

# Multicollector ICP-MS analysis of Pb isotopes using a $^{207}\text{Pb}$ - $^{204}\text{Pb}$ double spike demonstrates up to 400 ppm/amu systematic errors in Tl-normalization

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## Abstract

Pb isotope analyses using multicollector magnetic sector inductively coupled plasma mass spectrometers (ICP-MS) may potentially be corrected for mass bias, a major source of uncertainty, by assuming that the mass bias for Tl is similar to that of Pb. Around 7 ng of Pb has been analysed in this study using a Micromass IsoProbe MC-ICP-MS. With detailed attention to backgrounds arising from instrument memory and tailing from adjacent peaks, external precision of 55–180 ppm 2sd has been achieved over a year on Pb isotope ratios normalized to constant  $^{208}\text{Pb}/^{206}\text{Pb}$ . This involves use of a wide range of SRM981 solutions and two different nebulizers. Mean ratios are very close to multidynamic TIMS data normalized in the same way, provided that anomalous TIMS behaviour of  $^{207}\text{Pb}$  [Chem. Geol. Isot. Geosci. Sect. 163 (2000) 299] is corrected to the least fractionated ratios measured. Tl-normalized Pb isotope ratios vary substantially between different SRM981 solutions and between nebulizers, with external precision over the year being up to 541 ppm (2sd) on  $^{208}\text{Pb}/^{204}\text{Pb}$ . However, a  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  double spike (DS) can accurately correct for mass bias on the IsoProbe, and external precision of at worst 245 ppm (2sd) on  $^{208}\text{Pb}/^{204}\text{Pb}$  has been obtained over the year using a wide range of SRM981 solutions and two different nebulizers. Mean ratios on DS-corrected SRM981 and silicate samples are within error of DS-TIMS results, even using an independent calibration for the DS on the IsoProbe. A new  $^{208}\text{Pb}/^{206}\text{Pb}$  value for SRM981 of  $2.1677 \pm 2$  is proposed, normalized to SRM982  $^{208}\text{Pb}/^{206}\text{Pb} = 1.00016$ . Use of SRM981 to optimize the  $^{205}\text{Tl}/^{203}\text{Tl}$  normalizing ratio would give Tl-normalized sample ratios  $\sim 400$  ppm/amu higher than those calculated using the DS correction. It is shown that these problems with Tl normalization cannot result from isobaric interferences, but they appear to be due to unusual solution chemistry of Tl in the nebulizer. © 2002 Published by Elsevier Science B.V.

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## 1. Introduction

Variations in the relative abundances of Pb isotopes provide the most effective method of investigating

mixing in natural systems (e.g. Thirlwall et al., 1998; Abouchami et al., 1999). This is because three of the four Pb isotopes are daughter products of independent long-lived radioactive parents, and thus two and three components mixing define linear and planar arrays in three-dimensional Pb isotope ratio space. Further, the three decay systems allow age determinations over the range from a few ka (e.g. Richards et al., 1998) to 4.5

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Ga. The full potential of Pb isotope data for natural systems has not yet been realised owing to the difficulty of making an accurate correction for mass fractionation during mass spectrometric analysis. Unlike other natural radioactive decay systems (e.g. Sr, Nd, Os), Pb has only one non-radiogenic isotope of mass 204, so there is no ratio for which a constant natural value can be assumed to allow correction of all other measured isotope ratios for the observed mass bias. Instead, mass bias correction during thermal ionization mass spectrometry (TIMS) has conventionally been based on a combination of minimizing the variation in mass bias during analysis and assuming that repeated analysis of a standard sample, typically NIST SRM981, can accurately determine the mean mass bias of unknown samples. Although many laboratories report 2sd external precision of SRM981 of  $\pm 0.010$ – $0.020$  on  $^{206}\text{Pb}/^{204}\text{Pb}$  ( $\sim 0.015$ – $0.030\%$ /amu 1sd), it has been shown that this is a distinctly optimistic assessment of inter-laboratory sample reproducibility (Thirlwall, 2000).

Two methods have been successfully used over the past 5 years to improve on this external normalization technique. Firstly, a variety of Pb double spikes (DS, i.e. combinations of two, and sometimes more, strongly enriched Pb isotopes) have been used in TIMS to monitor mass bias. Todt et al. (1996) reported the use of a DS strongly enriched in the artificial  $^{202}\text{Pb}$  and  $^{205}\text{Pb}$  isotopes, and achieved much better reproducibility and defined a benchmark isotopic composition for the standard SRM981. Woodhead et al. (1995), Galer and Abouchami (1998) and Thirlwall (2000) have all used double or triple spikes enriched in  $^{207}\text{Pb}$  and  $^{204}\text{Pb}$ , which require separate isotopic analysis of unspiked and spiked aliquots of a sample. Together these can uniquely define the mass-bias-corrected isotopic composition of an element with four or more isotopes provided that the spike composition is known (e.g. Dodson, 1963). The latter two groups independently achieved 2sd external precision of  $\sim \pm 0.002$  in  $^{206}\text{Pb}/^{204}\text{Pb}$  and essentially identical ratios for SRM981 which are gradually replacing the benchmark values of Todt et al. (1996).

In parallel with the work on double/triple spikes, the development of commercial inductively coupled plasma mass spectrometers (ICP-MS) with magnetic sector geometry and multicollection has yielded a

second potential method for accurate mass bias correction of Pb isotope ratios. This is because these instruments have very stable mass bias (at times within counting statistics on  $5 \times 10^{-11}$  A ion beams over 1-h periods on the Royal Holloway instrument), and because the mass bias of one element is similar to that of another with similar atomic number (Longerich et al., 1987). Consequently thallium, with isotopes  $^{203}\text{Tl}$  and  $^{205}\text{Tl}$ , has been used to correct for Pb mass bias. Significantly better external precisions than conventional TIMS data have been obtained for SRM981, typically  $\pm 0.003$ – $0.006$  2sd on  $^{206}\text{Pb}/^{204}\text{Pb}$ , and  $^{207}\text{Pb}/^{206}\text{Pb}$  reproducibility comparable to DS TIMS (e.g. Hirata, 1996; Belshaw et al., 1998; Rehkämper and Halliday, 1998; Vance and van Calsteren, 1999; White et al., 2000; Rehkämper and Mezger, 2000). However, the Tl-normalized MC-ICP-MS data for SRM981 often do not agree within error with the DS-TIMS data (e.g. Rehkämper and Halliday, 1998; White et al., 2000), and in all studies the Tl isotope ratio must be optimized to provide the best fit to DS-TIMS data (e.g. Rehkämper and Mezger, 2000).

In this paper, I discuss the requirements for obtaining reproducible Pb isotope data on the IsoProbe at Royal Holloway. This is a MC-ICP-MS instrument manufactured by Micromass (UK), which uses a hexapole collision cell flushed with Ar to reduce the energy spread of ions produced in the plasma torch, instead of using an electrostatic analyser to focus the ion beam into the multicollector array. I show that with careful attention to backgrounds, in particular to tail corrections, it is straightforward to obtain internally normalized data for SRM981 of comparable external precision to DS-TIMS data on a wide range of Tl-bearing and Tl-free solutions. Further, these data lie within error of DS-TIMS data. However, different SRM981 solutions yield systematically different Tl-normalized Pb ratios implying that there is a sample-dependent effect on the ability of Tl to correct for Pb mass bias. Further, the isotopic ratio of Tl inferred to achieve accurate Pb ratios for SRM981 (c.f. Rehkämper and Halliday, 1998) yields systematically incorrect Tl-normalized Pb ratios for samples previously analysed by DS-TIMS. In contrast, correction of MC-ICP-MS mass bias using a  $^{207}\text{Pb}/^{204}\text{Pb}$  DS yields both SRM981 and sample ratios within error of DS-TIMS.

## 2. Analytical details

### 2.1. Sample/standard preparation

All reagents listed below were purified by 2–3× sub-boiling distillation, except water generated by a MilliQ element plant, and were checked by isotope dilution to have <2 ppt Pb before use. All work took place under a Class 100 cleanhood. SRM981 and 982 Pb and SRM997 Tl standard metals were dissolved in HNO<sub>3</sub> in FEP bottles and diluted with water to stock solutions in FEP bottles at 8–40 ppm. A “Reference” SRM981 solution at 50 ppb Pb–5 ppb Tl was made by diluting these in a FEP bottle, and was used for standard analyses in the early part of this study. The double spike solution of Thirlwall (2000) was also used in this study (~1.2 ppm <sup>207</sup>Pb, ~0.27 ppm <sup>204</sup>Pb).

Following leaching of rock chips or powders (Thirlwall, 2000), rock samples were prepared by conventional acid digestion in a 3-ml Savillex capsule. A single-pass HBr-based anion resin separation, with 6 M HCl collection, subsequently converted to nitrate, provides sufficiently clean samples. For each batch of analyses, fresh 1–2 wt.% HNO<sub>3</sub> was prepared in a FEP bottle as a blank solution. This was used to dilute a small drop of 37 ppm SRM997 solution to ~5 ppb Tl in a FEP dropper bottle. Based on an estimated (and very variable!) 50% loss of Pb in the leaching procedure, sufficient ~5 ppb Tl solution was added to the capsule to dissolve the samples and achieve ~50 ppb Pb in solution. To aid dissolution, capsules were placed on a hotplate for 1–6 h at 120 °C and then decanted into 1.5 ml centrifuge tubes on the morning of analysis. Centrifugation is important to avoid any particulates from blocking the uptake capillary tube, and also, since the double spike should not be introduced into the Savillex capsules, the centrifuge tubes provide a common container in which both the natural and natural-DS mix can be run. Initially, teflon tubes were used, but acceptable blanks were since achieved in polypropylene. Two procedure blanks, prepared in the same way and spiked with <sup>208</sup>Pb after column collection, were run with each 10 samples, and agreed to ~3 pg in the range 30–60 pg, apart from two early sample batches with 100–200 pg, due to contaminated cleaning acids.

SRM982 solutions were prepared by diluting 1–2 drops of the 6 ppm stock solution with the ~5 ppb Tl in a 6-ml Savillex capsule, and, sporadically during the early part of the study, and routinely later on, fresh SRM981 was prepared in a similar way with each batch of samples. In order to ensure comparable treatment to the samples, the drop of SRM981 was sometimes evaporated and nitrated prior to adding the ~5 ppb Tl, and on one occasion was taken through the full digestion and column procedure. Both SRM981 and 982 were also diluted with the Tl-free blank solution on some occasions. Pure double spike and DS-SRM981 or 982 mixtures were prepared by pipetting a small amount of DS into a teflon centrifuge tube containing the ~5 ppb Tl solution or the diluted Pb standards used for natural Pb composition analysis.

### 2.2. IsoProbe running parameters

Samples and standards were freely aspirated into either an Aridus desolvating nebulizer manufactured by Cetac or a Micromist nebulizer with cinnabar spray chamber made by Glass Expansion. Both have uptake rates of ca. 30 µl/min, and sensitivity of the instrument is typically ca.  $4 \times 10^{-9}$  A total ion beam per ppm dissolved Pb on the Aridus and  $5 \times 10^{-10}$  A/ppm Pb on the Micromist. For the latter, some more concentrated Pb standard solutions (~300 ppb) were run in addition to the Reference SRM981. The inlet system was cleaned with 5% HNO<sub>3</sub> followed by 2% HNO<sub>3</sub> between samples, until a stable Pb background was observed, before analysing the blank solution (15–30 min, Section 3.2). Gas flows were kept constant from day to day (at 14.0 l/min cool gas, 0.75 l/min intermediate and 0.85 l/min nebulizer gas), apart from using the nebulizer gas flow on the Micromist, and Ar sweep gas on the Aridus to optimize sensitivity each morning. Nitrogen was not used in the Aridus. Daily optimization was additionally performed on the torch position (without changing its nearly fully forward position) and on the beam focus voltages. On consecutive days, very little change was observed in these optimized parameters.

Ni sample and skimmer cones were changed infrequently (every ~2 months): the only effect of this was a reduction in sensitivity, particularly at maximum extraction potential (40%). Since lower extraction reduces baseline signal, values lower than

maximum were usually set each day to achieve near-maximum sensitivity but lower baseline. On some days, extraction voltage was varied to compensate for variations in solution Pb concentration, though usually constant extraction was used and an additional dilution with  $\sim 5$  ppb Tl solution was made if needed at the time of analysis. Changing extraction changes mass bias, and provides an important test for the mass bias correction procedure used. Where the absolute mass bias factor is discussed in this paper, extraction was held constant.

All analyses reported here were determined in static mode on Faraday collectors. Collectors were aligned High1= $^{203}\text{Tl}$  to High6= $^{208}\text{Pb}$ , with the axial Faraday used for  $^{202}\text{Hg}$  (early data) or  $^{201}\text{Hg}$  (later data), and the two low-mass collectors used for  $^{201}\text{Hg}$  and  $^{198}\text{Hg}$  (early data) or  $^{198}\text{Hg}$  and  $^{187}\text{Re}$  (later data). Cup efficiencies were set to unity as evidence from multidynamic and static Hf/Nd analysis suggests that they are within 100 ppm of unity, while little difference in Pb isotope ratios was observed when run with three different collector configurations. Resistor gains were calibrated each night before analysis; they vary by  $<10$  ppm between consecutive days. Raw signal intensities were corrected only for resistor gains before transfer to and further manipulation in an excel spreadsheet.

### 2.3. Precision and introduction to accuracy

With typical signal intensity of  $\sim 7 \times 10^{-11}$  A  $^{208}\text{Pb}$ , internal precisions of  $\pm 0.001$  (2se) on  $^{206}\text{Pb}/^{204}\text{Pb}$  in common Pb are usually obtained on means of 50 ratios at 5 s integration. At this signal intensity for common Pb, it was calculated that optimum use of analysis time required 25 5 s measurements on the blank solution. The same analysis time would require sample/blank of 44:31 integrations at  $^{206}\text{Pb}/^{204}\text{Pb}=100$  and 39:36 at  $^{206}\text{Pb}/^{204}\text{Pb}=500$  to optimize precision. For sample-DS mixed runs,  $^{204}\text{Pb}$  is no longer a minor isotope and adequate precision is obtained on  $\sim 25$  sample and 15 blank integrations. Total Pb sample consumption is ca. 7 and 44 ng Pb on the Aridus and Micromist, respectively, substantially lower than the 500, 200–300 and  $\sim 150$  ng used by Belshaw et al. (1998), Vance and van Calsteren (1999) and White et al. (2000), respectively.

Three main factors potentially affect the accuracy of the measured Pb isotope ratios that are not major

effects in TIMS Pb analysis, and are discussed in detail in the following sections.

(1) The IsoProbe has significantly worse abundance sensitivity than TIMS and most other MC-ICP-MS instruments (Thirlwall, 2001), resulting from relatively poor analyser vacuum ( $\sim 2.5 \times 10^{-8}$  mbar during the course of this study). The tailing of large peaks onto adjacent peaks caused by this forms a component of background.

(2) The whole inlet system to the torch has surface contact with the sample solution which inevitably results in some memory of prior samples. Further, other trace components of the sample solution, and the plasma and collision cell gases, are ionized as efficiently as sample Pb and may generate isobaric interference. Oxide production varies depending on the nebulizer being used (it should be lower on the Aridus, due to its desolvating character) and may generate additional isobaric interference. On the Royal Holloway IsoProbe,  $\text{NdO}^+/\text{Nd}$  was  $\sim 1\text{--}2\%$  on the Aridus in the early part of this work, and reduced to 0.2% after correction of leaks in the hexapole collision gas line. Again, all these effects contribute to the background.

(3) The magnitude of the mass bias is large ( $\sim -0.8$  to  $-1.2\%$ /amu) compared with TIMS ( $\sim +0.10\%$ /amu), and consequently, it is most important that an accurate mass bias correction procedure is used. Tl-normalization, as used in previous studies, and DS-normalisation are both used in this study. The algebraic form of the mass bias law is also an important consideration (Hirata, 1996; Rehkämper and Halliday, 1998).

## 3. Backgrounds

### 3.1. Tails

The ion current at a particular mass reflects the analyte Pb and Tl; tails from adjacent analyte masses onto the mass of interest; memory Pb and Tl in the introduction system through to the cones; blank Pb in the solution matrix; isobaric interferents derived from sample, inlet system and plasma gases; and the zero offset of the amplifiers. Tailing is a significant issue on the IsoProbe, as the specified abundance sensitivity of  $<15$  ppm of  $^{238}\text{U}$  at mass 237 is significantly worse than for other similar instruments (see

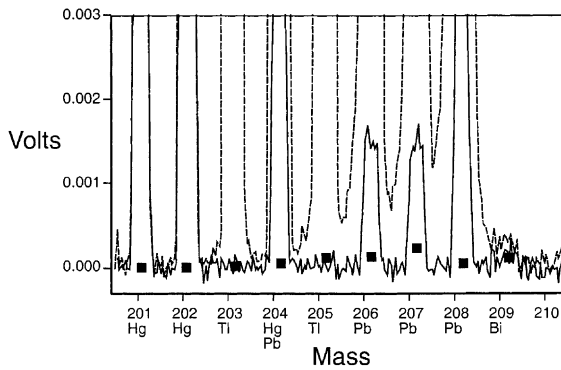


Fig. 1. Scan of Tl–Pb mass spectrum for Reference SRM981 (dashed line) and a wash solution (solid line) showing that tails derived from half-masses, whatever interpolation method is used, grossly overestimate the true tail at unit mass (solid squares). Tail curves are measured on monoisotopic Bi and the true tail shown here is calculated by integrating the contributions from masses up to 3 amu either side of the mass considered. For details, see Thirlwall, 2001.

comparison in Thirlwall, 2001). The observed abundance sensitivity on the Royal Holloway IsoProbe was 18–25 ppm of  $^{209}\text{Bi}$  at mass 208 during the course of this study, but improved to 8 ppm in May 2001, following rectification of two major leaks on the analyser. The abundance sensitivity is primarily controlled by analyser vacuum: Ar pressure in the hexapole has very little influence unless the hexapole is grossly detuned.

In static TIMS analysis, it is common to correct for tail using background measurements at  $\pm 0.5$  amu from the peak of interest, and a similar approach has been applied to MC-ICP-MS Pb analysis (Rehkämper and Mezger, 2000; while White et al., 2000 used only  $+0.5$  amu baselines). Using tails determined using a peakjumping routine up to  $\pm 3$  amu away from  $\sim 8$  V  $^{209}\text{Bi}$ , the true tails under the Pb peaks can be calculated from the observed Pb and Tl ion beam

intensities (Thirlwall, 2001). This is illustrated in Fig. 1, where the half-mass baselines on a scan are seen to be up to four times larger than the actual peak tails. It is straightforward to obtain precisions of  $<\pm 1$  ppm on the  $^{209}\text{Bi}$  tails, and they appear to be reproducible to  $\pm 1$  ppm over 7-day periods. All isotope ratios are calculated off-line, where these tails are applied to all measured ion beam intensities. Although these tail magnitudes may seem small, they have a substantial impact on measured isotope ratios (Table 1). Further, Thirlwall (2001) has shown that use of half-mass baselines for Tl-doped Pb-isotope analysis on the IsoProbe results in correlations between Pb/Tl ratios and Tl-normalized Pb isotope ratios very similar to those regarded as a matrix effect by Rehkämper and Mezger (2000). The success of this correction technique is judged by the fact that  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios for SRM981 standard are, after normalization to constant  $^{208}\text{Pb}/^{206}\text{Pb}$ , identical between Tl-spiked and Tl-free solutions (means  $16.9419 \pm 26$  and  $16.9417 \pm 17$  2sd, respectively).

### 3.2. Memory

Prior to each sample analysis, the 1–2%  $\text{HNO}_3$  used to prepare the  $\sim 5$  ppb Tl solution (Section 2.1) was analysed. These on-peak zeroes (OPZ) can correct for Pb in the blank solution, memory Pb and Tl in the inlet system, the amplifier offsets and some isobaric interferences. It is important that the blank solution measured should be identical to that used to dilute samples and standards, both in blank Pb content and in acid molarity, as changing acid molarity can strip additional Pb from the inlet system memory. In the early stages of this work, a single mixed SRM981–Tl solution was used as a standard, with different blank solutions daily: this appears to have caused no problems since the  $^{208}\text{Pb}/^{206}\text{Pb}$ -normalized Pb ratios

Table 1  
Pb and Tl isotope ratios based on three models for tail correction

	$^{208}\text{Pb}/^{206}\text{Pb}_m$	$^{204}\text{Pb}/^{206}\text{Pb}_N$	$^{207}\text{Pb}/^{206}\text{Pb}_N$	$^{205}\text{Tl}/^{203}\text{Tl}_N$
Half-mass zeroes	$2.20991 \pm 3$	$0.059007 \pm 3$	$0.914777 \pm 15$	$2.38980 \pm 8$
Measured tails	2.20979	0.059025	0.914910	2.39016
No tail correction	2.20969	0.059043	0.914963	2.39049

Data for SRM981 with  $^{205}\text{Tl}/^{206}\text{Pb} = 0.30$  measured in February 2000 before routine measurement of tails. Subscript m refers to measured ratio, subscript N refers to ratios normalized to  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677$ .

Half-mass zero correction used linear interpolation between the measured baselines.

are identical to those obtained subsequently. Although amplifier offsets are corrected by subtracting OPZ intensities, this loses valuable information on the nature of the memory. Thus, as well as subtracting the OPZ from the analyte signals, the absolute OPZ signal intensities are calculated for each sample by subtraction of the amplifier offsets, which are measured a few times each day with no ion beam in the analyser. Fig. 2 shows typical behaviour of the OPZ signals over the course of a few days.

The  $^{208}\text{Pb}$  signal of the OPZ ranged from 0.2 to 2 mV, representing on average 0.04% of the sample  $^{208}\text{Pb}$  ion beam intensity, apart from blank analyses. Increase in the signal with time at the start of an analytical session (e.g. Fig. 2) was traced to progressive contamination of the blank solution by the sampling probe: subsequently the blank solution was analysed from a 1.5-ml centrifuge tube replenished about every two samples from a stock bottle. OPZ intensity is controlled strongly by extract potential (Fig. 2), which can thus be used to improve signal/noise ratio.  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  of the OPZ average  $2.27 \pm 0.27$  and  $0.93 \pm 0.19$  (2sd on 116 unspiked runs studied), close to measured Pb isotope ratios for SRM981 (2.21 and 0.924, respectively), indicating that this is the dominant source of the memory. Analysis using the Aridus of a set of samples spiked with  $^{208}\text{Pb}$  to give beam intensities of  $2-6 \times 10^{-11}$  A and  $^{208}\text{Pb}/^{206}\text{Pb}$  of 14–60 caused a small increase in memory  $^{208}\text{Pb}/^{206}\text{Pb}$  from 2.2 to 2.5 (Fig. 2). Similarly, analysis of samples spiked with the  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  double spike (DS) of Thirlwall (2000) to give  $^{207}\text{Pb}/^{206}\text{Pb}$  of  $\sim 3.5$  caused increase in memory  $^{207}\text{Pb}/^{206}\text{Pb}$  from 0.9 up to 1.3 or even 1.7 on some days (e.g. Fig. 2). No clear differences in this effect were observed between the different types of inlet system used. In all cases, the changes in memory ratios are smooth with time, suggesting that accurate correction for memory should be possible.

Apart from some samples spiked with  $^{208}\text{Pb}$ , the observed memory correction to  $^{208}\text{Pb}/^{206}\text{Pb}$  on samples analysed so far is within the ratio error. For  $^{207}\text{Pb}/^{206}\text{Pb}$ , the changes caused by the memory correction are often larger than analytical error, so it is important to assess how accurately this correction can be made. The accuracy depends primarily on whether the OPZ  $^{208}\text{Pb}$  signal is really representative of the memory tapped by the sample solution, since

the uncertainty in memory  $^{207}\text{Pb}/^{206}\text{Pb}$  is also a function of memory  $^{208}\text{Pb}$  signal. This can be judged by the consistency of the memory  $^{208}\text{Pb}$  signal between samples: provided machine conditions such as extract potential are held constant, it rarely changes by more than 0.2 mV between samples (Fig. 2a), and some of this is probably a consequence of analysing the intervening sample. Drift in memory  $^{208}\text{Pb}$  signal without running samples is much less than 0.1 mV over 15 min. A 0.2 mV uncertainty on memory  $^{208}\text{Pb}$  signal propagates in most cases to an error on  $^{207}\text{Pb}/^{206}\text{Pb}$  much less than the counting statistics error. The only exceptions are runs for which the  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  DS has been added; in these the additional uncertainty is about twice the counting statistics error. The success of our clean-out and memory correction procedure can be judged by the fact that SRM981 analysed immediately after a set of samples with DS gives indistinguishable ratios from other SRM981 analyses.

### 3.3. Isobaric interferences

Three isobaric interferences have been identified in the samples analysed so far ( $^{204}\text{Hg}$ ,  $\text{WO}^+$  and  $\text{ReO}^+$ ), and the presence of more is suspected.  $^{204}\text{Hg}$  (6.85% of Hg) in plasma Ar and elsewhere in the instrument has long been recognised as an important isobaric interferent on  $^{204}\text{Pb}$ . This is conventionally corrected by measuring the  $^{202}\text{Hg}$  ion beam (29.8% of Hg; e.g. White et al., 2000), but since very little Hg is present in chemically processed samples, it may also be efficiently removed using the OPZ. This has the advantage that it is not necessary to know accurately the  $^{204}\text{Hg}/^{202}\text{Hg}$  ratio. The  $^{202}\text{Hg}$  signal in the OPZ varied from 3.8 to 24.8 mV on the Aridus, and is roughly linearly correlated with extract potential. On the Micromist nebulizer, the  $^{202}\text{Hg}$  signal is about five times lower at any given extract potential. This corresponds to a 0.4–6% contribution from Hg to measured 204 ion beam intensity on unspiked samples, rather less on samples with the DS, and often a lot more on  $^{208}\text{Pb}$ -spiked samples (for isotope dilution and blanks). This is much greater than the 200 ppm of mass 204 reported by White et al. (2000), in part due to the greater sensitivity of the IsoProbe, and requires an accurate correction procedure.

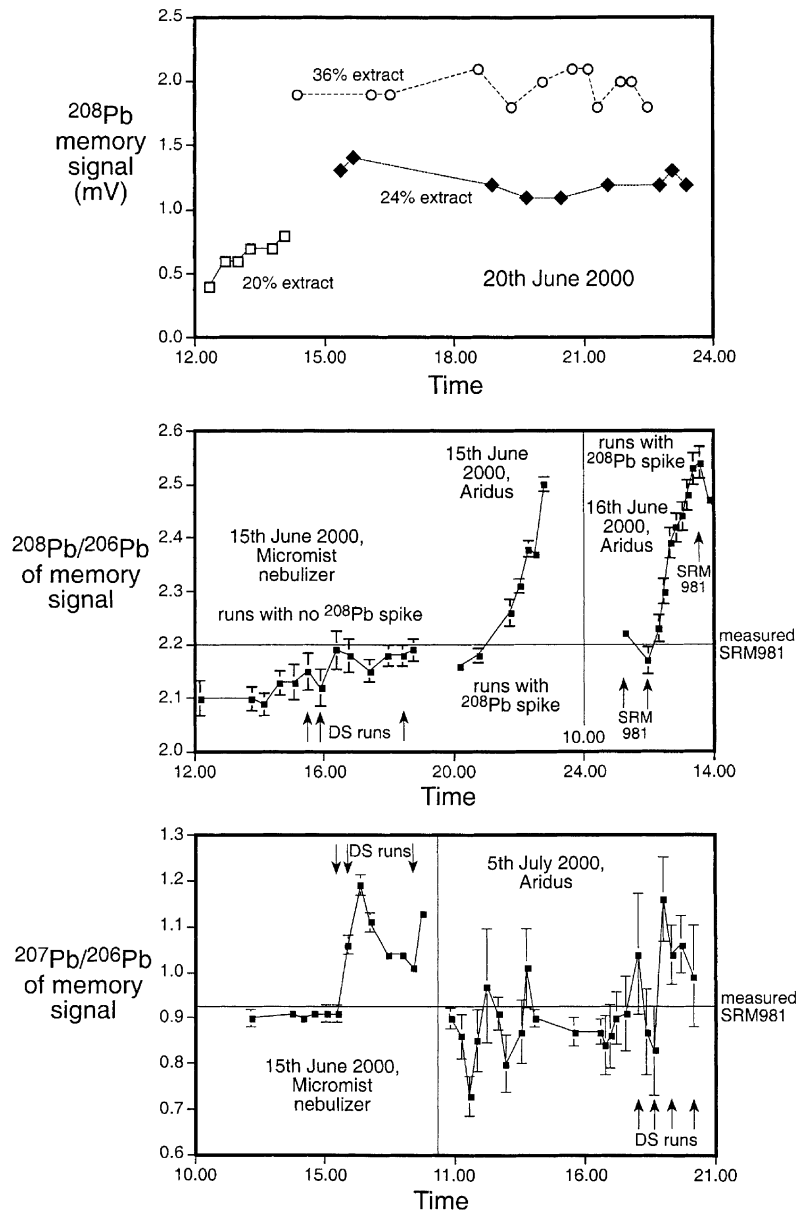


Fig. 2.  $^{208}\text{Pb}$  ion beam (mV),  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  for instrument memory and final wash solution, plotted against time on several days. Error bars are  $2\sigma$  calculated from counting statistics on 30 measurements at 5 s integration. Note dependence of memory ion beam intensity on extract potential; near-constant  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  close to SRM981 values when running unspiked samples; general increases in memory  $^{208}\text{Pb}/^{206}\text{Pb}$  on days when  $^{208}\text{Pb}$ -spiked samples were run (with  $^{208}\text{Pb}/^{206}\text{Pb} = 10\text{--}200$ ), and small increases in  $^{207}\text{Pb}/^{206}\text{Pb}$  in memory runs immediately after analysing samples spiked with a  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  double spike (DS,  $^{207}\text{Pb}/^{206}\text{Pb} = \sim 3$ ).

Measurement of several Hg masses, and subtraction of the amplifier offsets from the OPZ measurements, allows investigation of whether the OPZ

signal is pure Hg. The observed OPZ Hg isotopic ratios are corrected for  $^{204}\text{Pb}$  interference assuming common Pb compositions (0.3–4% of OPZ signal at

mass 204), and for the mass bias determined for the succeeding Pb sample. Means of some 80 OPZ Hg isotope ratios were within error of published natural Hg ratios but there are some significant exceptions. Memory  $^{204}\text{Hg}/^{201}\text{Hg}$  may be significantly higher following the analysis of samples with  $^{204}\text{Pb}$ -enriched DS (up to  $0.580$ , c.f.  $0.515 \pm 5$ ,  $2\text{sd}$ ,  $N=70$ , for other samples), implying minor DS contribution to the memory, as also observed for  $^{207}\text{Pb}/^{206}\text{Pb}$  (Fig. 2). On the Micromist nebulizer, memory  $^{198}\text{Hg}/^{201}\text{Hg}$  decreased from  $\sim 0.95$  to  $\sim 0.79$  on 1 day, significantly higher than published ratios and the Aridus values ( $0.765 \pm 7$ ,  $2\text{sd}$ ,  $N=70$ ). All ratios involving 202 were also anomalous on the Micromist nebulizer, while  $^{204}\text{Hg}/^{201}\text{Hg}$  was normal. These effects are thought to be due to  $\text{WO}^+$  interference, which has high-abundance isobars on all Hg masses except 201 and 204, and is inhibited by the desolvating characteristics of the Aridus. However, the source of the W in these Micromist OPZ is unclear. If  $\text{WO}^+$  is present, use of  $^{202}\text{Hg}$  to correct for Hg interference on  $^{204}\text{Pb}$ , as in all published MC-ICP-MS work, can lead to substantial error.  $\text{WO}^+$  can easily be recognised if the 198/202 and 198/201 ratios in the OPZ are checked for conformity to natural Hg ratios. Following the Micromist work,  $^{201}\text{Hg}$  was used to correct  $^{204}\text{Pb}$  instead. It has the added advantage of being little affected by tail from  $^{203}\text{Tl}$ .

After the OPZ subtraction,  $^{201,202}\text{Hg}/^{206}\text{Pb}$  commonly showed large variation (by  $\sim 0.0002$ ) during the course of a single analysis. These ratios were frequently negative. The residual signal (mostly  $\ll \pm 2$  mV) at mass 201 or 202 cannot be due to sample Hg as this cannot be negative, and the observed signal varies strongly with time. Since measured  $^{204}/^{206}\text{Pb}$  after OPZ subtraction was strongly correlated with  $\text{Hg}/^{206}\text{Pb}$ , with gradient consistent with natural Hg ratios, this effect is thought to result from secular variation in the Hg signal from the gas and machine. It is simply corrected using the observed  $^{201}\text{Hg}$  or  $^{202}\text{Hg}$  intensity and the relevant natural Hg isotope ratio corrected for the sample mass bias, and usually amounts to  $<0.1\%$  of the mass 204 signal. OPZ subtraction alone is insufficient to correct for Hg.

$\text{WO}^+$  has been identified in a number of sample runs, even on the Aridus, by studying the residual 198 and 202 ion intensities after OPZ subtraction. For most Aridus runs, the gradient of the 198–202 corre-

lation is similar to natural  $^{198}\text{Hg}/^{202}\text{Hg}$  with an intercept indicating small excess 198 in many sample but not standard runs. This is interpreted to be the result of a variable  $\text{Hg}^+$  ion beam with a near-constant small contribution from  $\text{WO}^+$ , consistent with common  $^{186}\text{W}^+$  ion beams in samples of 1–2 mV, and a  $\text{WO}^+/\text{W}^+$  ratio of 0.2% determined on W standard solutions. Many runs on the Micromist nebulizer show gradients of OPZ-corrected 198–202 consistent with  $\text{WO}^+$  rather than Hg, presumably as a result of the greater oxide production rate without desolvation. The most likely source of the W is from sodium polytungstate used in mineral separation, as  $\text{W}^+$  ion beams are greatest in mineral separates prepared by this technique.

Use of  $^{201}\text{Hg}$  to calculate the Hg correction on  $^{204}\text{Pb}$  avoids complications with  $\text{WO}^+$  interference but can still be compromised by the presence of  $^{185}\text{ReO}^+$ , and  $^{187}\text{ReO}^+$  can cause problems with mass bias corrections using  $^{203}\text{Tl}$ . The cup configuration of the Royal Holloway IsoProbe allows monitoring of  $^{187}\text{Re}$  on the low-3 Faraday simultaneously with Pb isotope analysis. Significant  $^{187}\text{Re}$  ion beams are observed for most samples and procedure blanks, but are absent from Pb standard solutions, implying that the Re originates as a chemistry blank. The  $^{187}\text{Re}$  signal intensity is commonly  $\sim 1$  mV, with a maximum of 40 mV, and tends to decrease with the extent of sample dilution used for analysis. Re standard solutions show very low  $\text{ReO}^+/\text{Re}^+$  ( $<0.03\%$ ), but it is unclear whether this also applies to sample solutions, in which the Re oxidation state may be different. For a sample with  $\sim 10$  mV  $^{187}\text{Re}$  at an oxide production rate of 0.2%,  $^{204}\text{Pb}$  will be overcorrected for Hg interference, and the  $^{205}\text{Tl}/^{203}\text{Tl}$  underestimated, resulting in a change to Tl-normalized  $^{206}\text{Pb}/^{204}\text{Pb}$  of a barely significant 0.003. Substantial  $\text{ReO}^+$  can be recognised by lower than natural  $^{198}\text{Hg}/^{201}\text{Hg}$  ratios after OPZ subtraction, while  $\text{WO}^+$  causes higher  $^{198}\text{Hg}/^{201}\text{Hg}$ .

Finally, high (6–9 mV) 201 and 198 ion signals after OPZ subtraction, with 198/201 ratios of 0.20–0.98, have been observed in three samples that appeared dirty after chemical separation. The origin of these isobars is at present unclear, but unreasonably low Hg-corrected  $^{204}\text{Pb}/^{206}\text{Pb}$  is obtained on such runs, implying that the excess signal at mass 201 is not Hg. Conformity of OPZ-subtracted 198/201 ratios



to natural  $^{198}\text{Hg}/^{201}\text{Hg}$  is an excellent test of the accuracy of isobaric corrections.

#### 4. Conventional mass bias correction

##### 4.1. Variations in apparent mass bias with time and sample

For a given element, the mass bias is controlled by several instrumental factors including extraction and other focus potentials, position of torch and gas flows. On most days, these parameters were held constant after initial ion beam optimization, in order that direct comparison of mass bias from sample to sample could be made. In addition, mass bias could be affected by sample parameters such as acid molarity and anions present, cleanliness of chemical separate and the solution chemistry of the element in question. In principle, mass bias corrections can be made by alternate analysis of samples and standards (e.g. Belshaw et al., 1998 for Pb), but this presupposes that the mass bias either stays constant with time or drifts in a systematic manner, and is unchanged by sample parameters.

After corrections for tail, Hg and memory, internal precision of Pb and Tl isotope ratios was for most runs  $1\text{--}2\times$  that expected from counting statistics, and

isotope ratios within runs showed no covariation apart from that expected for ratios with common denominators. A very few runs showed weak covariation between ratios with correlation gradients consistent with small variations in mass bias during the course of the run. Mass bias mostly therefore appears to be stable at the level of counting statistics on 7 V ion beams over 5-min periods.

On many days the measured  $^{205}\text{Tl}/^{203}\text{Tl}$  on a single SRM981 solution remains nearly constant or shows steady gentle drift ( $<0.1\%$  per day, e.g. 21/3/00 and 30/3/00, Fig. 3), but sometimes variation may be random and up to  $20\times$  internal precision despite holding machine parameters constant. On the former days, it is usual to observe systematically different  $^{205}\text{Tl}/^{203}\text{Tl}$  for different sample types. Fig. 3 demonstrates that, over four days, measured  $^{205}\text{Tl}/^{203}\text{Tl}$  in the Reference SRM981 solution is systematically  $\sim 500$  ppm higher than  $^{205}\text{Tl}/^{203}\text{Tl}$  measured on silicate samples where the Pb has been separated by ion exchange. A SRM981 solution prepared by using the complete silicate digestion and column separation chemistry prior to adding Tl shows  $^{205}\text{Tl}/^{203}\text{Tl}$  systematically 305 ppm higher than the Reference SRM981 solution (Fig. 3). Further,  $^{205}\text{Tl}/^{203}\text{Tl}$  in samples is often much more heterogeneous than in standards (e.g. Fig. 3, 23rd March). These data show that sample-standard bracketing is very unlikely to be an adequate method of

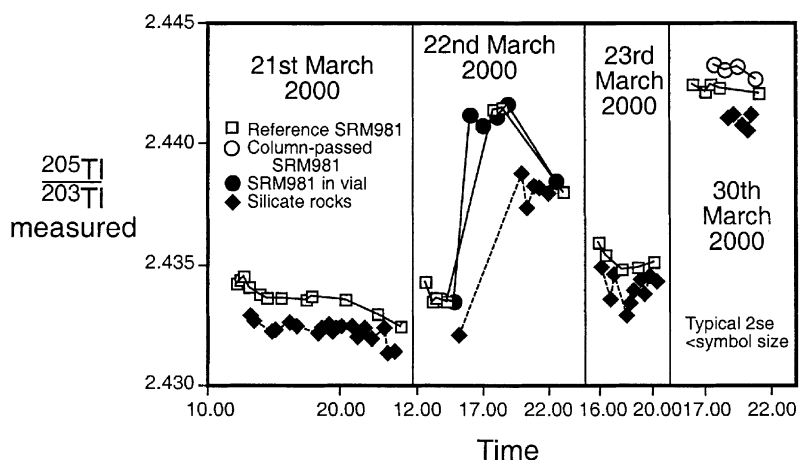


Fig. 3. Measured  $^{205}\text{Tl}/^{203}\text{Tl}$  ratios, corrected only for tail and memory, for standards and samples on three separate days. On each day, sample  $^{205}\text{Tl}/^{203}\text{Tl}$  is lower and more variable than that of the Reference SRM981 solution, but SRM981 given the same chemical treatment as samples has *higher*  $^{205}\text{Tl}/^{203}\text{Tl}$  than Reference SRM981 (30/3/00).

mass bias correction for real samples, and strongly suggest that there may be problems with using TI to correct for mass bias. It should be noted that the 40–250 ppm external precisions reported for sample-standard bracketing by Belshaw et al. (1998) were obtained using the same SRM981 solution for both “sample” and standard.

#### 4.2. The mass bias law

The extent of mass bias on MC-ICP-MS is very large relative to TIMS and there has been considerable discussion over the optimum algebraic law needed for correction. Most authors favour an exponential or similar law in which the extent of mass bias increases with decreasing mass (e.g. Hirata, 1996; Marechal et al., 1999). Following Russell et al. (1978), the exponential fractionation factor  $\beta$ , or  $f$  as used by White et al. (2000), may be defined by

$$\beta = \ln(R_t/R_m)/\ln(m_1/m_2)$$

where  $R_t$  and  $R_m$  are the true and measured values of an isotope ratio, and  $m_1$  and  $m_2$  are the numerator and denominator masses in amu. The exponential law requires that  $\beta$  should be invariant with mass, and Marechal et al. (1999) showed on their VG P54 MC-ICP-MS that  $\beta$  lay in the range  $-2.2 \pm 0.2$  over the full mass spectrum. However, it is unclear whether their instrument was individually optimized for each element. If instrumental parameters are held constant,  $\beta$  becomes less negative with increasing mass on the Royal Holloway IsoProbe (Fig. 4), suggesting that neither power nor exponential law, describe the true mass bias behaviour. This is true both over the mass spectrum as a whole and over the spectrum of single elements such as Nd (Vance and Thirlwall, submitted for publication) and Fe, and similar relationships appear to be present on other IsoProbes (S. Meffan-Main, personal communication, 2000), and may also be present on some double-focussing machines (Vance and Thirlwall, submitted for publication). From the relationships in Fig. 4, it may be anticipated that

$$\beta_{205/203} < \beta_{204/206} < \beta_{208/206}$$

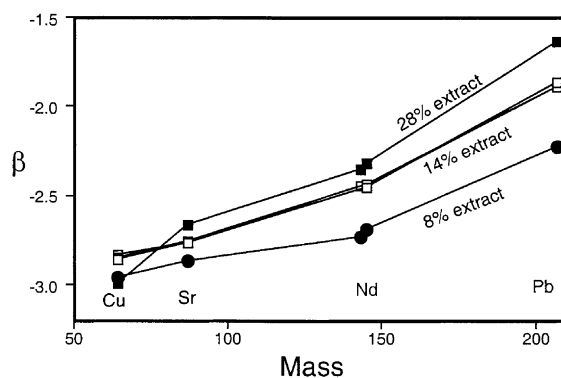


Fig. 4. Exponential mass fractionation parameter  $\beta$  (see text) plotted against mass for different extraction potentials. Negative slope is observed both between and within elements (e.g. Nd). Assumed true ratios:  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677$  (SRM981),  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ ,  $^{142}\text{Nd}/^{144}\text{Nd} = 1.141870$ ,  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ ,  $^{65}\text{Cu}/^{63}\text{Cu} = 0.4456$  (Marechal et al., 1999).  $\beta$  would be invariant with mass if the exponential mass bias law was valid; if the power law was valid a steep slope of reverse trend would be seen.

If the slope of the  $\beta$ -mass correlation (Fig. 4) were to remain constant as  $\beta$  changes for a given mass, then

$$\beta_{205/203} = k\beta_{208/206}$$

with  $k$  being a constant greater than 1.0, since  $\beta$  becomes progressively more negative with decreasing mass. The value of  $k$  for  $^{205}\text{Tl}/^{203}\text{Tl}$  can be determined from the slope of Fig. 4 as  $\sim 1.013$ . It is then simple to show that a graph of  $\ln(^{205}\text{Tl}/^{203}\text{Tl}_{\text{meas}})$  against  $\ln(^{208}\text{Pb}/^{206}\text{Pb}_{\text{meas}})$  should yield a straight line of gradient equal to  $1.013 \times$  the expected exponential law gradient.

Table 2 reports the  $\ln$ - $\ln$  relationships derived from 92 Aridus analyses of Reference SRM981 over 15 analytical days over 5 months. Unlike TIMS, where large temporal variations in mass bias allow gradients to be established for single runs (Thirlwall, 2000), on the Royal Holloway IsoProbe there is virtually no range in mass bias on single runs, and insufficient range on single days to define gradients with useful precision. This means that data from several days must be combined to define the results of Table 2, which will include variable instrumental settings. White et al. (2000) observed variation in mass bias of ca. 0.1%/

Table 2  
Regression statistics for natural logarithms of measured isotope ratios

	$\ln(^{204}\text{Pb}/^{206}\text{Pb})$	$\ln(^{207}\text{Pb}/^{206}\text{Pb})$	$\ln(^{205}\text{Tl}/^{203}\text{Tl})$
Gradient $\pm 2\text{se}$	$-0.993\pm 8$	$0.502\pm 3$	$1.013\pm 11$
$r^2$	0.9984	0.9993	0.9975
Expected gradients			
Exponential law	-1.0094	0.5014	1.0147
Power law	-0.9996	0.5002	0.9999
Based on Fig. 4	-1.0182	0.5025	1.028
TIMS, observed $\pm 2\text{se}$	$-1.013\pm 12$	$0.452\pm 9$	–

All gradients relative to  $\ln(^{208}\text{Pb}/^{206}\text{Pb})$  on the x-axis.

Gradients based on 92 runs of Royal Holloway Reference SRM981 solution between March and August 2000, runs with  $<3 \text{ V } ^{208}\text{Pb}$  omitted. TIMS data from Thirlwall (2000).

amu over a single day, and showed that the gradient of  $\ln(^{205}\text{Tl}/^{203}\text{Tl})$  vs.  $\ln(^{208}\text{Pb}/^{206}\text{Pb})$  was significantly different from the expected exponential law slope ( $1.041\pm 0.016$  compared with 1.0147). This they inter-

preted to be a result of different mass bias for Tl and Pb, but their gradient is within error of that predicted from the slope of Fig. 4 (1.028).

The Royal Holloway data show gradients of  $\ln(^{207}\text{Pb}/^{206}\text{Pb})$  and  $\ln(^{205}\text{Tl}/^{203}\text{Tl})$  vs.  $\ln(^{208}\text{Pb}/^{206}\text{Pb})$  that are nearly within error of those expected by either power or exponential mass bias laws (Table 2), but  $\ln(^{204}\text{Pb}/^{206}\text{Pb})$  vs.  $\ln(^{208}\text{Pb}/^{206}\text{Pb})$  shows a gradient within error of power law but just significantly lower than the exponential gradient. Gradients for  $^{205}\text{Tl}/^{203}\text{Tl}$  and  $^{204}\text{Pb}/^{206}\text{Pb}$  are substantially lower than expected from the  $\beta$ -mass slope of Fig. 4 (Table 2), perhaps implying that  $k$  is a function of  $\beta$  for a given mass. This would mean no linear relationships in  $\ln$ – $\ln$  space, invalidating the linear regressions used. Although the near  $-1.0000$   $r^2$  values in Table 2 appear to suggest linear relationships, virtually identical  $r^2$  values are obtained by regressing  $\ln(^{205}\text{Tl}/^{203}\text{Tl}_{\text{meas}})$  against  $(\ln(^{208}\text{Pb}/^{206}\text{Pb}_{\text{meas}}))^2$  and a wide range of other exponents. The narrow range in observed  $\beta$  means that it is

Table 3  
Pb and Tl isotope ratios for SRM981 and SRM982 mass bias corrected using  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677$  and 1.00016, respectively

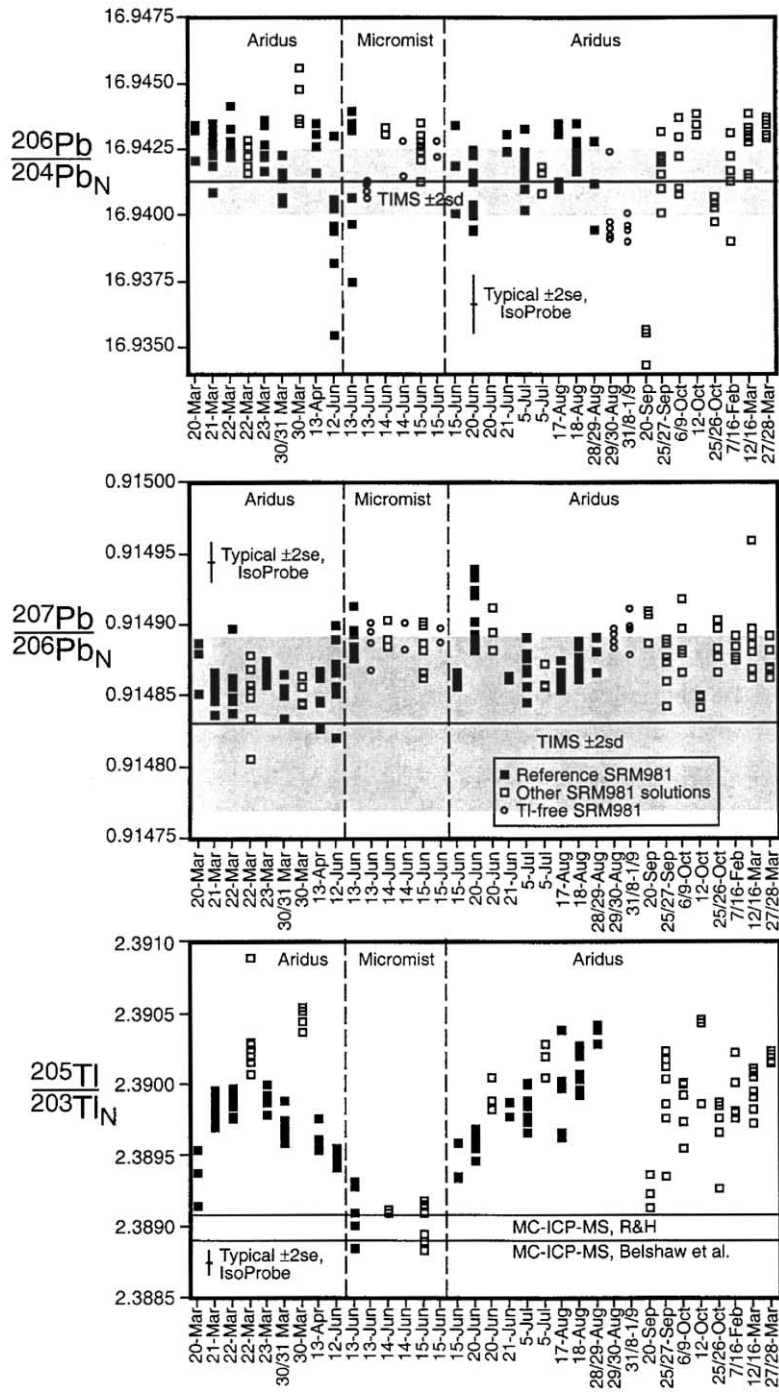
	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{205}\text{Tl}/^{203}\text{Tl}$	$N$
<i>SRM981 TIMS data</i>				
Todt et al. (1996), no $^{207}\text{Pb}$ correction	$16.9410\pm 31$	$0.91474\pm 9$	–	11
Thirlwall (2000), no $^{207}\text{Pb}$ correction	$16.9412\pm 12$	$0.91480\pm 9$	–	31
same, $^{207}\text{Pb}$ corrected to low $^{208}\text{Pb}/^{206}\text{Pb}$	$16.9412\pm 12$	$0.91483\pm 6$	–	31
Doucelance and Manhès (2001), $<1175 \text{ } ^\circ\text{C}$	$16.9406\pm 15$	$0.91489\pm 2$	–	16
<i>SRM981 IsoProbe data</i>				
All SRM981, exponential	$16.9418\pm 32$	$0.91487\pm 5$	$2.38979\pm 69$	171, 185, 150
All, power law	$16.9453\pm 31$	$0.91490\pm 5$	$2.39052\pm 76$	171, 185, 150
Reference soln., Aridus	$16.9419\pm 25$	$0.91487\pm 5$	$2.38977\pm 45$	89, 92, 85
Reference soln., Micromist	$16.9414\pm 51^a$	$0.91489\pm 3$	$2.38909\pm 36$	6, 6, 6
Micromist without Tl, over 3 days	$16.9417\pm 17$	$0.91489\pm 2$	–	8, 8, 0
Micromist with $^{205}\text{Tl}/^{206}\text{Pb} > 0.6$	$16.9432\pm 06$	$0.91489\pm 2$	$2.38913\pm 07$	5
<i>SRM982 TIMS data</i>				
Todt et al. (1996), no $^{207}\text{Pb}$ correction	$36.7498\pm 27$	$0.467023\pm 19$	–	11
Thirlwall (2000), no $^{207}\text{Pb}$ correction	$36.7431\pm 68$	$0.467038\pm 47$	–	11
Same, $^{207}\text{Pb}$ corrected to low $^{208}\text{Pb}/^{206}\text{Pb}$	$36.7431\pm 68$	$0.467063\pm 39$	–	11
Doucelance and Manhès (2001), $<1175 \text{ } ^\circ\text{C}$	$36.7485\pm 27$	$0.467080\pm 10$	–	5
<i>SRM982 IsoProbe data</i>				
Aridus	$36.7437\pm 45$	$0.467087\pm 12$	$2.38959\pm 10$	7, 7, 4

Means exclude  $^{206}\text{Pb}/^{204}\text{Pb}$  on runs with  $<3 \text{ V } ^{208}\text{Pb}$ , and  $^{205}\text{Tl}/^{203}\text{Tl}$  where there was no Tl, or  $<0.2 \text{ V } ^{203}\text{Tl}$ .

All errors  $2\times$  standard deviation. All data normalized using exponential law except for TIMS data and where indicated. Exponential-power law differences are insignificant for TIMS data.

<sup>a</sup> Poor 2sd on  $^{206}\text{Pb}/^{204}\text{Pb}$  due to only  $\sim 1.5 \text{ V } ^{208}\text{Pb}$ .

SRM981 normalized to  $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677$



near-impossible to define such curves algebraically, for although in principle they have to pass through the true isotopic ratios, in practice this means that it is no longer possible to test for accuracy of the normalized ratios.

#### 4.3. Standard Pb isotope ratios with internal mass bias correction

For standard samples such as SRM981 and SRM982, it is possible to mass bias correct measured Pb and Tl isotopic ratios relative to one assumed Pb isotopic ratio of each standard. This is equivalent to internal normalization used for Sr and Nd and, through comparison to TIMS data, indicates whether MC-ICP-MS can accurately measure Pb ratios. Table 3 and Fig. 5 present data for 185 runs of SRM981 and seven runs of SRM982 over the course of a year. The SRM981 runs include the Reference solution, SRM981 that has been evaporated and nitrated before redissolving in the same solution used to measure OPZ, and SRM981 that has gone through the full silicate chemical procedure. They also include runs with  $^{205}\text{Tl}/^{206}\text{Pb}$  from 0.00 to 0.93 ( $\text{Tl}/\text{Pb}=0.0\text{--}0.3$ , wider than the range used by Rehkämper and Mezger, 2000), and runs on both Micromist and Aridus nebulizers. Measured Pb and Tl isotope ratios are normalized using exponential and power laws to an assumed  $^{208}\text{Pb}/^{206}\text{Pb}$  value. For SRM982,  $^{208}\text{Pb}/^{206}\text{Pb}=1.00016$  is used as this is the assumption made in calibrating DS TIMS data (e.g. Todt et al., 1996; Galer and Abouchami, 1998; Thirlwall, 2000). For SRM981,  $^{208}\text{Pb}/^{206}\text{Pb}=2.1677$  is used as it is the mean value obtained using DS-TIMS by Galer and Abouchami (1998) and Thirlwall (2000).

Fig. 5 allows comparison between  $^{208}\text{Pb}/^{206}\text{Pb}$ -normalized Pb and Tl ratios of SRM981 for each day and for each mode of standard preparation and sample introduction used. The range in Pb ratios within a day is very close to the mean internal precisions (Fig. 5), which are  $\pm 0.0010$  and  $\pm 0.000015$  (2se), respectively, on  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$ . These are in turn close to counting statistics errors. Almost all

daily  $^{206}\text{Pb}/^{204}\text{Pb}$  results lie within 2sd of the mean of all SRM981 runs ( $^{206}\text{Pb}/^{204}\text{Pb}=16.9418\pm 32$ , 2sd,  $N=171$ ), despite different nebulizer types,  $\text{Tl}/\text{Pb}$  from 0.0 to 0.3, and different modes of solution preparation. The only exceptions are slightly high  $^{206}\text{Pb}/^{204}\text{Pb}$  (mean=16.9444) for 300 ng SRM981 “digested” with  $\text{HF-HNO}_3$  and passed through ion exchange columns, which might reflect a small blank contribution, and low ratios for 12/6/00 and 20/9/00. Further, the mean  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios for SRM981 and SRM982 derived by exponential law normalization are identical within error to published TIMS  $^{206}\text{Pb}/^{204}\text{Pb}$  for these standards when normalized to the same  $^{208}\text{Pb}/^{206}\text{Pb}$  values (Table 3). This agreement is remarkable given the issues of Hg correction, memory and tail from  $^{205}\text{Tl}$ , and particularly given the non-exponential mass bias behaviour of  $^{206}\text{Pb}/^{204}\text{Pb}$  demonstrated above.

$^{207}\text{Pb}/^{206}\text{Pb}$  ratios also show no significant differences between different standard preparation methods or between Tl-bearing or Tl-free standards, but there are small ( $\sim 30$  ppm) differences between mean  $^{207}\text{Pb}/^{206}\text{Pb}$  values from day to day (Fig. 5). This may reflect small changes in cup efficiencies. The mean  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios for SRM981 and SRM982 are slightly but significantly higher than TIMS values normalized in the same way (Table 3, Thirlwall, 2000; Todt et al., 1996), by 77 and 105 ppm, respectively, as also observed by other MC-ICP-MS studies (summarized in Thirlwall, 2000). This most probably indicates a discrepancy between TIMS and MC-ICP-MS measurement of  $^{207}\text{Pb}$ , as the  $^{206}\text{Pb}/^{204}\text{Pb}$  behaves so well. Thirlwall (2000) and Doucelance and Manhès (2001) observed systematic decrease in normalized  $^{207}\text{Pb}/^{206}\text{Pb}$  with increasing  $^{208}\text{Pb}/^{206}\text{Pb}$  in individual TIMS runs, with a gradient for  $\ln(^{207}\text{Pb}/^{206}\text{Pb}_{\text{meas}})$  vs.  $\ln(^{208}\text{Pb}/^{206}\text{Pb}_{\text{meas}})$  of  $0.435\pm 0.010$  (Thirlwall, 2000), substantially lower than the expected value (0.501) and the value observed on the IsoProbe ( $0.502\pm 3$ , Table 2). Thirlwall (2000) corrected TIMS data for this effect by extrapolating along the observed gradient to the estimated true  $^{208}\text{Pb}/^{206}\text{Pb}$ , but these results agree least well with the IsoProbe data. Mean

Fig. 5. Pb and Tl isotopic ratios in SRM981 normalized by exponential law to  $^{208}\text{Pb}/^{206}\text{Pb}=2.1677$  over the period March 2000–March 2001. Data for  $^{206}\text{Pb}/^{204}\text{Pb}$  not shown where  $^{208}\text{Pb}$  ion beam intensity was  $< 3\times 10^{-11}$  A, except for the Micromist data of 13th of June. TIMS values from Table 3. Comparative MC-ICP-MS data for  $^{205}\text{Tl}/^{203}\text{Tl}$  from R&H (Rehkämper and Halliday, 1998) and Belshaw et al. (1998) are normalized in the same way.

TIMS data, with no correction for  $^{207}\text{Pb}$ , agree better (Table 3), but the best agreement is obtained by extrapolating TIMS data along the gradient to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$  (Table 3). Doucelance and Manhès (2001) independently concluded that the best internally normalized TIMS data were those measured at low temperature. Thus there is excellent agreement between  $^{208}\text{Pb}/^{206}\text{Pb}$ -normalized IsoProbe and TIMS Pb isotope ratios provided that TIMS  $^{207}\text{Pb}/^{206}\text{Pb}$  are corrected for anomalous  $^{207}\text{Pb}$  behaviour to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio, or that only low-temperature TIMS data are used (Table 3).

#### 4.4. Pb isotope ratios normalized to Tl

Table 4 reports Pb isotope ratios for SRM981 and SRM982 corrected for mass bias to  $^{205}\text{Tl}/^{203}\text{Tl}=2.3889$ , a value which will be justified in Section 5.5. Sixteen runs of four different SRM981 solutions using

the Micromist nebulizer show similar means and 2sd values to MC-ICP-MS data reported by Rehkämper and Halliday (1988), Belshaw et al. (1998) and Vance and van Calsteren (1999) when renormalized to the same  $^{205}\text{Tl}/^{203}\text{Tl}$ . They are also similar to the DS-TIMS values of Thirlwall (2000) when corrected as described in Section 4.3. This is despite a range in  $^{205}\text{Tl}/^{206}\text{Pb}$  of 0.33–0.94, indicating that the tail correction procedure used works accurately (Thirlwall, 2001).

However, data for 92 runs of the Reference SRM981 solution using the Aridus are substantially less reproducible and show significantly lower Tl-normalized Pb ratios. Similarly, Tl-normalized SRM982 data are low relative to accepted values. Means of all Tl-spiked SRM981 solutions on both nebulizers are less reproducible still (Table 4), with 541 ppm 2sd on  $^{208}\text{Pb}/^{204}\text{Pb}$ , which is not vastly better than conventional TIMS (1140 ppm 2sd; Thirlwall, 2000). These data have similar reproducibility to

Table 4  
Pb isotope ratios of SRM981 and SRM982 mass bias corrected using  $^{205}\text{Tl}/^{203}\text{Tl}=2.3889$

	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	<i>N</i>	<i>S</i>
<i>Royal Holloway IsoProbe</i>					
Micromist, SRM981	16.9416±12	0.91486±06	2.16755±25	10–16	4
All Micromist, SRM981	16.9410±39	0.91486±06	2.16755±25	16	4
Reference solution on Aridus	16.9357±36	0.91470±10	2.16691±42	89–92	1
All data, SRM981	16.9356±48	0.91471±16	2.16691±66	159–168	22
SRM982, Aridus	36.734±7	0.46702±1	0.99966±4	4	1
<i>Double- and triple-spike TIMS, SRM981</i>					
Thirlwall (2000) <sup>a</sup>	16.9408±21	0.91483±07	2.16768±23	41	–
Galer and Abouchami (1998)	16.9405±15	0.91475±04	2.16771±10	60	–
<i>MC-ICP-MS, SRM981</i>					
Rehkämper and Halliday (1998)	16.9422±55	0.91485±5	2.16750±14	32	1
Belshaw et al. (1998)	16.9419±68	0.91489±6	2.16775±22	~80	?
Vance and van Calsteren (1999) <sup>b</sup>	16.9444±20	0.91484±3	2.16756±11	84	1
Rehkämper and Mezger (2000) <sup>c</sup>	16.9498±59	0.91494±14	2.16858±44	48	4
Same, corrected for tail <sup>d</sup>	16.9389	0.91491	2.16761		

All errors 2sd.

$^{206}\text{Pb}/^{204}\text{Pb}$  data where  $^{208}\text{Pb}<3\times 10^{-11}$  A are excluded from Royal Holloway IsoProbe means, except for “All Micromist” data. The lower value for *N* refers to  $^{206}\text{Pb}/^{204}\text{Pb}$ .

All MC-ICP-MS data normalized or renormalized from published data using exponential law to  $^{205}\text{Tl}/^{203}\text{Tl}=2.3889$ . Data from Hirata (1996) and White et al. (2000) are not included, as they cannot be simply recalculated using exponential law from the information given.

*S*=number of different solutions used in the study. Belshaw et al. (1998) used several different solutions but maintained constant Tl/Pb ratios.

<sup>a</sup> Data from Thirlwall (2000) and subsequent Royal Holloway DS-TIMS data, with anomalous  $^{207}\text{Pb}$  behaviour corrected to lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$ .

<sup>b</sup> Modified by personal communication, Vance (2001).

<sup>c</sup> Mean and 2sd of all data reported after renormalization: original data used a different Tl normalization ratio for each day.

<sup>d</sup> Their data are also recalculated using an estimate of the abundance sensitivity on their IsoProbe from Thirlwall (2001).

those reported for the IsoProbe by Rehkämper and Mezger (2000) when their data are corrected to a single Tl isotope ratio (Table 4), but their data are substantially higher with this normalization, probably due to inadequate tail correction (Table 4; Thirlwall, 2001). The much better external precision of Tl-normalized Pb data reported by Rehkämper and Halliday (1988), Belshaw et al. (1998) and Vance and van Calsteren (1999) may reflect their use of a single Tl-doped SRM981 solution or constant Tl/Pb ratios, their use of Cetac MCN6000 nebulizers, their use of much more Pb (4–50 times that used in the IsoProbe work), or their use of different instruments.

#### 4.5. Tl isotope ratios normalized to $^{208}\text{Pb}/^{206}\text{Pb}$ : implications for Tl-based mass bias correction

$^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios of SRM981 and SRM982 normalized to constant  $^{208}\text{Pb}/^{206}\text{Pb}$  show <54 and <188 ppm 2sd external precision respectively and agree closely with TIMS data (Table 3). If  $^{205}\text{Tl}/^{203}\text{Tl}$  is to be used for normalization of Pb isotope ratios then it should be equally precise and accurate when normalized to  $^{208}\text{Pb}/^{206}\text{Pb}$ . Table 3 and Fig. 5 show that this is not the case, with 2sd external precision being 289 ppm for all SRM981 analyses. Within any 1 day, the range in Pb-normalized  $^{205}\text{Tl}/^{203}\text{Tl}$  on the Reference SRM981 solution is close to that expected from the average internal precision of  $\pm 0.000083$  (2se; Fig. 5), but the mean ratio differs by up to 419 ppm from day to day (e.g. 28/8/00 and 20/3/00, Fig. 5). Similarly, Rehkämper and Mezger (2000) needed inter-day differences of up to 377 ppm in the  $^{205}\text{Tl}/^{203}\text{Tl}$  normalizing ratio to yield their preferred Pb isotopic composition for SRM981. Thus, the Royal Holloway Pb data could be normalised using the mean Pb-normalized  $^{205}\text{Tl}/^{203}\text{Tl}_N$  ratios for each day. This would inevitably result in an apparently accurate  $^{208}\text{Pb}/^{206}\text{Pb}$  of 2.1677 with external precision comparable to the internally normalized Pb isotope ratios, because the daily  $^{205}\text{Tl}/^{203}\text{Tl}_N$  is derived from the very same Pb ratios that are used to assess external precision.

This Tl-based correction method assumes that the inter-day differences are due to a general instrument effect on the relative mass bias of Tl and Pb that is applicable to all samples, and not to a sample-dependent

effect. The assumption can be tested by comparing data obtained on a single day for SRM981 prepared in different ways. Substantial differences (up to 325 ppm) in  $^{205}\text{Tl}/^{203}\text{Tl}_N$  are observed (22nd March, 30th March, 20th June, 5th July; Fig. 5), despite alternate running of the different SRM981 solutions. On a single day, the differences seen in  $^{205}\text{Tl}/^{203}\text{Tl}_N$  between different SRM981 solutions are identical to those observed in their raw measured  $^{205}\text{Tl}/^{203}\text{Tl}$  (compare Figs. 5 and 3 for 30/3/00, 325 and 305 ppm difference, respectively). The difference in  $^{205}\text{Tl}/^{203}\text{Tl}_N$  between the two SRM981 solutions of 30/3/00 would give rise to normalized Pb ratios up to 650 ppm different for  $^{208}\text{Pb}/^{204}\text{Pb}$ .

Since the difference between these two SRM981 solutions must be a sample-dependent effect, it is difficult to ascertain whether either  $^{205}\text{Tl}/^{203}\text{Tl}_N$  derived from the SRM981 solutions can accurately correct for mass bias in silicate sample runs. Fig. 3 demonstrates that the raw measured  $^{205}\text{Tl}/^{203}\text{Tl}$  is systematically lower in silicate samples than standards; through comparison with the two SRM981 solutions this suggests that the Tl normalizing ratio required for silicates would be appreciably lower than that for either SRM981 solution. Fortunately, many of the silicate samples analysed in March 2000 (Fig. 3) had previously been analysed by DS-TIMS and thus  $^{205}\text{Tl}/^{203}\text{Tl}_N$  can be calculated by normalization to their known  $^{208}\text{Pb}/^{206}\text{Pb}$ . For example,  $^{205}\text{Tl}/^{203}\text{Tl}_N = 2.38843 \pm 63$  (2sd,  $N = 5$ ) for the silicate samples of 30/3/00, 528–855 ppm below the  $2.38969 \pm 24$  and  $2.39047 \pm 16$  of the two SRM981 solutions run that day. Using the  $^{205}\text{Tl}/^{203}\text{Tl}_N$  derived from the SRM981 solutions to normalize the silicate Pb data gives  $^{208}\text{Pb}/^{204}\text{Pb}_N$  that are 1050–1710 ppm higher than DS-TIMS data, a discrepancy worse than the external precision of conventional TIMS analysis. It is only possible to show this by analysis of samples previously studied by DS-TIMS, which has not been done in any previous MC-ICP-MS studies.

It thus appears that Tl mass bias correction of Pb isotope ratios measured on the IsoProbe at Royal Holloway introduces substantial systematic errors, both from day to day and using different solutions on the same day. It is unclear whether other MC-ICP-MS laboratories might have similar effects: in general, data has only been reported elsewhere for SRM981, or for samples analysed by conventional TIMS, and it is rare that more than one SRM981 solution has been analysed.

## 5. Double spike mass bias corrections on the IsoProbe

IsoProbe SRM981 Pb isotope ratios normalized to constant  $^{208}\text{Pb}/^{206}\text{Pb}$  are accurate relative to multi-dynamic TIMS and are insensitive to Tl/Pb, matrix and nebulizer (Fig. 5, Table 3). This suggests that a Pb double spike should be able to correct accurately for mass bias on the IsoProbe just as it can on TIMS (e.g. Thirlwall, 2000). While a  $^{205}\text{Pb}$ - $^{202}\text{Pb}$  spike (Todt et al., 1996) would be ideal, the spikes involved are expensive and carry the problem of being additional isotopes with additional interferences (e.g.  $^{186}\text{WO}^+$ ,  $^{202}\text{Hg}$ ,  $^{205}\text{Tl}$ ) on MC-ICP-MS. A  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  spike avoids extra interferences, and also allows continued use of Tl in order to identify the cause of the problems with the Tl-based mass bias correction. It does however mean that two runs must be performed on each sample, an unspiked run, and a “mix” run containing a mixture of sample and DS (e.g. Thirlwall, 2000). Since the precision on the “mix” run is not limited by counting statistics on the  $^{204}\text{Pb}$ -ion beam, fewer ratios (typically 20–25) need be collected than the natural run to achieve adequate precision. Although Pb-normalized data for SRM981 analysed immediately after “mix” runs are indistinguishable from those determined before, to avoid blank problems it is preferred to run all the natural isotopic compositions first, and then all the “mix” runs at the end of a day. Usually, three SRM981 naturals are run interspersed with the natural samples, and two SRM981-DS mixes are run among the sample-DS mixes.

### 5.1. Exponential solutions to DS algebra

Algebraic solutions to the DS equations are only possible if a linear mass fractionation law is assumed (Thirlwall, 2000): while this is an adequate approximation for TIMS, an exponential law is often thought to be most suitable for MC-ICP-MS (e.g. Marechal et al., 1999). Johnson and Beard (1999) have proposed a linear expansion of the exponential law that allows algebraic solution; while appropriate for TIMS, the error introduced at the more extreme mass bias of MC-ICP-MS can be substantial. In this study, the spreadsheet used by Thirlwall (2000) has been modified to use the linear solution as a first step to solve iteratively the exponential mass bias equations. The

calculated linear fractionation factors for natural and “mix” runs are converted to first-estimate  $\beta$ -values (Section 4.2) by multiplying by the mass of  $^{206}\text{Pb}$ . These are used to calculate first-estimate exponential-law-normalized Pb ratios for both runs, which are then used to calculate residuals in the two sample-DS mixing equations (p. 301 of Thirlwall, 2000). The operator then adjusts multipliers to the two first-estimate  $\beta$ -values until the two residuals are zero, which takes  $\sim 15$  s in the spreadsheet. The  $\beta$ -multiplier is highly variable for the natural run, where it is strongly dependent on the sample/spike mixing ratio  $Q$  (Thirlwall, 2000), but it shows limited variation for the “mix” run, where it is primarily dependent on  $\beta$  for the “mix” run.

### 5.2. DS calibration

An independent calibration of the DS isotopic composition was carried out on the IsoProbe, using the standard method used for DS-TIMS (e.g. Todt et al., 1996; Thirlwall, 2000). IsoProbe SRM982 Pb ratios normalized to  $^{208}\text{Pb}/^{206}\text{Pb}=1.00016$  (Table 3) are used as a spike composition in the DS solution spreadsheet, with pure DS runs treated as the unknown sample. In addition, the TIMS DS calibration data of Thirlwall (2000) were reprocessed with the  $^{207}\text{Pb}$ -effect being corrected to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$  (Section 4.3). The IsoProbe results for the DS composition appear to be within error of the TIMS calibration (Table 5), though, as with TIMS, the spread of calculated DS compositions is largely due to small amounts of blank contamination, and it is impossible to define meaningful external precision on the DS ratios. The individual data points show  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{204}\text{Pb}/^{206}\text{Pb}$  blank mixing lines, with the TIMS mixing line having 100 ppm higher  $^{208}\text{Pb}/^{206}\text{Pb}$  at any  $^{204}\text{Pb}/^{206}\text{Pb}$ . This may be due to the use of static data with unit cup efficiencies on the IsoProbe.

### 5.3. SRM981 results mass bias corrected using DS

Table 6 presents data for 36 DS-corrected SRM981 analyses between June 2000 and June 2001 in which independent natural and “mix” runs were used for each analysis. The data were obtained on 20 separate days, and include data from both Micromist (4) and



Table 5  
Pb isotope ratios of the Royal Holloway  $^{207}\text{Pb}$ – $^{204}\text{Pb}$  double spike

	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	<i>N</i>
TIMS	3.38905±110	15.2690±45	1.22374±37	7
IsoProbe	3.38884±051	15.2702±11	1.22369±18	3
Mean 2se, IsoProbe	±018	±05	±07	

Results obtained by calibration against SRM982, using mean  $^{204}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  for natural SRM982 determined on the respective instruments (Table 3).

TIMS data corrected for anomalous  $^{207}\text{Pb}$  behaviour to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$ .

Errors 2sd but largely reflect blank mixing. Mean 2se is based on internal errors propagated through the double-spike mass bias correction.

Aridus (32) nebulizers, on the Reference solution (twice) and on 12 other solutions with variable Tl/Pb, and included 12 analyses without admixed Tl. *Q*-values ( $^{204}\text{Pb}_{\text{sample}}/^{204}\text{Pb}_{\text{spike}}$ ) varied from 0.045 to 0.38 in order to mimic a possible range in sample *Q*-values. The mean values and external precisions are almost identical to those obtained by DS-TIMS at Royal Holloway (Thirlwall, 2000; recalibrated to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$  in Table 6). Slightly high values for IsoProbe  $^{207}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$  and  $^{207}\text{Pb}/^{204}\text{Pb}_{\text{DS}}$  are most probably a consequence of insufficient correction to the TIMS  $^{207}\text{Pb}$ .  $^{207}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$  is significantly higher than the TIMS triple-spike result of Galer

and Abouchami (1998), but identical to the TIMS result of Doucelance and Manhès (2001) when normalized to the same  $^{208}\text{Pb}/^{206}\text{Pb}$ . It is suspected that this is a consequence of small unrecognised anomalous  $^{207}\text{Pb}$  behaviour in the triple-spike TIMS data.

The TIMS data of Doucelance and Manhès (2001) were reported normalised to the certified  $^{208}\text{Pb}/^{206}\text{Pb}$  for SRM981. It is clear through three consistent independent double/triple spike calibrations (Galer and Abouchami, 1998; Thirlwall, 2000; this paper) that this  $^{208}\text{Pb}/^{206}\text{Pb}$  is inconsistent with  $^{208}\text{Pb}/^{206}\text{Pb} = 1.00016$  for SRM982, and thus a new  $^{208}\text{Pb}/^{206}\text{Pb}$  of 2.16770±2 is proposed for SRM981. It is important to note that this value is *independent* of whether or how TIMS data are corrected for  $^{207}\text{Pb}$  behaviour. Table 8 of Thirlwall (2000) erroneously suggested that results without  $^{207}\text{Pb}$  correction showed different  $^{208}\text{Pb}/^{206}\text{Pb}_N$ , a mistake resulting from failure to process the DS calibration in the same way without a  $^{207}\text{Pb}$  correction.

The external precisions reported for the DS-IsoProbe in Table 6 are substantially better than achieved using Tl-normalization on multiple solutions and different nebulizers (Table 4). To ensure that this is not a function of a smaller number of DS-SRM981 analyses, Table 6 reports data from the same natural SRM981 runs used to calculate the DS-normalization, but mass bias corrected instead using Tl. The

Table 6  
Pb isotope ratios of SRM981 mass bias corrected using a  $^{207}\text{Pb}$ – $^{204}\text{Pb}$  double spike

	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	<i>N</i>
<i>Royal Holloway IsoProbe</i>						
All data, DS-norm	16.9417±29	15.4996±31	36.724±09	0.91488±08	2.16770±24	36
Mean 2se	±13			±03	±13	
Same runs, Tl-norm	16.9356±55	15.4911±74	36.697±23	0.91470±16	2.16686±68	25 <sup>a</sup>
<i>Royal Holloway TIMS- same double spike, independent calibration</i>						
DS-TIMS	16.9408±21	15.4980±25	36.722±08	0.91483±07	2.16768±23	41
<i>Triple-spike-TIMS, Galer and Abouchami (1998)</i>						
	16.9405±15	15.4963±16	36.722±04	0.91475±04	2.16771±10	60
<i>TIMS, Doucelance and Manhès (2001), normalized to <math>^{208}\text{Pb}/^{206}\text{Pb} = 2.1677</math></i>						
Low-T TIMS	16.9406±15	–	–	0.91489±02	–	16

Errors 2sd. Mean 2se is based on internal errors propagated through the double-spike mass bias correction.

TIMS data corrected for anomalous  $^{207}\text{Pb}$  behaviour to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$ .

<sup>a</sup> Data for the natural runs used in the DS mass-bias correction, normalized instead to  $^{205}\text{Tl}/^{203}\text{Tl} = 2.3889$ . There are only 25 of these because 10 had no admixed Tl, and one had too little Tl for precise correction.

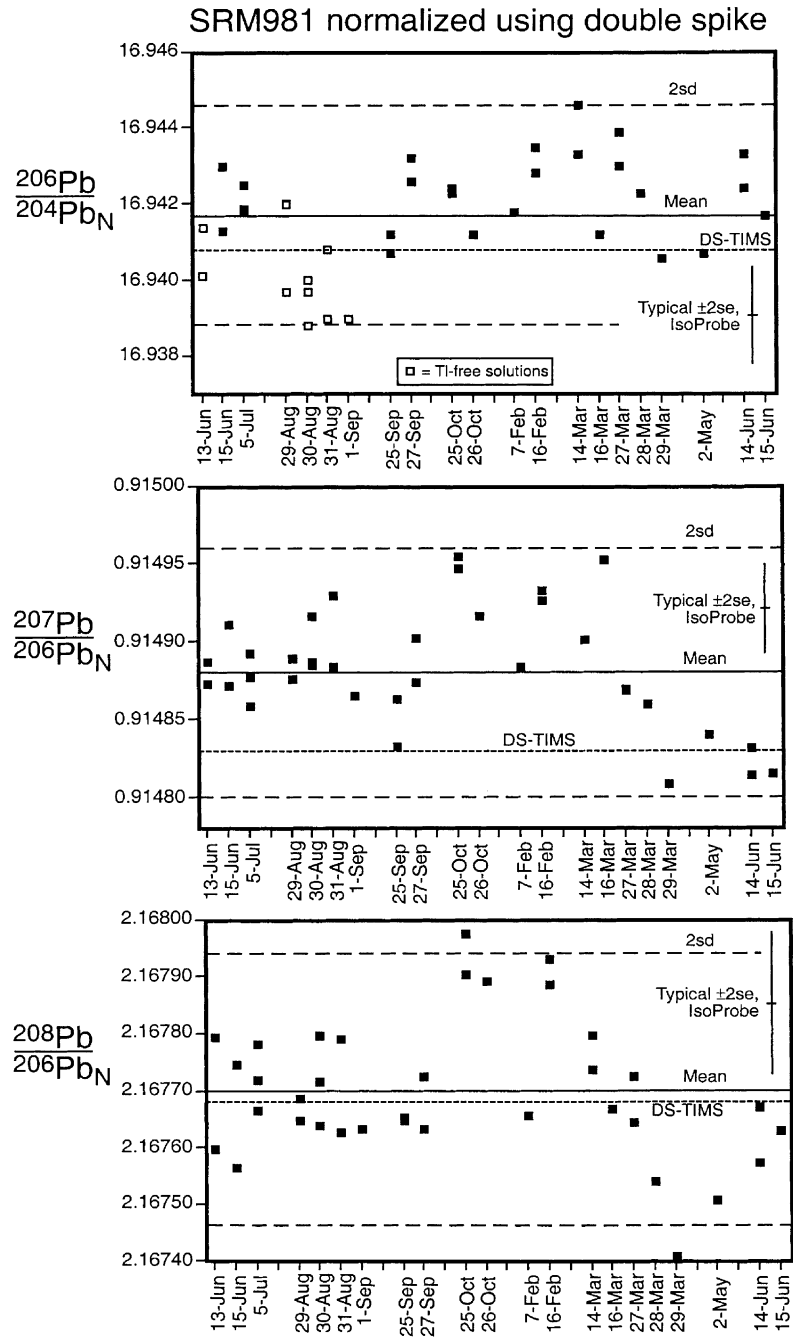


Fig. 6. Pb isotopic ratios in SRM981 normalized by independent double spike runs over the period June 2000 to June 2001. Note conformity to Royal Holloway DS-TIMS values. 2se values are means of internal precision propagated through the double spike algorithms.

mean and 2sd values of this subset of samples are virtually identical to those of the whole Tl-normalized data set (Table 4).

Although the external precisions of the DS-IsoProbe data are similar to those of Royal Holloway DS-TIMS, they are significantly worse than the mean internal precisions. In the DS-TIMS data, this is because the correction for  $^{207}\text{Pb}$  is only an approximation of a process that is not understood (Thirlwall, 2000). Using DS-IsoProbe, this does not apply, and it should be possible to attain better external precision values. The DS-normalized IsoProbe data for SRM981 show no relationships with  $Q$  or  $\beta$ -values.  $^{206}\text{Pb}/^{204}\text{Pb}_{\text{DS}}$  is slightly lower in runs with no added Tl (Fig. 6), with means being  $16.9405 \pm 21$  (2sd on 10) on Tl-free and  $16.9425 \pm 21$  (2sd on 26) on Tl-bearing solutions, possibly reflecting a minor common Pb contaminant in the Tl solution. However, there is no correlation with  $^{205}\text{Tl}/^{206}\text{Pb}$  ratio over the range from 0.1 to 0.94, and this effect is not noticeable in the internally normalised Micromist data (Fig.

5).  $^{208}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$  and  $^{207}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$  are always within 2se internal errors on a single day, but do show small changes from day to day (Fig. 6).  $^{207}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$  is low in June 2001 and high on 16/3/01, where it is accompanied by normal  $^{208}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$ , due to respectively anomalous low and high internally normalized  $^{207}\text{Pb}/^{206}\text{Pb}$  on the natural run (see 16/3/01 on Fig. 5). The low values in June 2001 are associated with a change to a new PFA nebulizer in the Aridus. The high values for both  $^{207}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$  and  $^{208}\text{Pb}/^{206}\text{Pb}_{\text{DS}}$  in October 2000 and on 16/2/01, and low values on 29/3/01 are due to problems with the “mix” run: processing natural runs from these days with “mix” runs from other days results in normal DS-normalized ratios. Although the causes of these small effects are under investigation, small cup efficiency changes affecting  $^{204}\text{Pb}$  would not be noticed on the natural run but would have a significant effect on the “mix” run. Such changes could be accurately corrected by normalization to the standards run each day.

Table 7  
Comparative Pb isotope data for silicate samples using DS-TIMS and DS-IsoProbe

		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	
IsoProbe	R010	18.3940±12	15.4951±11	37.845±3	
TIMS	RO10	<i>18.3904±14</i>	15.4934±12	37.840±3	
IsoProbe	121D3	18.2870±16	15.4521±14	37.860±4	
TIMS	121D3	18.2854±34	15.4490±29	37.858±7	
IsoProbe	RP91L	18.9126±14	15.5181±12	38.487±3	
TIMS	RP91L	18.9141±12	<i>15.5157±10</i>	38.484±3	
IsoProbe	SV2	19.3968±13	15.7348±12	38.945±3	
TIMS	SV2	19.3950±13	15.7347±11	38.945±3	
IsoProbe	105D1	18.2274±15	15.4518±14	37.809±4	
TIMS	105D1	18.2247±24	<i>15.4481±21</i>	37.800±5	
IsoProbe	131D1	18.2324±14	15.4312±13	37.795±4	
TIMS	131D1	18.2343±28	15.4337±24	37.804±6	
IsoProbe	128D6	18.4778±17	15.4733±16	38.058±5	
TIMS	128D6	18.4716±49	15.4687±41	38.048±10	
IsoProbe	AD21	19.9271±40	15.6330±26	39.605±9	mean±2sd of four digestions
IsoProbe	AD21	19.9281±13	15.6290±11	39.592±3	separate digestion
TIMS	AD21	<i>19.9411±21</i>	15.6304±17	39.604±4	large blank correction
TIMS	AD21	19.9315±21	15.6301±17	39.595±4	same assuming less blank

Italics denote failure to agree within the propagated internal precision.

IsoProbe data corrected for the small daily variations in DS-normalised SRM981.

TIMS data corrected for anomalous  $^{207}\text{Pb}$  behaviour to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$ .

All data blank corrected using procedure blanks prepared with the set of samples.

Samples include MORB, ocean island and arc basalts and are <1 Ma old except for AD21 (ca. 11 Ma). TIMS digestions carried out 1998–1999; fresh digestions were used for the IsoProbe work.

#### 5.4. Silicate samples normalized using DS on both TIMS and IsoProbe

Eight silicate samples have been prepared from HCl-leached rock chips and run using DS-normalization on both TIMS and IsoProbe. Results (Table 7) agree within propagated internal precision for most samples, the main exception being sample AD21, where the differences are attributable to uncertain blank corrections. The initial preparation of four separate digestions for this sample took place at a time when the blank was rather unpredictable.

#### 5.5. Comparison between DS and Tl normalization

The DS correction allows calculation of the Pb mass bias,  $\beta_{\text{DS}}$ , on both natural and “mix” runs. Addition of Tl to both runs used for the DS correction allows the independent calculation of the Tl mass bias,  $\beta_{\text{Tl}}$ , for the same runs. Fig. 7 shows the variation of  $\beta_{\text{Tl}}/\beta_{\text{DS}}$  for 23 silicate natural runs, 25 silicate “mix” runs, 4 SRM981 natural runs and 4 SRM981 “mix” runs over three consecutive days. Of 14 days when DS normalisation has been used, 10 show a pattern very similar to that of 27/3/01. Silicate samples, whether natural or “mix” runs, show  $\beta_{\text{Tl}}/\beta_{\text{DS}} = 1.000 \pm 0.005$ , while SRM981 naturals show  $\beta_{\text{Tl}}/\beta_{\text{DS}} = 1.020 \pm 0.005$ , and SRM981 “mix” runs show  $\beta_{\text{Tl}}/\beta_{\text{DS}} = 1.007 - 1.020$ . Obviously,  $\beta_{\text{Tl}}/\beta_{\text{DS}}$  depends on the  $^{205}\text{Tl}/^{203}\text{Tl}_{\text{N}}$  used to calculate  $\beta_{\text{Tl}}$ . The value of 2.3889 was chosen to yield  $\beta_{\text{Tl}}/\beta_{\text{DS}} = 1.000 \pm 5$  for the majority of silicate samples, and interestingly yields SRM981 values nearly identical to DS-TIMS and DS-IsoProbe data when applied to the Royal Holloway Micromist data and to the MC-ICP-MS data of Belshaw et al. (1988), Rehkämper and Halliday (1998) and Vance and van Calsteren (1999) (Table 4). On these 10 days, the observed Tl ion beam intensity in SRM981 solutions was typically 45–65% of the intensity in silicate solutions (Fig. 7), despite using the same  $\sim 5$  ppb Tl solution to dissolve both silicates and SRM981 prior to analysis. Reagent and procedure blanks usually show similar Tl intensities to the silicates, but the pure  $\sim 5$  ppb Tl solution shows  $\sim 33\%$  of the Tl signal of the silicates.

One silicate sample on 27/3/01 has  $\beta_{\text{Tl}}/\beta_{\text{DS}} = 1.012$ , and sporadic other silicate samples behave similarly on the nine other days like 27/3/01. Commonly, if  $\beta_{\text{Tl}}/\beta_{\text{DS}}$  is high for the natural run, it will also be high for the “mix” run. However, they do not usually show reduced Tl ion beams (Fig. 7). The remaining 4 days show silicate  $\beta_{\text{Tl}}/\beta_{\text{DS}}$  that diverge markedly from 1.000, and 28/3/01 is a good example. On 28/3/01 many silicates show  $\beta_{\text{Tl}}/\beta_{\text{DS}} \sim 1.02$ , and  $\beta_{\text{Tl}}/\beta_{\text{DS}}$  decreases with time from 1.02 as both the natural runs and “mix” runs are analysed (Fig. 7). SRM981 shows reduced Tl ion beam intensity but this is not apparent in the silicates. In the case of these 2 days, the silicate samples were prepared in two different laboratories, but samples prepared using identical chemistry at Royal Holloway can behave in both ways. On days when the silicates show variable  $\beta_{\text{Tl}}/\beta_{\text{DS}}$ , low Tl intensities are sometimes observed on the most discrepant samples, but sometimes not.

## 6. Causes of failure of Tl normalization

DS-normalized data are considered to be the most accurate Pb isotope results for all sample types on the Royal Holloway IsoProbe. This is because

- $^{208}\text{Pb}/^{206}\text{Pb}$ -normalized Pb data have good external precision for all SRM981 analysed and are accurate relative to DS-TIMS (Table 3);
- DS-normalized SRM981 results on the IsoProbe are equally reproducible and are also accurate relative to DS-TIMS (Table 6);
- DS-normalized silicate samples agree within error with DS-TIMS (Table 7), but so far, unfortunately, these all have  $\beta_{\text{Tl}}/\beta_{\text{DS}}$  close to unity.

Accordingly, it seems clear that Tl is unable to provide accurate normalization of most SRM981 solutions and about 30% of silicate samples run at Royal Holloway. In addition to the poor reproducibility of Tl-normalized SRM981 data, evidence in support of the problem lying with Tl includes the differences in measured  $^{205}\text{Tl}/^{203}\text{Tl}$  between different SRM981 solutions and silicates (Fig. 3), and the reduction of Tl signal intensities in SRM981 relative to samples (Fig. 7). Given that all other ICP-MS laboratories use Tl-normalisation,

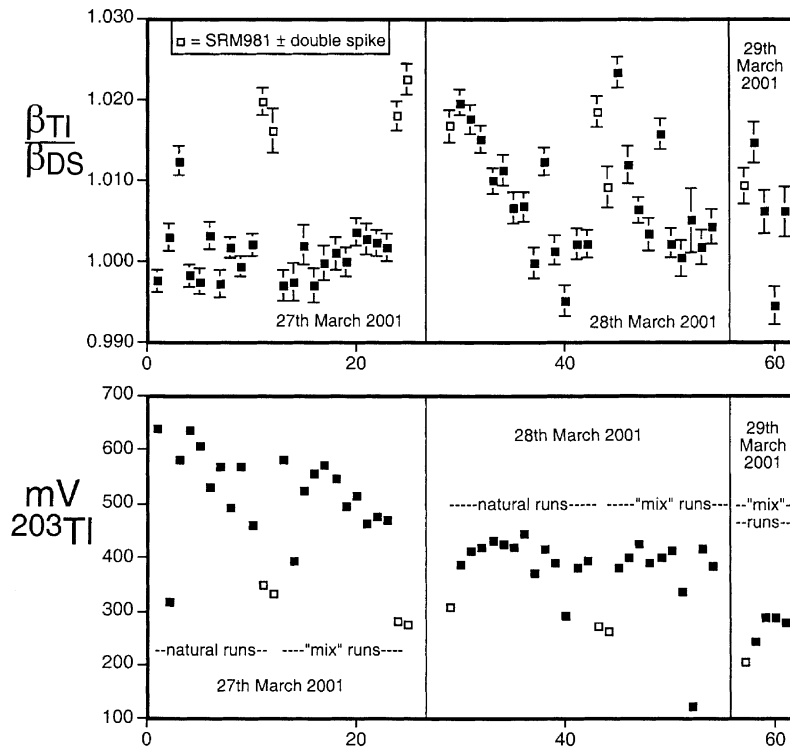


Fig. 7. Comparison between the exponential normalization parameter  $\beta$  independently determined for each run using Tl ( $\beta_{Tl}$ , assuming  $^{205}\text{Tl}/^{203}\text{Tl}_N = 2.3889$ ), or double spike ( $\beta_{DS}$ ). Data are shown for chemically separated silicate samples with and without DS, and for SRM981 samples with and without DS, over three consecutive days. All samples were dissolved in a single  $\sim 5$  ppb Tl solution, and the lower diagram shows the observed  $^{203}\text{Tl}$  signal intensities for the same runs. Error bars are 2se from propagating the errors on the raw ratios. Note that high  $\beta_{Tl}/\beta_{DS}$  in SRM981 is associated with  $\sim 40\%$  drop in Tl signal intensities, but that Tl signal is not a good predictor of  $\beta_{Tl}/\beta_{DS}$  in silicates.

it is important to discuss possible reasons for these problems.

### 6.1. Residual sample Tl in silicate samples or an interference on the Tl masses

If Tl was not fully removed from the silicate samples during ion exchange chemistry, residual Tl in the samples could have undergone extensive column mass fractionation and be isotopically different to natural Tl, resulting in an incorrect Tl mass bias correction for silicates. Similarly, an interference on Tl masses present only in silicate samples (e.g.  $\text{ReO}^+$  originating in the chemistry blank, Section 3.3), could cause the apparent difference in Tl mass bias between silicates and SRM981. The  $\text{ReO}$  hypothesis is inconsistent with  $<1$  mV  $\text{Re}^+$

ion beams observed in most silicates, and with the higher measured  $^{205}\text{Tl}/^{203}\text{Tl}$  in column-processed SRM981 than in unprocessed SRM981 than in silicates (Fig. 3). Both hypotheses are inconsistent with the accuracy and reproducibility of Tl-normalized Pb data being worse for SRM981 than for silicates (Table 4, Fig. 7). Both hypotheses have been tested by analysing a single SRM981 solution and two separate digestions of hawaiiite AD21 before and after adding Tl, on a day with very stable mass bias (Table 8). Pb isotope ratios are nearly identical between Tl-free and Tl-spiked samples. As usual, measured  $^{205}\text{Tl}/^{203}\text{Tl}$  is 450 ppm higher in SRM981 than in the silicates. All three had very small ion signals at masses 203 and 205 prior to adding the Tl solution. If the measured  $^{205}\text{Tl}/^{203}\text{Tl}$  is assumed to be a mixture between

Table 8

Measured isotope ratios for two silicate digestions and one SRM981 solution before and after adding Tl solution

	$^{205}\text{Tl}/^{203}\text{Tl}$	$^{205}\text{Tl}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$
SRM981	1.1±0.2	0.000011±2	2.21268±3	17.2922±9
SRM981	2.44037±10	0.24494	2.21264±3	17.2933±9
AD21/1	1.8±0.2	0.000019±1	2.02859±3	20.3399±9
AD21/1	2.43920±8	0.29149	2.02858±3	20.3411±9
AD21/2	1.7±0.2	0.000021±1	2.02865±4	20.3411±9
AD21/2	2.43935±6	0.43634	2.02867±2	20.3438±9

No correction for mass bias. Data measured over 6-h period. Other AD21 digestions had similar  $^{205}\text{Tl}/^{203}\text{Tl}$  both before and after analysing three SRM981, which all had elevated  $^{205}\text{Tl}/^{203}\text{Tl}$ .

these small signals and the added Tl solution, the true  $^{205}\text{Tl}/^{203}\text{Tl}$  of the added Tl solution can be calculated for each. This is ~22 ppm higher than the observed ratio for AD21 and 54 ppm higher for SRM981. Since these are trivial relative to the observed difference in  $^{205}\text{Tl}/^{203}\text{Tl}$ , it is concluded that neither isobaric interference nor residual sample Tl can explain the Tl problem.

### 6.2. Contamination with blank Pb

Environmental Pb is a major problem for high-precision Pb isotope analysis (Thirlwall, 2000). Blank contamination cannot explain the difference in Pb-normalized  $^{205}\text{Tl}/^{203}\text{Tl}$  between normal and chemically processed SRM981 (Fig. 5) as ~300 ng of Pb was used in this chemical experiment, and procedure blanks were ~40 pg. Our laboratory blank  $^{208}\text{Pb}/^{206}\text{Pb}$  (2.130) is very close to that of SRM981 so heterogeneity in Tl-normalized SRM981 Pb data cannot be explained by blank.

### 6.3. Mass fractionation of Pb isotopes during chemical separation

Column-induced mass fractionation is a known problem for light elements such as Cu (Marechal et al., 1999), and there could be a small effect for heavy elements. Addition of the double spike after chemistry does not correct for this possible effect, but consistency between the two separate digestions of silicates (for DS-TIMS and DS-IsoProbe, Table 7), suggests it is minor. The effect cannot explain the higher apparent  $^{205}\text{Tl}/^{203}\text{Tl}_N$  needed to correct column-passed SRM981, but lower apparent  $^{205}\text{Tl}/^{203}\text{Tl}_N$  needed

for silicates. The low Tl-normalized  $^{206}\text{Pb}/^{204}\text{Pb}$  of SRM981 (Table 4) cannot be explained by blank contamination as our laboratory blank has much higher  $^{206}\text{Pb}/^{204}\text{Pb}$ .

### 6.4. Sample matrix effect on the relative mass bias of Tl and Pb

Sample matrix change may indeed change mass bias, and the relative effects on Tl and Pb can be studied by comparing variation in  $\beta_{\text{DS}}$  and  $\beta_{\text{Tl}}$  with time. In general,  $\beta_{\text{Tl}}$  is more negative for SRM981 than for silicates (higher  $^{205}\text{Tl}/^{203}\text{Tl}$ , Fig. 3), and  $\beta_{\text{DS}}$  for SRM981 is similar to that of bracketing silicates, although there are some cases where  $\beta_{\text{DS}}$  is slightly less negative in SRM981. For the data of 30/3/00 (Fig. 3),  $\beta_{\text{Pb}}$  was calculated assuming  $^{208}\text{Pb}/^{206}\text{Pb}=2.1677$  for the SRM981 runs, and DS-TIMS  $^{208}\text{Pb}/^{206}\text{Pb}$  values for the silicates.  $\beta_{\text{Pb}}$  shows a common trend for all samples getting slightly less negative with time. These results imply that any matrix effect on Pb is small relative to that on Tl. Further, matrix effects *sensu stricto* must be caused by something in the matrix. The fact that Tl-normalisation works for about 70% of silicate samples but only for ~10% of SRM981 runs is difficult to reconcile with a matrix effect in the chemically pure SRM981. A matrix effect is inconsistent with the observation that silicate samples have systematically lower measured  $^{205}\text{Tl}/^{203}\text{Tl}$  than SRM981 whether they are the product of single pass chemistry of rocks with ~0.5 ppm Pb (data of 30/3/00) or double pass chemistry of rocks with ~10 ppm Pb (data of 21/3/00, Fig. 3). Matrix in the latter should be very dilute, a view confirmed

by a scan showing no element with  $>0.1$  V ion beam from mass 48 upward. The matrix of the chemically processed SRM981 should be similar to that of a sample if the chemistry actually introduces matrix (e.g. resin), but it has radically higher  $^{205}\text{Tl}/^{203}\text{Tl}_\text{N}$  than silicate samples processed in the same batch (Fig. 3).

### 6.5. Solution chemistry of Tl

The low intensity of the Tl ion signal in SRM981 solutions (Fig. 7) is thought to be the best indicator of the cause of the inconsistent Tl mass bias behaviour. Since the same  $\sim 5$  ppb Tl solution is used to dissolve both SRM981 and silicates, it should produce the same ion beam intensity in both solutions. The Tl signal is not being suppressed by the Pb ion beam, since signal intensity is lower still in the pure Tl solution, and high Tl signals are observed in procedure and reagent blanks. The pure Tl solution has even higher measured  $^{205}\text{Tl}/^{203}\text{Tl}$  than bracketing SRM981 solutions, and thus it is suspected that whatever causes the Tl signal reduction preferentially affects the lighter isotope. A reagent blank with 1 V  $^{205}\text{Tl}$  and 0.6 V  $^{208}\text{Pb}$  was mixed in various proportions with the pure Tl solution (0.4 V  $^{205}\text{Tl}$  and no Pb). If signal intensities were proportional to concentration in solution, linear mixing should be observed. Pb signals decreased as expected with mixing proportion, but Tl signals decreased much more slowly, implying that the effect is a consequence of anomalous solution chemistry of Tl, perhaps during interaction with the nebulizer. Despite this apparently simple explanation, all prior chemical or heat treatment to ensure similar solution behaviour of silicates and SRM981 has so far failed to change the relationships described in this paper.

## 7. Conclusions

(1) Pb isotope data of similar external and internal precision (55–180 ppm 2sd) can be achieved on  $\sim 7$  ng of Pb using a wide range of SRM981 solutions on the Royal Holloway IsoProbe through mass bias normalization to constant  $^{208}\text{Pb}/^{206}\text{Pb}$ . To achieve this, it is essential to understand the behaviour of background,

with accurate tail corrections (Thirlwall, 2001) being the most important. It is possible to change dramatically the isotopic composition of samples being measured without significantly affecting the instrument memory.

(2) Data so obtained are indistinguishable from multidynamic TIMS data corrected in the same way for mass bias provided that the TIMS data are corrected for the anomalous behaviour of  $^{207}\text{Pb}$  (Thirlwall, 2000) to the lowest measured  $^{208}\text{Pb}/^{206}\text{Pb}$ , rather than to the fractionation-corrected  $^{208}\text{Pb}/^{206}\text{Pb}$ .

(3) The Royal Holloway  $^{207}\text{Pb}$ - $^{204}\text{Pb}$  double spike (DS) has been independently calibrated against SRM982 on the IsoProbe and yields nearly identical results to those obtained by TIMS.

(4) 36 IsoProbe analyses of SRM981 solutions using independent SRM981-DS mixtures to correct for mass bias yield mean values and external precisions nearly identical to Royal Holloway DS-TIMS data (87–245 ppm maximum 2sd for  $^{208}\text{Pb}/^{204}\text{Pb}$ ). Since this is an independent calibration and also agrees with the triple spike data of Galer and Abouchami (1998), a new value for SRM981  $^{208}\text{Pb}/^{206}\text{Pb}$  of  $2.1677 \pm 2$  is proposed. The other Pb ratios in SRM981, determined by TIMS and most published MC-ICP-MS studies, agree with the values reported here when normalized to this value for  $^{208}\text{Pb}/^{206}\text{Pb}$ . DS-normalized SRM981 data show small variations with time possibly reflecting changes in cup efficiencies. They are essentially independent of nebulizer, Tl/Pb ratio, and type of SRM981 solution.

(5) Eight DS-normalized IsoProbe analyses of silicate samples are within error of DS-TIMS data for separate digestions of these samples.

(6) Tl-normalization of Pb isotope ratios can provide moderately reproducible data for a single SRM981 solution over a few months. However, differences of 500–800 ppm exist between  $^{205}\text{Tl}/^{203}\text{Tl}$  measured on samples and different solutions of SRM981 on any 1 day, and between the same SRM981 solution measured on different nebulizers, and over a longer time period. Comparison between DS- and Tl-normalized sample and SRM981 data shows that use of SRM981 to optimize the  $^{205}\text{Tl}/^{203}\text{Tl}_\text{N}$  normalizing ratio would give systematic errors in Tl-normalized Pb ratios of  $\sim 400$  ppm/amu. While adequate for some applications, the only major advantage of Tl-normalization over conventional

TIMS is then speed. If  $^{205}\text{Tl}/^{203}\text{Tl}_N = 2.3889$  is assumed,  $\sim 70\%$  of silicate samples analysed show good agreement between Tl- and DS-normalized results; Tl-normalized SRM981 determined with a Micromist nebulizer agree with the DS-normalized results, and several published datasets for MC-ICP-MS SRM981 also conform to the DS-normalized results.

(7) The problems with Tl-normalization can be shown to not be due to isobaric effects or residual sample Tl. They most probably reflect processes affecting Tl in solution in the nebulizer. This is suggested because, for identical Tl concentrations, Tl signal intensities are depressed in SRM981 and pure Tl solutions relative to solutions of Pb chemically separated from silicates. It is highly likely that this behaviour affects other MC-ICP-MS instrumentation: its absence can only be confirmed by analysis of samples that have known Pb isotope ratios from DS studies.

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