

An assessment of mass discrimination in MC-ICPMS using Nd isotopes

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Abstract

The stability of mass discrimination in multiple-collector magnetic-sector inductively coupled mass spectrometry (MC-ICPMS)—with time, between elements and between samples—makes it potentially much simpler to deal with than in TIMS. However, while the stability of mass bias across limited areas of the mass spectrum is critical to the derivation of precise isotope ratios, the fundamentals of mass bias behaviour of MC-ICPMS instruments are still incompletely characterised. In this paper, we present Nd isotope data for standards and samples with the aim of using the well-known Nd isotopic system to obtain systematic information on the nature of the mass bias in MC-ICPMS. An extensive Nd dataset was obtained on a Micromass IsoProbe and more limited data on two different Nu Instrument machines. The IsoProbe data were obtained over 18 months between March 2000 and September 2001. The standard approach of using $^{146}\text{Nd}/^{144}\text{Nd}$ to normalise other Nd isotope ratios leads to both inaccurate (by around 100 ppm in the case of the exponential-law normalised $^{143}\text{Nd}/^{144}\text{Nd}$ ratio) and relatively imprecise (2 rsd = 45 ppm for $^{143}\text{Nd}/^{144}\text{Nd}$) results. On the IsoProbe, this is due to the fact that the magnitude of the exponential mass bias itself varies, albeit by a small amount, over limited mass ranges such as that for Nd. The result is that the inaccuracy is much greater for isotope ratios that have an average mass further away from that of the normalising ratio—for example, > 500 ppm for $^{150}\text{Nd}/^{144}\text{Nd}$ vs. < 30 ppm for $^{145}\text{Nd}/^{144}\text{Nd}$. Both accuracy and precision increase dramatically if a normalising ratio is used that is close in mass to the ratio to be normalised. $^{143}\text{Nd}/^{144}\text{Nd}$ (average mass = 143.5) normalisation with $^{145}\text{Nd}/^{142}\text{Nd}$ (average mass = 143.5) yields a value identical to TIMS. An alternative approach is to use post-normalisation linear correlations between isotope ratios to do a secondary mass bias correction. Such an approach with the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio using $^{142}\text{Nd}/^{144}\text{Nd}$ yields a value identical to the TIMS value and a long-term reproducibility of 14–20 ppm. This compares with a reproducibility of 45 ppm using simple normalisation to $^{146}\text{Nd}/^{144}\text{Nd}$. We have tested both these approaches on standards and samples with $^{143}\text{Nd}/^{144}\text{Nd}$ up to 30 ϵ units different from our in-house standard and identical results to TIMS are obtained. Post-normalisation correlations between isotope ratios obtained on the Nu Instruments MC-ICPMS are qualitatively very similar to those obtained on the IsoProbe and suggest a common cause. This, despite the very different physical characteristics of the various instruments. Furthermore, it also appears that qualitatively very similar effects, though at much smaller magnitude, are observed in TIMS. The data suggest that the quasi-empirical exponential law does not perfectly correct for mass discrimination on any mass spectrometer. This inadequacy becomes important, for precise isotope ratio analysis, when dealing with the large mass discriminations inherent in MC-ICPMS. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Multiple-collector ICPMS; Mass discrimination; Neodymium isotopes; Accuracy; Precision

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1. Introduction

Multiple-collector magnetic-sector inductively coupled mass spectrometry (hereafter MC-ICPMS) is rapidly becoming the method of choice for the measurement of the isotopic composition of a wide range of elements in the earth and environmental sciences. These range from the well-known heavy radiogenic isotope systems such as Sr, Nd, Hf and Pb (see Halliday et al., 1995, 2000 for reviews) to less familiar, lighter, stable isotope systems like Mg (Galy et al., 2001), Ca (Halicz et al., 1999), Fe (Belshaw et al., 2000), Cu (Maréchal et al., 1999; Zhu et al., 2000) and Zn (Maréchal et al., 1999, 2000). Among the advantages of these instruments is their versatility and the rapidity of analysis. Perhaps the greatest step forward, however, concerns their mass bias behaviour. Though mass discrimination is greater than on conventional TIMS (about 1.8% amu^{-1} at Nd on the Royal Holloway IsoProbe as compared to 0–0.2% on a TIMS), its apparent stability with time, over large mass ranges and between different elements, makes correction for it apparently much more straightforward than on TIMS for a number of key applications. For example, the ability to fractionation-correct isotope ratios of one element with those of another allows much more precise corrections for isobaric interferences and, hence, permits the use of much simpler chemical separation procedures (e.g. Luais et al., 1997). More importantly, however, mass bias correction for elements, such as Pb, without an invariant isotope ratio can be made using other elements that do, for example, Tl (Hirata, 1996; Rehkämper and Halliday, 1998; Belshaw et al., 1998; Vance and van Calsteren, 1999). A similar approach has been used for mass bias correction of Zn and Cu isotopes (Maréchal et al., 1999; Zhu et al., 2000). Finally, where this approach is not possible or not desirable, the temporal stability of the mass bias behaviour allows correction to be done using interpolated standards (e.g. Belshaw et al., 1998; Zhu et al., 2000).

However, the details of the mass bias behaviour of these instruments are still incompletely characterised. For example, in the many papers now published on Pb isotopic analysis, there is some disagreement on the nature of the mass bias law—with suggestions varying from the exponential law (Belshaw et al., 1998; Vance and van Calsteren, 1999), through the power law

(Rehkämper and Halliday, 1998), to a modified version of the power law (Hirata, 1996). In addition, several laboratories (Rehkämper and Halliday, 1998; Belshaw et al., 1998; Vance and van Calsteren, 1999) have found a discrepancy between Tl-normalised Pb ratios involving ^{208}Pb and the best TIMS data as obtained using double spike techniques (Galer and Abouchami, 1998; Thirlwall, 2000). The reasons for this disagreement are as yet unclear. While for many applications these issues are of only marginal importance, for others, they significantly degrade confidence in the accuracy and precision of the technique. In the case of Pb, the discrepancies between double spike and MC-ICPMS measurements of the $^{208}\text{Pb}/^{206}\text{Pb}$ ratio are of the order of 200–300 ppm—up to an order of magnitude greater than the long-term reproducibility of the measurements. Such effects are likely to be of major importance where precise isotope ratio measurements are required, such as with Nd and Hf.

The characterisation of the mass bias behaviour of MC-ICPMS machines with the Pb isotopic system is hampered by these uncertainties and by the lack of generally accepted benchmark TIMS values (e.g. Todt et al., 1996; Galer and Abouchami, 1998; Thirlwall, 2000) for the isotope ratios. In this paper, we present Nd isotopic data for various standards and samples obtained recently on the Royal Holloway IsoProbe. We also present smaller data sets for Nd isotopes from two different Nu Instruments machines—at the Open and Oxford Universities, UK. The principal objective is to use the well-known Nd isotopic system (Wasserburg et al., 1981; Thirlwall, 1991a,b) to examine, in detail and in general, the mass bias behaviour of MC-ICPMS instruments. We observe very systematic deviations from conventional mass bias laws. The effects are so systematic that for Nd, they are readily dealt with, and the insights gained may have relevance for the behaviour of other isotopic systems. We show that a slightly more complex but robust correction procedure, analogous to one previously used in TIMS (Thirlwall et al., 1991a,b), yields accurate $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios and a long-term reproducibility for static analysis of 14–20 ppm (2 rsd). Furthermore, internal precisions of 35 ppm (2 rse) are achieved on 4 ng of Nd—a sensitivity more than a factor of 10 better than that reported previously for various elements by several groups (e.g. Rehkämper and Halliday, 1998; Belshaw et al., 1998; Luais et al., 1997).

2. Instruments and procedures

The results presented here have been obtained on a Micromass IsoProbe instrument at Royal Holloway between March 2000 and September 2001 and during one analytical session each on the Open University and Oxford Nu Instruments machines (see Halliday et al., 2000 for a description of the IsoProbe instrument and comparisons with other MC-ICPMS).

2.1. RHUL IsoProbe

The Nd was introduced into the mass spectrometer in 2% HNO₃ via an Aridus desolvating nebulizer in free-aspiration mode. The uptake rate varied between 30 and 45 µl/min, resulting in total signals of 2.5–4 × 10⁻⁹ A/ppm Nd. For most of the analyses reported here, Nd concentrations in solutions were 70–80 ppb and these yielded a ¹⁴⁶Nd ion beam of 3–5 × 10⁻¹¹ A. Internal precisions of less than 20 ppm on the ¹⁴³Nd/¹⁴⁴Nd ratios were obtained after thirty–fifty 5-s integrations. This corresponds to a sample usage of about 30–50 ng Nd. The inlet system was cleaned between analyses using distilled 5% HNO₃ followed by a blank solution of 2% HNO₃ from which the sample solutions were prepared. Washout takes no more than about 5 min. Static multicollection was used for most of the data collected during this study with Faraday amplifier gains being calibrated using a constant current source before each analytical session. The static data are split into two periods—March–June 2000 and July–September 2000—between which there was a change in relative cup efficiencies. In addition, to eliminate residual uncertainties associated with cup efficiency variations, multidynamic data

were obtained for one analytical session in September 2001.

The analysis procedure is virtually identical to that described for Pb in Thirlwall (2002a,b) and will be only briefly described here. The correction for blank in the analyte solution is not so critical for Nd as for Pb, both because of the lower blank signal from the solution and because of the lesser variability of natural Nd. Cleaning between analyses was always done until the 142 total signal was stable. Corrections for blank Nd in the solution, memory and amplifier offsets were done by measuring on-peak zeroes (OPZs) for the 2% HNO₃ solution before each sample measurement. The signal for these OPZ measurements was less than 300 ppm of the sample signal for most analyses reported here and usually around 150 ppm. Tail-correction is important for the IsoProbe because of the lower abundance sensitivity relative to TIMS. Tails were measured here using a Pr solution that gives a ¹⁴¹Pr signal of ~ 7 × 10⁻¹¹ A, by measuring signals at mass 141 and at half-masses away from mass 141. Tails at integer masses were then calculated by fitting a curve to the resulting data. Relative to the size of the ¹⁴¹Pr signal, the tails measured during this study are 8–14 ppm at -1 amu, 4–9 ppm at -2 amu and 5 ppm at +1 amu. The tails do not change by more than 1–2 ppm within periods between analyzer bakes.

For the analysis of the marine sediment from Hawaii, Nd was separated using standard techniques (Cohen et al., 1988). The DEP chemistry used reduces ¹⁴⁴Sm interference on ¹⁴⁴Nd to insignificant levels but is not efficient at separating Ce. A correction for ¹⁴²Ce interference on ¹⁴²Nd was determined using Ce-doped standards and the ¹⁴²Ce/¹⁴⁰Ce used for correction was 0.12584.

Table 1

Measured Nd isotope ratios^a normalised using an exponential law to ¹⁴⁶Nd/¹⁴⁴Nd=0.7219 for the two analysis periods, compared to TIMS values.^b Multidynamic data for a single analysis period are also given

	¹⁴² Nd/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	¹⁴⁵ Nd/ ¹⁴⁴ Nd	¹⁵⁰ Nd/ ¹⁴⁴ Nd
TIMS	1.141876	0.511421	0.348415	0.236446
March–June 2000	1.141582 (95)	0.511378 (22)	0.348417 (22)	0.236299 (69)
July–September 2000	1.141628 (97)	0.511377 (23)	0.348426 (13)	0.236329 (48)
Multidynamic September 2001	1.141509 (63)	0.511353 (16)	0.348421 (9)	0.236279 (20)

^a All reproducibilities here, and throughout the paper, are 2 standard deviations.

^b TIMS data for the ¹⁴³Nd/¹⁴⁴Nd ratio from Thirlwall (1991a,b). Other ratios are the power-law normalised values of Wasserburg et al. (1981) re-normalised to 0.7219 using an exponential law.

2.2. Oxford and OU Nu Instruments

Most of the analysis procedures were as described above for the IsoProbe. Data were collected statically. The important differences in procedure to that described above were: (a) the solution concentration and sample usage were about an order of magnitude higher; (b) on-peak zeros were measured once at the end of the day rather than before each analysis—for Nd, where blank levels are very low, this is adequate; (c) tail corrections were not necessary and have not been applied.

3. Results—ratios normalised to $^{146}\text{Nd}/^{144}\text{Nd}$

The most commonly used procedure for the elimination of mass-discrimination effects in Nd isotopic analysis is to assume an exponential dependence on mass and to normalise to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ (O’Nions et al., 1977). An alternative normalisation, to $^{146}\text{Nd}/^{142}\text{Nd}$, has been used by Wasserburg et al. (1981). For two isotope ratios, $R_1 = a/b$ and $R_2 = c/d$, a general mass discrimination law can be written as follows:

$$\left[\frac{R_1^{\text{meas}}}{R_1^{\text{mbc}}} \right]^x = \left[\frac{R_2^{\text{meas}}}{R_2^{\text{mbc}}} \right]^y \quad (1)$$

where superscripts “meas” and “mbc” are for measured and mass bias-corrected ratios, respectively. In the case of the exponential law, exponent $x = \ln(m_c/m_d)$ and exponent $y = \ln(m_a/m_b)$, where $m_i =$ mass of isotope i . For the power law, exponent $x = m_d - m_c$ and exponent $y = m_b - m_a$.

Table 1 shows the data obtained on our internal Aldrich Nd standard, by normalising measured isotope ratios to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ using an exponential law. The data are compared with TIMS analyses using the same mass-bias correction (Thirlwall, 1991a,b; Wasserburg et al., 1981). In Fig. 1, the data for the $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 1a) and $^{150}\text{Nd}/^{144}\text{Nd}$ ratios (Fig. 1b) are illustrated. Clearly, for both ratios, the data are both inaccurate relative to the TIMS values and are also much less precise. The effect is much greater for the $^{150}\text{Nd}/^{144}\text{Nd}$ ratio (2 rsd=200–300 ppm, deviation relative to TIMS 500–600 ppm) than for the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (2 rsd=45 ppm, deviation relative to TIMS=84 ppm).

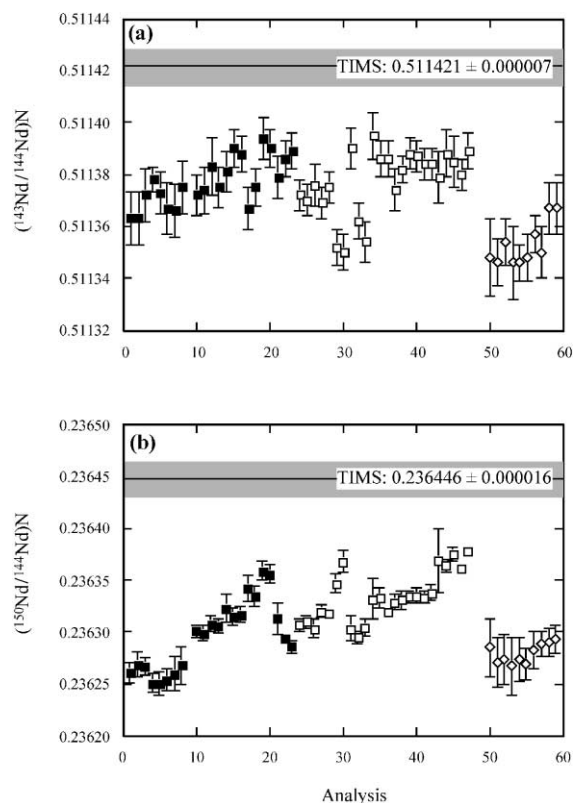


Fig. 1. $^{143}\text{Nd}/^{144}\text{Nd}$ (a) and $^{150}\text{Nd}/^{144}\text{Nd}$ (b) ratios for our in-house Aldrich Nd standard, normalised to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ assuming an exponential dependence of mass discrimination on mass. Each data point represents the average and 2 standard errors of fifty 5-s integrations. The filled squares are for static analyses for the period March–June 2000 and the open squares those for the period July–September 2000. The open diamonds are multidynamic analyses obtained in one analysis session in September 2001. The values obtained by TIMS (see Table 1) are given by the shaded bands. The mean data from the IsoProbe lie some 84 and 500–600 ppm below the TIMS data for the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{150}\text{Nd}/^{144}\text{Nd}$ ratios respectively (see Table 1).

The greater imprecision in the $^{150}\text{Nd}/^{144}\text{Nd}$ ratio immediately leads one to suspect an origin in inappropriate mass bias correction given the large mass difference between the numerator and denominator isotopes for this ratio. The imprecision and inaccuracy in the data are not due to cup efficiency problems for two reasons. Firstly, the cup efficiencies have been measured and corrections applied where necessary. Secondly, and most importantly, the multidynamic data in Fig. 1, for which any non-unity cup efficiencies are irrelevant, display the same/greater inaccuracy as do

the static data. A further examination of the mass discrimination issue is clearly merited.

4. Discussion

4.1. Nature of mass-discrimination behaviour

Eq. (1) makes predictions about the relationships between un-normalised isotope ratios—specifically, that plots of $\ln(R_1)$ vs. $\ln(R_2)$ should be straight lines with slopes defined by the exponents in Eq. (1). Fig. 2 shows such plots for $^{146}\text{Nd}/^{144}\text{Nd}$ vs. both $^{143}\text{Nd}/^{144}\text{Nd}$ (Fig. 2a) and $^{150}\text{Nd}/^{144}\text{Nd}$ (Fig. 2b). The first important observation is that the MSWDs of the lines are greater than 1. In the case of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, the factor of 2 (sqrt MSWD) excess scatter over that expected from the internal uncertainties (about 18 ppm on average) almost wholly accounts for the poor reproducibility in Fig. 1a. For the $^{150}\text{Nd}/^{144}\text{Nd}$, about half of the scatter in Fig. 1b is explained by the high MSWD in Fig. 2b. The other important feature of these plots is the slopes. The expected gradients for the exponential and power mass bias laws are given in Table 2 as well as the gradients observed from the data. The uncertainties quoted on these gradients take full account of the large MSWDs. In the case of the

$^{143}\text{Nd}/^{144}\text{Nd}$ ratio, the observed gradients do not correspond exactly to those for the power or exponential laws. The uncertainty on the gradients means that they are indistinguishable from the power law—though only at the very limit of the uncertainty in the case of the March–June 2000 data. For the $^{150}\text{Nd}/^{144}\text{Nd}$ ratio, the observed gradients are certainly different from that expected from an exponential law. They are closer to the power law but are not within error of it. One obvious possible approach here is simply to use the observed gradients of these correlations in Eq. (1) in a modified mass-bias law that fits the MC-ICPMS data. Clearly, such an approach would be predicted to improve the reproducibility since the correction is now done using a relationship that actually fits the data, but it will only be accurate relative to TIMS if these best fit lines to the MC-ICPMS data go through the TIMS values. In fact, this is not the case and a correction using these best-fit lines to the MC-ICPMS data in a modified mass-bias law results in even more inaccurate ratios. The implication is that if a full description of mass bias across the entire range of discrimination were possible, it would only be achieved by a curve in \ln – \ln space.

Hart and Zindler (1989) have observed previously that Ca isotope fractionation on TIMS does not match the exponential law and proposed mixing between two

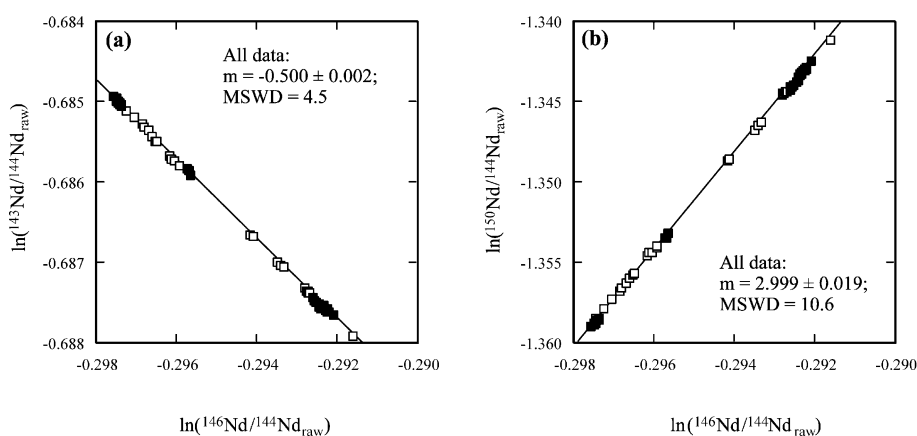


Fig. 2. Plot of natural logs of the raw $^{143}\text{Nd}/^{144}\text{Nd}$ (a) and $^{150}\text{Nd}/^{144}\text{Nd}$ (b) ratios vs. the natural log of the raw $^{146}\text{Nd}/^{144}\text{Nd}$ for the Aldrich Nd standard. Symbols as in Fig. 1. Each data point represents the average of fifty 5-s integrations. Error bars are smaller than the symbols. Note that in neither case do the best-fit lines to the IsoProbe data have slopes that correspond to mass bias laws established for TIMS data. Neither do these best-fit lines pass through a set of consistent isotope ratios obtained by TIMS (see Table 2 and text for details).

Table 2
Normalisation of Nd isotope ratios to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ using three different correction schemes

Analysis period		$^{142}\text{Nd}/^{144}\text{Nd}$	Slope ^a	$^{143}\text{Nd}/^{144}\text{Nd}$	Slope	$^{145}\text{Nd}/^{144}\text{Nd}$	Slope	$^{150}\text{Nd}/^{144}\text{Nd}$	Slope
<i>TIMS</i>									
		1.141876		0.511421		0.348415		0.236446	
<i>Royal Holloway IsoProbe</i>									
March– June 2000	Exponential Law	1.141582 (95)	– 1.014	0.511378 (22)	– 0.505	0.348417 (22)	0.502	0.236299 (69)	2.960
	Power Law	1.141090 (74)	– 1.000	0.511288 (22)	– 0.499	0.348442 (20)	0.500	0.235996 (36)	3.001
	Observed data fit	1.141162 (73)	– 1.002 (5)	0.511337 (21)	– 0.502 (3)	0.348474 (19)	0.497 (5)	0.235907 (33)	3.013 (10)
July– September 2000	Exponential Law	1.141628 (97)	– 1.014	0.511377 (23)	– 0.505	0.348426 (13)	0.502	0.236329 (48)	2.960
	Power Law	1.141139 (60)	– 1.000	0.511287 (19)	– 0.499	0.348450 (11)	0.500	0.236028 (40)	3.001
	Observed data fit	1.141032 (57)	– 0.997 (2)	0.511271 (18)	– 0.498 (2)	0.348483 (11)	0.497 (1)	0.236087 (39)	2.993 (8)
Multidynamic September 2001	Exponential Law	1.141509 (63)		0.511353 (16)		0.348421 (9)		0.236279 (20)	
	Power Law	1.140973 (88)		0.511272 (20)		0.348448 (9)		0.235956 (36)	

^a Slopes predicted by the power and exponential laws. The “observed data fit” line gives the slope defined by the actual data and its uncertainty (in parentheses) at 95% confidence [2σ (sqrt (MSWD))].

independently fractionating reservoirs as a possible reason for deviations from conventional mass bias laws. This is a potentially attractive explanation for the data presented here also. For example, in MC-ICP-MS, there is the potential for mixing between a heavy-enriched ion beam extracted from the plasma with a light-enriched ion beam generated from the residues of past samples on the cones. However, in our case, this explanation is precluded for two reasons. Firstly, Nd released from the cones is incorporated into the on-peak zeroes measured before, and subtracted from, the measured sample signals. More importantly, the curvature of the exponential mass-bias relationships means that exponential normalisation of a mixture of these two sources would result in normalized ratios— $^{150}\text{Nd}/^{144}\text{Nd}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ —that are higher than the true value, not lower as we observe.

All these observations are summarized in Table 2 where the values for various isotope ratios are given using different approaches to mass-bias correction using the $^{146}\text{Nd}/^{144}\text{Nd}$ ratio. Table 2 shows that in all cases, the power law and an empirical law based on a best-fit line to the data yield better reproducibility.

However, they also yield even more inaccurate isotope ratios than the exponential law. There is one further very significant feature of Table 2, that is, that the inaccuracy generally increases the further the average of the numerator and denominator isotopes in the ratio is from that for the $^{146}\text{Nd}/^{144}\text{Nd}$ ratio. For example, for the values obtained using an exponential law, the $^{142}\text{Nd}/^{144}\text{Nd}$ is lower than the TIMS value by 220–260 ppm and the $^{150}\text{Nd}/^{144}\text{Nd}$ ratio by 500–600 ppm. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, on other hand, is only 85 ppm too low while the $^{145}\text{Nd}/^{144}\text{Nd}$ ratio is, within the uncertainties, exactly the same as the TIMS value.

The above observations suggest that the mass discrimination on this instrument does not display a simple exponential dependence on mass. Another way of looking at this is to calculate a “beta” factor (Russell et al., 1978; or the f of Luais et al., 1997) which is defined as follows:

$$\beta \text{ (or } f) = \ln \left[\frac{R_{\text{ref}}}{R_{\text{meas}}} \right] / \ln \left[\frac{m_a}{m_b} \right] \quad (2)$$

where R_{meas} and R_{ref} are measured and reference values for the ratio a/b and m is the mass of isotope

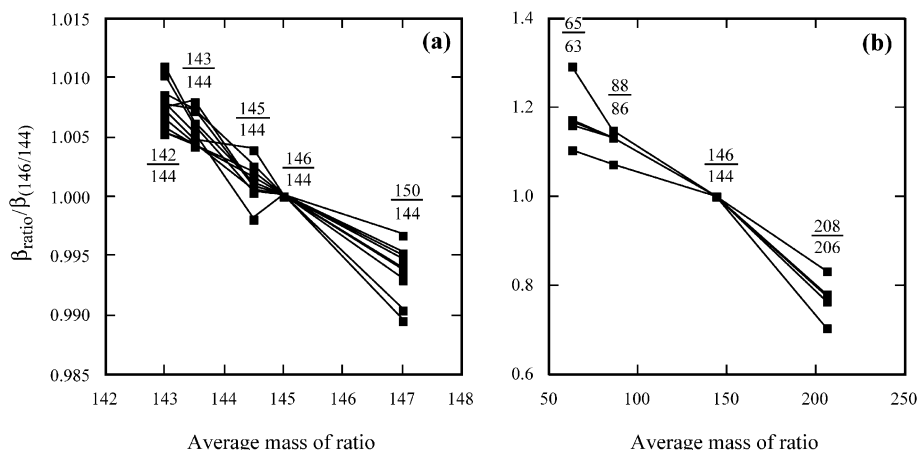


Fig. 3. Variation in exponential mass bias with mass for (a) the Nd mass range and (b) the mass range from Cu to Pb, plotted as a function of the average mass of the normalised ratio. β values (Russell et al., 1978) in both cases are normalised to that for the $^{146}\text{Nd}/^{144}\text{Nd}$ ratio. In (a), each set of points connected by lines represents averages for nine separate analysis sessions over a period of 7 months. The typical range in β from run-to-run *within* an analysis session is of the same order as the variation seen in the diagram *between* analysis sessions. In (b), each set of points represents different operating conditions within a single analysis session.

i. If mass bias is a simple exponential function of mass, then these beta values should be the same across the entire mass range. Fig. 3a shows the beta values for the Nd isotope ratios measured here, normalised to the

beta value for the $^{146}\text{Nd}/^{144}\text{Nd}$ ratio and plotted as a function of the numerical average of the masses in the numerator and denominator. Clearly, the beta value is not constant, even across the limited mass range of Nd.

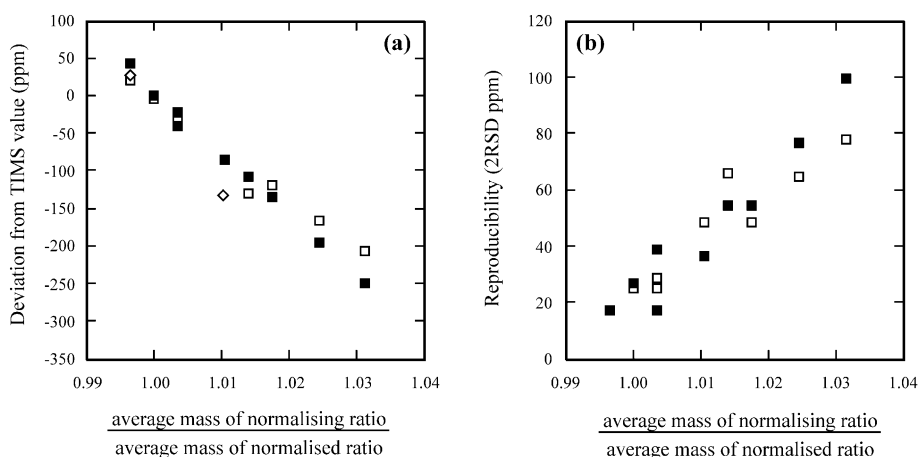


Fig. 4. (a) The relationship between the normalised $^{143}\text{Nd}/^{144}\text{Nd}$ (ordinate) and the ratio of the average mass of the numerator and denominator in the normalising ratio to that for $^{143}\text{Nd}/^{144}\text{Nd}$ (abscissa). The data are plotted as the deviation (in ppm) from the TIMS value (Table 2). Each data point represents the average for the analysis period March–June 2000 (filled squares) or July–September 2000 (open squares). Where available, data are also shown for multidynamic runs (open diamonds). Accurate ratios are only obtained if the normalising ratio has exactly the same average mass as the ratio normalised. (b) The relationship between the reproducibility (2 rsd over the two analysis periods) of the normalised $^{143}\text{Nd}/^{144}\text{Nd}$ (ordinate) and the ratio of the average mass of the numerator and denominator in the normalising ratio to that for $^{143}\text{Nd}/^{144}\text{Nd}$ (abscissa). Each data point represents the reproducibility for the analysis period March–June 2000 (filled squares) or July–September 2000 (open squares). The most precise ratios are obtained if the normalising ratio has close to the same average mass as the ratio normalised.

In fact, the data in Fig. 3a are simply a particular case of a general phenomenon we have observed on the IsoProbe. A similar plot to Fig. 3a is shown in Fig. 3b, where the beta values for a much wider mass range are shown—again normalised to those for $^{146}\text{Nd}/^{144}\text{Nd}$. Over the mass range stretching from Cu to Pb, the beta values change, in a rather systematic fashion, by about 35%. At this stage, we put forward the hypothesis, based on Fig. 3, that the variation in beta with mass explains the imprecision and inaccuracy of the data in Fig. 1. Below we show that this hypothesis can explain many of the observations that we have made concerning $^{146}\text{Nd}/^{144}\text{Nd}$ -normalised isotope ratios. In addition, we perform some simple tests of it that serve to further illustrate the nature of the mass bias behaviour.

For Nd, there are many possible choices of ratios with which to normalise—for example, $^{146}\text{Nd}/^{144}\text{Nd}$ as we have used here, $^{146}\text{Nd}/^{145}\text{Nd}$, $^{142}\text{Nd}/^{144}\text{Nd}$, $^{146}\text{Nd}/^{142}\text{Nd}$ or even $^{145}\text{Nd}/^{142}\text{Nd}$. Each of these, of course, has average masses for the numerator and denominator that differ from that for the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio to varying degrees. The prediction of the hypothesis outlined above is that there should be a simple relationship between the mass differences and the imprecision and inaccuracy of the normalised ratios. This is quite simple to test and this is done in Fig. 4a, which shows that such a simple, linear relationship does indeed exist. Fig. 4a suggests that the most accurate approach to mass-bias correction is to choose a normalising ratio that has exactly the same average mass as the ratio to be normalised. In the case of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio, the $^{145}\text{Nd}/^{142}\text{Nd}$ is such a ratio. As expected, the value of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio obtained using $^{145}\text{Nd}/^{142}\text{Nd}$ as a normalising ratio is identical to the TIMS value. Fig. 4b also shows that this approach also yields the most reproducible data—around 26 ppm using the $^{145}\text{Nd}/^{142}\text{Nd}$ as the normalising ratio as opposed to 90 ppm using the $^{150}\text{Nd}/^{146}\text{Nd}$ ratio.

Returning to the relationships between the natural logs of raw ratios such as those in Fig. 2, a further consequence of the above discussion is that such a correlation for $^{145}\text{Nd}/^{142}\text{Nd}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$ should yield a perfect linear fit with a slope that is close to that predicted by the mass bias laws. The slope for the $^{145}\text{Nd}/^{142}\text{Nd}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$ correlation is very close to that predicted by conventional mass bias laws (Fig. 5). In addition, the MSWD of this line is 2.4—an

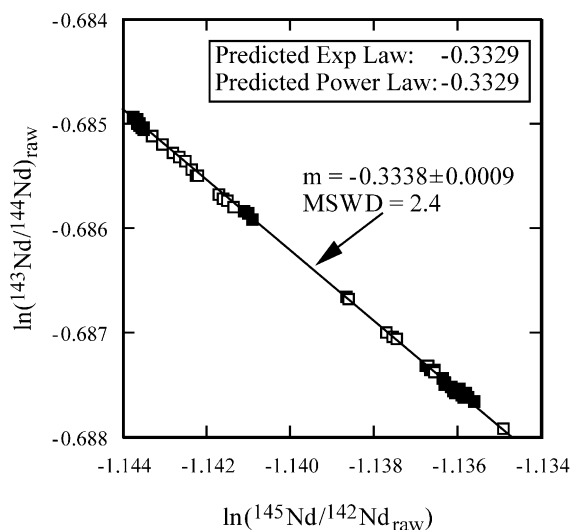


Fig. 5. Plot of natural log of the raw $^{143}\text{Nd}/^{144}\text{Nd}$ vs. the natural log of the raw $^{145}\text{Nd}/^{142}\text{Nd}$ for the Aldrich Nd standard. Each data point represents the average of fifty 5-s integrations. Symbols as in Fig. 1. Error bars are smaller than the symbols. The best-fit line to the IsoProbe data has a smaller error than those in Fig. 2 and has a slope very close to that predicted by conventional mass bias laws. Unlike the data in Fig. 2, the best-fit line does pass through a set of consistent isotope ratios obtained by TIMS. Note that when the average mass of two isotope ratios is the same the mass bias laws have the same slope in \ln - \ln space.

improvement over those for the correlations in Fig. 2 and reflecting the more coherent behaviour of these two isotope ratios as a consequence of their proximity in mass.

If the approach described above holds in general, then any pair of isotope ratios with the same average mass for the numerator and denominator should yield a pair of normalised isotope ratios that are consistent with those of TIMS. Because Nd has many isotopes, and because of the many possible combinations of normalising and normalised ratios, there are many further tests of this approach that can be made. Here we describe just one of those. One appropriate pair of ratios is $^{150}\text{Nd}/^{144}\text{Nd}$ and $^{148}\text{Nd}/^{146}\text{Nd}$. The prediction of our hypothesis is that the $^{150}\text{Nd}/^{144}\text{Nd}$ ratio, corrected using the $^{148}\text{Nd}/^{146}\text{Nd}$ ratio, should give accurate and precise values. We have modified our normal cup setup, which does not measure ^{148}Nd , for one analytical session to obtain the appropriate data. The $^{150}\text{Nd}/^{144}\text{Nd}$ ratio, normalised to both $^{146}\text{Nd}/^{144}\text{Nd}$ and to $^{148}\text{Nd}/^{146}\text{Nd}$, is shown in Fig. 6. Note that on any one day, the

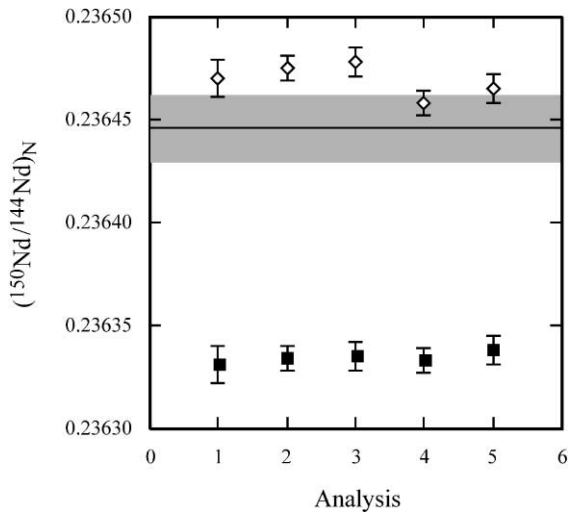


Fig. 6. $^{150}\text{Nd}/^{144}\text{Nd}$ ratio obtained via normalisation to $^{148}\text{Nd}/^{146}\text{Nd}=0.334654$ (open diamonds) compared to those obtained via normalisation to a $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ (filled squares). These data were obtained during a single analytical session. The shaded band represents values obtained by TIMS (Table 2; Wasserburg et al., 1981). The value of 0.334654 for the $^{148}\text{Nd}/^{146}\text{Nd}$ was obtained from the values of Wasserburg et al. (1981) re-normalised to 0.7219 using an exponential law (as for Table 2). The $^{148}\text{Nd}/^{146}\text{Nd}$ -normalised values are accurate to 97 ± 68 ppm while the $^{146}\text{Nd}/^{144}\text{Nd}$ -normalised values are inaccurate by 470 ppm.

$^{150}\text{Nd}/^{144}\text{Nd}$ normalised to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ can be quite precise if the mass bias is stable, which it was for the hour or so that it took to obtain the data in Fig. 6. However, as already described, this leads to inaccurate values for $^{150}\text{Nd}/^{144}\text{Nd}$ by 500–600 ppm on average over 3 months (Fig. 1). The $^{148}\text{Nd}/^{146}\text{Nd}$ corrected values are, however, virtually identical to those from TIMS analysis (Fig. 6). The rather surprising result is that the normalised $^{150}\text{Nd}/^{146}\text{Nd}$ ratios are significantly less reproducible than expected. This may be due to poor counting statistics on the less abundant ^{148}Nd isotope—particularly since these errors are then magnified considerably in applying a mass bias correction to a ratio with 6 mass units between numerator and denominator.

4.2. Relationships between normalised isotope ratios

The reason for the slopes in the beta vs. mass plots is as yet unclear but they obviously have serious consequences for precision and accuracy in MC-ICPMS. In

Section 4.1, it became obvious that the way to obtain more accurate and precise isotope ratios is to normalise with a ratio that is as close as possible in average mass to that for the ratio of interest. In the case of Nd, this approach is eminently feasible but there may be cases where it is not possible—for example, where there are no isotopes both lighter and heavier than those of interest. An alternative approach is therefore required. In this section, we explore some very systematic relationships between normalised isotope ratios which, at least in the case of Nd, can be used to eliminate the deviations from conventional mass bias behaviour described above and which may be useful for other applications.

One of the expected consequences of the deviations from conventional mass bias laws presented above is post-normalisation correlations between isotope ratios. Fig. 7a shows an example of this for the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios normalised to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$. The slope of the line for the March–June 2000 data set (filled symbols) is 0.18 ± 0.02 and the excellent quality of the fit is indicated by an MSWD of 0.7. This relationship has been noted before for TIMS data (Thirlwall, 1991a,b and Fig. 7a) and it appears from Fig. 7a that the MC-ICPMS data are simply a more extreme manifestation of the effect seen on TIMS—presumably because of the greater mass bias inherent in MC-ICPMS. Furthermore, the mean slope of lines fitted to the TIMS data is 0.20—clearly close to that obtained from the MC-ICPMS data. The data for the period July–September (open symbols) are displaced to slightly lower $^{142}\text{Nd}/^{144}\text{Nd}$ for any given $^{143}\text{Nd}/^{144}\text{Nd}$ but the correlation has the same slope (0.22 ± 0.02 ; MSWD = 1.3). We also note that the data for the July–September period, along with the multidynamic data, are co-linear with the TIMS data, whereas the March–June data lie slightly above the correlation defined by the rest of the data. The slight discrepancy between the data sets in Fig. 7a is probably due to slightly inaccurate cup efficiency corrections for the March–June period. The expected slope for these correlations, if they were simply due to residual mass bias effects, would be 0.22—close to those for the real data (Fig. 7a).

The $^{142}\text{Nd}/^{144}\text{Nd}$ ratio is a constant in virtually all Earth materials. The consequence of this is that the relationship in Fig. 7a can be used to apply an empirical correction to $^{146}\text{Nd}/^{144}\text{Nd}$ -normalised ratios in the

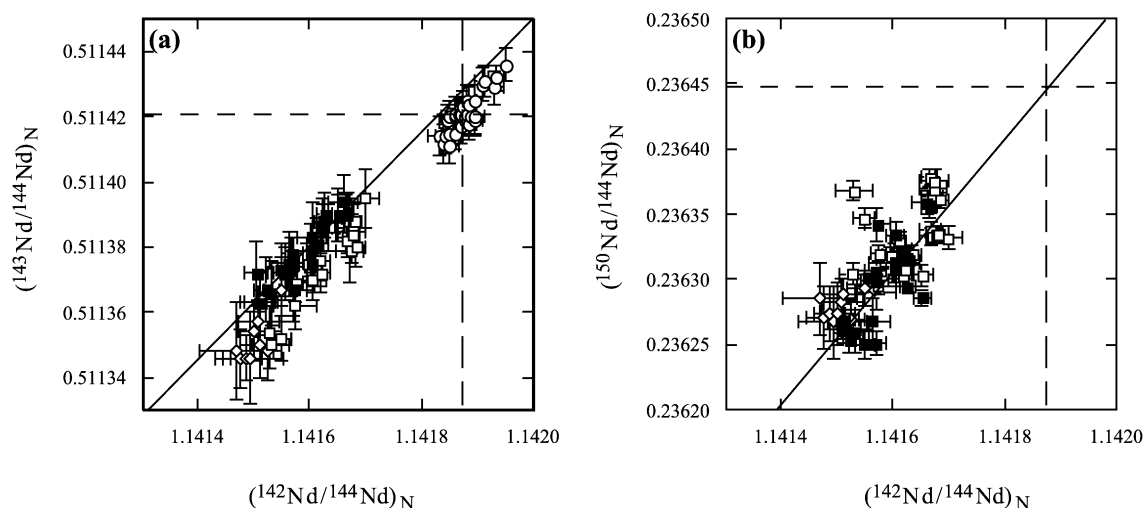


Fig. 7. The relationship between the normalised (to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$) $^{142}\text{Nd}/^{144}\text{Nd}$ and (a) $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and (b) $^{150}\text{Nd}/^{144}\text{Nd}$ ratios. Symbols for MC-ICPMS data as in Fig. 1. RHUL TIMS data (open circles; Thirlwall, 1991a) are also plotted. In both panels, the benchmark TIMS values are given by the dashed lines and solid lines are best fits to the correlations defined by the data for the March–September 2000 analysis period. The IsoProbe data in (a) define a tight linear array with a slope — of 0.18–0.22 — very similar to the TIMS data. The data in (b) define a weaker correlation with a slope of 0.51. However, the best-fit line does pass through the pair of ratios obtained by TIMS.

manner first suggested by Thirlwall (1991a). The resulting data are shown in Fig. 8. This procedure is important for a number of reasons. Firstly, it transpires that this method yields the most reproducible final $^{143}\text{Nd}/^{144}\text{Nd}$ ratios — 14–20 ppm (2 rsd) over periods of months. Secondly, the resulting $^{143}\text{Nd}/^{144}\text{Nd}$ is accurate to within 14 ppm of the TIMS value for the period March–June 2000 and is identical to the TIMS value for July–September 2000 static data and for the multidynamic data. Finally, this approach may be of more utility for other isotope systems where there are not sufficient or appropriate isotope ratios to do a conventional mass bias correction using the approach outlined in Section 4.1. We note that the approach described above is exactly the same as that which has been used previously for TIMS by Thirlwall (1991a,b). However, we also note that the approach is robust even for mass discriminations an order of magnitude greater than those observed in TIMS. To test the generality of the approach, Fig. 7b shows the data for the $^{150}\text{Nd}/^{144}\text{Nd}$ ratio against the $^{142}\text{Nd}/^{144}\text{Nd}$ ratio. The quality of the fit on Fig. 7b is clearly not nearly as good as for Fig. 7a (MSWDs of 10 and 18 for the two analysis periods). However, the correlation on Fig. 7b does explain 75% of the variation in the $^{146}\text{Nd}/^{144}\text{Nd}$ -normalised $^{150}\text{Nd}/^{144}\text{Nd}$ ratio. Significantly, also, the

best-fit line does go through the exponential-law normalised TIMS values (Table 2) and the result of applying an empirical correction based on Fig. 7b is a $^{150}\text{Nd}/^{144}\text{Nd}$ ratio of 0.236452 ± 0.000048 for all the data on Fig. 7b (cf. Table 2).

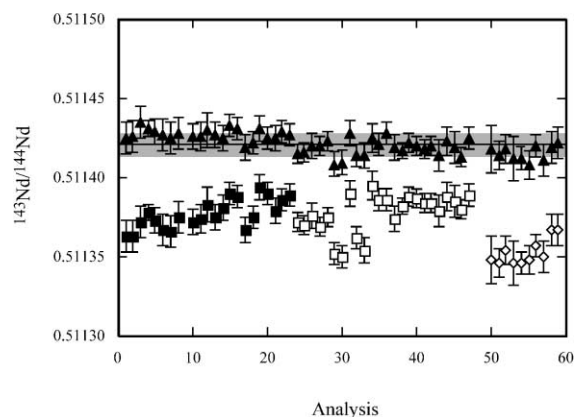


Fig. 8. $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for the Aldrich standard normalised to $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$ (symbols as in Fig. 1) compared to those that have undergone an additional correction based on the correlation in Fig. 7a (filled triangles). The TIMS data for the standard are given by the shaded band. Data corrected using the $^{142}\text{Nd}/^{144}\text{Nd}$ – $^{143}\text{Nd}/^{144}\text{Nd}$ correlation are accurate to 14 ppm or better. The data are precise to 14–20 ppm over long time periods (Table 3).

Table 3
 $^{143}\text{Nd}/^{144}\text{Nd}$ for three different samples by TIMS and MC-ICPMS

	TIMS	Pure
Aldrich (March–June 2000)	0.511421 (7) ^a	0.511427 (7) <i>n</i> = 22
Aldrich (July–September 2000)		0.511419 (10) <i>n</i> = 24
Aldrich (Multidynamic September 2001)		0.511415 (9) <i>n</i> = 10
La Jolla (40 ng)	0.511853 (7) ^b	0.511856 (13) <i>n</i> = 11
La Jolla (4 ng)		0.511857 (20) ^c <i>n</i> = 7
Hawaii Marine Sediment	0.512921 (7) <i>n</i> = 4	0.512925 (7) <i>n</i> = 4

^a TIMS data from Thirlwall (1991a).

^b TIMS data from Vance and Harris (1999) and Thirlwall (1991a).

^c Average internal error = 0.000018.

4.3. Experiments with other Nd isotope compositions

The procedure outlined for the mass bias correction of $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in Section 4.2, using the relationship between the $^{146}\text{Nd}/^{144}\text{Nd}$ -normalised $^{143}\text{Nd}/^{144}\text{Nd}$

and $^{142}\text{Nd}/^{144}\text{Nd}$ ratios, is the most precise way of obtaining isotope ratios. However, the approach is also empirical and it is important to demonstrate that it applies to isotope compositions other than that of the in-house standard we have used here ($\epsilon_{\text{Nd}} = -23.7$). In this section, we describe experiments with La Jolla Nd ($\epsilon_{\text{Nd}} = -15.3$) and a marine sediment from near Hawaii ($\epsilon_{\text{Nd}} = +5.7$). These three standards/samples have been multiply analysed by TIMS and span a range of nearly 30 epsilon units. They thus provide a good test of the generality of the approach.

The data for the two standards and samples are presented, along with TIMS data, in Table 3. The data for the in-house Aldrich standard have already been presented (Fig. 8). The in-house standards are reproducible to 14–20 ppm over a period of months. The data are accurate relative to TIMS to 14 ppm or better. Both the pure La Jolla standards and the marine sediment also agree with the TIMS values to better than 16 ppm. The result on the three analyses of 4 ng La Jolla samples—which yield internal errors of 36 ppm—is particularly noteworthy and is a reflection of the excellent sensitivity of the IsoProbe.

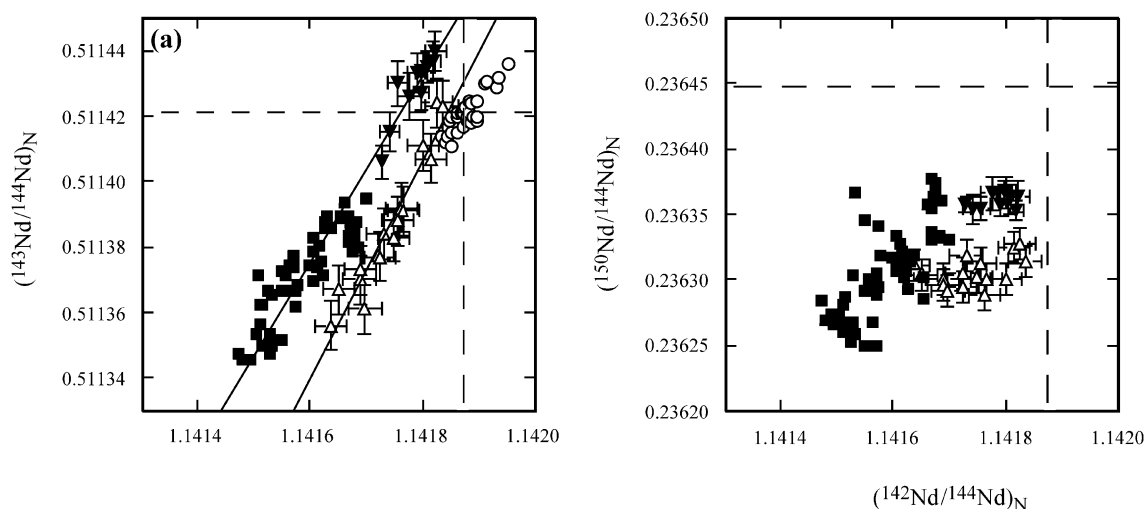


Fig. 9. The same data as in Fig. 7 (all IsoProbe data plotted as filled squares in this case and TIMS data as open circles, error bars omitted for clarity) compared to data from the Open University (open triangles) and Oxford (filled inverted triangles) Nu Instruments MC-ICPMS. For the $^{142}\text{Nd}/^{144}\text{Nd}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$ (both normalised to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$) correlations in (a), all three sets of MC-ICPMS data define tight linear arrays—though with markedly different slopes (0.18–0.22 for the IsoProbe vs. 0.33 for the OU Nu and 0.29 for the Oxford Nu). All of the arrays pass close to the accepted TIMS values for these two ratios. The $^{142}\text{Nd}/^{144}\text{Nd}$ vs. $^{150}\text{Nd}/^{144}\text{Nd}$ (both normalised to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$) correlations in (b) exhibit much more scatter. The limited data from the Nu Instruments MC-ICPMS (one analytical session in each case) yield a $^{150}\text{Nd}/^{144}\text{Nd}$ that is consistent with that of the IsoProbe and with the non-exponential law mass discrimination discussed in the text.

4.4. Relevance to other MC-ICPMS instruments

It is clearly desirable to ascertain whether the effects described here are peculiar to the IsoProbe or general to all MC-ICPMS instruments. This is particularly important given that it is conceivable that the unique design of the IsoProbe, incorporating a hexapole in a collision cell as a means of reducing the energy spread of the ions, could induce these phenomena. The data in Fig. 7a for the IsoProbe and TIMS are reproduced in Fig. 9, along with limited data obtained on two different Nu Instruments MC-ICPMS. The principal noteworthy point is that, qualitatively, the effects we have described for the IsoProbe are also observed on another instrument of a very different design. The rather surprising observation, however, is that for the Nu ICPMS data, the slopes of the relationships between the normalised $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are 0.29 (Oxford) and 0.33 (OU)—higher than those observed for the IsoProbe and the TIMS data in Fig. 7a and 9a. Moreover, the $^{150}\text{Nd}/^{144}\text{Nd}$ ratio measured on the Nu Instruments machines is 0.23630–0.23638—300–600 ppm below the TIMS value and very close to that obtained on the IsoProbe. Recent data for a MAT Neptune instrument (Schweikers et al., 2000; oral comm.) also display, qualitatively, the same general effects as observed for the IsoProbe: that is, all the corrected isotope ratios lie below the TIMS values and the magnitude of the deviation increases for ratios involving masses whose averages are further away from that of $^{146}\text{Nd}/^{144}\text{Nd}$ —exactly as we have observed here. In the latter case, however, the effects are apparently smaller than those that we describe here.

5. Concluding remarks—general significance

In this paper, we have described non-standard mass bias effects on the IsoProbe MC-ICPMS, have traced their origin to variation in mass bias with mass and pointed the way forward for dealing with them. The two approaches that we have suggested are: (a) normalisation with an isotope ratio that is identical (or at worst close) in average mass to the ratio being normalised; (b) a post-normalisation empirical correction based on correlations between different isotope ratios.

These two approaches yield isotope ratios for Nd that are comparable with the best TIMS in precision and accuracy. In addition, we have demonstrated that qualitatively similar effects are observed on another MC-ICPMS instrument.

The two MC-ICPMS instruments for which we have presented Nd data have very different physical characteristics (see Halliday et al., 2000 for a review). For example, the IsoProbe instrument reduces the energy spread inherent in plasma sources using a hexapole lens system surrounded by a gas cell, while the Nu Instruments machine employs an electrostatic analyser. Additionally, the IsoProbe handles the mass dependence of the spatial separation between adjacent isotopes using conventional movable Faraday cups while the Nu employs fixed Faraday cups and a variable dispersion zoom optic device behind the magnetic sector. On the other hand, the important common characteristic of all the MC-ICPMS instruments that sets them apart from TIMS machines is the design of the source and interface. This, and the fact that the effects we have observed here are common to at least two and perhaps more MC-ICPMS instruments (Schweikers et al., 2000; oral comm.), suggest that the mass bias effects we observe here have their origin in the source or the interface. Such a conclusion is consistent with the conventional view (e.g. Maréchal et al., 2000) that the mass-discrimination features observed in MC-ICPMS originate in the area of the interface between the source and the mass analyser—the sampler and skimmer cones.

Any attempt to take further the search for a physical explanation of the mass discrimination effect we observe is hampered by one very significant observation. We have already noted that the MC-ICPMS data display very similar relationships to the TIMS data in Fig. 7a. Moreover, we note that Palacz et al. (2000) has reported similar phenomena to those on Fig. 7a on other TIMS instruments. This is a strong argument for these effects being common, not only to MC-ICPMS but to all mass spectrometers, and suggests a general inadequacy, for high-precision isotope ratio measurements, in the empirical exponential law. The smaller spread in the TIMS data on Fig. 7a would then, in this view, simply be ascribed to the smaller mass biases on these instruments.

We therefore suggest that conventional mass discrimination laws, themselves quasi-empirical, do not

perfectly correct for mass discrimination on any mass spectrometer. Moreover, we suggest that the extent of their imperfection is merely a function of the magnitude of the original mass bias. (The one problem with this idea is that, though we observe correlations between the raw $^{146}\text{Nd}/^{144}\text{Nd}$ and the inaccuracy of the $^{146}\text{Nd}/^{144}\text{Nd}$ -normalised $^{143}\text{Nd}/^{144}\text{Nd}$ in single analysis sessions, no such correlation exists over long time periods. However, between analysis sessions, there are major changes in the instrument operating conditions.) The origin of the deviations from conventional mass-bias laws are at present unclear and it is very difficult at this stage to put forward a physical explanation—not least because the conventionally used mass discrimination laws themselves have little physical basis. What is clear, however, is that linear fits to MC-ICPMS data in \ln – \ln space do not pass through values obtained by TIMS at much lower levels of mass discrimination. It may be that a more complex law may ultimately be found that fits the whole spectrum of mass discrimination. The correction procedure we adopt here, as with all procedures for the elimination of mass bias, is empirical but is clearly successful for Nd and may be applicable to other isotopic systems.

Finally, we wish to note that the data presented here also have implications for an observation made by others using Tl to correct Pb isotope ratios. The normalising $^{146}\text{Nd}/^{144}\text{Nd}$ ratio that would, in theory, be required by our data to bring the normalised $^{143}\text{Nd}/^{144}\text{Nd}$ ratio into line with TIMS is 0.72177—in other words 180 ppm below the TIMS value. The mass shift from $^{143}\text{Nd}/^{144}\text{Nd}$ to $^{146}\text{Nd}/^{144}\text{Nd}$ is about 1%. By analogy, the mass shift from $^{207}\text{Pb}/^{206}\text{Pb}$ to $^{205}\text{Tl}/^{203}\text{Tl}$ is -1.2% . The prediction of our analysis, then, would be that the $^{205}\text{Tl}/^{203}\text{Tl}$ ratio required to obtain a normalised $^{207}\text{Pb}/^{206}\text{Pb}$ value identical to TIMS double spike analyses would be 216 ppm higher than the true value. This observation goes some way (about 40–50% in fact) to explaining the difference between the certified value for the $^{205}\text{Tl}/^{203}\text{Tl}$ of NIST SRM997 Tl and those required by several MC-ICPMS laboratories (Rehkämper and Halliday, 1998; Belshaw et al., 1998; Vance and van Calsteren, 1999) to obtain the published double spike values (Galer and Abouchami, 1998; Thirlwall, 2000).

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