

Accurate and precise Pb isotope ratio measurements in environmental samples by MC-ICP-MS[☆]

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Received 11 January 2004; accepted 14 January 2004

Abstract

Analytical protocols for accurate and precise Pb isotope ratio determinations in peat, lichen, vegetable, chimney dust, and ore-bearing granites using MC-ICP-MS and their application to environmental studies are presented. Acid dissolution of various matrix types was achieved using high temperature/high pressure microwave and hot plate digestion procedures. The digests were passed through a column packed with EiChrom Sr-resin employing only hydrochloric acid and one column passage. This simplified column chemistry allowed high sample throughput. Typically, internal precisions for approximately 30 ng Pb were below 100 ppm ($\pm 2\sigma$) on all Pb ratios in all matrices. Thallium was employed to correct for mass discrimination effects and the achieved accuracy was below 80 ppm for all ratios. This involved an optimization procedure for the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio using least square fits relative to certified NIST-SRM 981 Pb values. The long-term reproducibility ($\pm 2\sigma$) for the NIST-SRM 981 Pb standard over a 5-month period (35 measurements) was better than 350 ppm for all ratios. Selected ore-bearing granites were measured with TIMS and MC-ICP-MS and showed good correlation (e.g., $r = 0.999$ for $^{206}\text{Pb}/^{207}\text{Pb}$ ratios, slope = 0.996, $n = 13$). Mass bias and signal intensities of Tl spiked into natural (after matrix separation) and in synthetic samples did not differ significantly, indicating that any residual components of the complex peat and lichen matrix did not influence mass bias correction. Environmental samples with very different matrices were analyzed during two different studies: (i) lichens, vegetables, and chimney dust around a Cu smelter in the Urals, and (ii) peat samples from an ombrotrophic bog in the Faroe Islands. The presented procedure for sample preparation, mass spectrometry, and data processing tools resulted in accurate and precise Pb isotope data that allowed the reliable differentiation and identification of Pb sources with variations as small as 0.7% for $^{206}\text{Pb}/^{207}\text{Pb}$.

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Keywords: Accuracy; Precision; Pb isotope ratios; MC-ICP-MS; Source assessment; Environmental samples; Sample preparation

1. Introduction

The use of Pb isotopes has had a tremendous effect on our understanding of the geochemical cycling of Pb in the environment and the anthropogenic impact [1]. Lead isotopes in environmental samples, i.e., soil, plant, sediment, peat, surface and subsurface waters, have mainly been measured using thermal ionization mass spectrometry (TIMS) or quadrupole-based inductive coupled plasma source mass

spectrometry (ICP-QMS). The advantage of TIMS is that ratios including the least abundant ^{204}Pb isotope are measured with high reproducibility (down to 200 ppm) and it achieves good accuracy also in samples with low [Pb]. However, analytical procedures for TIMS are time consuming and involve intensive sample preparation steps, e.g., two column passages are needed to achieve stable emission of Pb^+ ions from the filament analyzing organic rich matrices, such as lichen or peat. This severely restricts the sample throughput. Yet, many environmental problems require a large sample number to infer statistically significant conclusions. This is due to inherent temporal and spatial variability in the environmental context.

Consequently, most environmental investigations to date use ICP-QMS (e.g., Refs. [2,3]), which performs single mea-

[☆] The program code written for the Tl optimization can be obtained from the authors.

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measurements at the nominal mass value of each peak using either scanning or peak hopping modes. This results in poor peak shape and consequently in less precise measurements than using multi-collector sector instruments [4]. Typically, precisions of around 0.1–1.0% are achieved [5,6], depending on the concentration or matrix and the ^{204}Pb isotope is seldom measured. However, isotopic ratios including the ^{204}Pb isotope are of crucial importance for source assessments.

Multiple-collector inductively coupled plasma source mass spectrometry (MC-ICP-MS) combines the high ionization efficiency of the Ar-plasma with the precision attainable using multi-collector array. It is thus of great interest for the environmental geochemist as it allows the inclusion of the ^{204}Pb for routine measurements in low [Pb] samples and a large sample throughput with less sample preparation and measurement time is possible. A number of papers have investigated Pb isotope ratio measurements with MC-ICP-MS using different mass spectrometer designs, i.e., double [7–12] or single focussing [13–16] sector field MC-ICP-MS. These papers showed that external precisions achieved are similar to TIMS and that mass fractionation, abundance sensitivity, baseline correction, etc. affect data quality significantly.

With respect to instrumental mass fractionation, arguably a major source of error, the major drawback is that Pb has only one non-radiogenic isotope (^{204}Pb) and mass fractionation cannot be corrected internally. One way to correct for mass bias is to spike the sample with an element of similar mass and with two stable isotopes. In the case of Pb, Tl with isotopes 203 and 205 is the preferred choice [7,12,13]. However, it was shown that the $^{205}\text{Tl}/^{203}\text{Tl}$ normalizing ratio of the NIST-SRM 997 Tl (used as dopant) had to be adjusted to higher ratios than the certified value to generate normalized values within error for NIST-SRM 981 Pb determined using double and triple spikes [13]. The latter vary significantly themselves from laboratory to laboratory, i.e., for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios with values of 16.9405 ± 0.0015 [17], 16.9409 ± 0.0022 [18], and 16.9356 ± 0.0023 [19]. White et al. [7] assessed the graphical technique previously developed for Cu and Zn isotope analysis [20], which plots measured ratios of the Tl dopant versus the Pb isotope pair of interest in log–log space. This technique is not applicable on first generation *IsoProbe* instruments due to the small mass bias variations using dry plasma conditions, which consequently results in poor linear fits with high errors and inaccurate isotope ratios [13,21].

To date, most investigations have been limited to synthetic and ‘simple’ silicate matrices and the Tl mass bias correction procedure has been the object of intense discussions [8,13,15]. Consequently, more investigations on accurate and precise Pb isotope ratio measurements, especially with a focus on environmental samples, are needed. Recent applications of MC-ICP-MS to environmental geochemistry included Pb isotope measurements in seawater matrices [9,16].

The purpose of this contribution is to present a reliable and robust analytical protocol (including sample prepara-

tion and mass spectrometry) and data processing methodology for precise and accurate Pb isotope measurements in a wide range of environmental samples. To achieve this, we (i) re-assessed the Tl mass bias correction procedure using a simple optimization procedure, (ii) assessed its analytical merits, and (iii) demonstrated its application in two environmental geochemical studies.

2. Experimental

2.1. MC-ICP-MS and TIMS instrumentation

A Micromass *IsoProbe* MC-ICP-MS based at the Imperial College London/Natural History Museum Joint Analytical Facility (ICL/NHM JAF) was used during the study. The instrument is equipped with seven independently adjustable Faraday cups and a hexapole collision cell. A CETAC Aridus desolvating system (Omaha, NE, USA) with a T1-H microconcentric nebulizer was used for sample introduction. The optimized data acquisition parameters selected for Pb isotope ratio measurements are summarized in Table 1. For comparative purposes, Pb isotope analyses were also conducted at the Geochronology Laboratory of the University of Heidelberg using a Finnigan *MAT 261* TIMS with multi-cup system for Pb isotopes and standard sample preparation techniques. Raw TIMS data were normalized to NIST-SRM 981 Pb international standard with reference values of Galer and Abouchami [17] and long-term reproducibility on the 95% confidence level was below 0.03% for ratios normalized to ^{204}Pb . Details of the TIMS procedure have been described in detail before [22].

2.2. Measurement procedures

All isotope measurements were performed by static multiple collection. The ion currents were measured using

Table 1
Typical instrument operating conditions of the *IsoProbe* MC-ICP-MS and the CETAC nebulizer

Instrument settings	
Accelerating voltage (V)	~6000
rf power (W)	~1375
Reflected power (W)	<2
Coolant Ar flow (l min^{-1})	~14
Auxiliary Ar flow (l min^{-1})	1.0–1.2
Nebulizer flow (l min^{-1})	0.6–0.8
Ar collision gas flow (ml min^{-1})	1–2
Abundance sensitivity (ppm)	~25
Analyzer pressure (mbar)	$\sim 4.8 \times 10^{-8}$ under full gas load
Sensitivity for Pb (V ppm^{-1})	~300
Cones (skimmer and sample)	Ni
Sample introduction	
Spray chamber temperature ($^{\circ}\text{C}$)	75
Desolvator temperature ($^{\circ}\text{C}$)	160
Ar sweep gas flow (ml min^{-1})	~2.8–3.5
Sample flow rate ($\mu\text{l min}^{-1}$)	~40–60

Faraday collectors at masses 200 (Hg), 203 (Tl), 204 (Pb and Hg), 205 (Tl), 206 (Pb), 207 (Pb), and 208 (Pb). The collector efficiencies were calibrated on a daily basis. Ion beam intensities of Pb and Tl were optimized adjusting accelerating voltage, lens system, torch settings, and gas flows. Data collection was made using two blocks with 25 measurements each when analyzing samples and using one block with 20 measurements when analyzing the acid blank before the sample. Internal errors ($\pm 2\sigma$) for synthetic solutions of 50 ng ml^{-1} were below 50 ppm for all ratios. A 10-s integration and 5-s sample admission delay guaranteed stable signals before measurements started. The rinse out time between samples and acid blank was 6 min using 2% (v/v) HNO_3 . A typical measurement procedure included five samples taken up in 2% (v/v) HNO_3 and spiked with NIST-SRM 977 Tl and one NIST-SRM 981 Pb standard spiked with NIST-SRM 977 Tl in 2% (v/v) HNO_3 to assess the reproducibility and to optimize the Tl ratio (see below).

Analytical blanks for the total procedure, estimated from intensity data, were below 1 ng and can be accounted for by the Aristar grade acids used during sample preparation. The blank was always below 1% of the total Pb and mixing calculation showed that contributions were insignificant at any time at the level encountered.

2.3. Data reduction and mass discrimination correction

To correct for Faraday cup offset, solvent blank and instrumental blank, averaged acid blank intensities were subtracted from individually measured raw isotope intensities and then the average was calculated. To account for the ^{204}Hg isobaric interference, the ^{200}Hg was measured on L2. This correction was very small and typically amounted to $\leq 0.1\%$. Previous work suggests that average abundance sensitivities are stable on the *IsoProbe* to approximately $\pm 2 \text{ ppm}$ ($\pm 2\sigma$) under same vacuum conditions [16]. Consequently, abundance sensitivity correction during this study was achieved by fixing the Pb/Tl ratio and concentration matching between samples and standards to within 10%.

The run intensities corrected for background and isobaric interference were used to calculate the raw ratios, which then were corrected for instrumental mass bias using Tl as external dopant and the Tl mass fractionation factor f_{Tl} . The $^{205}\text{Tl}/^{203}\text{Tl}$ ratio used to calculate the mass fractionation factor f_{Tl} was optimized each measurement session from repeated NIST-SRM 981 Pb standard measurements dispersed between sample measurements (see below details of procedure). The exponential law proved to be the most accurate. The mass fractionation coefficient for Tl (f_{Tl}) was calculated as

$$f_{\text{Tl}} = \frac{\ln(R_{\text{Tl}}/r_{\text{Tl}})}{\ln(M_{205}/M_{203})} \quad (1)$$

where R_{Tl} is the ‘true’ Tl ratio, r_{Tl} the measured ratio, and M represents the atomic masses of Tl (202.9723 and 204.9745, respectively). The Tl mass correction factor f_{Tl} was used to

correct the raw Pb isotope ratios (baseline, interference and abundance sensitivity corrected)

$$R_{\text{Pb}} = r_{\text{Pb}} \left(\frac{M_1}{M_2} \right)^{f_{\text{Tl}}} \quad (2)$$

where R_{Pb} is the ‘true’ Pb ratio, r_{Pb} is the measured ratio, $M_{1,2}$ are the atomic masses of isotopes 1 and 2, respectively, and f_{Tl} is the mass fractionation coefficient derived from Eq. (1).

2.4. Tl ratio optimization procedure

Instrumental mass fractionation was determined during a measurement session by repeated analyses of the NIST-SRM 981 Pb standard spiked with the NIST-SRM 997 Tl using the same Pb/Tl ratio and concentrations as the samples. The Tl ratio was optimized against the $^{206}\text{Pb}/^{204}\text{Pb}$ value of Galer and Abouchami [17]. The optimization was achieved using a least squares method. The approach is based on the logarithmic law, which assumes that the ‘true’ Tl and Pb ratios are given by

$$R_i^{\text{Tl}} = r_i^{\text{Tl}} (c^{\text{Tl}})^f \quad (3)$$

and

$$R_i^{\text{Pb}} = r_i^{\text{Pb}} (c^{\text{Pb}})^f \quad (4)$$

where f is the mass bias fractionation factor given by $f = \ln(R_i^x/r_i^x)/\ln(c^x)$ (with $x = \text{Pb}$ or Tl), R^{Tl} and R^{Pb} are the ‘true’ ratios, i is a given number of measured NIST-SRM 981 Pb standards, r^{Pb} and r^{Tl} are measured ratios of $^{205}\text{Tl}/^{203}\text{Tl}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, respectively, $c^{\text{Tl}} = M_2/M_1 = 205/203 = 1.008852$, and $c^{\text{Pb}} = M_2/M_1 = 206/204 = 1.009804$.

Using repeated NIST-SRM 981 Pb measurements (between 6 and 12) during a measurement session, we defined \bar{R}^{Pb} (the mean value) as

$$\bar{R}^{\text{Pb}} = \frac{1}{N} \sum_{i=1}^N R_i^{\text{Pb}}, \quad \text{with } R_i^{\text{Pb}} = r_i^{\text{Pb}} (c^{\text{Pb}})^{\ln(R^{\text{Tl}}/r_i^{\text{Tl}})/\ln(c^{\text{Tl}})} \quad (5)$$

where N is the number of NIST-SRM 981 Pb measurements during the measurement session. \bar{R}^{Pb} is a function of the ‘true’ Tl ratio (R^{Tl}), which we do not know reliably. Given \bar{R}^{Pb} should be close to the certified value for Pb ($R_{\text{cert.}}^{\text{Pb}}$), we adjusted the unknown R^{Tl} , such that we minimized the prediction error for \bar{R}^{Pb} . Therefore, we chose an objective function $\varphi = (\bar{R}^{\text{Pb}}/R_{\text{cert.}}^{\text{Pb}} - 1)^2$, which has a minimum (of zero) when $\bar{R}^{\text{Pb}} = R_{\text{cert.}}^{\text{Pb}}$. The value of R^{Tl} was found by taking the denominator of φ with respect to R^{Tl} and setting this to zero ($\partial\varphi/\partial R^{\text{Tl}} = 0$). This leads to the final form

$$R^{\text{Tl}} = \ln(c^{\text{Tl}}) \left(\frac{NR_i^{\text{Pb}}}{\sum_{i=1}^N r_i^{\text{Pb}} (c^{\text{Pb}})^{\ln(r_i^{\text{Tl}})/\ln(c^{\text{Tl}})}} \right)^{\ln(c^{\text{Tl}})/\ln(c^{\text{Pb}})} \quad (6)$$

2.5. Materials and reagents

Environmental samples included peat from an ombrotrophic bog in the Faroe Islands [23], lichens, vegetables, and chimney dust collected around a Cu smelter in Karabash, Southern Urals [24], and ore-bearing and barren granites from the Orlovka-Spokoinie mining district in Eastern Transbaikalia [25]. The acids were of ultra-pure (Merck and sub-boiling acid) or Aristar (Merck) quality. Dilute solutions of acids for mass spectrometry were prepared with purified water obtained from quartz still or an 18 M Ω grade Millipore system (Bedford, MA, USA). Lead, Tl, and mixed Pb–Tl standard solutions were made up from previously prepared stock solutions of NIST-SRM 981 Pb (1240 $\mu\text{g ml}^{-1}$ in 2% (v/v) HNO₃, from S. Bowering, MIT, Cambridge) and NIST-SRM 997 Tl (732 $\mu\text{g ml}^{-1}$ in 2 M HNO₃, from M. Rehkaemper, ETH, Zürich). All solutions and samples were prepared and handled in laminar flow hoods. Solutions were concentration matched to get a signal of ≥ 100 mV on ²⁰⁴Pb and a Pb/Tl ratio of approximately 5:1.

2.6. Sample preparation of environmental samples

Peat samples were digested using a Milestone high pressure/high temperature microwave oven system [26]. Lichens and vegetables samples from the Karabash smelter were digested using an MARSX high pressure/high temperature microwave oven system [27]. Both microwave digestion methods have been recently developed and showed quantitative recoveries for Pb. The barren and Ta–Nb–W bearing granites from the Orlovka-Spokoinie mining district and the chimney dust samples were dissolved using standard HNO₃/HF acid mixtures on a hot plate in closed Teflon beakers [25].

After digestion, all solutions were dried and the residues redissolved in 2 ml of 2.4 M HCl prior to the passage through the column. After conversion to the chloride form, Pb was separated using the Pb selective extraction chromatographic Sr-resin from EiChrom [28] and following the distribution factor dependencies for Pb as reported elsewhere [29]. The method uses only hydrochloric acid and one column pas-

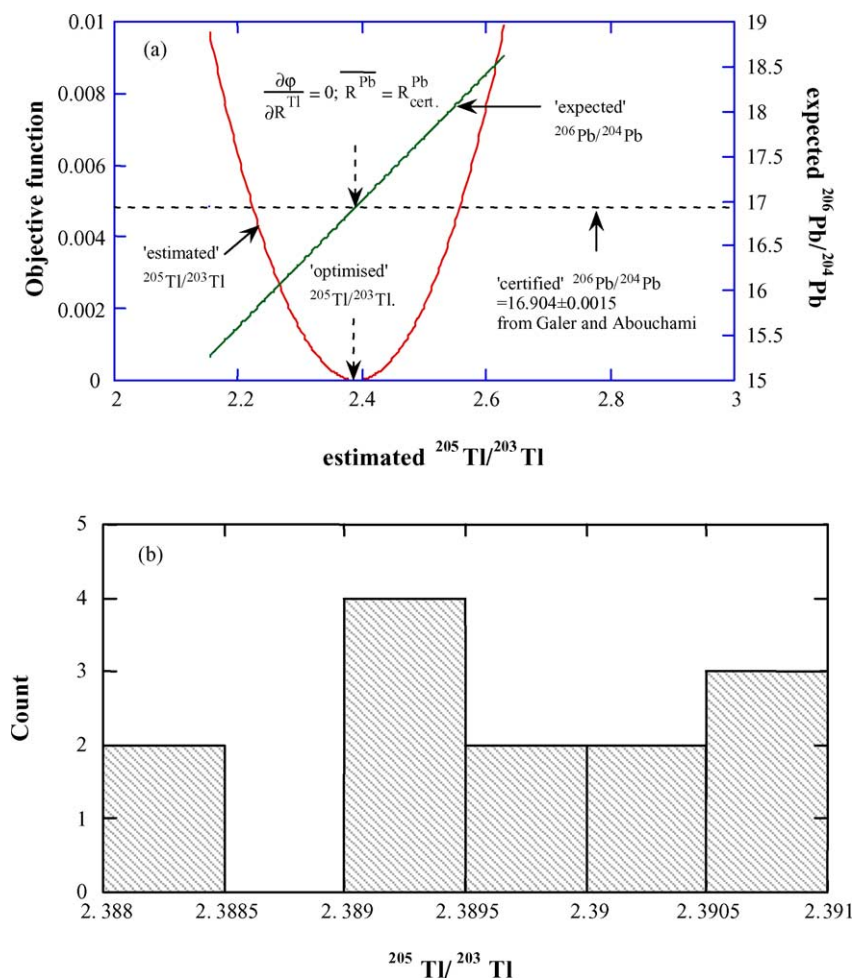


Fig. 1. (a) Distribution of estimated ²⁰⁵Tl/²⁰³Tl (x-axes) as a function of the expected ²⁰⁶Pb/²⁰⁴Pb ratios (\bar{R}^{Pb}) and the objective function (φ). The optimized ²⁰⁵Tl/²⁰³Tl ratio of this measurement session (29.1.03) is given by 2.3905 and fulfills the conditions of $\partial\varphi/\partial R^{Tl} = 0$ and $\bar{R}^{Pb} = R_{cert}^{Pb}$. (b) The distribution of optimized Tl ratios during 13 measurement sessions at the ICL/NHM JAF during 1 year (August 2002 to August 2003).

Table 2
Ion exchange column procedure for separating Pb from sample matrix

Stage	Acid strength of HCl and volume used
1. Cleaning step	6 M (6 × 1 ml)
2. Conditioning step	2.4 M (2 × 0.5 ml)
3. Sample loading step	2.4 M (1 × 1.5 ml)
4. Matrix elution step	2.4 M (4 × 1 ml)
5. Pb elution step	6 M (3 × 1 ml)
6. Cleaning step	6 M (3 × 1 ml)

The columns were made in-house using Teflon tubing and packed with 600 μ l of EiChrom Sr-resin resulting in a bed height of about 0.5 cm.

sage. It consists of a cleaning step with 6 M HCl, a preconditioning and a loading step, both with 2.4 M HCl and an elution step using 6 M HCl (Table 2). The recovery of Pb from the column is quantitative from biological and silicate matrices.

3. Results and discussion

3.1. Assessing the Tl optimization procedure

Fig. 1a shows the results of a Tl optimization calculation from one measurement session (16.8.2002) using 12 individual analyses of NIST-SRM 981 Pb standards doped with NIST-SRM 997 Tl. Plotted is the estimated $^{205}\text{Tl}/^{203}\text{Tl}$ ratio (R^{Tl}) versus the objective function. Also shown are the corresponding estimated (\bar{R}^{Pb}) and certified Pb ratios ($R^{\text{Pb}}_{\text{cert}}$). Fig. 1b shows a frequency distribution histogram of optimized Tl ratios determined during 13 individual measurement sessions in a time period of 1 year (August 2002 to August 2003). No systematic trend or bias is visible in the frequency distribution of the optimized Tl ratio. The $^{205}\text{Tl}/^{203}\text{Tl}$ ranged between 2.3885 and 2.3907 with a mean value of 2.3897 ± 0.0015 ($\pm 2\sigma$). The mean value is slightly higher than the originally ‘certified’ ratio of 2.38714 ± 0.00101 [30] but has a similar error.

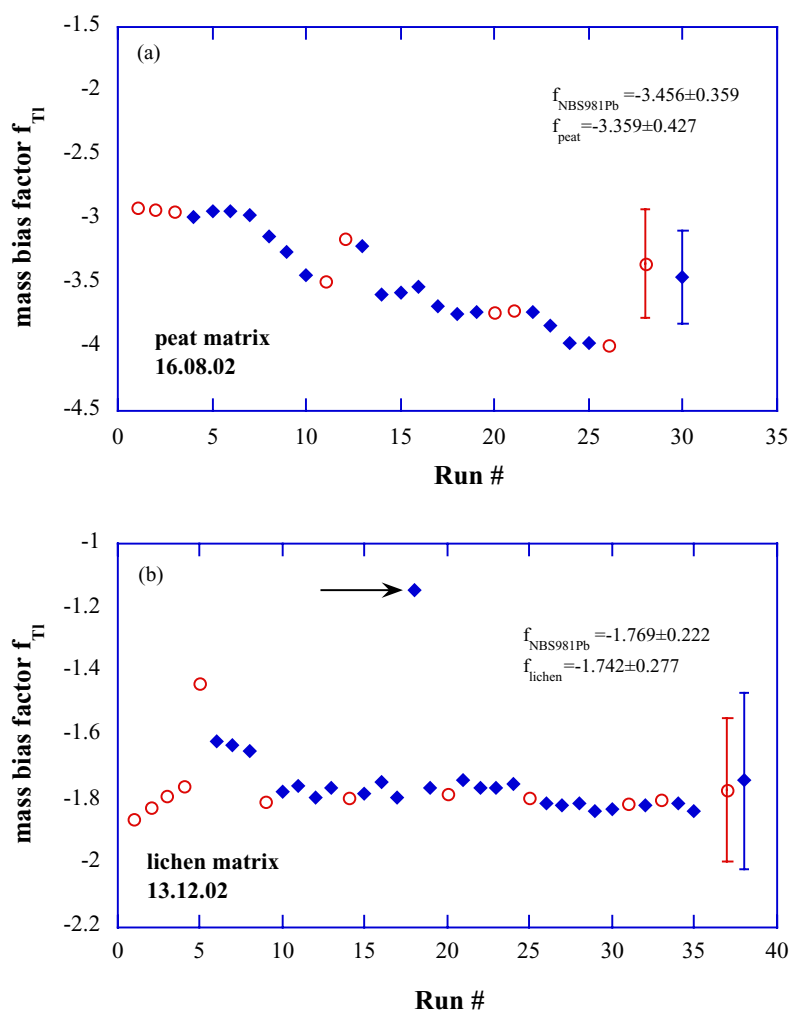


Fig. 2. Changing mass bias factors (f_{Tl}) of the spiked Tl during two measurement sessions in samples and NIST-SRM Pb 981: (a) measuring peat samples from the Faroe Islands, and (b) measuring lichens from the Karabash smelter. Open circles represent the NIST-SRM Pb 981 standard and the closed quadrangles represent the peat and lichen samples. The points with the error bars represent the mean value and the $\pm 2\sigma$ standard deviation.

Table 3

Comparison of selected published Pb isotopic composition of NIST-SRM 981 Pb measured by TIMS and MC-ICP-MS

Authors	Mass spectrometer	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Todt et al. (1995)	TIMS	2.16701 (43)	0.914585 (132)	16.9356 (23)	15.4891 (30)	36.7006 (112)
Galer and Abouchami [17]	TIMS	2.16771 (10)	0.914750 (35)	16.9405 (15)	15.4963 (16)	36.7219 (44)
Thirlwall [18]	TIMS	2.16770 (21)	0.91469 (7)	16.9409 (22)	15.4956 (26)	36.7228 (80)
Hirata [12]	MC-ICP-MS— <i>Plasma 54</i>	2.16636 (82)	0.914623 (37)	16.9311 (90)	15.4856	36.6800 (210)
Rehkaemper and Halliday (1995)	MC-ICP-MS— <i>Plasma 54</i>	2.16677 (14)	0.91469 (5)	16.9364 (55)	15.4912 (51)	36.7219 (44)
Belshaw et al. [11]	MC-ICP-MS— <i>Nu Plasma</i>	2.1665 (2)	0.91463 (6)	16.932 (7)	15.487	36.683
White et al. [7]	MC-ICP-MS— <i>Plasma 54</i>	2.1646 (8)	0.91404	16.9467 (76)	15.4899 (39)	36.6825 (78)
Rehkaemper and Mezger [13]	MC-ICP-MS— <i>IsoProbe</i>	2.16691 (29)	0.91459 (13)	16.9366 (29)	15.4900 (17)	36.7000 (23)
Reuer et al. [16]	MC-ICP-MS— <i>IsoProbe</i>	2.16639 (304)	0.91460 (18)			
This study	MC-ICP-MS— <i>IsoProbe</i>	2.16767 (63)	0.914767 (120)	16.9413 (39)	15.4974 (51)	36.7239 (115)

The Tl ratios used in this study were adjusted to the Galer and Abouchami value. The TIMS data are based on double and triple spike measurements. Errors shown refer to the least significant digits and are all given as $\pm 2\sigma$.

To achieve also accurate Pb isotope measurements in real samples using optimized Tl values derived from repeated NIST-SRM 981 Pb measurements, the mass bias of Tl in standard and samples has to be similar. Fig. 2 shows the calculated mass bias factors f_{Tl} for spiked sam-

ples and NIST-SRM 981 Pb standards using the optimized $^{205}\text{Tl}/^{203}\text{Tl}$ during two measurement sessions: 16.8.02 (Fig. 2a) when peat matrices were measured and 13.12.02 (Fig. 2b) when lichen matrices were measured. The average f_{Tl} in peat (-3.359 ± 0.427 ; $n = 18$) or lichen

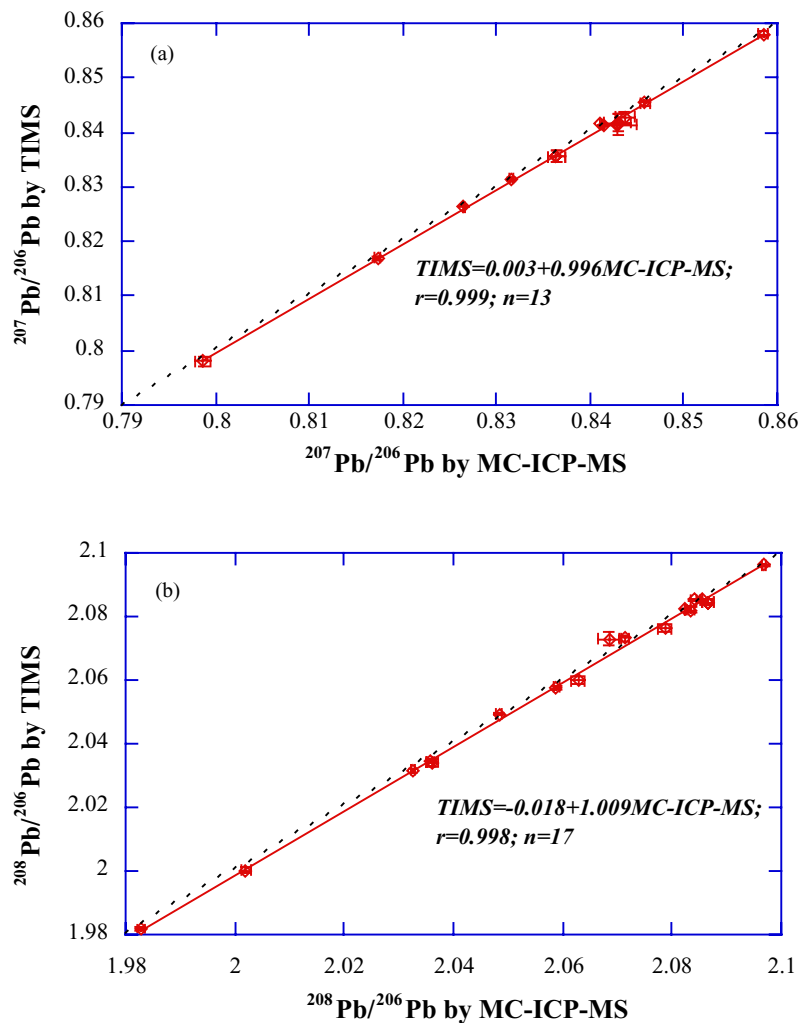


Fig. 3. TIMS and MC-ICP-MS data from selected silicate samples (whole rock and mineral separates from Ta–W ore-bearing granites). Shown is the best linear fit along with the theoretical (dashed) 1:1 line.

Table 4
Complete Pb isotope data set measured during the two environmental geochemical studies

Sample number	Sample ID	Sample type	Pb ($\mu\text{g g}^{-1}$)	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$ (%)	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$ (%)	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2\sigma$ (%)	$^{207}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)	$^{208}\text{Pb}/^{206}\text{Pb}$	$\pm 2\sigma$ (%)
Cu smelter near Karabash													
1	I 15 3	Lichen	68.0	17.911	0.0051	15.550	0.0044	37.874	0.0109	0.86816	0.0038	2.11455	0.0051
2	I 17 3	Lichen	120.0	17.897	0.0151	15.535	0.0131	37.847	0.0327	0.86798	0.0038	2.11469	0.0056
5	I 19 3	Lichen	111.0	17.975	0.0032	15.607	0.0028	38.065	0.0070	0.86824	0.0030	2.11767	0.0164
6	I 34 12 (1)	Lichen	213.0	17.916	0.0025	15.571	0.0020	37.856	0.0050	0.86908	0.0032	2.11293	0.0164
7	I 35 12 (2)	Lichen	151.0	17.906	0.0074	15.549	0.0067	37.830	0.0163	0.86837	0.0051	2.11265	0.0041
8	I 37/C	Lichen	n.d.	17.929	0.0018	15.572	0.0013	37.908	0.0033	0.86852	0.0032	2.11427	0.0042
9	I 1 K1	Lichen	112.8	17.935	0.0036	15.557	0.0029	37.840	0.0073	0.86741	0.0030	2.10983	0.0069
10	I 2 K2	Lichen	64.0	17.801	0.0269	15.457	0.0232	37.635	0.0555	0.86831	0.0065	2.11424	0.0041
11	I 4 K3	Lichen	118.2	17.896	0.0040	15.545	0.0036	37.788	0.0087	0.86860	0.0030	2.11152	0.0040
12	II 5 (D-2)	Vegetable	n.d.	17.831	0.0126	15.506	0.0109	37.684	0.0270	0.86962	0.0036	2.11338	0.0085
13	II 40 3	Lichen	100.6	17.854	0.0144	15.518	0.0130	37.718	0.0322	0.86913	0.0052	2.11251	0.0039
14	II 41/4	Lichen	446.5	17.899	0.0026	15.553	0.0021	37.798	0.0055	0.86890	0.0032	2.11173	0.0059
15	II 42/5	Lichen	1199.9	17.824	0.0142	15.505	0.0127	37.708	0.0313	0.86988	0.0050	2.11558	0.0075
16	II 43/6	Lichen	482.7	17.830	0.0223	15.489	0.0195	37.616	0.0487	0.86871	0.0048	2.10966	0.0045
17	II 44 (2)	Lichen	278.3	17.710	0.0186	15.463	0.0161	37.517	0.0399	0.87313	0.0059	2.11839	0.0071
18	II C1 (D-9)	Chimney dust	n.d.	17.841	0.0014	15.596	0.0007	37.822	0.0019	0.87414	0.0036	2.11990	0.0089
19	II C2 (D-10)	Chimney dust	n.d.	17.844	0.0009	15.599	0.0006	37.833	0.0014	0.87419	0.0028	2.12016	0.0075
20	II C4	Chimney dust	n.d.	17.921	0.0022	15.618	0.0019	37.952	0.0047	0.87149	0.0031	2.11770	0.0044
21	III 46	Lichen	n.d.	17.875	0.0188	15.488	0.0164	37.683	0.0410	0.86646	0.0063	2.10814	0.0047
22	III 49 C/12	Vegetable	175.6	17.913	0.0015	15.574	0.0012	37.864	0.0029	0.86943	0.0036	2.11380	0.0035
23	III 14/1	Vegetable	n.d.	18.044	0.0007	15.727	0.0004	38.342	0.0010	0.87156	0.0021	2.12489	0.0043
24	III 14/2	Vegetable	n.d.	18.003	0.0015	15.599	0.0010	38.015	0.0027	0.86648	0.0035	2.11155	0.0085
25	III KA 26/5	Vegetable	n.d.	17.813	0.0066	15.533	0.0057	37.689	0.0144	0.87201	0.0045	2.11582	0.0045
26	III 26	Vegetable	n.d.	17.901	0.0078	15.527	0.0069	37.776	0.0173	0.86740	0.0034	2.11032	0.0029
27	III KA 4/2	Vegetable	n.d.	17.961	0.0017	15.570	0.0012	37.899	0.0030	0.86687	0.0034	2.11002	0.0045
Average					0.0079		0.0068		0.0169		0.0039		0.0063
Myrarnar peat core													
1	Myr Neo 01	Peat	6	17.738	0.0046	15.583	0.0048	37.606	0.0053	0.87853	0.0015	2.12014	0.0037
2	Myr Neo 02	Peat	14.8	17.688	0.0044	15.582	0.0046	37.577	0.0050	0.88092	0.0018	2.12441	0.0051
3	Myr Neo 03	Peat	45.3	17.657	0.0028	15.562	0.0026	37.503	0.0030	0.88133	0.0046	2.12393	0.0108
4	Myr Neo 04	Peat	65	17.774	0.0061	15.567	0.0054	37.651	0.0054	0.87587	0.0017	2.11838	0.0041
5	Myr Neo 05	Peat	109.1	18.043	0.0030	15.599	0.0029	38.004	0.0036	0.86454	0.0015	2.10633	0.0036
6	Myr Neo 07	Peat	107.1	18.307	0.0078	15.621	0.0086	38.326	0.0094	0.85331	0.0017	2.09358	0.0048
7	Myr Neo 09	Peat	95.9	18.383	0.0124	15.616	0.0161	38.348	0.0203	0.84948	0.0046	2.08601	0.0114
8	Myr Neo 15	Peat	28.1	18.404	0.0018	15.637	0.0020	38.443	0.0022	0.84962	0.0013	2.08879	0.0032
9	Myr Neo 17	Peat	26	18.396	0.0043	15.620	0.0056	38.381	0.0067	0.84911	0.0018	2.08640	0.0043
10	Myr Neo 19	Peat	6.2	18.470	0.0067	15.629	0.0059	38.505	0.0058	0.84618	0.0022	2.08479	0.0062
11	Myr Neo 32	Peat	6.4	18.428	0.0046	15.626	0.0048	38.452	0.0053	0.84796	0.0015	2.08666	0.0035
12	Myr Neo 42	Peat	5.4	18.557	0.0054	15.614	0.0054	38.600	0.0059	0.84137	0.0018	2.08003	0.0043
Average					0.0053		0.0057		0.0065		0.0022		0.0054

The errors shown represent 'with-in run' precisions, which are in general better than the long term reproducibility (see text for details).

(-1.742 ± 0.277 ; $n = 23$) matrix does not differ significantly from the f_{Tl} in the NIST-SRM 981 Pb standards during the same measurement session (-3.456 ± 0.359 ; $n = 8$, and -1.769 ± 0.222 ; $n = 11$, respectively). The Tl mass bias is similar in samples and standards, suggesting that the ion exchange chemistry, high plasma temperature and/or the sample dilution prior to the measurements remove any possible interference. The significant different mass bias factors between two measurement sessions reflect the effect of an instrument upgrade which included a new interface.

3.2. Accuracy, precision, and reproducibility

3.2.1. Accuracy

Table 3 shows the average Pb isotope ratio of the NIST-SRM 981 Pb standard from repeated measurements ($n = 35$) during a 5-month period using optimized $^{205}\text{Tl}/^{203}\text{Tl}$ ratios for mass bias correction (August to December 2002). Also shown are TIMS and MC-ICP-MS data for the NIST-SRM 981 Pb standard from other laboratories. Average accuracy of 48, 70, 55, 41, and 77 ppm for the ratios $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$, and $^{208}\text{Pb}/^{206}\text{Pb}$, relative to the Galer and Abouchami value are achieved.

To get an estimate for the data accuracy for real samples, selected ore-bearing and barren granites (whole rock)

from the Orlovka-Spokoino mining district were measured with the *IsoProbe* MC-ICP-MS and with the *MAT 261* TIMS. Fig. 3 shows the $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios measured in the same aliquot using the different instruments. Linear regressions ($[^{207}\text{Pb}/^{206}\text{Pb}]_{\text{TIMS}} = 0.003 + 0.996[^{207}\text{Pb}/^{206}\text{Pb}]_{\text{MC-ICP-MS}}$; $r = 0.999$; $n = 13$; $[^{208}\text{Pb}/^{206}\text{Pb}]_{\text{TIMS}} = 0.018 + 1.009[^{208}\text{Pb}/^{206}\text{Pb}]_{\text{MC-ICP-MS}}$; $r = 0.998$; $n = 17$) and the theoretical 1:1 line are shown. A systematic offset between TIMS and MC-ICP-MS exists, which has been described also with the *VG Plasma 54* [7]. The results agree on average within 0.08% for both $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios. Similar agreements between MC-ICP-MS and TIMS data for real samples were described for ferromanganese crust [11], volcanic rocks [7], archeological samples [13], and peat samples [31].

3.2.2. Precision and reproducibility

Table 4 shows an entire set of isotope ratios and internal precision expressed in $\pm 2\sigma$ (%) measured during the two environmental studies in various different environmental matrices. The error of the internal isotope measurements is considerably better (on average below 100 ppm) than the errors estimated from the long-term reproducibility. The measured solutions were diluted to a concentration, which allowed a signal of ≥ 100 mV on ^{204}Pb . Typically, that was 50 ng ml^{-1} .

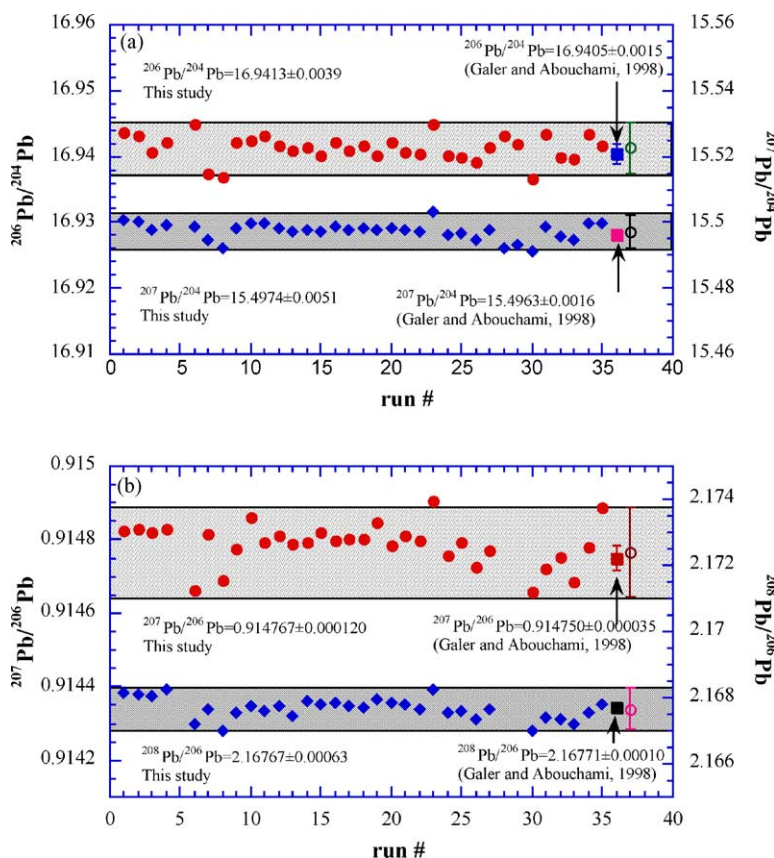


Fig. 4. Typical long-term reproducibility achieved for the ratios (a) $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$, and (b) $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios on the Micromass *IsoProbe* MC-ICP-MS determined from repeated measurements of NIST-SRM 981 Pb standards spiked with NIST-SRM 997 Tl over the time period of 5 months (August to December 2002).

Fig. 4 shows the long-term reproducibility of the *Iso-Probe* MC-ICP-MS using repeated NIST-SRM 981 Pb measurements over a 5-month period (August to December 2002). Errors (in ppm) are 227 for $^{206}\text{Pb}/^{204}\text{Pb}$, 326 for $^{207}\text{Pb}/^{204}\text{Pb}$, 314 for $^{208}\text{Pb}/^{204}\text{Pb}$, 126 for $^{207}\text{Pb}/^{206}\text{Pb}$, and 292 for $^{208}\text{Pb}/^{206}\text{Pb}$. The errors estimated using the long-term reproducibility are significantly higher than the ones estimated from a single measurement session (short-term reproducibility), which was in general below 200 ppm for the $^{208}\text{Pb}/^{204}\text{Pb}$ ratio and below 150 ppm for all the other ratios (data not shown). The long-term reproducibility of the MC-ICP-MS is similar to the Heidelberg TIMS and agrees well with other laboratories using MC-ICP-MS [7,10–13,32]. Reproducibility estimated from ‘true’ replicate measurements (different aliquots of same solution) showed similar errors to the ones determined by the repeated measurements of NIST-SRM 981 Pb [31].

3.3. Applications to environmental geochemical studies

Using these new analytical (ion exchange column, high temperature/high pressure microwave digestions) and modified data processing ($^{205}\text{Tl}/^{203}\text{Tl}$ optimization) procedures, we achieved high precision Pb isotope ratio measurements in peats, lichens, vegetables, and chimney dust during two environmental geochemical projects conducted in London and Heidelberg. One study aimed to assess the local dispersal of Pb and other heavy elements from a Cu smelter using lichen as biomonitors [24], the second study aimed to characterize sources and pathways of Pb and Hg in the sub-Arctic region using a dated peat core in the Faroe Islands [23].

Fig. 5 shows three isotope plots including ^{208}Pb , ^{207}Pb , and ^{206}Pb measured during the two studies. The differences in the isotope ratios among the individual samples are significant on the $\pm 2\sigma$ confidence level and the errors (derived from the long-term reproducibility) plot within the symbols.

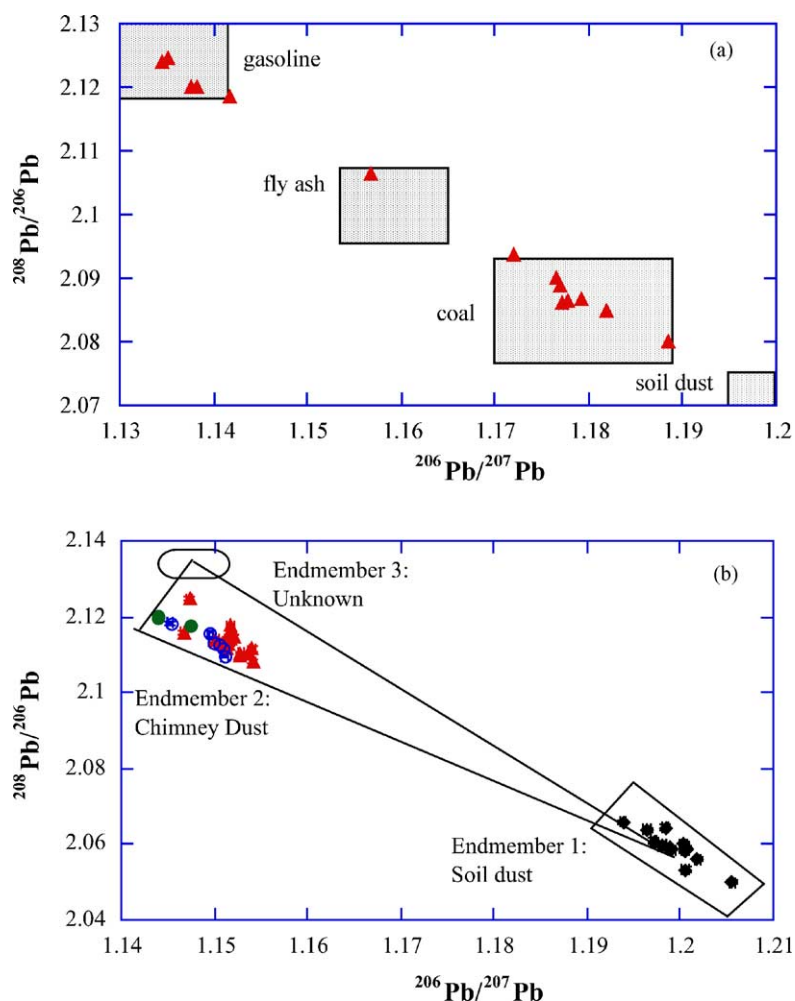


Fig. 5. Three isotope plots including the isotopes ^{208}Pb , ^{207}Pb , and ^{206}Pb of the two different environmental geochemical studies assessing Pb dispersal into the environment: (a) Pb isotope data from chimney dust, vegetable and lichens within the vicinity of a Cu smelter in the Urals (Purvis et al. [24]) and (b) Pb isotope data from a peat core in the Faroe Islands (Shotyck et al. [23]).

3.3.1. Lead sources from long-range atmospheric transport in the sub-Arctic

Fig. 5a represents Pb isotope data measured in a peat bog profile collected in the Faroe Islands (representing ca. 2500 years of atmospheric Pb deposition) with variations of $^{206}\text{Pb}/^{207}\text{Pb}$ (1.13–1.19) and $^{208}\text{Pb}/^{206}\text{Pb}$ (2.07–2.12) ratios, which are significantly larger (5 and 2%, respectively) than the estimated long-term reproducibility for these isotope pairs (0.013 and 0.029%, respectively). The large variations of isotope signatures in the peat samples are due to the different Pb sources (gasoline, coal, soil dust, waste incineration, represented as gray fields in Fig. 5a and estimated from data taken from Ref. [33]), which characterized the atmospheric Pb deposition in Europe during the last 2500 years [1,34]. The error bars plot well within the symbols and the individual samples are clearly discernible. The detailed geochemical discussion is given elsewhere [23], but the conclusions agree well with other peat records in Europe covering the last 2500 years of atmospheric Pb deposition [33,35].

3.3.2. Lead sources around a Cu smelter

Fig. 5b shows Pb isotope data measured in lichens, vegetables, and chimney dust around the Cu smelter in Karabash, Southern Urals. The range of $^{206}\text{Pb}/^{207}\text{Pb}$ and of $^{208}\text{Pb}/^{206}\text{Pb}$ (1.14–1.15 and 2.11–2.12, respectively) is considerably smaller (0.9 and 0.7%, respectively) than in the peat study, but the variations are still an order of magnitude larger than the estimated errors of the individual data points using the long-term reproducibility. Most ratios of the lichens and vegetables plot on a mixing line between two end members—smelter dust (represented by the isotopic composition of the chimney dust) and natural background Pb (represented by pre-anthropogenic aerosols [36]). However, a statistically significant scatter in the data is revealed and several samples are off the simple two component mixing line, which suggests that a third end member (most likely anthropogenic) with higher ^{208}Pb and higher ^{207}Pb concentrations remains unidentified. The data set shows that with the precision achieved, even on a local scale pollution with small variations, new end members can be identified hinting to additional sources. Such detailed source assessment in a local pollution study has previously been achieved using TIMS [37] but not ICP-QMS [38].

4. Conclusions

A wide range of environmental samples was dissolved using microwave-assisted acid digestion for biological samples or conventional hot plate acid digestion for silicates. After digestion, the solutions were passed through an ion exchange column packed with EiChrom Sr-resin applying a new simple monoacid elution procedure. The column chemistry yielded quantitative recoveries of Pb and allowed a high sample throughput.

Analysis of ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb in 50 ng ml⁻¹ solutions on an *IsoProbe* MC-ICP-MS resulted typically in internal precisions of below 100 ppm ($\pm 2\sigma$) on all Pb isotope ratios in all matrices. Mass bias correction using optimized $^{205}\text{Tl}/^{203}\text{Tl}$ ratios achieved accuracies below 80 ppm for all ratios. The Tl optimization was achieved using repeated measurements of NIST-SRM 981 Pb spiked with NIST-SRM 977 Tl during a measurement session and fitting the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio using a least square approximation. The optimized Tl ratio used for mass bias correction had to be adjusted for each measurement session up to 2.3907. The long-term reproducibility (expressed as $\pm 2\sigma$) determined over a 5-month period using repeated measurements of the NIST-SRM 981 Pb standard and optimized Tl values was below 350 ppm for all ratios. Ore-bearing granites samples passed through the columns and measured with TIMS and MC-ICP-MS showed excellent correlation. The mass bias of Tl spiked into natural and synthetic samples during a measurement session did not differ significantly, indicating that the complex peat and lichen matrix did not affect the mass bias behavior of the Tl spike.

Acknowledgements

We thank Sara Russell, Eta Mullane, Caroline Smith, Teresa Jeffries, Derek Jones, Mathieu Gounelle, Dietlinde Pingel, and Nicole Rausch for the help in the laboratory and William Shoty, William Purvis, and Reimar Seltmann for the stimulating collaborative research. Mike Warner, Andy Fleet, and Terry Williams are thanked for support. Financial support from NERC, the Leverhulme Trust, Imperial College London, and The Natural History Museum is gratefully acknowledged. This paper benefited greatly from the discussions with other isotope and environmental geochemists, especially Matthew Thirlwall, Mark Rehkaemper, Ed Boyle, Kevin Foy, Matt Reuer, and Jan Kramers. We also thank the anonymous reviewer and Professor Schwarz for editorial handling. D.W. dedicates this paper to Rosa, Jakob and Claudia.

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