ratios and the results agree within the 2σ errors of the measurements (filled symbols in Fig. 1). A slightly better agreement with the reference values is obtained using an optimized exponential correction procedure, where the deviations of the MC-ICPMS data from the results of Todt et al. [9] are $<$ 150 ppm for all Pb isotope ratios. It is also evident from Table 2 that application of an optimized linear correction function produces much larger deviations, and this suggests that this procedure is the least suitable technique for correction of mass discrimination.

A further comparison of the three correction techniques is obtained by plotting the corrected Pb isotope ratios of each individual analysis versus an index of the mass bias that was observed during the isotope ratio measurement by MC-ICPMS. Such diagrams are shown in Fig. 2, where we plot the relative deviation of $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$ and $^{207}\mathrm{Pb}/^{206}\mathrm{Pb}$ for individual runs from the respective mean values (in ϵ-units) versus the Tl bias factor per atomic mass unit, α. The optimized correction factors for the linear, power, exponential law functions were used to correct the individual run data for mass discrimination. The respective $^{205}\mathrm{Tl}/^{203}\mathrm{Tl}$ ratios that were used for external normalization are discussed above and summarized in Table 2. It is noteworthy, however, that the data correlations obtained in Fig. 2 are insensitive to changes in the Tl isotopic composition that is used for external normalization. All slopes and the respective uncertainties remain nearly constant for $2.387 \leq {}^{205}\mathrm{Tl}/^{203}\mathrm{Tl} \leq 2.390$.

Ideally, correction for mass discrimination would lead to plots in which the corrected data display only random scatter, such that we obtain best fit lines with slopes that are statistically identical to zero [19]. With respect to $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$, the Pb isotope ratio with the biggest mass spread, all three correction techniques produce data that display a small, but statistically significant slope. For the power law corrected results the slope is just larger then the 2σ statistical uncertainty, whereas the data corrected by an exponential and linear law are both characterized by a more significant relationship with mass bias. For $^{207}\mathrm{Pb}/^{206}\mathrm{Pb}$, all slopes are smaller, but because the analytical scatter is also reduced, even a small slope may carry a large statistical significance. In this case, both the power and exponential law functions generate results that are associated with slopes that are within error of zero. The data obtained by a linear correction procedure, however, are again characterized by a statistically significant relationship with mass discrimination.

These results underline our previous conclusion that external correction for mass discrimination of Pb is best performed using a power or exponential law function, whereas a linear correction technique is not appropriate for this purpose. Surprisingly, these results also suggest that a power law is better suited for correction of Pb mass discrimination by external normalization than an exponential function. This result is unexpected, because a power law, unlike an exponential function, does not reduce the correction factors for mass discrimination with increasing atomic mass [19]. A variety of isotopic measurements by MC-ICPMS for elements such as Hf, W, and U [12,20,21] have demonstrated that an exponential function is well suited for the correction of mass discrimination by internal normalization. Furthermore, TIMS results obtained for Ca suggest that an

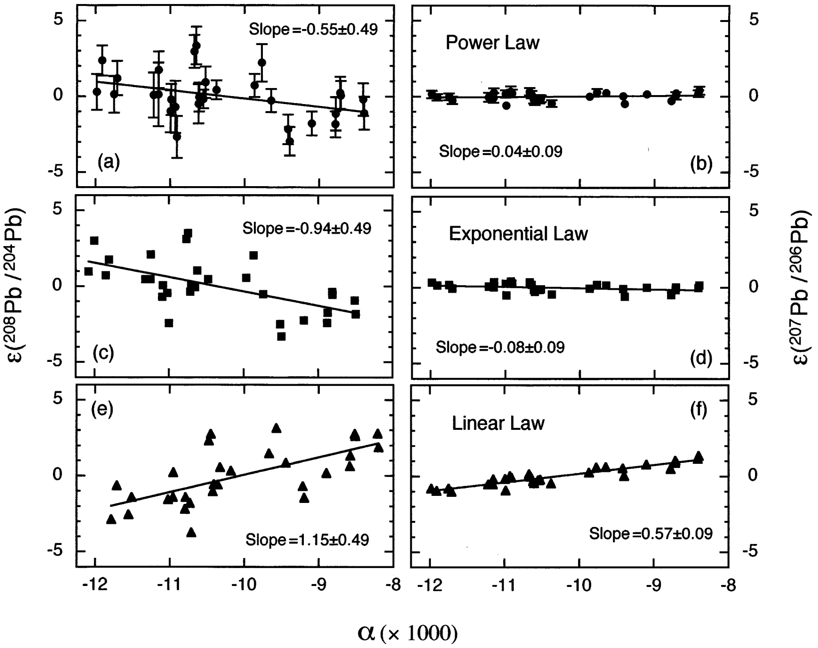

Fig. 2. Plots of the relative deviation of ^{208}Pb/^{204}Pb and ^{207}Pb/^{206}Pb for individual analyses from the respective mean ratios (in ϵ notation) vs. α for the three investigated techniques of mass discrimination correction. The mass discrimination per atomic mass unit α was calculated as: $\alpha = [(^{205}\text{Tl}/^{203}\text{Tl})_N/(^{205}\text{Tl}/^{203}\text{Tl})_M - 1]/2$, where the subscripts M and N indicate measured and normalization values, respectively. $\epsilon(^{208}\text{Pb}/^{204}\text{Pb}) = [(^{208}\text{Pb}/^{204}\text{Pb})_M/(^{205}\text{Tl}/^{203}\text{Tl})_{AV} - 1] \times 10^4$, where the subscript AV denotes the average value of the respective dataset. $\epsilon(^{207}\text{Pb}/^{206}\text{Pb})$ was calculated in an equivalent manner. Bold lines are least squares fit of the data. The slopes and 2σ uncertainties of these best-fit lines are given in each case. (a), (b): Power law correction relative to $^{205}\text{Tl}/^{203}\text{Tl} = 2.38854$; error bars refer to the $2\sigma_{\text{mean}}$ in-run statistics. (c), (d): Exponential correction relative to $^{205}\text{Tl}/^{203}\text{Tl} = 2.38808$. (e), (f): Linear correction relative to $^{205}\text{Tl}/^{203}\text{Tl} = 2.38951$.

exponential law function is superior to a power law technique for the correction of relatively large mass fractionation effects [15,19]. However, it is also apparent that none of the correction procedures investigated in this study are able to provide data with zero slope for all of the different Pb isotope ratios. This indicates either the presence of other systematic sources of error in our results or the inability of the examined correction techniques to accurately describe the mass discrimination effects that are encountered during analysis.

3.2. Reproducibility

In Table 2 and Fig. 1 we also document the precision of our Pb isotope ratio measurements for SRM-981 Pb and compare these results with previously published data from the literature. In the following we discuss only the data obtained using an exponential and power law correction, because a linear correction procedure is not considered to yield reliable Pb isotopic results. For ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb, where only relatively large ion beams are collected, we achieve relative standard deviations (RSD, 1σ) of approximately 20–30 ppm, whereas ratios with ^{204}Pb are characterized by RSD values of $\sim$150 ppm. In general, the power law results have a somewhat better precision than the exponentially corrected data. This is clearly associated with the observation that a power law function produces data that are characterized by lower residual correlations with mass bias (Fig. 2).

A comparison of our new results with the MC-ICPMS data of Hirata [6] for SRM-981 (Table 2) is particularly interesting, because it appears that his smaller dataset was collected within a relatively short period of time, whereas our analyses were performed over a period of over 7 months. Nevertheless, the precision of our data is significantly better for all Pb isotope ratios, with the exception of ^{207}Pb/^{206}Pb. This may be related to the use of a high-efficiency desolvating nebulizer in this investigation, whereas a conventional nebulization system was utilized in the study of Hirata [6]. First, this enabled us to obtain significantly larger ion beam intensities (by about a factor of 2), even though our measurements were performed with a less concentrated solution of SRM-981 Pb (0.15 as opposed to 2.0 μg g^{-1}); furthermore, the MCN 6000 is able to produce highly stable ion beam signals that are characterized by significantly less noise than other nebulization systems. The Nu-Plasma MC-ICPMS data of Belshaw et al. [11], were also obtained using an MCN 6000 nebulizer at beam intensities comparable to our analyses and were compiled over a period of several weeks. The precision of this dataset is similar, but slightly worse, than our long-term reproducibility for 7 months (Table 2). The differences are, however, quite small and may be related to the fact that we applied a 2σ filter to our dataset in order to identify outliers.

A comparison of the precision obtained in this study with the data of Todt et al. [9] for SRM-981 is of interest, because the latter results are the most precise TIMS data presently available for this isotopic reference material. Inspection of Table 2 demonstrates that we achieve a significantly better precision with respect to the measurement of ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb, but that the TIMS results have a similar or better reproducibility for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{208}Pb/^{204}Pb. This is almost certainly just a function of signal/noise ratio differences between the measurements of ratios that include the low-intensity ^{204}Pb ion beam. Nonetheless, it is apparent that the long-term reproducibility of Pb isotope ratio determinations by MC-ICPMS is comparable to, or only slightly worse than, the precision of state-of-the-art TIMS measurements using a double-spike technique for the correction of mass fractionation. It is noteworthy that our results are significantly more precise than standard TIMS data that generally quote a 2σ precision, based upon the reproducibility of standards, of approximately 0.02–0.03% per amu. This is equivalent to a reproducibility of 400–600 ppm and 800–1200 ppm for the measurement of ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb, respectively.

The excellent reproducibility of our results indicates that the mass discrimination factors of Pb and Tl display only negligible changes with respect to one another. Previous MC-ICPMS studies, however, have shown that the relative mass bias of two elements can be altered by changes in the instrumental operating conditions of the Plasma 54 [4,22]. During the 7 month period of this study, all measurements were conducted using the same radio frequency (rf) power setting for the ICP source (1.2 kW). All other instrumental settings, however, were adjusted on a daily basis to ensure proper peak shapes and in order to obtain maximum signal intensities for Pb and Tl. These adjustments included changes in the acceleration and extraction voltages (5990 ± 10 V and 4100 ± 200 V, respectively), the settings of the lens stacks in the quadrupole region, torch box positions, and gas flow rates. Our results demonstrate that the relative mass discrimination of Pb and Tl remains highly constant for long periods of time with proper attention to instrumental adjustments, thus enabling us to achieve excellent levels of long-term reproducibility for Pb isotope ratio measurements using an external method to correct for mass discrimination.

4. Conclusions

The MC-ICPMS data compiled in this study and by other laboratories for SRM-981 indicate that use of the certified isotopic composition of SRM-997 Tl for the external normalization of Pb isotope data generates results that are systematically lower than the reference values of Todt et al. [9]. Furthermore, they are lower than the true, certified isotopic composition of SRM-981 Pb [7] with respect to ^{208}Pb/^{206}Pb and ^{208}Pb/^{204}Pb, regardless of whether a power-law or an exponential function are used for normalization. Therefore, an empirical procedure is required to improve the accuracy of the mass discrimination correction. In this study we apply a least squares technique to obtain an empirical correction factor for mass discrimination that minimizes the differences between our data and the reference values of Todt et al. [9] for SRM-981 Pb. Once calculated, this empirical mass bias factor can be applied during further analyses, because the relative mass discrimination of Pb and Tl is nearly constant over long periods of time.

A possible alternative approach for the external correction for mass discrimination of Pb may be the empirical normalization of the results relative to a common standard ratio that is known to a high degree of accuracy. This technique would then be similar to the internal normalization methods that are commonly used for isotopic analysis of Sr, Nd, or Hf. If a similar approach was used by several laboratories, this would significantly ease the comparison of Pb results obtained by MC-ICPMS. Presently there exists no standard procedure for the external normalization of Pb isotopic data acquired by MC-ICPMS. Therefore all current Pb isotopic results are somewhat arbitrary, because the measured values are corrected for mass discrimination using different normalization techniques. The ^{207}Pb/^{206}Pb ratio of SRM-981 Pb would be suitable for normalization purposes, for example, because this ratio is close to unity such that it is easily measured to high precision and relatively insensitive to any instrumental bias effects. A further advantage of this procedure is that ratios that include ^{204}Pb, which are generally characterized by relatively large uncertainties and may also be biased by systematic errors because of the presence of hydrocarbons during TIMS analyses, are excluded from the calculation of the empirical mass discrimination factor.

Application of such an external correction technique for Pb would be similar to the least squares optimized procedures described above. A standard dataset for a mixture of SRM-981 Pb with SRM-997 Tl is used for the calculation of the appropriate Tl isotopic composition which generates a mean ^{207}Pb/^{206}Pb ratio for SRM-981 that is identical to the reference value. Because of the stability of the relative mass discrmination for Tl and Pb, this factor can then be used for the correction of the measured ratios for samples with an unknown Pb isotopic composition. In Table 3 we show our results for SRM-981 Pb renormalized to the Tl isotopic compositions that produce ^{207}Pb/^{206}Pb ratios, corrected for mass discrimination using either a power-law or exponential function, that are identical to the TIMS reference values of Todt et al. [9]. It is apparent that our Pb data corrected by an exponential law function relative to ^{205}Tl/^{203}Tl $= 2.38755$ are very similar to the results of Hirata [6] that were obtained using a modified power law technique with Tl normalization (Table 2). The similarity of the results is caused by the use of related correction techniques, because the latter study [6] also employed an empirical mass bias factor that was determined with the aid of the relative mass discriminations observed for Tl and ^{207}Pb/^{206}Pb. Furthermore, our data are also identical, within error, to the values of Belshaw et al. [11] shown in Table 2, because the later study applies an exponential normalization (relative to ^{205}Tl/^{203}Tl $= 2.3875$) that is very similar to our correction.

The excellent agreement of the MC-ICPMS data with one another was previously discussed with respect to the isotopic results summarized in Table 1. From the values shown in Tables 2 and 3 it is also apparent, however, that the MC-ICPMS datasets are more comparable to one another (given a similar method of mass discrimination correction) than to the TIMS reference values of Todt et al [9]. This conclusion is independent of the normalization procedure that is used for the correction of the MC-ICPMS results. A detailed analysis reveals that the different MC-ICPMS datasets can achieve excellent agreement with one another for all of the considered Pb isotope ratios, whereas this is not possible with the reference values of Todt et al. [9]. In the latter case, a close match for one Pb ratio is always related to an increasing difference for another. It is possible, albeit unlikely, that this results from the introduction of a nearly identical analytical bias (potentially related to instrumental or mass discrimination effects) by the three different MC-ICPMS instruments. Alternatively, it is conceivable that the TIMS reference values of Todt et al. [9] do not constitute a self-consistent dataset of isotopic ratios, and may require slight revisions in the future. The possibility of small systematic errors in these reference values was dis-

Table 3
Pb isotope data for SRM-981 Pb obtained in this study by MC-ICPMS using an external correction technique for mass discrimination. The mass bias factors are adjusted to generate $^{207}Pb/^{206}Pb$ ratios in agreement with the reference values of Todt et al. [9]

	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Todt et al. (TIMS) [9]	2.16701 (43)	**0.914585** (132)	16.9356 (23)	15.4891 (30)	36.7006 (112)
This study:					
Power law correction to $^{205}Tl/^{203}Tl = 2.38817$	2.16619 (10)	**0.914585** (47)	16.9353 (53)	15.4886 (47)	36.6848 (112)
Δ_{Ref}	−380	±0	−20	−35	−431
Exponential correction to $^{205}Tl/^{203}Tl = 2.38755$	2.16629 (14)	**0.914585** (49)	16.9326 (55)	15.4861 (51)	36.6808 (128)
Δ_{Ref}	−331	±0	−175	−192	−538

The 2σ errors of the data are given in parentheses and refer to the least significant digits. Δ_{Ref} is the relative deviation of a result from the reference value of Todt et al. [9] in parts per million.

cussed by Todt et al. [9], who remarked that their results were less precise than would be expected from the mass spectrometric uncertainties alone and suggested that this may be related to the presence of unknown interferences during the measurements.

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