Multi-collector ICP-MS Analysis of Pb Isotope Ratios in Rocks: Data, Procedure and Caution

LI Huaikun
ACQUIRE, The University of Queensland, Brisbane, Qld 4072, Australia
Tianjin Institute of Geology and Mineral Resources, Tianjin, 300170, China;
E-mail :tjlhuaikun@cgs.gov.cn
and NIU Yaoling
Department of Earth Sciences, Cardiff University, Cardiff, CF10 3YE, UK
ACQUIRE, The University of Queensland, Brisbane, Qld 4072, Australia

Abstract The authors measured Pb isotope compositions of seven USGS rock reference standards, i.e. AGV-1, AGV-2, BHVO-1, BHVO-2, BCR-2, BIR-1/1 and W-2, together with NBS 981 using a micromass isoprobe multi-collector inductively-coupled plasma mass spectrometer (MC-ICP-MS) at the University of Queensland. ^{203}Tl-^{205}Tl isotopes were used as an internal standard to correct for mass-dependant isotopic fractionation. The results for both NBS 981 and USGS rock standards AGV-1 and BHVO-1 are comparable to or better than double- and triple-spike TIMS (thermal ionization mass spectrometry) data in precision. The data for BHVO-2 and, to a lesser extent, AGV-2 and BCR-2 are reproducibly higher for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb than double-spike TIMS data in the literature. The authors also obtained the Pb isotope data for BIR-1/1 and W-2, which may be used as reference values in future studies. It is found that linear correction for Pb isotopic fractionation is adequate with the results identical to those corrected following an exponential law or a power law. Precise ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb and ^{208}Pb/^{207}Pb ratios can be acquired for sample solutions with Pb≥1 ppb. However, Pb isotope ratios involving ^{204}Pb (i.e., ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb) are reliable for solutions with Pb≥40 ppb. The errors for Pb isotope ratio analysis using the MC-ICP-MS are dominated by errors in the analysis of ^{204}Pb, which is commonly ascribed to the difficulty and imprecise correction for a ^{204}Hg isobaric interference. It is found however that the major errors on ^{204}Pb come from the tailings of mass ^{203}Tl and mass ^{205}Tl. These mass tailings lead to over-subtraction of the baseline for ^{204}Pb, which is measured at ±0.5 amu on both sides of mass-204 (i.e., at amu 203.5 and 204.5 respectively). Such errors are insignificant for Pb-rich sample solutions (i.e., high Pb/Tl ratios), but can be severe for low-Pb sample solutions when over-"spiked" with Tl. Experiments in this study suggest that a minimum concentration ratio of Pb/Tl>5 in Tl-"spiked" solutions be required to ensure reliable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb isotopic ratios. The tailings of ^{203}Tl and ^{205}Tl can also lead to over-subtraction of baselines for ^{202}Hg (at amu 202.5) and ^{206}Pb (at amu 205.5). Therefore, the elegance of using ^{203}Tl and ^{205}Tl isotopes for mass fractionation correction becomes a severe problem in low-Pb rock solutions—caution is required. Alternative internal standards for mass fractionation correction may be considered. Of course, significant instrumental refinement in abundance sensitivity is in demand.

Key words: MC-ICP-MS, Pb isotope ratios, reference materials

1 Introduction

It has been demonstrated that the MC-ICP-MS is the instrument of choice for precise measurement of isotope ratios of geochemical significance and, in particular, those of elements with high ionization potentials (e.g., Cu, Zn, Hf and W) that cannot be measured otherwise using the TIMS thanks to the innovative application of the superior ionization efficiency of a plasma source to Magnetic Sector multi-collector instruments (Bradshaw et al., 1989; Walder and Freeman, 1992; Lee and Halliday, 1995; Thirlwall and Walder, 1995; Blichert-Toft and Albarede, 1997; Marechal et al., 1999; Collerson, 2000; White et al., 2000). The MC-ICP-MS is particularly capable of high-precision and high-accuracy analysis for Pb isotopes (Rehkämper and Mezger, 2000; Thirlwall, 2000a; White et al., 2000). For Sr, Nd and Hf isotope analyses with the conventional TIMS method, mass fractionations occurring in mass spectrometers can be corrected accurately using the observed mass fractionation of two or more non-radiogenic isotopes of the same elements. This procedure is, however, impossible for Pb because the latter has only one non-radiogenic isotope, ^{204}Pb. Alternatively, a correction is applied by comparing this with the observed isotopic fractionation in a synthetic standard solution such as NBS 981. However, this procedure may not be valid because of the potentially different isotopic fractionation behaviors between pure-metal standard solutions and actual sample solutions, and the time dependence of mass fractionations (e.g., Hirata, 1996; White et al., 2000; Woodhead and Hergt, 2000). Double- and triple-spike techniques have been successful (e.g., Oversby and Gast, 1968; Hamelin et al., 1985; Todt et al., 1996; Galer and Abouchami, 1998), but they are labor-intensive and time-consuming. These problems might be overcome by the recently developed MC-ICP-MS method with the ^{203}Tl-^{205}Tl isotopes as an internal standard (e.g. White et al., 2000).

The purpose of this paper is to show that by using the MC-ICP-MS, a Micromass Isoprobe, we can acquire high-quality Pb isotopic ratio analyses in actual rock solutions (e.g., the USGS rock reference standards) as well as in the synthetic reference standard (e.g., NBS 981) (Collerson, 2000). The precisions are comparable to or better than those done by the TIMS. The requirements for small sample size, simplified sample preparation, fast throughput, and great detection capacity make the MC-ICP-MS the instrument of choice. However, caution is necessary for low-Pb solutions, in which case imprecise background mass 204 correction (e.g., the effect of ^{204}Hg and other possible isobaric interferences) and, in particular, excessive use of Tl can lead to unreliable Pb isotope ratios involving ^{204}Pb.

2 Instrument, Sample Preparation and Analytical Details

The MC-ICP-MS that we used at the University of Queensland (UQ) is a Micromass^{TM} Isoprobe (Collerson and Palacz, 1999; Collerson, 2000). NBS 981 solution was diluted to 100 ppb in 2% HNO_3 with 5−10 ppb of Tl added as an internal standard. About 200 mg of rock powder for each of the studied USGS rock standards was dissolved in a mixture of triple-distilled HF and HNO_3 acids using tightly sealed Teflon Savilex^{TM} beakers on a hot plate at ~150°C for ~ 24 hours. The sample solutions were then placed lid off on a hot plate at ~120°C to evaporate to incipient dryness. Two ml 6N HCl was added to remove the fluorides if any. Sample powders were unleached prior to digestion. Lead was separated by the conventional anion exchange procedure on micro-columns containing BioRad^{TM} AG 1-X8 (200–400 mesh) resin and using one column pass in HBr/HCl media (e.g., Woodhead and Hergt, 2000). All wares used in sample preparation were cleaned following a strict procedure: boiled in detergent decon^{TM} 90, Aquaregia, 6N HNO_3 and then leached with concentrated triple-distilled HNO_3 on a hot plate for over 24 hours. The total Pb procedure blank for the whole-rock analyses is between 60 and 100 pg per analysis (Wendt et al., 1999), which is in all cases insignificant for Pb-rich samples studied (Pb **~2 ppm for BHVO-1, BHVO-2 and** BIR-1; **10 ppm for AGV-1, AGV-2, BCR-2 and W-2).**

Isoprobe operating conditions have been discussed by Collerson and Palacz (1999) and Collerson (2000), and the technical details will be discussed elsewhere (Collerson et al., 2002). The Aridus Desolvating system was used for sample solution introduction. Note that the blank level for the Aridus if any is negligible because no Pb isotope signal is detected after our four-step washouts (see below). The sample up-take rate is ~ 60 μl per minute. The between-sample wash includes 5 minutes flush using each of the following solutions: (1) 10% HNO_3, (2) 0.01% HF, (3) isopropyl alcohol and (4) 2% HNO_3 (a total of 20 minutes). Sample solutions were “spiked” with ~5–10 ppb Tl for mass fractionation correction. On-peak zeros were measured to correct for the background Hg effect (in argon or solution or both?) and for the possible Pb memory from the sample introduction system. A ±0.5-amu background was measured for baseline subtraction prior to the measurements of isotopic peaks for each unknown sample solution. 100 ppb solution typically yielded a Pb ion beam of >12 volts. Sufficient precision can be achieved by acquiring < 50 cycles in less than 10 minutes (i.e., < 12 s per cycle) consuming about 1 ml solution provided that the solutions have Pb ≥ 40 ppb. Masses 202, 203, 204, 205, 206, 207 and 208 were measured simultaneously via a multi-Faraday Cup array. Mass 202 (assumed to be ^{202}Hg) was measured to correct for ^{204}Hg contribution to ^{204}Pb, assuming that ^{204}Hg/^{202}Hg = 0.229866 (White et al., 2000). Pb isotope mass fractionation was corrected against the observed ^{203}Tl-^{205}Tl mass fractionation. The correction is done by assuming that Tl and Pb behave similarly in ICP-MS (e.g., Longerich et al., 1987; Walder and Furuta, 1993; White, 1993; Belshaw et al., 1998; Rehkämper and Halliday, 1998;).

3 Results and Discussion

3.1 Mass fractionation correction

Mass fractionation occurring in the ICP-MS is always larger than in the TIMS. However, for Pb isotope analysis, the mass fractionation in ICP-MS can be corrected effectively via simultaneously measuring ^{203}Tl/^{205}Tl and Pb isotopic ratios. Previous MC-ICP-MS studies of Pb isotopes followed either an exponential law (e.g., Blichert-Toft et al., 1997; Luais et al., 1997; Belshaw et al., 1998; Marechal et al., 1998; Rehkämper and Mezger, 2000; Thirlwall, 2000; White et al., 2000) or a power law (e.g., Hirata, 1996, 1997; Rehkämper and Halliday, 1998) to correct for mass-dependent Pb isotopic fractionation. White et al. (2000) gave an excellent account of the issue and dealt with this rigorously. However, we have observed a simple linear relationship in mass-dependent isotopic fractionation in the measured mass range of 203 to 208. Simple linear correction is therefore adequate for Pb mass fractionation, at least for Pb isotope ratios within the range of natural rocks.

In our analysis, isotope ratio calculation includes subtraction of baseline, on-peak zeros to correct for possible Pb memory from the sample introduction system and the possible ^{204}Hg contribution to ^{204}Pb, and most importantly the mass fractionation correction. Mass fractionation correction is achieved by correcting against the observed ^{203}Tl-^{205}Tl fractionation, assuming that Pb has the same mass fractionation coefficient as Tl and a reference value of $(^{203}\mathrm{Tl}/^{205}\mathrm{Tl})_R$ = 0.41865, which is obtained empirically to be the optimal value for the Isoprobe at UQ (Collerson, 2000). This value is similar to the value (0.41892) of Dunstan et al. (1980). Rehkämper and Mezger (2000) preferred to adjust this reference value on a daily basis, but we have found that such adjustment is not necessary. This is because the relative errors on NBS 981 we measured over a 5-month period (N = 154) corrected using a single $(^{203}\mathrm{Tl}/^{205}\mathrm{Tl})_R$ value are acceptably small (see below).

We have found that the measured $^{203}\mathrm{Tl}/^{205}\mathrm{Tl}$ values are always less than the actual values. For example, the average measured $^{203}\mathrm{Tl}/^{205}\mathrm{Tl}$ value of 154 analyses over a 5-month period is 0.41343 ± 0.00076 (mean±1σ). This value is significantly smaller than all reference values, including the reference value that we use (e.g., 0.41865 of Collerson (2000)) and the value 0.41892 by Dunstan et al. (1980). This suggests that the mass fractionation seen in the MC-ICP-MS differs physically from that in the TIMS. In the TIMS, the mass fractionation occurs during ionization, that is, heavier isotopes of an element form stronger bonds and have slightly lower translational velocities than lighter isotopes (Urey, 1947; White et al., 2000) and therefore the lighter isotopes preferentially ionize and enter the analyzer. In the MC-ICP-MS, little mass fractionation occurs during ionization because the ionization efficiencies approach 100% (~ less than 1% in the TIMS) (White et al., 2000). Mass fractionation in the MC-ICP-MS is thought to result from space-charge effects in the low electrostatic field regions of the instrument; as the ion beam expands, lighter ions migrate to the exterior of the plasma and are focused less efficiently in the mass analyzer (Ross and Hieftje, 1991; Marechal et al., 1999; Niu and Houk, 1996; Hirata, 1996; White et al., 2000).

In mass fractionation correction following an exponential law, a fractionation coefficient, termed the Beta value, is defined as follows:

$$b = \ln(0.41865/\,(^{203}\mathrm{Tl}/^{205}\mathrm{Tl})_M)\,/\ln(203/205) \quad (1)$$

where subscript M denotes the measured value, and 0.41865 is the reference value of the $^{203}\mathrm{Tl}/^{205}\mathrm{Tl}$ ratio (Collerson, 2000). The β value is essentially the same as the factor f proposed by of Marechal et al (1999) and White et al. (2000). The corrected ratios (with subscript C) are calculated, for example, for Tl as:

$$(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_C = (^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_M \times (205/203)^{b} \quad (2)$$

We corrected Pb isotopic ratios using equation (2) accordingly assuming Pb behaves the same as Tl in mass fractionation in the ICP-MS (also see section 3.2). For example, $^{208}\mathrm{Pb}/^{206}\mathrm{Pb}$ is calculated as:

$$(^{208}\mathrm{Pb}/^{206}\mathrm{Pb})_C = (^{208}\mathrm{Pb}/^{206}\mathrm{Pb})_M \times (208/206)^{b} \quad (3)$$

All other Pb isotopic ratios are corrected accordingly using Equation (3).

Our study of NBS 981 shows that both the exponential law and the power law are indeed effective in using ^{203}Tl-^{205}Tl to correct for Pb mass fractionation in the MC-ICP-MS. We found, however, that a linear correction is adequate for Pb isotope ratios within the range defined by natural rocks. Our linear method does not need b values, but simply uses the ratio of measured $(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_M$ over reference $(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_R$, i.e.

$$\begin{aligned}&(\text{Corrected ratio})_C=\\&(\text{Measured ratio})_M/(1+((^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_M/(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_R-1)\times\\&(\text{mass difference})/2)\end{aligned} \quad (4)$$

For example,

$$\begin{aligned}&(^{208}\mathrm{Pb}/^{206}\mathrm{Pb})_C = (^{208}\mathrm{Pb}/^{206}\mathrm{Pb})_M/\\&(1+((^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_M\,/(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_R-1)\times(208-206)/2)\end{aligned}$$

Figure 1 plots the measured and corrected Pb isotopic ratios against $(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_M/(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_R$ for NBS 981. The 154 measurements for NBS 981 plotted in Fig. 1 include those previously reported by Collerson (2000), those determined along with USGS rock standards of this study, and those collected together with about 80 abyssal peridotite samples (Niu and Li in preparation) over a period of 5 months. Clearly, the measured $^{206}\mathrm{Pb}/^{204}\mathrm{Pb}$, $^{207}\mathrm{Pb}/^{204}\mathrm{Pb}$, $^{208}\mathrm{Pb}/^{204}\mathrm{Pb}$, $^{207}\mathrm{Pb}/^{206}\mathrm{Pb}$ and $^{208}\mathrm{Pb}/^{206}\mathrm{Pb}$ ratios all define linear trends against $(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_M/(^{205}\mathrm{Tl}/^{203}\mathrm{Tl})_R$. In other words, $y = ax+b$ with the correlation coefficients>0.99, statistically significant at confidence levels>99.99%. The y values at x=1 are the geometrical means when no mass fractionation occurs. These geometrical mean y values are in good agreement with both exponential and linear arithmetic mean values (Table 1). Such linear variations are unexpected (e.g., Maréchal et al., 1999; White et al., 2000), but our observations in Fig. 1 are robust. In fact, Fig. 1 demonstrates that linear correction is sufficient for correcting mass-dependent Pb isotope fractionation in the MC-ICP-MS, and confirms the suggestion/assumption in the literature that Pb and Tl behave sufficiently similar, if not identical, in terms of mass fractionation in the MC-ICP-MS. The latter is particularly important in understanding the physics of isotope fractionation in the MC-ICP-MS.

Figure 2 compares the results corrected linearly with those following the exponential law. Note that such excellent correlations are unexpected because if both correction procedures were perfect there should be a single value with random errors associated with the means. However, such within-error (±2σ) correlations demonstrate that the linear correction is as effective as those following the exponential and power laws.

3.2 mean and median values of NBS 981

Tables 1 and 2 present the mean and 2σ values of 154 measurements of Pb isotope ratios on NBS 981. The mean values of our NBS 981 data corrected using both methods are very similar to each other and similar to the median values (not shown), indicating that the variations are close to a normal distribution and reflect a random analytical error vs. artificial or procedure caused error.

Table 2 shows that our data are in good agreement within errors (2σ) with the existing double- and triple-spike TIMS data and MC-ICP-MS data from other laboratories. The external reproducibility on 154 runs over a 5-month period is 170 ppm (relative standard deviation, RSD = $1\sigma/\text{Mean} \times 10^6$) on ^{206}Pb/^{204}Pb, 253 ppm on ^{207}Pb/^{204}Pb, 308 ppm on ^{208}Pb/^{204}Pb, 118 ppm on ^{207}Pb/^{206}Pb and 160 ppm on ^{208}Pb/^{206}Pb respectively. Such reproducibility demonstrates not only a good long-term instrumental stability, but also the fact that the Isoprobe can indeed obtain precise Pb isotope ratios comparable in precision to the double- and triple-spike TIMS data. Note that such reproducibility is based on the correction using a single reference value of $(^{203}\text{Tl}/^{205}\text{Tl})_R = 0.41865$ over a 5-month period. This demonstrates that daily adjustment of this reference ratio (Rehkämper and Mezger, 2000) is unnecessary, at least for the Isoprobe at UQ.

3.3 USGS reference rock standards: AGV-1, AGV-2, BHVO-1, BHVO-2, BCR-2, BIR-1 and W-2

In order to investigate the potential of the Isoprobe for analyzing Pb isotopes in actual rocks, we analyzed seven USGS rock reference standards. Table 3 gives the data and Fig. 3 provides a comparison of our data with the available double-spike corrected TIMS data for 5 USGS rock standards: AGV-1, AGV-2, BCR-2, BHVO-1 and BHVO-2 (Woodhead and Hergt, 2000). The average of 10 runs of NBS 981 done during the analysis of these rock standards is in good agreement with the means of the 154 runs achieved in the 5-month period (see Tables 1 and 2). Our Isoprobe data for AGV-1 and BHVO-1 are in good

Table 1 Comparisons of Pb isotopic ratios in NBS 981 corrected linearly and exponentially

Isotopic ratios	^{206}Pb/^{204}Pb±2ó	^{207}Pb/^{204}Pb±2ó	^{208}Pb/^{204}Pb±2ó	^{207}Pb/^{206}Pb±2ó	^{208}Pb/^{206}Pb±2ó
Mean of Exp.	16.9445±60	15.4945±78	36.722±22	0.91443±22	2.16722±68
Mean of Lin.	16.9436±60	15.4936±80	36.722±22	0.91435±23	2.16686±74
Y (at *X=1*)	16.9485	15.5013	36.735	0.91468	2.16782

Note: ±2σ refers to the last 2 digits.

Table 2 Comparison of published Pb isotope data for NBS 981

		^{206}Pb/^{204}Pb±2ó	^{207}Pb/^{204}Pb±2ó	^{208}Pb/^{204}Pb±2ó	^{207}Pb/^{206}Pb±2ó	^{208}Pb/^{206}Pb±2ó	N
This study	Exponential	16.9445±60	15.4945±78	36.722±22	0.91443±22	2.16722±68	154
	Linear	16.9436±60	15.4936±80	36.722±22	0.91435±23	2.16686±74	
MC-ICPMS							
Hirata (1996)		16.9311±90		36.680±21	0.914623±37	2.16636±82	8
Belshaw et al., (1998)		16.9320±70			0.914630±60	2.16650±22	80
Rehkämper & Halliday (1998)		16.9326±55	15.4861±51	36.6808±128	0.914585±49	2.16629±14	32
White et al. (2000)		16.9467±76	15.4899±39	36.6826±78		2.1646±8	33
Rehkämper & Mezger (2000)		16.9366±29	15.4900±17	36.7000±29	0.91459±13	2.16691±29	N/A
*NBS TIMS		16.937±11	15.491±15	36.721±36	0.91464±33	2.1681±8	
Double Spike TIMS							
Todt et al. (1996)		16.9356±24	15.4891±30	36.7006±114	0.914585±13	2.16701±43	11
Woodhead et al. (1995)		16.937±4	15.492±5	36.708±13			109
Thirlwall (2000)		16.9409±22	15.4956±26	36.7228±80	0.91469±7	2.16770±21	31
Triple Spike TIMS							
Galer & Abouchami (1998)		16.9405±15	15.4963±16	36.7219±44	0.91475±4	2.16771±10	60

Note: ±2 refers to the last 2 digits. *NBS TIMS is the recommended TIMS value by Catanzaro et al. (1968). Note that such inter-laboratory comparison may not always be valid. For example, the values by White et al. (2000) are not claimed to be the true values of NBS 981, but only reference values or "prescribed standard" used to "normalize" the values of the rock sample data.

agreement with the double-spike TIMS data of Woodhead and Hergt (2000). The analytical precision is comparable to or better than the TIMS data. However, we observed that our Isoprobe data for BHVO-2, and to a lesser extent AGV-2 and BCR-2, differ from the double-spike TIMS data of Woodhead and Hergt (2000). The difference for BHVO-2 is beyond the analytical error. Given the similar precisions by the two techniques (Fig. 3), we suggest that the difference for BHVO-2 could be inherited from the difference of the two batches of rock reference materials studied. This difference for BHVO-2, plus the small but recognizable differences for AGV-2 and BCR-2, suggests the probable heterogeneity of these USGS standards, perhaps due to incomplete homogenization or contamination during preparation. Caution is therefore necessary when considering their Pb isotope measurements as standards (White, person. Comm., 2001).

We corrected for Pb isotopic mass fractionation for all the rock standards both linearly and exponentially. The two cases agree well with each other and are close to the double-spike TIMS data of Woodhead and Hergt (2000), particularly for AGV-1 and BHVO-1. We ran the same chemically separation solutions for some samples (BCR-2, BHVO-2 and W-2) at different times, and we also measured two different separation solutions of BCR-2 and BHVO-2 (Table 3). Especially, the data obtained for BCR-2, statistical analyses of three different Batches 0295, 0373 and 0376, including re-digestion and re-separation of Batch 0295 are all reproducible, and in good agreement with the double-spike TIMS data within 2σ errors

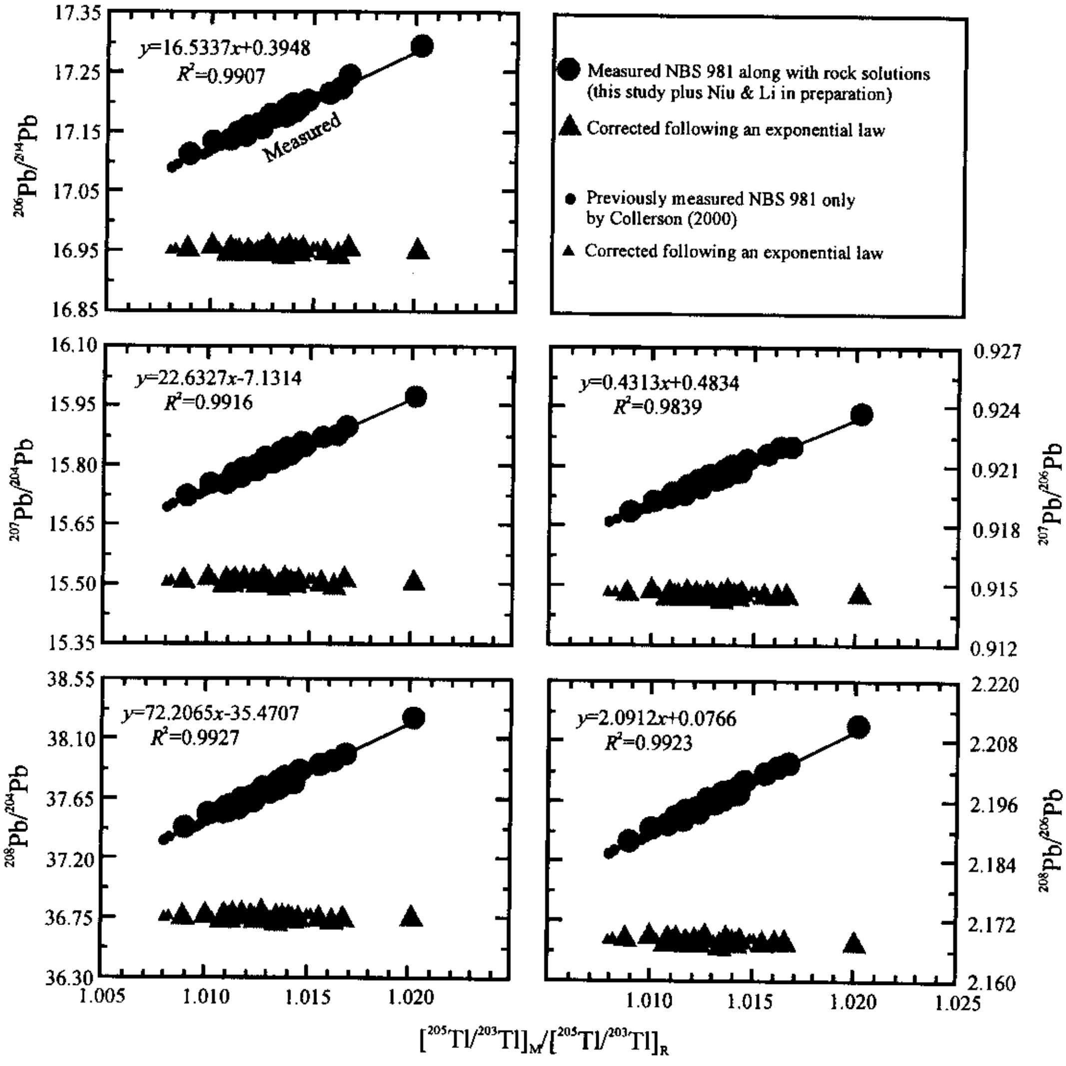

Fig. 1. Plots of measured and fractionation-corrected Pb isotopic ratios against $[^{205}Tl/^{203}Tl]_M/[^{205}Tl/^{203}Tl]_R$ for NBS 981.

The correction follows an exponential law (Equation 3). Note that the measured ratios defined almost perfect linear trends on these plots, which substantiate the validity and effectiveness of linear correction for mass dependent Pb isotopic fractionation (Equation 4). The intercepts or *Y* values of the regression lines at *X = 1* give geometric means (Table 1) of the corresponding isotopic ratios as if no mass fractionation occurred. Bigger grey circles and triangles are analyses done along with the USGS rock standards of this study and those done together with about 80 abyssal peridotite samples (Niu and Li, in preparation). Smaller solid circles and triangles are NBS 981 analyses of Collerson (2000).

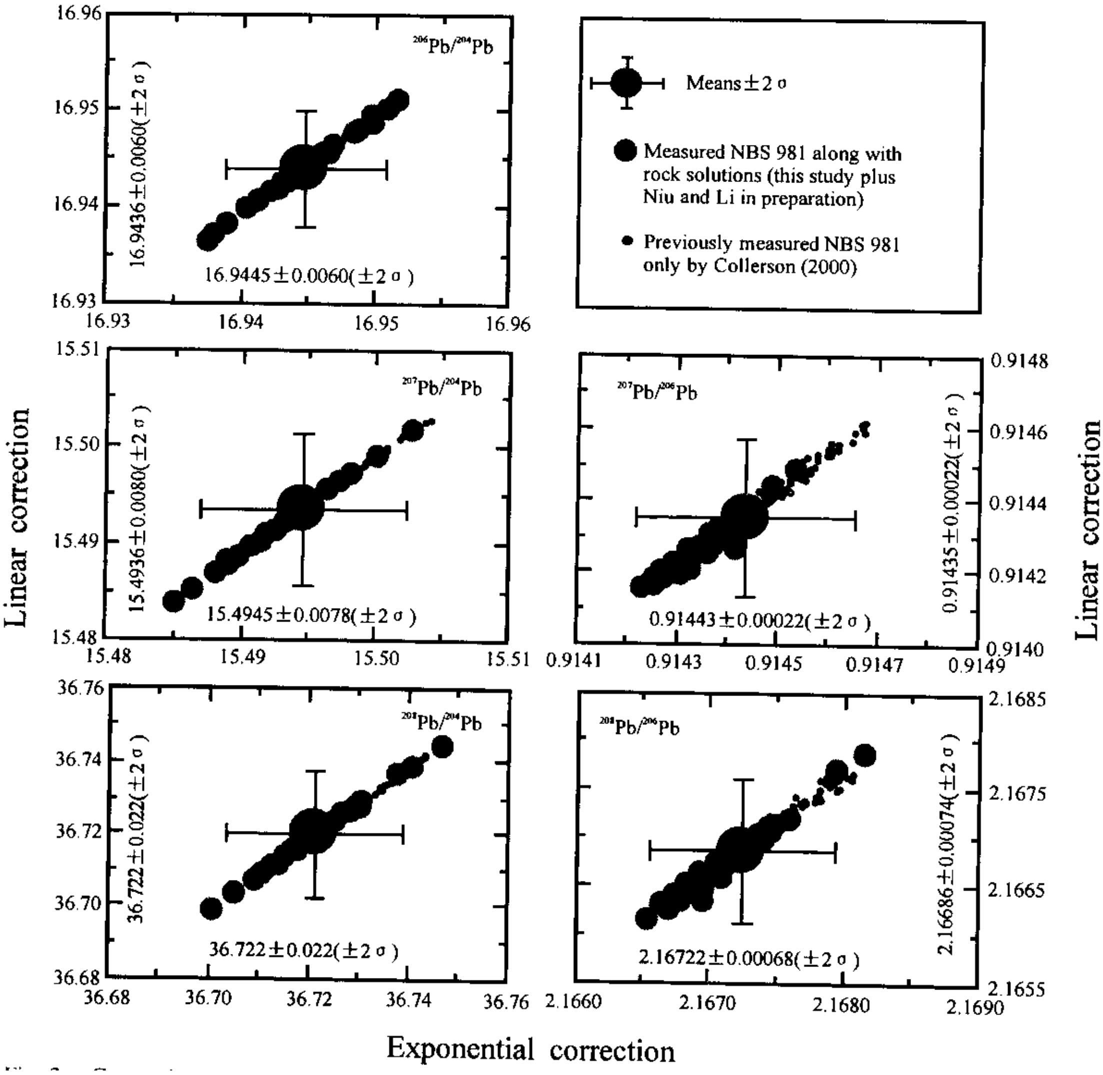

Fig. 2. Comparison of Pb isotopic ratio analyses of NBS 981 with mass fractionation corrected following an exponential law (Equation 3) and by the linear treatment of this study (Equation 4).

Almost perfect linear correlations are unexpected if both correction procedures were perfect as there should be a single value with random errors about the means, but the within-error (±2σ) correlations demonstrate that the simple linear correction is adequate.

(Woodhead and Hergt, 2000). We thus conclude that our chemical procedure, Isoprobe stability as well as our fractionation correction method are all acceptably good.

We also obtained Pb isotopic data for the USGS rock standards BIR-1/1 (Batch 1003) and W-2 (Batch 1020), which are, to our knowledge, the first analyses available. We think that these new Pb isotopic data for BIR-1/1 and W-2 have good quality and may be used as reference for future studies. We wish to point out however that these rock standards may not be homogeneous. Caution is thus necessary when using these data (W. M. White, person. Comm., 2001).

3.4 Matrix effect and dilution experiments

It has been discussed in the literature that purified (essentially mono-element) materials such as NBS 981 and 982. exhibit markedly different mass fractionation behaviors from actual rock samples with complex matrices (e.g., major elements etc.) in the TIMS (Woodhead et al., 1995; Woodhead and Hergt, 1997). Leads, chemically separated from rock solutions, may still contain trace amounts of elements such as Cd, Zn and Mg. Such matrix may suppress (or even enhance) ionization in an unpredictable manner, i.e., matrix effect (e.g., Woodhead et al., 1995; Woodhead and Hergt, 1997, 2000; Thirlwall, 2000). The so-called matrix effect within the ICP-MS is poorly understood and is thought to vary from one instrument to another. Ross and Hieftje (1991) showed apparent matrix-induced interferences on ion intensities. White et al. (2000) proposed that the relatively large standard deviation of real rock analysis might be partially caused by matrix effect; impurities in the analyte

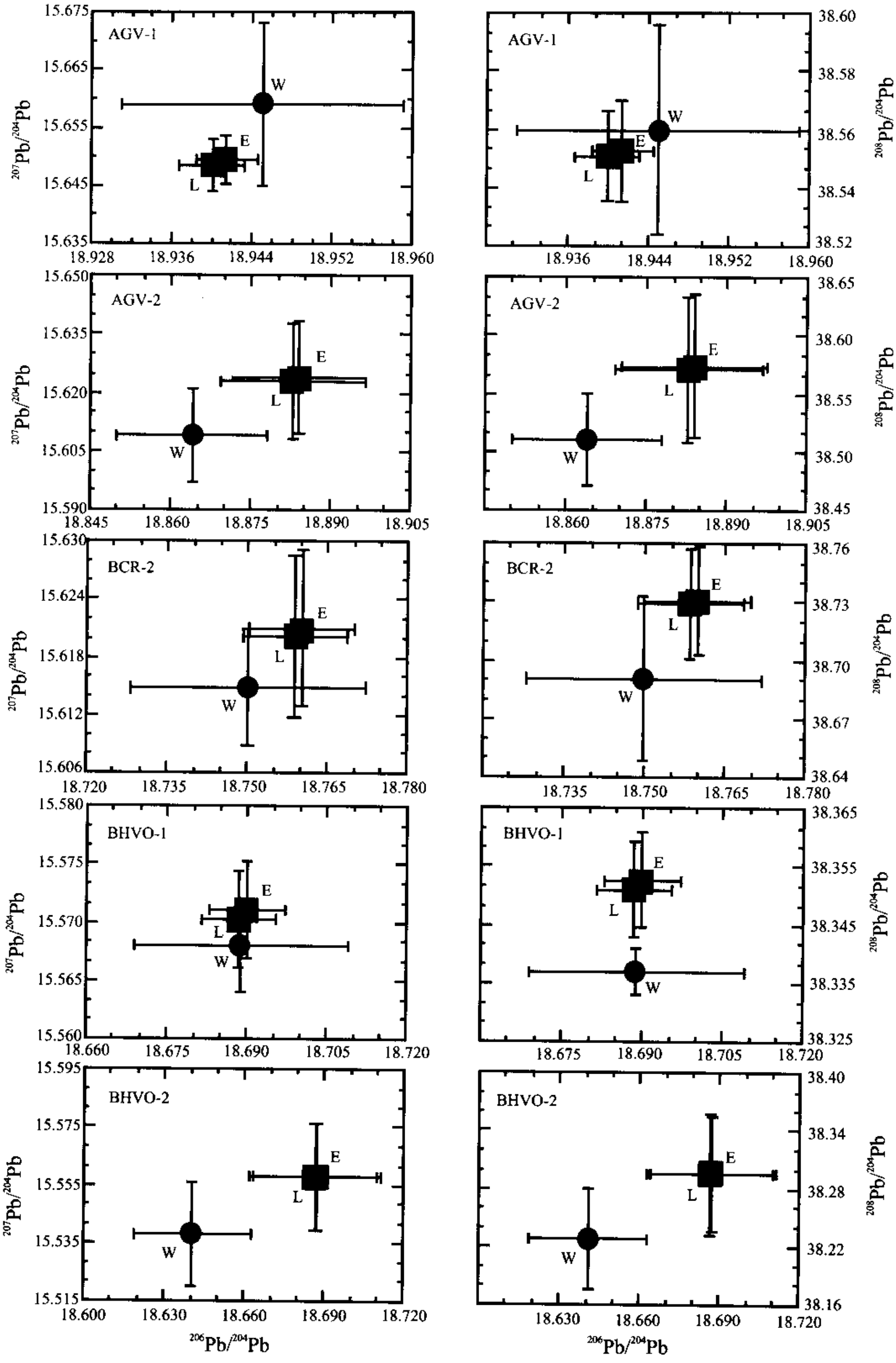

Fig. 3. Comparisons of Pb isotope ratios of USGS rock reference standards AGV-1, AGV-2, BCR-2, BHVO-1 and BHVO-2.

Analyzed by the UQ Isoprobe (grey squares labeled with "L" – corrected linearly, and black squares with "E" – corrected exponentially) with those of double-spike corrected TIMS data of Woodhead and Hergt (2000) (grey circles labeled with "W").

Table 3 Pb isotope data for USGS rock reference standards

Sample	Batch	Runs*	Pb (ppb)#	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$
AGV-1$_E$	62/31	3	134	2.0354	0.82621	38.553	15.649	18.941
2σ				0.0007	0.00016	0.017	0.004	0.003
AGV-1$_L$				2.0350	0.82612	38.551	15.648	18.940
2σ				0.0007	0.00015	0.016	0.005	0.003
AGV-1$_W$	20/3 61/13			2.0354	0.82655	38.560	15.659	18.945
2σ						0.036	0.014	0.014
AGV-2$_E$	604	2	115	2.0417	0.82723	38.547	15.618	18.879
2σ				0.0004	0.00007	0.017	0.008	0.011
AGV-2$_L$				2.0413	0.82714	38.545	15.617	18.878
2σ				0.0003	0.00006	0.017	0.009	0.012
AGV-2$_W$	833			2.0415	0.82745	38.511	15.609	18.864
2σ						0.040	0.012	0.014
BCR-2$_E$	0295 0373 0376	11	123 147 148 153	2.0646	0.83269	38.731	15.621	18.760
2σ				0.0008	0.00019	0.028	0.008	0.010
BCR-2$_L$				2.0641	0.83259	38.730	15.620	18.759
2σ				0.0008	0.00020	0.029	0.008	0.010
**BCR-2$_E$	0295		35	2.0635	0.83259	38.701	15.616	18.755
2σ			17	2.0636	0.83260	38.741	15.631	18.774
**BCR-2$_L$			35	2.0631	0.83251	38.699	15.614	18.754
2σ			17	2.0633	0.83253	38.739	15.630	18.773
BCR-2$_W$	3756			2.0635	0.83280	38.691	15.615	18.750
2σ						0.042	0.006	0.022
BHVO-1$_E$	21/8	3	139	2.0521	0.83312	38.353	15.571	18.690
2σ				0.0003	0.00008	0.008	0.004	0.007
BHVO-1$_L$				2.0516	0.83303	38.351	15.570	18.689
2σ				0.0003	0.00009	0.008	0.004	0.007
BHVO-1$_W$	56/23 40/11			2.0513	0.83300	38.337	15.568	18.689
2σ						0.004	0.004	0.020
BHVO-2$_E$	0363	4	29 38 115	2.0492	0.83255	38.294	15.558	18.687
2σ				0.0010	0.00043	0.060	0.019	0.024
BHVO-2$_L$				2.0489	0.83247	38.294	15.558	18.687
2σ				0.0010	0.00041	0.062	0.018	0.024
BHVO-2$_W$	3251			2.0508	0.83354	38.228	15.538	18.641
2σ						0.052	0.018	0.022
BIR-1/1$_E$	1003	3	85	2.04067	0.83012	38.4493	15.6407	18.8417
2σ				0.00003	0.00001	0.0022	0.0012	0.0004
BIR-1/1$_L$				2.04022	0.83001	38.4491	15.6398	18.8405
2σ				0.00004	0.00003	0.0019	0.0004	0.0004
W-2$_E$	1020	5	68 75	2.0622	0.83551	38.670	15.680	18.766
2σ				0.0014	0.00024	0.032	0.007	0.004
W-2$_L$				2.0618	0.83543	38.697	15.678	18.765
2σ				0.0016	0.00030	0.031	0.008	0.005
NBS 981$_E$		10	100	2.1672	0.91436	36.722	15.493	16.944
2σ				0.0009	0.00019	0.033	0.010	0.008
NBS 981$_L$				2.1668	0.91427	36.720	15.492	16.944
2σ				0.0010	0.00021	0.033	0.011	0.008

Note: Subscripts L and E denote data calculated linearly and exponentially respectively. Subscript W refers to double spike TIMS data of Woodhead and Hergt (2000). "Runs*" refers to the number of repeated analyses at different times of the same chemistry separation-solutions: BCR-2, BHVO-2 and W-2, or multiple runs of replicate digestion/chemistry separation solutions: BCR-2 and BHVO-2. Pb (ppb)# indicates Pb concentrations in sample solutions estimated from ^{208}Pb-intensity by comparison with that of NBS 981solutions. The 10 analyses of NBS 981 were done during the same period of these rock standards analyzed. **denotes the measurements of two diluted BCR-2 (Batch 295) to lower concentrations of about one fourth (~ 35 ppb) and one eighth (~ 17 ppb) of the first run (147 ppb).

could affect ion beam stability as well as cause isobaric interferences.

We have found that significant amounts of impurities such as Mg, Zn, Cu, W, B and Ag still exist in our chemically separated Pb solutions. The concentrations of some of these elements such as Mg are comparable to those of Pb in terms of signal intensities. However, as our Isoprobe Pb isotope data of the USGS rock standards are reproducible, and agree well with the double-spike TIMS data (Woodhead and Hergt, 2000), we consider that the matrix effect, if any at all, is insignificant in terms of Pb isotopic ratio analysis. This is perhaps not surprising because most rock constituents have been removed during Pb chemical separation.

In order to further understand the potential matrix effect and its extent as well as errors associated with Isoprobe Pb isotope ratio analyses, we measured the Pb isotope ratios of progressively diluted solutions of the same initial solution of BCR-2 (Batch 0295) and an abyssal peridotite sample AP3-26 (Tables 4–5; Figs. 4–5). We acquired 36 ratios for each of the diluted sample solutions and 50 ratios for NBS 981. We have not observed any obvious matrix effect on data precision. This is again not surprising as the solutions are overall further diluted. However, Tl is kept more or less the same, and the Tl/Pb ratios are higher in more diluted solutions. We can conclude at least that the matrix effect of Tl on Pb isotopic ratio analysis is not obvious, which others may not agree with (e.g., Rehkämper and Mezger, 2000).

Our dilution experiments demonstrate that the varying Tl/Pb ratio (varying Pb but similar Tl concentrations of ~10–20 ppb) does affect the measured Pb isotopic ratios involving ^{204}Pb, but this is not because of the matrix effect, but because of baseline correction problems as discussed below. We found that Pb isotopic ratios with ^{204}Pb as the denominator become larger and unreliable in more diluted sample solutions; the isotopic ratio increases rapidly with decreasing Pb concentration (Fig. 4). However, the ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb ratios vary very little and remain reliable in sample solutions with Pb $\geq$ 1 ppb (Tables 4–5 and Fig. 4).

Figure 5 is a close-up of Fig. 4 excluding solutions with Pb<1 ppb. This further demonstrates that ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb can certainly be obtained in highly diluted solutions with Pb < 1 ppb, yet ≥ 40 ppb Pb in the solutions is required to obtain reliable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios. The increase in these isotopic ratios with decreasing Pb concentration follows neither an exponential nor a power law, but is a hyperbolic function of the form $Y = [aX+b]/[cX+d]$, where Y represents the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios and X is the Pb concentration. Such a hyperbolic function often reflects a binary mixing in geochemistry (Langmuir et al., 1978; Albarède, 1995). Understanding the origin of such a trend is important in the improved MC-ICP-MS Pb isotope ratio analysis (see Section 3.6 below).

3.5 Hg interference on mass 204 and its correction

The Hg interference on mass 204 has always been a problem in Pb isotope analysis (e.g. Walder and Furuta, 1993; Hirata and Nesbitt, 1995; Rehkämper and Halliday, 1998; White et al., 2000). We have observed the same using the Isoprobe at UQ despite the generally weak signals. The origin of Hg is likely to be laboratory-dependant. For example, Hirata and Nesbitt (1995) and Rehkämper and Halliday (1998) concluded that Hg was present in the plasma supporting the Ar gas. White et al. (2000) speculated that Hg might come from a non-operating Hg pump in their laboratory. We observed roughly the same ^{202}Hg signal intensity during sample up-take and between-sample washes using three different acid solutions (10% HNO_3, 0.01% HF and 2% HNO_3) and pure Mili-Q water. However, we observed no ^{202}Hg signal when introducing isopropyl alcohol, one of our wash solutions. This could suggest that (1) there is no Hg in the Ar used in the UQ lab, or alternatively (2) Hg could in fact exist in the Ar, but may have combined with isopropyl alcohol in plasma (or collision cell?) forming some complex ions with masses different from 202. When no solutions of any kind, but just air and Ar were introduced, no signal on mass 202 was observed. This suggests to us that Hg is potentially present only in the Mili-Q water, which is used for sample preparation and to dilute distilled acids.

As the baseline subtraction and masses 202 through 208 are all measured simultaneously from the same (^{203}Tl-^{205}Tl "spiked") sample solutions dominated by the same Mili-Q water (2% HNO_3) "matrix", they thus have similar Hg abundances and isotopic compositions. Therefore, correction of ^{204}Hg isobaric interferences on ^{204}Pb using the intensity at ^{202}Hg should be effective assuming that ^{204}Hg/^{202}Hg = 0.229883 (e.g., White et al., 2000) is constant. Therefore, the high and unreliable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios in sample solutions with Pb < 40 ppb seen in Figs. 4–5 are not caused by inaccurate and imprecise measurements of Hg. As both Pb and Tl exhibit mass-dependent isotopic fractionations, there must also be a ^{202}Hg-^{204}Hg fractionation. Therefore, neglecting the Hg isotopic fractionation may contribute to the inaccuracy on the resultant ^{204}Pb. Also, some of the signals on mass 202 measured may not be Hg, so there could also be over-correction on mass 204 (W.M. White, Person. Comm.). Calculations show that all these effects are small

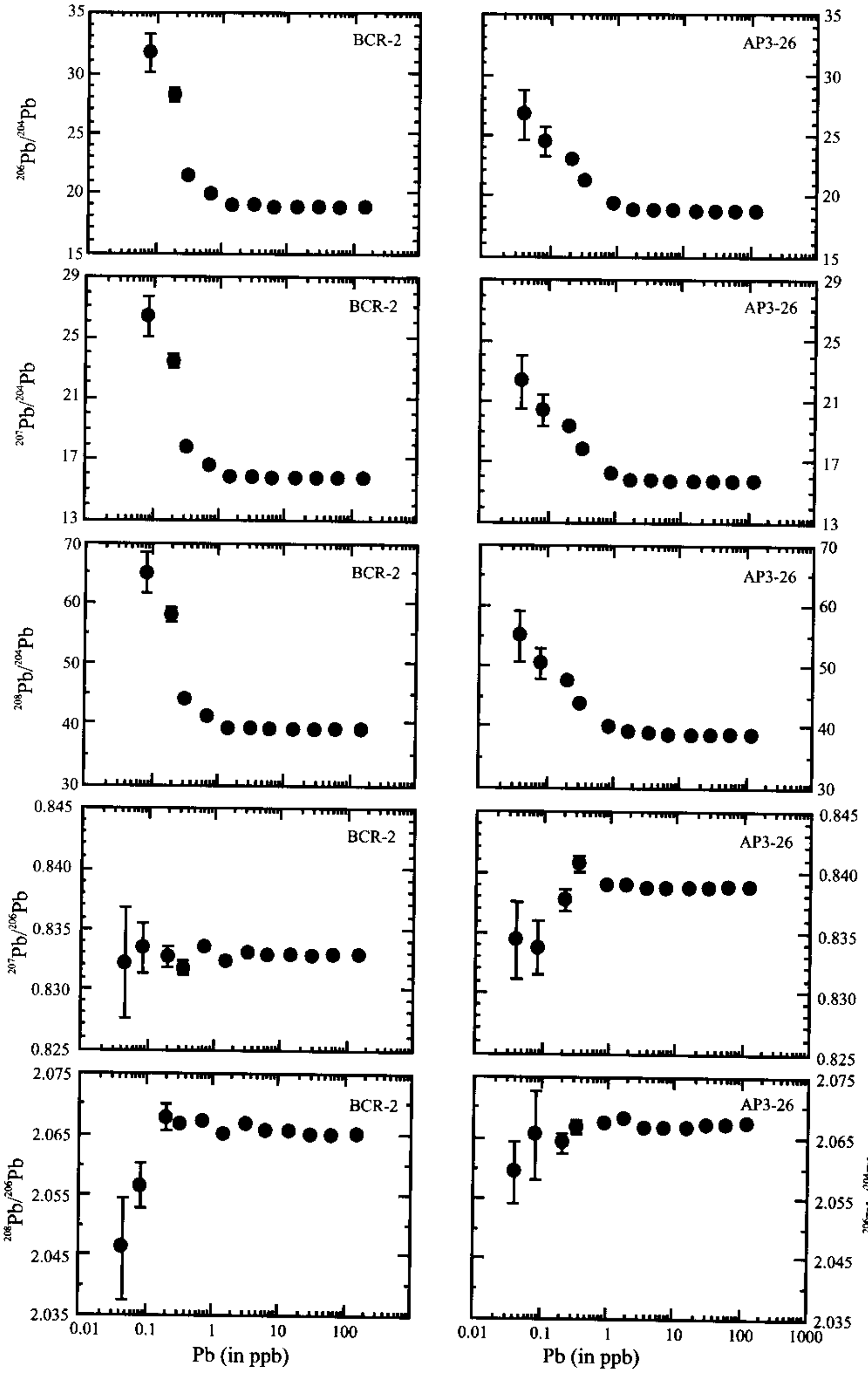

Fig. 4. Results of dilution experiments on USGS rock reference standard BCR-2 and an abyssal peridotite sample AP2-36.

Plotted are Pb isotope ratios of the two rock solutions progressively diluted in Pb concentrations from ~150 ppb down to ~0.05 ppb (variation over 3 orders of magnitude). The more-or-less uniform ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb variations suggest that these two ratios can be determined reliably in Pb-diluted solutions (Pb $\geq$ 1 ppb). However, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios are unrealistically high in Pb-diluted solutions, but they approach reasonable values with increasing Pb concentration.

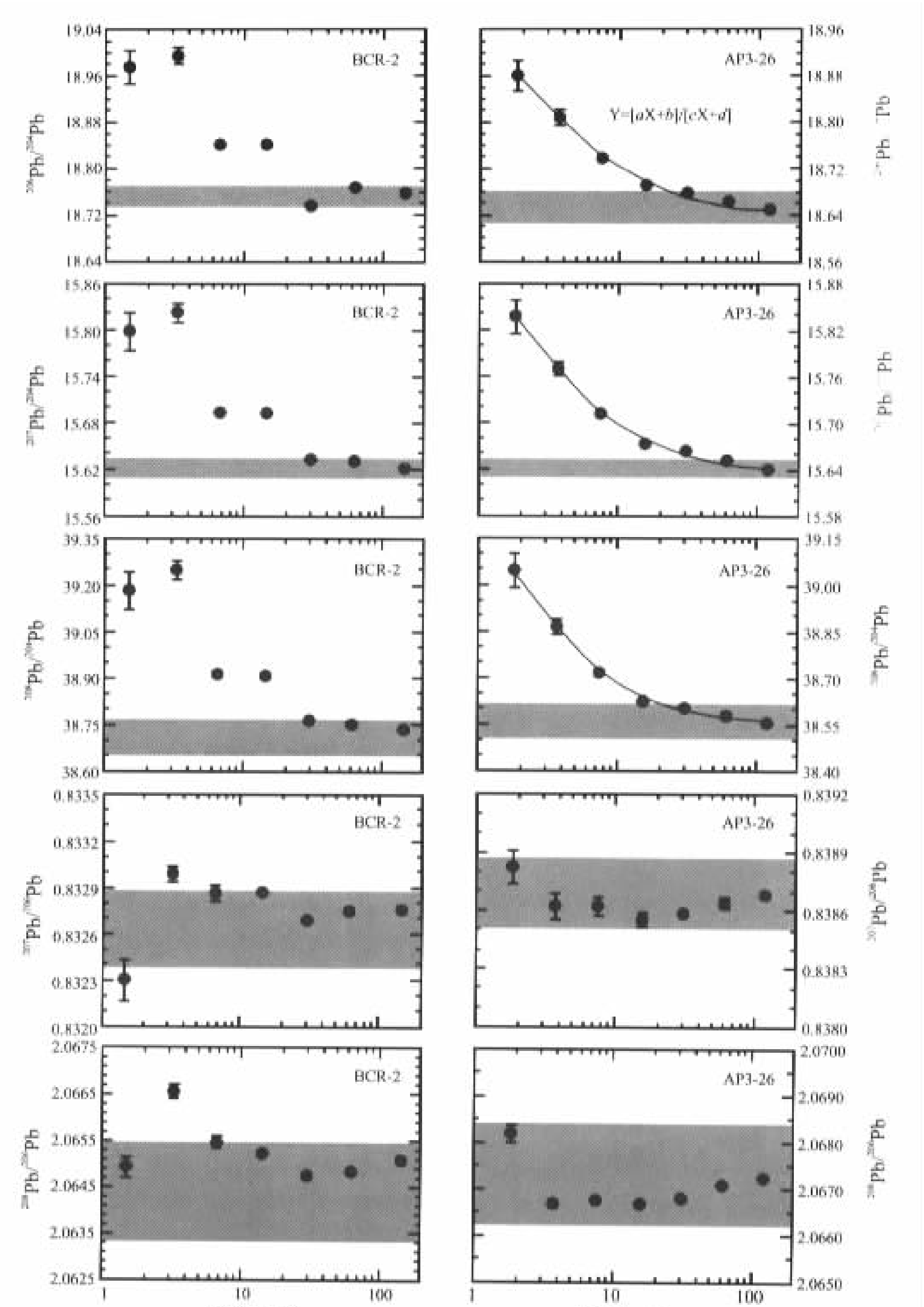

Fig. 5. Close-up of Fig. 4 with solutions having Pb > 1 ppb only plotted.

Note again that reliable ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb ratios can certainly be obtained in solutions of 1–2 ppb, but reliable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios can only be obtained in solutions with Pb $\geq$ 40 ppb). Note also that the decreasing ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios with increasing Pb in the solutions as better defined by AP2-36 are best described by a hyperbolic function of the form $Y = (aX+b)/(cX+d)$, suggesting a greater decreasing rate of ^{204}Pb than ^{206}Pb, ^{207}Pb and ^{208}Pb as Pb is progressively diluted in the solutions. Such a function is consistent with a "mixing" relationship, and is caused by over subtractions at mass 204 (see text for details). The grey bands in BCR-2 plots are the 2σ range of the mean values of Isoprobe analyses (see Table 3) extended to include the double-spike TIMS data of Woodhead and Hergt (2000) (Table 3). The grey bands in AP2-36 plots are from the same plots of BCR-2 with the mid-band coinciding with isotopic ratios of the solution with the highest Pb concentration (right most on the plots).

and can be readily corrected for as demonstrated by White et al. (2000), and cannot cause the elevated $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios in Figs. 4–5.

3.6 Pros and cons of using ^{203}Tl-^{205}Tl as an internal standard

Rehkämper and Mezger (2000) suggested that addition of large amounts of Tl to the samples is unfavorable for accurate measurements of low-intensity ^{204}Pb due to inaccurate baseline subtraction. Thirlwall (2000) noted the same and suggested the need of accurate Tl tail correction. We independently discovered the same through our systematic Pb-dilution experiments. As reviewed above (Section 3.1), there is much discussion in the literature on the elegance of using ^{203}Tl-^{205}Tl to correct for mass-dependent isotopic fractionation in Pb isotope ratio analysis, but we stress and illustrate here that the use of ^{203}Tl-^{205}Tl can in fact cause severe problems and caution is necessary! The fact that the $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios are essentially independent of Pb concentrations suggests that the hyperbolic curve in ratios involving ^{204}Pb (Fig. 4) is not caused by ^{206}Pb, ^{207}Pb or ^{208}Pb, but by mass-204 itself. In other words, increases of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ with the decrease of the Pb concentration results from a rapid decrease of "^{204}Pb intensity" (denominator) relative to the slow decrease of the ^{206}Pb, ^{207}Pb or ^{208}Pb intensity (numerators). This explains why the inverse correlations in Figs. 4 and 5 are best described by a hyperbolic function. This apparently perplexing phenomenon is readily explained by the subtraction of some similar amount at mass-204 regardless of actual Pb concentrations in the solutions in the course of our data collection and reduction. The subtraction of such a similar amount at mass-204 will inevitably increase the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios as the Pb concentration in the solution decreases. So, there is an over-subtraction on mass-204, and progressively more so in more Pb-diluted solutions. If the ^{202}Hg-^{204}Hg fractionation follows the same trend as those of Pb and Tl, correction of the ^{204}Hg effect based on the measured ^{202}Hg (assuming a constant $^{204}Hg/^{202}Hg$) would only "under-subtract" but not "over-subtract" an amount on mass-204.

Table 4 Pb isotope analyses of systematically Pb-diluted solutions of BCR-2 (Batch 0295)

BCR-2	$^{208}Pb/^{206}Pb$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	Pb (ppb)	208 (volts)
BCR-2-12	2.045966	0.832221	Negative	Negative	Negative	0.05	0.002
2ó	0.008478	0.004577					
BCR-2-11	2.056430	0.833480	64.9302	26.31632	31.55956	0.08	0.004
2ó	0.003685	0.002077	3.2655	1.32434	1.58341		
BCR-2-10	2.067657	0.832720	58.0141	23.35815	28.04935	0.20	0.010
2ó	0.002035	0.000881	1.1407	0.45618	0.56121		
BCR-2-9	2.066587	0.831768	44.0341	17.69418	21.27576	0.34	0.017
2ó	0.000905	0.000546	0.3718	0.14400	0.18646		
BCR-2-8	2.066766	0.833509	41.1395	16.58926	19.89028	0.72	0.035
2ó	0.000496	0.000268	0.1550	0.06204	0.07833		
BCR-2-7	2.064914	0.832308	39.1826	15.79708	18.97459	1.48	0.072
2ó	0.000235	0.000132	0.0585	0.02477	0.02785		
BCR-2-6	2.066548	0.832985	39.2479	15.82021	18.99232	3.31	0.161
2ó	0.000145	0.000052	0.0296	0.01209	0.01466		
BCR-2-5	2.065451	0.832862	38.9099	15.69025	18.83843	6.62	0.322
2ó	0.000132	0.000048	0.0142	0.00574	0.00671		
BCR-2-4	2.065193	0.832870	38.9067	15.69051	18.84018	14.55	0.707
2ó	0.000087	0.000030	0.0097	0.00383	0.00445		
BCR-2-3	2.064713	0.832690	38.7618	15.63204	18.73378	30.69	1.492
2ó	0.000078	0.000030	0.0033	0.00125	0.00131		
BCR-2-2	2.064793	0.832753	38.7484	15.62788	18.76659	62.98	3.062
2ó	0.000062	0.000018	0.0032	0.00109	0.00131		
BCR-2-1	2.065038	0.832758	38.7341	15.62004	18.75702	146.97	7.186
2ó	0.000062	0.000017	0.0027	0.00091	0.00083		
NBS 981	2.167244	0.914384	36.7315	15.49721	16.94815	100	4.862
2ó	0.000069	0.000024	0.0026	0.00099	0.00075		
NBS 981	2.166958	0.914296	36.7186	15.49257	16.94451	100	4.862
2ó	0.000052	0.000015	0.0020	0.00074	0.00061		

Notes: **2ó** is two standard deviations from means of 50 ratios acquired for NBS 981 and of 36 ratios acquired for each of the diluted BCR-2 solutions. The NBS 981 data were obtained during the same analysis period of these diluted solutions. Pb concentrations in sample solutions were estimated from ^{208}Pb-intensity by comparison with that of NBS 981.

It is possible that the measured signals at mass 202 may not all be Hg, in which case there could be an over-correction for mass 204, but this effect is negligible. Therefore, the ^{202}Hg-^{204}Hg related correction is not the cause of the elevated ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios in Figs. 4 and 5 for Pb-diluted solutions.

The fact that there is always an "over-subtraction" but not "under-subtraction" on mass-204 is important. Also, the observation that more mass-204 is subtracted in more Pb-diluted solutions (i.e., lower-Pb and higher ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios in Figs. 4 and 5) indeed points to some similar amount on mass-204 being subtracted. Correctly, the only thing that is in common or similar in amount in these otherwise variably Pb-diluted solutions is the spiked Tl, ~10 ppb in NBS 981 solutions and ~10–20 ppb in diluted rock solutions (vs. a large range in Pb, from ~0.05 ppb to ~ 50 ppb). How could such a similar amount of Tl affect mass-204? The logical answer comes from our "±0.5 amu" baseline subtraction applied. The tailing of ^{203}Tl at amu 203.5 and the tailing of ^{205}Tl at amu 204.5 are thus considered to be the true baseline for ^{204}Pb in each unknown solution. As the Tl concentration in Pb-diluted sample solutions is similar, and thus a similar amount is being subtracted on mass-204 for the ^{204}Pb-baseline correction in all the sample solutions. The net effect is the greater amount subtraction for mass-204 in more Pb-diluted solutions. In other words, what is left on mass-204 after baseline subtraction is smaller in more Pb-diluted solutions. Consequently, "^{204}Pb" declines at a greater rate than ^{206}Pb, ^{207}Pb and ^{208}Pb as Pb is progressively diluted in the solution, thus the progressively elevated ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios (Figs. 4 and 5). In summary, the elegance of ^{203}Tl-^{205}Tl in correcting Pb isotopic fractionation becomes problematic if the sample solution is over-"spiked", particularly, in low-Pb solutions, as also noted by Rehkämper and Mezger (2000) and Thirlwall (2000). The tailings of ^{203}Tl and ^{205}Tl also cause baseline over-subtraction for ^{202}Hg (at amu 202.5) and ^{206}Pb (at amu 205.5). This effect may be relatively small (only on one side of the peak), but must be carefully evaluated in order to produce totally reliable data. We observed that the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios approach the expected mean values in solutions of Pb/Tl > 5. We

Table 5 Pb isotope analyses of systematically Pb-diluted solutions of abyssal peridotite sample AP3-26

	^{208}Pb/^{206}Pb	^{207}Pb/^{206}Pb	^{208}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{206}Pb/^{204}Pb	Pb (ppb)	208 (volts)
AP3-26-12	2.059272	0.834259	54.8813	22.25007	26.66739	0.04	0.002
2σ	0.005144	0.003184	4.3024	1.72416	2.08171		
AP3-26-11	2.065291	0.833633	50.3678	20.38029	24.43328	0.08	0.005
2σ	0.007295	0.002403	2.5591	1.03797	1.22992		
AP3-26-10	2.064115	0.837644	47.3851	19.28996	22.95296	0.22	0.012
2σ	0.001532	0.000848	0.7560	0.29209	0.36445		
AP3-26-9	2.066813	0.840576	43.7133	17.77918	21.15179	0.34	0.018
2σ	0.001079	0.000624	0.4347	0.16944	0.20128		
AP3-26-8	2.067168	0.838940	39.7506	16.14091	19.23419	0.93	0.051
2σ	0.000322	0.000174	0.0895	0.03612	0.04424		
AP3-26-7	2.068173	0.838822	39.0464	15.83698	18.87950	1.82	0.099
2σ	0.000190	0.000087	0.0529	0.02166	0.02549		
AP3-26-6	2.066652	0.838624	38.8665	15.76944	18.80406	3.77	0.205
2σ	0.000087	0.000067	0.0239	0.00858	0.01091		
AP3-26-5	2.066732	0.838620	38.7167	15.71204	18.73544	7.69	0.419
2σ	0.000107	0.000049	0.0117	0.00478	0.00525		
AP3-26-4	2.066673	0.838552	38.6286	15.67357	18.69153	15.72	0.856
2σ	0.000079	0.000039	0.0060	0.00245	0.00299		
AP3-26-3	2.066796	0.838586	38.6018	15.66259	18.67726	31.22	1.701
2σ	0.000054	0.000020	0.0033	0.00138	0.00168		
AP3-26-2	2.067058	0.838641	38.5778	15.65171	18.66297	61.31	3.340
2σ	0.000074	0.000030	0.0042	0.00150	0.00142		
AP3-26-1	2.067213	0.838683	38.5520	15.64051	18.64897	122.62	6.680
2σ	0.000054	0.000018	0.0028	0.00084	0.00082		
NBS 981	2.167265	0.914374	36.7256	15.49455	16.94557	100	5.448
2σ	0.000056	0.000022	0.0022	0.00087	0.00075		
NBS 981	2.167433	0.914402	36.7287	15.49534	16.94597	100	5.448
2σ	0.000056	0.000022	0.0022	0.00087	0.00075		

Note: **2σ** is two standard deviations from means of 50 ratios acquired for NBS 981 and of 36 ratios acquired for each of the diluted AP3-26 solutions. The NBS 981 data were obtained during the same analysis period of these diluted solutions. Pb concentrations in sample solutions were estimated from ^{208}Pb-intensity by comparison with that of NBS 981.

therefore suggest that a minimum concentration ratio with Pb/Tl > 5 in Tl-“spiked” solutions be required to ensure reliable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios by using the MC-ICP-MS. This requirement is critical for Pb-depleted samples because the amount of Tl added must be well above its detection limits while ensuring Pb/Tl > 5. For this purpose, a prior Pb concentration is certainly needed.

Alternatively, a well-characterized mixture of ^{209}Bi (mono-isotopic) and enriched ^{202}Hg isotope (with well characterized ^{202}Hg/^{204}Hg ratios) may be used as the internal standard to correct for mass dependent Pb isotopic fractionation. This ^{209}Bi-^{202}Hg “spike” may in fact be advantageous for two reasons. (1) This mass range (202–209) covers all the Pb isotopes of interest (i.e., masses 204, 206, 207 and 208), and mass fractionation correction by interpolation is better constrained than by extrapolation as is the case when using ^{203}Tl-^{205}Tl. (2) The simple linear fractionation relationship in the mass range of 203 to 208 we discovered (Fig. 1) might well extend to mass 202 to 209. This suggestion requires experimental tests.

The observations (Figs. 4–5) and foregoing discussion suggest that the MC-ICP-MS in general and perhaps the Isoprobe in particular are yet to be refined in abundance sensitivity. We do not consider this a negative sign, but emphasize an urgent need for instrumental improvement.

4 Conclusions

The major conclusions of this study are as follows.

(1) An MC-ICP-MS, such as the Isoprobe at UQ, can produce precise Pb isotope ratios on both high-purity reference solutions such as NBS 981 and actual rock samples such as the USGS reference standards. Our data on these rock standards are comparable to the double- and triple-spike TIMS data in precision and accuracy.

(2) We demonstrate that a linear correction for Pb isotopic fractionation is adequate with the results identical to those corrected following an exponential law or power law at least for Pb isotope ratios within the range of natural rocks.

(3) Precise ^{207}Pb/^{206}Pb, ^{208}Pb/^{206}Pb and ^{208}Pb/^{207}Pb ratios can be readily acquired for sample solutions with Pb $\geq$ 1 ppb. However, reliable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios were obtained in solutions with Pb $\geq$ 40 ppb Pb.

(4) We agree with the previous conclusion that the error in ^{204}Pb analysis is the main source of the error for Pb isotope ratio analysis using the MC-ICP-MS. This ^{204}Pb-associated error is commonly ascribed to the difficulty and imprecise correction for a ^{204}Hg isobaric interference. We show that the Hg effect is trivial and can be readily corrected for. The origin of Hg could be laboratory-dependent; our experiments suggest that Hg is potentially present only in the Mili-Q water in the UQ laboratory, not in the Ar carrier or acids or any other sources.

(5) We demonstrate that the major source of error on ^{204}Pb comes from the tailings of ^{203}Tl and ^{205}Tl. These mass tailings lead to the over-subtraction of the baseline for ^{204}Pb, which is measured at ±0.5 amu on both sides of mass-204 (i.e., at amu 203.5 and 204.5 respectively). Such errors are insignificant for Pb-rich samples, but can be severe for low-Pb sample solutions when over-“spiked” with Tl. The tailings of ^{203}Tl and ^{205}Tl also cause baseline over-subtraction for ^{202}Hg (at amu 202.5) and ^{206}Pb (at amu 205.5). Our experiments suggest that a minimum concentration ratio of Pb/Tl > 5 in Tl-“spiked” solutions is required to produce reliable ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios in actual rock samples.

(6) We emphasize that the MC-ICP-MS in general and perhaps the Isoprobe in particular are yet to be refined in abundance sensitivity. This by no means negates the instrumentation or the techniques, but does demonstrate the necessity of further improvement.

Acknowledgements

We thank the Australian Research Council and the University of Queensland for supporting this research. We also thank Ken Collerson for making the Isoprobe available for this study and for providing some of his NBS 981 analyses. YN acknowledges the support from NERC and Cardiff University that allowed the final completion of the manuscript. Discussion with Bill McDonough and Alan Greig has been helpful. Critical and constructive reviews by Francis Albarède, Catherine Chauvel, Mark Rehkämper, and Bill White are extremely helpful, and are acknowledged with great gratitude although we do not always agree.

Manuscript received Nov. 8, 2001
accepted March 9, 2002
edited by Liu Xinzhu

References

Albarède, F., 1995. *Introduction to Geochemical Modeling.* Cambridge: Cambridge University Press, 543.

Belshaw, N.S., Freedman, P.A., O'Nions, R.K., et al., 1998. A new variable dispersion double-focusing plasma mass spectrometer with performance illustrated for Pb isotopes. *Int. J. Mass Spec. Ion Proc.,* 181: 51–58.

Blichert-Toft, J., and Albarede, F., 1997. The Lu-Hf geochemistry of chondrites and the evolution of the mantle-crust system. *Earth Planet. Sci. Lett.,* 148: 243–258.

Bradshaw, N., Hall, E.F.H. and Sanderson, N.E., 1989. Inductively coupled plasma as an ion-source for highresolution mass-spectrometry. *J. Anal. At. Spectrom*., 4: 801−803.

Catanzaro, E.J., Murphy T.J., Shields W.R., et al., 1968. Absolute isotopic abundance ratios of common, equal atom, and radiogenic lead isotopic standards. *J. Res. Natl. Bur. Stand*., 72A: 261.

Collerson, K.D., 2000. Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS): Accurate, precise and rapid measurement of Pb and Th isotope ratios. *31st IGC Abstr*., 193.

Collerson, K.D., Kamber, B.S., and Schoenberg R., 2002. Applications of accurate, high-precision Pb isotope ratio measurement by multi-collector ICP-MS. *Chem. Geol*. 188, 65– 83.

Collerson, K.D., and Palacz, Z.A., 1999. Accurate and precise isotopic ratio measurements of NBS 981 lead by multiple collector inductively coupled plasma mass spectrometry: why are the ratios different from TIMS measurements? *Ninth Goldschmidt Conf. Abs*., 9.

Dunstan, L.P., Gramlich, J.W., Barnes, I.L., et al., 1980. Absolute isotopic abundance and the atomic weight of a reference sample of thallium. *J. Res. Nat. Bur. Stand*., 85: 1−10.

Galer, S.J.G., and Abouchami, W., 1998. Practical application of lead triple spiking for correction of instrumental mass discrimination. *Mineral. Mag*., 62: 491–492.

Hamelin, B., Manhes, G., Albarède, F., et al., 1985. Precise lead isotope measurements by the double spike technique: a reconsideration. *Geochim. Cosmochim. Acta*, 49: 173–182.

Hirata, T., 1996. Lead isotopic analysis of NIST standard reference materials using multiple collector-inductively coupled plasma mass spectrometry coupled with modified external correction method for mass discrimination effect. *The Analyst*, 121: 1407−1411.

Hirata, T., 1997. Isotopic variations of germanium in iron and stony meteorites. *Geochim. Cosmochim. Acta*, 61: 4439–4448.

Hirata, T., and Nesbitt, R.W., 1995. U-Pb isotope geochronology of zircon: evaluation of laser probed-inductively coupled plasma mass spectrometry technique. *Geochim. Cosmochim. Acta*, 59: 2491−2500.

Langmuir, C.H., Vocke, R.D., and Hanson, G.N., 1978. A general mixing equation with application to Icelandic basalts. *Earth Planet. Sci. Lett*., 37: 380−392.

Lee, D.C., and Halliday, A.N., 1995. Hafnium-tungsten chronometry and the timing of terrestrial core formation. *Nature*, 378: 771−774.

Longerich, H.P., Fryer, B.J., and Strong, D.F., 1987. Determination of lead isotope ratios by inductively coupled-plasma mass spectrometry (ICP-MS). *Spectrochim. Acta*, 42: 39–48.

Luais, B., Télouk, P., and Albarède, F., 1997. Precise and accurate neodymium isotopic measurements by plasma-source mass spectrometry. *Geochim. Cosmochim. Acta*, 61: 4847–4854.

Marechal, C., Télouk, P., and Albarède, F., 1999. Precise analysis of Cu and Zn isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.*, 156: 251−273.

Niu, B.S., and Hieftje, G.M., 1991. Alteration of the ion-optic lens configuration to eliminate mass-dependent matrix-interference effects in inductively coupled plasma-mass spectrometry. *Spectrochim. Acta*, 46: 1263−1273.

Oversby, V.M., and Gast, P.W., 1968. Lead isotope compositions and uranium decay series disequilibrium in recent volcanic rocks. *Earth Planet. Sci. Lett.*, 5: 199−206.

Rehkämper, M., and Halliday, A.N., 1998. Accuracy and long-term reproducibility of lead isotopic measurements by MC-ICP-MS using an external method for correction of mass discrimination. *Int. J. Mass Spec.*, 181: 123–133.

Rehkämper, M., and Mezger, K., 2000. Investigation of matrix effects for Pb isotope ratio measurements by multiple collector ICP-MS: verification and application of optimized analytical protocols. *J. Anlyt. Atom. Spectr.*, 15: 1451−1460.

Ross, B.S., and Hieftje, G.M., 1991. Alteration of the ion-optic lens configuration to eliminate mass-dependent matrix-interference effects in inductively coupled plasma-mass spectrometry. *Spectrochim. Acta*, 46: 1263−1273.

Thirlwall, M.F., 2000a. Precise Pb isotope analysis of standards and samples using an Isoprobe Mulicollector ICP-MS: Comparisons with doublespike thermal ionization data. *J. Conf. Abstr.*, 52: 996.

Thirlwall, M.F., 2000b. Inter-laboratory and other errors in Pb isotope analyses invested using a ^{207}Pb-^{204}Pb double spike. *Chem. Geol.*, 163: 299–322.

Thirlwall, M. F., and Walder, A. J., 1995. In situ hafnium isotope ratio analysis of zircon by inductively coupled plasma multiple collector mass spectrometry. *Chem. Geol*., 122: 241–247.

Todt, W., Cliff, R.A., Hansen, A., Hofmann, A. W., 1996. Evaluation of a ^{202}Pb-^{205}Pb double spike for high-precision lead isotope analysis. In: Hart, S.R., and Baso, A. (eds.), Earth Processes: Reading the Isotope Code, Am. Geophys. Union, Geophys. Monogr. Ser. 95: 429-437.

Urey, H.C., 1947. The thermodynamics of isotopic substances. *J. Chem. Soc.*, 1947: 562–581.

Walder, A.J., and Freeman, P.A., 1992. Isotope ratio measurement using a double focusing magnetic sector mass analyser with inductively coupled plasma as an ion source. *J. Anal. Spectrom.*, 7: 571−575.

Walder, A.J., and Furuta, N., 1993. High precision lead isotope ratio measurement by inductively coupled plasma multiple collector mass spectrometry. *Anal. Sci.* 9: 675−680.

Wendt, J.I., Regelous, M., Niu, Y., et al., 1999. Geochemistry of lavas from the Garrett Transform Fault: insights into mantle heterogeneity beneath the eastern Pacific. *Earth Planet. Sci. Lett.*, 173: 271−284.

White, W.M., 1993. ^{238}U-^{204}Pb in MORB and open system evolution of the depleted mantle. *Earth Planet. Sci. Lett*., 115: 211−226.

White, W.M., Albarède, F., and Télouk, P., 2000. High-precision analysis of Pb isotope ratios by multi-collector ICP-MS. *Chem. Geol.*, 167: 257–270.

Woodhead, J.D., and Hergt, J.M., 1997. Application of the “double spike” technique to Pb isotope geochronology. *Chem. Geol.*, 138: 311–321.

Woodhead J.D., Volker, F., and McColluch, M.T., 1995. Routine lead isotope determinations using a ^{207}Pb-^{204}Pb double spike: A long term assessment of analytical precision and accuracy. *The Analyst*, 120: 35−39.

Woodhead, J.D., and Hergt, J.M., 2000. Pb-isotope analysis of USGS reference materials. *Geostand. Newslett*., 24: 33–38.