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Sr isotope ratio measurements by double-focusing MC-ICPMS: techniques, observations and pitfalls

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Abstract

Routine techniques for Sr isotope analysis on a double-focusing multiple collector inductively coupled plasma mass spectrometer (MC-ICPMS) are described that for unspiked samples yield accurate and precise results (e.g., $^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.710255 \pm 24$; 0.003%; 2 S.D.) similar to those obtainable by thermal ionisation mass spectrometry. Prior to a 5-min analysis, backgrounds are measured on-mass to correct for interferences on masses 84 and 86 derived from small amounts of Kr in the Ar supply, and stable, residual memory Sr and Rb signals from sample material on the torch and cones. Each analysis consumes ca. 300 ng of Sr, which compares unfavourably to TIMS where loads of ca. 1 ng can be measured. Simultaneous ionisation of all elements during plasma-based ionisation proves to be a disadvantage during Sr isotope analysis as extra chemical clean-up steps, beyond those necessary for TIMS analyses, are required to remove potential isobaric interference problems such as Rb, doubly charged rare earth element (REE) and Ca dimers and argides. Reproducibility for spiked Sr samples is significantly worse than for unspiked samples, largely due to an inability to determine the exact isotopic composition of interfering Rb. This problem can be avoided by splitting the digested sample into isotopic composition and dilution aliquots prior to spiking. Laser ablation (LA)-MC-ICPMS Sr isotope ratio measurements of various geological and biological samples have shown significant deviations in the naturally constant $^{84}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio and the radiogenic $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio from values obtained by analysis of Sr chemically separated from the sample matrix. The precise reasons for this remain unclear but likely reflect a combination of isobaric interferences from Ca dimers and Ca argides and doubly charged REE, as well as disruption of mass bias effects due to differential loading of the plasma. It is also unclear whether this is an instrument- or technique-specific problem and we suggest great care be taken when attempting Sr isotope analyses by in situ LA-MC-ICPMS techniques. (Int J Mass Spectrom 221 (2002) 229–244)

Keywords: MC-ICPMS; Sr isotopes; Laser ablation; Isobaric interferences

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1. Introduction

The radioactive β decay of $^{87}\mathrm{Rb}$ to $^{87}\mathrm{Sr}$ is a widely exploited isotope system in the earth sciences for both petrogenetic and environmental tracing and geochronological purposes. Nevertheless, the relatively large disparities in abundance between the different Sr isotopes, and the often relatively small variation in $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios in, for example, mantle-derived rocks, makes Sr one of the more difficult isotope systems to analyse well, i.e., ≤±20 ppm (e.g., [1]). The advent of multiple collector inductively coupled plasma mass spectrometry (MC-ICPMS) has revolutionised isotope geosciences by allowing (i) analysis

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of elements previously considered difficult or impossible by thermal ionisation mass spectrometry (TIMS) due to their high first ionisation potentials (e.g., W, Hf) (e.g., [2–8]) and (ii) in situ isotopic analysis through laser ablation (LA) of samples [9–11].

Small scale Sr isotopic investigations by TIMS have proved to be extremely informative in the geosciences [12–14], yet are time consuming as they require micro-sampling and wet chemistry separations. The feasibility of more rapid LA-MC-ICPMS Sr isotope analyses without the need for time-consuming chemistry could, therefore, prove to be a major breakthrough in analytical geosciences. While MC-ICPMS instruments have been mainly used to study new isotope systems not easily analysable by other methods, many institutions are acquiring these instruments and will need to perform all their isotopic work by MC-ICPMS, including traditional isotope systems such as Sr. It is, therefore, important that the techniques (and complications) are well described and discussed in the literature. Previously published MC-ICPMS Sr isotope studies have been carried out using single-focusing spectrometers, often with collision cells that help to reduce molecular interferences [9,15]. For this reason we describe here our experiences with Sr isotopic analysis using a double-focusing MC-ICPMS and, in particular, we focus on a number of critical limitations for Sr isotope analysis on these instruments. Previous studies (e.g., [9,15]) have also shown that LA Sr isotope analyses are feasible by MC-ICPMS, although the method has yet to be widely applied. With this in mind, we also present the results of investigations of LA-MC-ICPMS Sr isotope analysis which indicate some caveats and potential complications to the technique.

2. Analytical techniques

2.1. Standard and sample aqueous solution preparation

To determine the reproducibility of unspiked Sr solutions, a ∼300 ppb solution of NIST isotope standard reference material Sr-carbonate SRM987 (in 0.2% HNO_3) was analysed in replicate during all analytical sessions. To test analysis of spiked Sr samples, three rock powders (fine grained volcanic rocks from Yemen), previously analysed at Royal Holloway University of London by TIMS [16], and several international standards (Colombia River basalt BCR-2 and alkali feldspar SRM607) were analysed in replicate [17]. All samples discussed in the text were either conventionally crushed and milled whole rock samples or small samples collected using a dentist drill (see [14] for technique details). LA-MC-ICPMS analyses were carried out directly on freshly broken and/or polished surfaces of samples.

2.2. Sample dissolution and chemical separation of Sr

Rock, mineral and shell samples were weighed into Savillex™PFA vials, spiked with a mixture of highly enriched ^{84}Sr and ^{87}Rb tracer, where appropriate, and then dissolved to completion using conventional HF–HNO_3–HCl dissolution techniques in closed beakers. Three mixed spikes with different Rb/Sr were used, with concentrations and isotopic compositions previously measured using both TIMS and MC-ICPMS. Rb and Sr are first separated from the dissolved samples on a cation exchange column loaded with AG50W-X 100–200 mesh resin by elution of 2.0 M HCl. In order to minimise isobaric interferences on ^{87}Sr from ^{87}Rb and vice versa, an extra clean step using Eichrom Sr-specific resin is necessary for both the Sr and Rb cuts [17]. In the case of Sr, the cut from the cation columns is redissolved in 3 M HNO_3 and loaded onto small single use columns loaded with ∼200 μL of Sr-Spec resin. Several reservoir volumes of 3 M HNO_3 are passed to remove Rb from the sample; Sr is then re-collected with one to two reservoir volumes of Milli-Q water. For unspiked samples, chemistry can be simplified to one or two passes through Sr-Spec resin. In most cases, this technique resulted in Sr fractions with only small Rb interferences ($^{87}\mathrm{Rb}/^{87}\mathrm{Sr} < 0.0001$). Full procedural blanks for this technique amounted to less than 50 pg of Rb and Sr.

2.3. MC-ICPMS and LA-MC-ICPMS procedures

All analyses were determined on a VG Axiom MC-ICPMS, a double-focusing, sector field MC-ICPMS. Samples were taken up in 0.2% HNO_3. Most aqueous solutions were introduced into the mass spectrometer using a Micromist glass nebuliser in free-aspiration mode with an uptake rate of 0.1 mL/min using methods similar to those described in Ref. [17]. This introduction technique typically yields a sensitivity of ca. 25 V/ppm of Sr. Smaller samples (e.g., micro-drilled feldspar) were introduced using the higher sensitivity (ca. 120 V/ppm) Cetac Aridus microcentric desolvating nebuliser, where the advantages of increased signal size and aqueous solution life are juxtaposed against the need for slightly longer washouts.

With both introduction systems, background signals of up to 0.5–3 mV of ^{85}Rb and ^{88}Sr remain even after protracted washout times. These backgrounds slowly rise by 1–2 mV over analytical sessions (∼days), but remain stable with respect to the timeframe of an individual Sr isotope analysis. The background signal is significantly enriched in ^{87}Rb and ^{84}Sr after analysis of spiked samples, indicating it is an accumulation of material from samples on the introduction system, rather than an environmental contribution. Background signals disappear after cleaning of the entire introduction system and fitting of clean cones.

LA-MC-ICPMS analyses were carried out using either a Cetac LSX-200 266 nm quadrupled Nd-YAG laser or a New Wave LUV frequency-quintupled Nd-YAG 213 nm laser. Ablated material was carried into the plasma using Ar as a carrier gas. The spot size used (10–200 μm) was varied depending on the material analysed to maximise signal strength, whereas laser energy (∼4 mJ) and pulse rate (20 Hz) were kept at maxima. More details on the LA apparatus and MC-ICPMS analytical protocols are given by Willigers et al. [18].

2.4. Mass spectrometry

The Axiom MC-ICPMS in Copenhagen is equipped with one fixed and eight movable Faraday collectors; all fitted with 10^{11} Ω resistors. Instrumental operating conditions are summarised in Table 1. The Faraday collector set-up used for Sr isotope analyses comprises an array from ^{83}Kr (L4) to ^{89}Y (H2) (Fig. 1), monitoring Kr, Rb, Sr and Y. Kr provides an isobaric interference on masses 84 and 86 and, therefore, must be monitored to yield accurate stable and radiogenic Sr isotope ratios. The main source of Kr is from air leaks in the Ar gas system or from the Ar supply itself, but signals are stable and generally very low (<2 mV ^{83}Kr). Cup efficiencies for Sr on the Axiom

Table 1
Summary operating conditions for the Axiom MC-ICPMS

RF power	1300 W
Ar cooling gas flow rate	14 L/min
Interface cones	Nickel
Acceleration voltage	6 kV
Ion-lens settings	Optimised for maximum sensitivity and optimal peak shape
Mass resolution	∼400
Mass analyser pressure	Low 10^{-8} mbar
Detection system	Nine Faraday collectors and one electron multiplier
Sampling mode	One run = three to four blocks of 100 × 2 s
Backgrounds	1 min on peak in 0.2% HNO_3
Nebuliser 1	Micromist 100
Uptake mode	Free aspiration
Spray chamber temperature	7 °C
Sample uptake rate	∼0.1 mL/min
Typical sensitivity on ^{88}Sr	∼25 V/ppm
Ar auxiliary gas flow rate	∼1.4 L/min (optimised daily)
Ar nebuliser gas flow rate	∼0.8 L/min (optimised daily)
Nebuliser 2	Aridus microcentric
Spray chamber temperature	70 °C
Desolvator temperature	160 °C
Sample flow rate	0.07 mL/min
Typical sensitivity on ^{88}Sr	∼100 V/ppm
Ar auxiliary gas flow rate	∼1.2 L/min (optimised daily)
Ar nebuliser gas flow rate	∼1.0 L/min (optimised daily)
Ar sweep gas rate	∼4 L/min (optimised regularly)
Laser	Cetac LSX-200 266 nm or New Wave LUV 213 nm
Spot size	Varied (10–200 μm)
Laser energy	4 MJ
Pulse rate	20 Hz
Ar auxiliary gas flow rate	∼1.2 L/min (optimised daily)
Ar nebuliser gas flow rate	∼1.0 L/min (optimised daily)
Carrier gas	Ar

Collector	L4	L3	L2	L1	Axial	H1	H2	H3	H4
	^{83}Kr$_{11.55\%}$	^{84}Kr$_{57.0\%}$		^{86}Kr$_{17.3\%}$					
			^{85}Rb$_{72.2\%}$		^{87}Rb$_{27.8\%}$				
		^{84}Sr$_{0.56\%}$		**^{86}Sr$_{9.86\%}$**	**^{87}Sr$_{7.00\%}$**	**^{88}Sr$_{82.6\%}$**			
							^{89}Y$_{100\%}$		

Fig. 1. Faraday collector set-up used for Sr isotopic measurement illustrating direct isobaric interferences on Sr masses.

are stable and are not changed over long periods (weeks) of analysis. All Sr isotopic measurements are carried out at a mass resolution of 400 in static mode.

2.5. Data acquisition and reduction

An on-peak-zeroes (OPZ) baseline measurement is made prior to every analysis, primarily to eliminate the effects of the small, persistent yet stable Rb and Sr backgrounds from the torch and cones. Following washout in 2% HNO_3 to stable background signals (ca. 1–2 mV ^{85}Rb and ^{88}Sr), the solution introduction system is pre-treated and equilibrated using an OPZ solution of the exact same molarity as that used to dilute aqueous solutions (0.2% HNO_3); background signals will change if the aqueous solution and OPZ solution have different molarities. The intensity of these background signals are measured for 1 min. The sample solution is then aspirated and once a stable signal has been achieved, data collection begins. The background signals are subsequently subtracted on-line from the measured signals. The OPZ measurement also negates small isobarically interfering Kr signals from the plasma but, on occasion, relatively high Kr levels (10 mV ^{83}Kr) occur due to enrichment of the heavier noble gases as the tanks deplete in Ar. In these rare instances, error magnification during correction of the isobaric interferences make Sr isotopic analysis problematic, and analytical sessions must be delayed until delivery of cleaner Ar.

Data are generally acquired as two to four blocks of 100 × 2-s data measurements. A single analysis, including washouts and OPZ carried out in this way lasts 10–15 min. At signal intensities of 5–6 V on ^{88}Sr, this results in an internal error on the ^{87}Sr/^{86}Sr ratio $\leq \pm 0.001\%$ (1 S.D.). A typical Sr analysis carried out in this fashion using the Micromist glass nebuliser consumes ∼1–1.5 mL of solution, equivalent to ∼300 ng of Sr. The lower-uptake Aridus desolvating nebuliser consumes ∼0.5–1.0 mL of solution, equivalent to 50–60 ng of Sr.

Although isobaric interferences from Kr on masses 84 and 86 are effectively cancelled by the OPZ measurement, any subsequent fluctuations in Kr are corrected by monitoring ^{83}Kr. The isobaric interference of ^{87}Rb on ^{87}Sr is corrected by monitoring mass 85 and a user-specified ^{87}Rb/^{85}Rb ratio, corrected for mass bias using the measured ^{86}Sr/^{88}Sr ratio. A natural ^{87}Rb/^{85}Rb ratio (0.3855) for interference corrections is suitable if samples are unspiked or the amount of interfering Rb is low (^{87}Rb/^{87}Sr $< 0.01\%$). Following interference corrections, the Sr isotope ratios are then fractionation corrected using the exponential law and the accepted value for ^{86}Sr/^{88}Sr $= 0.1194$, or in the case of spiked samples, the ^{86}Sr/^{88}Sr ratio calculated for the sample/spike mixture after calculating the Sr concentration of the sample.

3. Results

3.1. Isotope standard solutions and unspiked rock samples

Replicate analyses ($n = 81$) of a ∼300 ppb SRM987 isotope standard solution carried out over several analytical sessions by a number of different users between July 2000 and June 2002 have yielded an average value of ^{87}Sr/^{86}Sr $= 0.710255 \pm 23$ (0.003%; 2 S.D.) and ^{84}Sr/^{86}Sr $= 0.056482 \pm 32$ (0.06%; 2 S.D.) (Fig. 2). These values and reproducibilities are comparable to those obtainable by high quality TIMS techniques [1] (^{87}Sr/^{86}Sr $= 0.710241 \pm 12$ (0.002%)) and in good agreement with

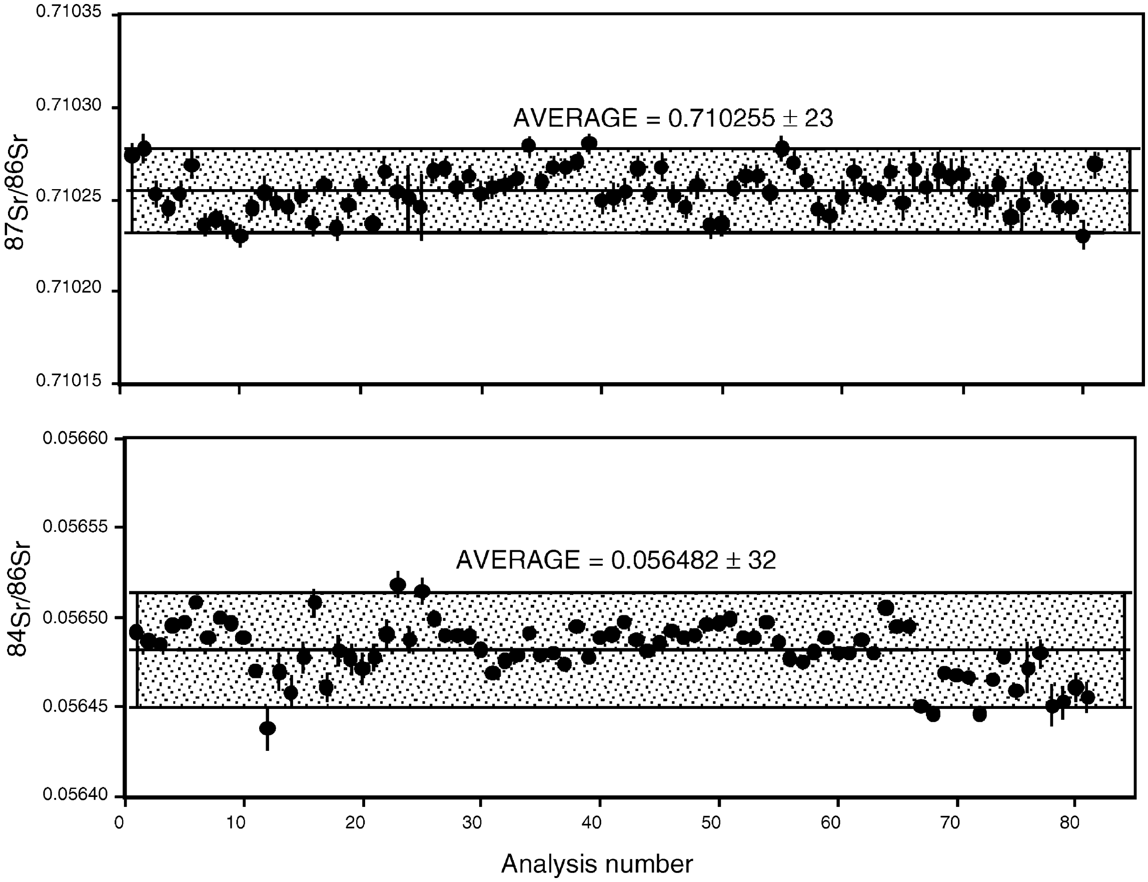

Fig. 2. Replicate analyses of Sr isotopic standard SRM987 measured over a 2-year period.

other Sr isotope data collected by MC-ICPMS [19]. A typical internal precision for such an analysis is better than ±0.001% (1 S.E.) for $^{87}Sr/^{86}Sr$ and better than ±0.01% (1 S.E.) for $^{84}Sr/^{86}Sr$. Reproducibility of standard analyses during a single analytical session are generally better than this long-term average, for example, replicate analyses ($n = 7$) of Sr separated from two clinopyroxene crystals carried out over 3 days yielded an average $^{87}Sr/^{86}Sr$ of 0.704468 ± 21 (0.003%; 2 S.D) (Table 2). These data indicate that reproducibilities for isotope standard solutions and samples dissolved and processed through chemistry are comparable. All analyses presented in Fig. 2 were run interspersed with analyses of both spiked and unspiked rock and mineral samples with widely varying

Table 2
Replicate analyses of duplicate dissolutions of separate clinopyroxene crystals from the Batbjerg Intrusion (Greenland) analysed over three separate analytical sessions

	$^{87}Sr/^{86}Sr$ ± 2 S.E.	$^{84}Sr/^{86}Sr$ ± 2 S.E.
	0.704464 ± 13	0.056402 ± 15
	0.704474 ± 10	0.056468 ± 14
	0.704463 ± 11	0.056426 ± 16
	0.704462 ± 10	0.056527 ± 16
	0.704488 ± 11	0.056495 ± 5
	0.704472 ± 11	0.056510 ± 6
	0.704457 ± 10	0.056548 ± 4
Average	0.704468 ± 21 (0.003%)	0.056482 ± 11 (0.019%)

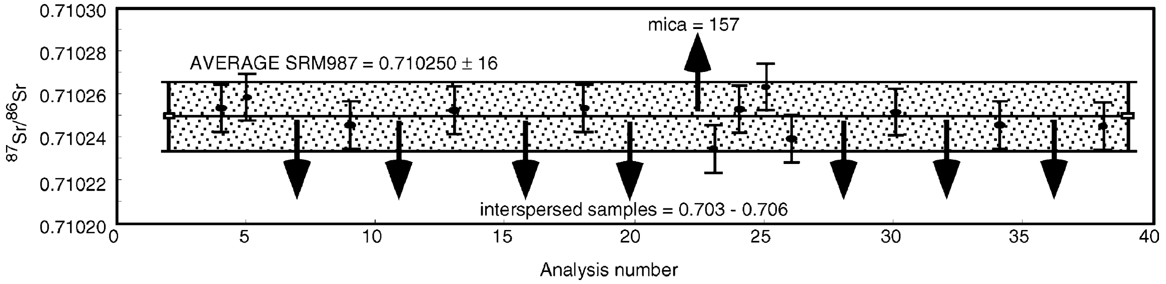

Fig. 3. Plot illustrating reproducibility of ^{87}Sr/^{86}Sr determinations on SRM987 when interspersed with geological samples of distinct composition over a period of 2 days.

^{87}Sr/^{86}Sr (0.703–7.5) and ^{84}Sr/^{86}Sr (0.0565–1). The efficiency of washouts and the OPZ method are illustrated in Fig. 3 which shows ^{87}Sr/^{86}Sr data for SRM987 over a 2-day period, analysed interspersed with geological samples with ^{87}Sr/^{86}Sr mostly between 0.703 and 0.706 and one sample (a mica) with an extreme ^{87}Sr/^{86}Sr of 157. During this analytical session, the SRM987 standard data yielded an average value of 0.710250 ± 16 (0.002%; 2 S.D.), well within our long-term standard average.

During the early stages of this project, unspiked dissolutions of some rock samples yielded consistently incorrect results for both radiogenic and stable ratios. Mass scans across these solutions at a resolving power of ca. 3000 revealed the presence of doubly charged rare earth elements (REEs) (e.g., $^{166}\text{Er}^{2+}$ = mass 88) (Fig. 4). Doubly charged REE interferences at mass 85 ($^{170}\text{Er}^{2+}$ and $^{170}\text{Yb}^{2+}$) and mass 83 ($^{166}\text{Er}^{2+}$) will result in incorrect isobaric interference corrections for Rb and Kr, respectively. Furthermore, the presence of doubly charged REE will also create artificially high baselines at half-masses (e.g., $^{173}\text{Yb}^{2+}$ = mass 86.5) and result in incorrect baseline corrections if conventional half-mass baselines are measured whilst aspirating the sample solution (e.g., Fig. 4). The presence of REE in these aqueous solutions was the result of poorly calibrated cation exchange columns, and the solutions yielded accurate data following further processing through Sr-spec resin. Such interferences should be unimportant during MC-ICPMS analysis as long as careful chemistry is carried out, however, they are potentially very important for LA-MC-ICPMS

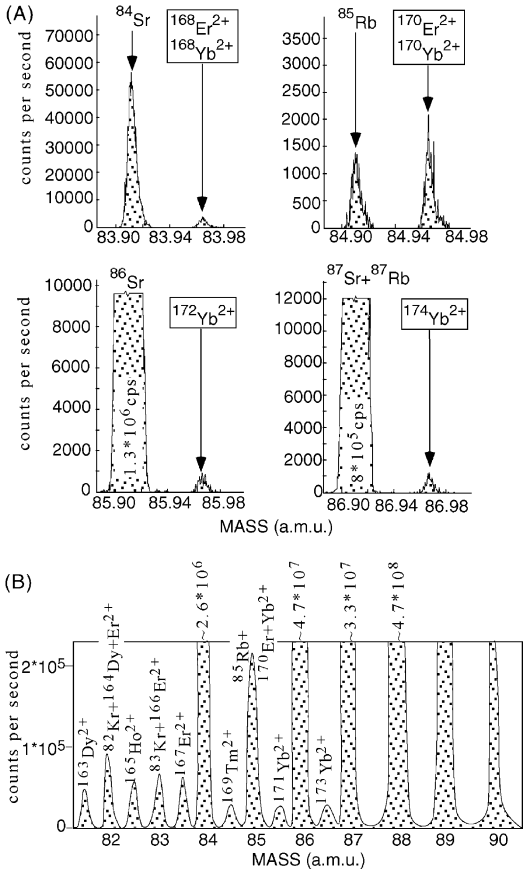

Fig. 4. (A) Mass spectra at approximate resolving power of 3000 indicating the presence of doubly charged REE interferences on Sr and Rb masses in an Sr aliquot processed using poorly calibrated cation exchange columns. (B) Scan at normal resolving power (400) across a similar sample illustrating the presence of half-mass interferences that would disrupt conventional half-mass baseline measurements.

analyses of Sr and REE-rich minerals, such as apatite. Mass 89 (Y) is monitored as an indication of the presence of doubly charged REE isobaric interferences. As discussed later, significant shifts in $^{84}Sr/^{86}Sr$ from 0.0565 are also indicative of isobaric interferences. However, this cannot be monitored in spiked Sr isotope analyses.

3.2. Spiked samples

The reproducibility of spiked Sr isotopic analyses on geological samples was determined by replicate isotope dilution analyses of several volcanic rock samples and international rock and mineral standards. These samples have a wide range in Rb/Sr (0.03–13.3) and $^{87}Sr/^{86}Sr$ (0.7039–1.2004). The results have been previously presented and discussed (with respect to Rb) in Waight et al. [17] and are summarised in Table 3.

As stated previously, the isobaric interference of ^{87}Rb on ^{87}Sr is corrected for on-line with a user-specified $^{87}Rb/^{85}Rb$ ratio. If interfering Rb is entirely derived from environmental blanks, then a natural $^{87}Rb/^{85}Rb$ (0.3855) may be most appropriate [17]. However, if interfering Rb is derived from imperfect chemical separation, then the isotopic composition of the complementary Rb analysis (enriched in ^{87}Rb) may be more appropriate. In reality, the Rb will be some unknown mixture between natural blank and spiked sample. Therefore, the results of replicate analyses are presented in Table 3 using both methods to correct for isobaric interferences on mass 87. Sr concentration determinations reproduce to <0.5% (2 S.D.) and Rb/Sr ratios reproduce to ∼0.2% (2 S.D.) in the moderate and high Rb/Sr samples, but are somewhat worse in the low Rb/Sr sample and SRM607 (±0.5%). In these cases, we attributed these poorer reproducibilities to relatively large Sr interferences during the Rb isotope dilution analysis, and uncertainties in determining $^{87}Sr/^{86}Sr$ ratio to use for correcting isobaric interferences in the case of NYJB140, and relatively small sample sizes and sample heterogeneity in the case of SRM607 [17]. Providing isobaric interferences are kept to a minimum ($^{87}Sr/^{87}Rb < 1\%$, $^{87}Rb/^{87}Sr < 0.01\%$), it is possible to replicate Rb/Sr ratios to ±0.2% (2 S.D.) using these techniques [17].

The $^{87}Sr/^{86}Sr$ ratio in replicate isotope dilution analyses of whole rock samples reproduces poorly (0.005–1.3%, Table 3) in comparison to unspiked samples and standards (0.003%). In general, a considerable improvement in both the reproducibility and accuracy of the $^{87}Sr/^{86}Sr$ ratio occurs when natural Rb compositions are used to correct for isobaric interferences, although reproducibilities remain worse than unspiked standard analyses. In contrast, SRM607 yields a better reproducibility (albeit for only three replicates) when the isotopic composition of the complementary Rb isotope dilution analysis is used.

3.3. LA-MC-ICPMS analyses

The potential for isobaric interferences is large during LA as all material ablated is ionised simultaneously. The direct isobaric interference of ^{87}Rb on ^{87}Sr, and the inability to determine parent/daughter ratios to adequate levels of precision, effectively limits in situ Sr isotope analyses to materials with either low Rb/Sr ratios or relatively young samples where age corrections are insignificant [15]. High Sr contents (hundreds of ppm) are also required to generate sufficiently sized signals to guarantee adequate data quality. Despite these limitations, many potential geological and environmental problems could be investigated by in situ Sr isotope analyses (e.g., plagioclase and apatite in volcanic rocks, seawater compositional variations in carbonates and shell material, environmental tracing using bone material, etc.). We have undertaken LA-MC-ICPMS Sr isotope analyses on a number of samples, the results of which are summarised in the following description.

3.3.1. Plagioclase (1.19 Ga)

A plagioclase megacryst (1.5 cm diameter) from Gardar Province dikes in South Greenland was sampled using a small drill to investigate possible Sr isotopic variation within the crystal [20]. This data revealed that the crystal has generally very low

Table 3
Results of replicate isotope dilution analyses of whole rock volcanic samples and international standards (see also [17])

Sample	*n*	Sr (ppm) ± 1 S.D.[a] (2 S.D.%)	Sr (ppm) ± 1 S.D[b] (2 S.D.%)	Rb/Sr ± 1 S.D[a] (2 S.D.%)	Rb/Sr ± 1 S.D[b] (2 S.D.%)	$^{87}Sr/^{86}Sr$ ± 1 S.D[a] (2 S.D.%)	$^{87}Sr/^{86}Sr$ ± 1 S.D[b] (2 S.D.%)
NYJB140	6	1104.30 ± 1.66 (0.30)	1104.30 ± 1.66 (0.30)	0.03098 ± 8 (0.49)	0.03102 ± 8 (0.49)	0.703883 ± 72 (0.021)	0.703915 ± 19 (0.005)
Rec.		1104.3		0.03097		0.70391	
NYJB271	5	391.33 ± 0.91 (0.47)	391.34 ± 0.91 (0.47)	0.14878 ± 15 (0.20)	0.14877 ± 14 (0.19)	0.706000 ± 222 (0.063)	0.706319 ± 99 (0.028)
Rec.		391.7		0.14884		0.70622	
NYJB232	5	13.32 ± 0.03 (0.39)	13.32 ± 0.02 (0.35)	13.361 ± 16 (0.24)	13.358 ± 14 (0.20)	0.72169 ± 468 (1.296)	0.72453 ± 428 (1.180)
Rec.		12.45		14.289		0.72102	
SRM607	3	65.50 ± 0.15 (0.47)	65.52 ± 0.14 (0.44)	8.011 ± 0.015 (0.37)	8.008 ± 0.017 (0.43)	1.20033 ± 124 (0.207)	1.20263 ± 256 (0.425)
		65.49		8.000		1.20039 ± 20	
BCR-2	3	324.20 ± 3.85 (2.4)	324.20 ± 3.85 (2.4)	0.13949 ± 9 (0.13)	0.13949 ± 10 (0.14)	0.705003 ± 91 (0.026)	0.705027 ± 11 (0.003)

Rec., recommended results previously determined by TIMS [16].

[a] Using measured Rb isotopic composition to correct for isobaric interference.

[b] Using natural Rb isotopic composition to correct for isobaric interference.

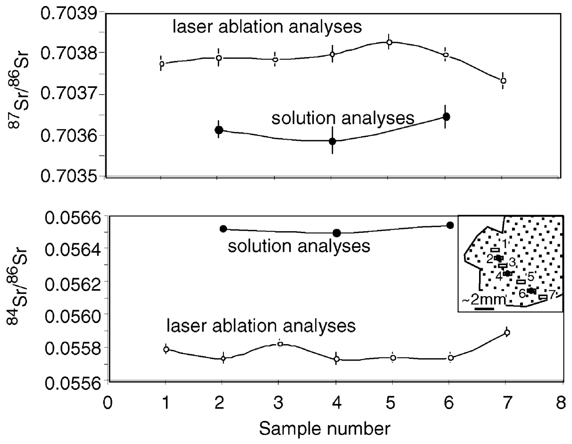

Fig. 5. Comparative $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ isotope data from LA-MC-ICPMS and MC-ICPMS analyses on processed drilled samples collected from Gardar Province plagioclase. Inset shows schematic diagram of sampled crystal, small boxes represent laser ablation sites and small dots represent drill sites for MC-ICPMS analyses.

$^{87}Rb/^{86}Sr$ (~0.002) and consequently age corrections are insignificant, despite the rock being relatively old (1.19 Ga). It was also found to have constant initial $^{87}Sr/^{86}Sr$ except in the core. The high Sr contents (1500+ ppm), isotopic homogeneity and low Rb/Sr make this crystal an ideal target to test the accuracy of LA-MC-ICPMS Sr isotopic analyses of plagioclase.

Several LA-MC-ICPMS analyses were made of the isotopically homogenous region of the crystal (Table 4, Fig. 5) using a 100 μm spot size. Five-minute analyses were carried out by rastering the laser over a 500 μm × 500 μm area at a scan speed of 5 μm/s, yielding internal errors comparable to those for MC-ICPMS Sr isotope analyses. Three of these LA sites were then sampled using a drill and chemically processed to yield a clean Sr split which was then analysed unspiked.

It is apparent from Fig. 5 that, while the LA-MC-ICPMS technique gives reproducible $^{87}Sr/^{86}Sr$ data, with precisions comparable to MC-ICPMS data, there is a large discrepancy (~0.025%) between absolute values derived from LA-MC-ICPMS and conventional MC-ICPMS analyses from the same locations; the laser data consistently yielding higher $^{87}Sr/^{86}Sr$ values. Furthermore, the $^{84}Sr/^{86}Sr$ ratio is consistently ~1.2% too low in the LA-MC-ICPMS analyses.

3.3.2. *Carbonate material (0 Ma)*

In a similar investigation, but on markedly different material, LA-MC-ICPMS Sr isotope analyses were made in a profile across an ear bone (otolith) from an Arctic Char. These fish hatch and grow in freshwater regions in Greenland, then after several years migrate to the open sea, returning to the inland waters each year to breed. We hoped to investigate if this lifestyle change was recorded in the Sr isotopic signature of the otolith which grew over the life of the fish [21,22] as the inland waters may have considerably more radiogenic Sr isotopic signatures derived by erosion of the relatively old surrounding continental crust compared with modern seawater ($^{87}Sr/^{86}Sr \sim 0.709$ [23]). Results are presented in Table 4 and Fig. 6, and while there is a marked changed in the $^{87}Sr/^{86}Sr$ composition about halfway through the otolith that may reflect migration from freshwater to seawater, this change is matched by a shift in $^{84}Sr/^{86}Sr$ ratio which is again consistently different from the accepted stable ratio of 0.0565, in this case being 1.8–5.3% higher. These changes also coincide with an increase in Sr signal (i.e., Sr concentration and likely a change in Sr/Ca).

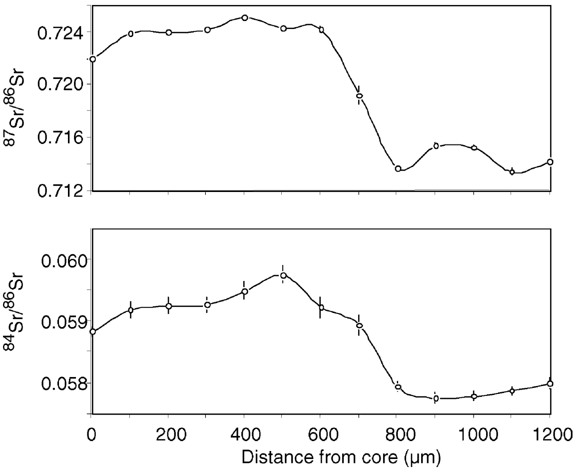

Fig. 6. $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ isotope data collected using LA-MC-ICPMS in a traverse across an otolith from an Arctic Char.

Table 4
LA-MC-ICPMS and MC-ICPMS (on bulk dissolutions and processed solutions) results for plagioclase from the Gardar Province, an otolith from an Arctic Char, apatite, pyroxene and sphene from the Gardiner Intrusion, and a modern seashell

Sample		$^{87}Sr/^{86}Sr \pm 2$ S.E. (absolute)	$^{84}Sr/^{86}Sr \pm 2$ S.E. (absolute)
Gardar feldspar (1.19 Ga)			
	Laser ablation analyses		
	GM 1680-1 LA	0.703777 ± 18	0.05579 ± 3
	GM 1680-3 LA	0.703787 ± 15	0.05583 ± 3
	GM 1680-5 LA	0.703829 ± 18	0.05575 ± 3
	GM 1680-7 LA	0.703734 ± 18	0.05590 ± 3
	GM 1680-6 LA	0.703798 ± 17	0.05575 ± 3
	GM 1680-4 LA	0.703800 ± 20	0.05574 ± 3
	GM 1680-2 LA	0.703792 ± 21	0.05574 ± 4
	Solution analyses		
	GM 1680-10 (ablation spot 2)	0.703616 ± 20	0.05653 ± 1
	GM 1680-11 (ablation spot 4)	0.703589 ± 32	0.05650 ± 1
	GM 1680-12 (ablation spot 6)	0.703648 ± 28	0.05655 ± 1
Arctic Char otolith			
	Laser ablation analyses[a]		
	0	0.72203 ± 14	0.05884 ± 7
	100	0.72395 ± 9	0.05919 ± 13
	200	0.72403 ± 10	0.05926 ± 12
	300	0.72422 ± 12	0.05927 ± 12
	400	0.72515 ± 13	0.05950 ± 14
	500	0.72433 ± 21	0.05975 ± 14
	600	0.72422 ± 24	0.05923 ± 17
	700	0.71924 ± 66	0.05894 ± 15
	800	0.71376 ± 22	0.05794 ± 8
	900	0.71541 ± 22	0.05777 ± 8
	1000	0.71530 ± 14	0.05779 ± 7
	1100	0.71348 ± 26	0.05788 ± 6
	1200	0.71427 ± 19	0.05800 ± 9
	Modern seawater	0.7092	0.0565
Gardiner clinopyroxene (55 Ma)			
	Laser ablation analyses		
		0.703748 ± 83	0.05656 ± 6
		0.703881 ± 84	0.05612 ± 9
		0.703825 ± 86	0.05641 ± 6
		0.703730 ± 55	0.05654 ± 8
		0.703717 ± 52	0.05671 ± 10
		Average = 0.70378 ± 14	0.05650 ± 44
	Solution analyses[b]		
		0.703920 ± 10	
		0.703931 ± 11	
		0.703891 ± 10	
		Average = 0.703907 ± 44	
Gardiner sphene (55 Ma)			
	Laser ablation analyses		
		0.703639 ± 42	0.05771 ± 4
		0.703632 ± 39	0.05776 ± 4
		0.703628 ± 82	0.05748 ± 4
		Average = 0.70363 ± 1	0.0576 ± 3

Table 4 (*Continued*)

Sample		^{87}Sr/^{86}Sr ± 2 S.E. (absolute)	^{84}Sr/^{86}Sr ± 2 S.E. (absolute)
	Solution analyses		
	Bulk (no chemistry)	0.704174 ± 11	0.05827 ± 0
	Bulk (no chemistry)	0.704050 ± 14	0.05510 ± 2
	Sr-spec	0.703882 ± 10	0.05646 ± 1
Gardiner apatite			
	Laser ablation analyses		
		0.70362 ± 10	0.05720 ± 15
		0.70369 ± 8	0.05687 ± 9
		0.70360 ± 17	0.05708 ± 19
		0.70380 ± 16	0.05665 ± 4
		0.70371 ± 10	0.05668 ± 4
		0.70367 ± 13	0.05667 ± 4
		0.70368 ± 11	0.05686 ± 5
		Average = 0.70368 ± 12	0.05686 ± 12
	Solution analyses		
	Bulk (no chemistry)	0.703732 ± 14	0.05604 ± 2
	Bulk (no chemistry)	0.704020 ± 23	0.05684 ± 1
	Sr-spec	0.703682 ± 11	0.05646 ± 2
Seashell			
	Laser ablation analyses		
		0.709543 ± 35	0.05689 ± 4
		0.709613 ± 34	0.05676 ± 4
	Solution analyses		
	Sr-spec	0.709536 ± 13	0.05649 ± 1

[a] Distance from core (in micrometers).

[b] No ^{84}Sr/^{86}Sr as samples were spiked with ^{84}Sr-enriched tracer.

Correlations also exist between all ratios, including the measured ^{86}Sr/^{88}Sr which is used for fractionation correction. While we have not carried out wet chemical analyses of the otolith to determine its ‘true’ isotopic composition, we note that the observed ^{87}Sr/^{86}Sr compositions are considerably higher than would be expected if they were derived from modern seawater. LA-MC-ICPMS analyses of modern seashell material reveal ^{87}Sr/^{86}Sr ratios within error of the conventional MC-ICPMS analysis on separated material, but ^{84}Sr/^{86}Sr values that are again marginally higher than the accepted value (Table 4).

3.3.3. *Igneous Ca silicate, phosphate and titanite (55 Ma)*

LA-MC-ICPMS Sr isotope analyses were made of apatite, sphene and clinopyroxene crystals from the Gardiner Intrusion in Greenland (Table 4). Significant discrepancies are also observed in these minerals between LA-MC-ICPMS analyses and conventional MC-ICPMS analyses of Sr separated from the same materials. In all cases ^{84}Sr/^{86}Sr is generally higher than the accepted value of 0.0565, whereas ^{87}Sr/^{86}Sr values are either within error of, or lower than that obtained by MC-ICPMS (Table 4).

In summary, much of our in situ LA-MC-ICPMS analyses are discrepant from conventional MC-ICPMS analyses on separated material for radiogenic Sr isotope ratios, and show offsets from accepted values of stable isotope ratios that cast serious doubts on the validity of the LA-MC-ICPMS data. The variations in stable isotopic ratios suggest the presence of complex molecular isobaric interferences that are not accounted for during data reduction or OPZ measurements. Attempts to reduce interferences by changing gas flows and increasing torch–cone spacing had no effect.

4. Discussion

4.1. Reproducibility and accuracy of Sr concentrations and isotope ratio determinations by MC-ICPMS

Replicate analyses of whole rock samples have shown that Sr concentration determinations from isotope dilution analyses reproduce to $\leq 0.5\%$. Isobaric interferences from Rb do not interfere on the ratio used to determine Sr concentration ($^{84}Sr/^{86}Sr$), and thus the difficulties in determining which Rb isotope ratio to use to correct for isobaric interferences has no effect on Sr concentration determinations. The opposite, however, is not true for Rb isotope dilution analyses [17]. Unspiked Sr isotope analyses reproduce to levels ($^{87}Sr/^{86}Sr = 0.003\%$; 2 S.D.) similar to those obtainable by most TIMS laboratories. The main cause of poor standard reproducibility is insufficient washouts.

The poor reproducibility of the $^{87}Sr/^{86}Sr$ ratio in isotope dilution samples, compared to that obtained for standard isotopic solutions, is directly attributable to errors resulting from an inability to precisely determine the isotopic composition of isobarically interfering Rb [17] which represents an unknown mixture of natural Rb, and enriched spike Rb. This makes this isobaric interference difficult to correct for, unless the Rb interference is small enough (i.e., $^{87}Rb/^{87}Sr < 0.0005\%$) to be insignificant. In a recent contribution, Moens et al. [24] presented a method for effectively removing this Rb interference by reacting Sr with CH_3F in a dynamic reaction cell and measuring SrF^+ free of RbF^+ interferences. There are a number of potential problems with this method such as the possibility of other isobaric interferences (Rh, Pd, Ag), the long analysis time (30 min) and subsequent large amounts of Sr required, large matrix effects resulting in a need to run interspersed matrix matched standards and relatively poor in-run precisions (0.03%). While this technique may prove extremely advantageous in the future, especially when applied to multiple collector instruments with collision cells, in this contribution we concentrate on isotopic ratio determinations on our double-focusing, multiple collector instrument (without a collision cell) which is similar to many others in the geoscience community.

Given our observations, TIMS may remain the method of choice for determining high quality Sr isotopic compositions from isotope dilution aliquots, such as are needed for geochronological studies. Moreover, the MC-ICPMS technique requires >200 ng Sr for a high precision analysis. This compares poorly to TIMS, where samples on the order of 1 ng can be analysed precisely using TaF activator techniques.

If Sr isotope dilution analyses are necessary by MC-ICPMS, we recommend that samples are digested prior to addition of spike, and then quantitatively split into two aliquots once fully in solution in 6N HCl. An unspiked aliquot is analysed to yield a high quality $^{87}Sr/^{86}Sr$ determination where the natural Rb isotopic composition can be used confidently to correct for isobaric interferences which should be minimal provided careful chemical separations take place, and, therefore, reproducibilities determined from unspiked standards are applicable. Tracer is added to the second aliquot which is processed for Rb and Sr concentrations determinations only.

4.2. Causes of inaccurate LA-MC-ICPMS Sr isotope analyses

The apparent coupled discrepancies in both $^{87}Sr/^{86}Sr$ and $^{84}Sr/^{86}Sr$ ratios during LA-MC-ICPMS analyses suggests the presence of isobaric interferences. This is particularly well illustrated in the otolith data where $^{84}Sr/^{86}Sr$, $^{86}Sr/^{88}Sr$ and $^{87}Sr/^{86}Sr$ all correlate with each other and even show correlated changes with a change in Sr intensity (concentration) and Sr/Ca. As most material suitable for LA-MC-ICPMS Sr isotope studies have high Ca contents (15 wt.% or higher), Ca dimers and/or Ca argides represent potential interferences on all Sr isotope masses (Table 5). The most problematic of these will be the dominant ^{40}Ca (96.9%) plus ^{44}Ca, the second most abundant Ca isotope (2.09%), interfering with ^{84}Sr and representing ~89% of the Ca dimers interfering on Sr masses. The presence of such an interference is consistent with the observed

Table 5
Summary of potential Ca dimer, Ca argide and doubly charged REE interferences which may interfere on Sr masses, and Kr and Rb peaks used to monitor isobaric interferences

Mass					
83	84	85	86	87	88
^{40}Ca^{43}Ca^{+} ^{40}Ar^{43}Ca^{+}	^{40}Ca^{44}Ca^{+} ^{40}Ar^{44}Ca^{+} ^{42}Ca^{42}Ca	^{42}Ca^{43}Ca	^{40}Ca^{46}Ca ^{40}Ar^{46}Ca ^{42}Ca^{44}Ca ^{43}Ca^{43}Ca ^{48}Ca^{38}Ar	^{44}Ca^{43}Ca	^{40}Ca^{48}Ca ^{40}Ar^{48}Ca ^{46}Ca + ^{42}Ca ^{44}Ca + ^{44}Ca
^{166}Er^{2+}	^{168}Er^{2+} ^{168}Yb^{2+}	^{170}Er^{2+} ^{170}Yb^{2+}	^{172}Yb^{2+}	^{174}Yb^{2+} ^{174}Hf^{2+}	^{176}Yb^{2+} ^{176}Hf^{2+} ^{176}Lu^{2+}

A resolving power of ca. 1300 would be required to distinguish Sr masses from the doubly charged REE, and a corresponding resolving power of ca. 9200+ is required to distinguish Ca argides from Sr.

discrepancies in the measured ^{84}Sr/^{86}Sr ratio. The second largest combined dimer interference (∼10% of total) will be on mass 88 (^{40}Ca^{48}Ca^{+}, ^{44}Ca^{2+}, ^{42}Ca^{46}Ca^{+}), affecting ^{86}Sr/^{88}Sr and thus disrupting mass fractionation corrections. Most other Ca dimer interferences are relatively minor, except for the possibility of a small ^{40}Ca^{43}Ca^{+} dimer creating a signal at mass 83, resulting in incorrect isobaric interference corrections for Kr at mass 86 (Table 5). Furthermore, as the samples are carried and ionised in Ar, Ca argides (dominated by ^{40}Ar^{4*}Ca^{+}) will create similar interferences, particularly on mass 84 (^{40}Ar^{44}Ca^{+}).

To determine if Ca dimers and argides are the cause of the shift in Sr isotope ratios observed during LA-MC-ICPMS analyses, we analysed a series of aqueous mixtures of SRM987 and Ca (Sr/Ca = 0–50) (Fig. 7). Significant divergence is observed in the Sr isotopic composition of Sr/Ca mixtures compared to pure Sr standards (and aqueous solutions) run in the same analytical session. Values of ^{84}Sr/^{86}Sr (0.05650–0.05665) and ^{87}Sr/^{86}Sr (0.71014–0.71025) are generally higher and lower, respectively, than the accepted values and standard reproducibility (0.71025 ± 2 and 0.05648 ± 7 over the analytical session). Changes in ^{87}Sr/^{86}Sr may also reflect addition of unradiogenic Sr impurities from the Ca solution, however, this will have no effect on the stable ratios. Furthermore, the measured ^{86}Sr/^{88}Sr ratio for the Sr/Ca mixtures is generally distinctly higher than enclosing pure Sr standards, and will cause very different mass fractionation corrections, higher measured ^{86}Sr/^{88}Sr yielding lower fractionation corrected ^{87}Sr/^{86}Sr. Moreover, duplicate analyses of the same solutions often gave quite different values (outside of standard reproducibility), even when analysed in series, and these variations were often linked to large drifts in the amount of mass fractionation during the analysis. These variations are observed even at Ca/Sr ratios of 50 which is considerably lower

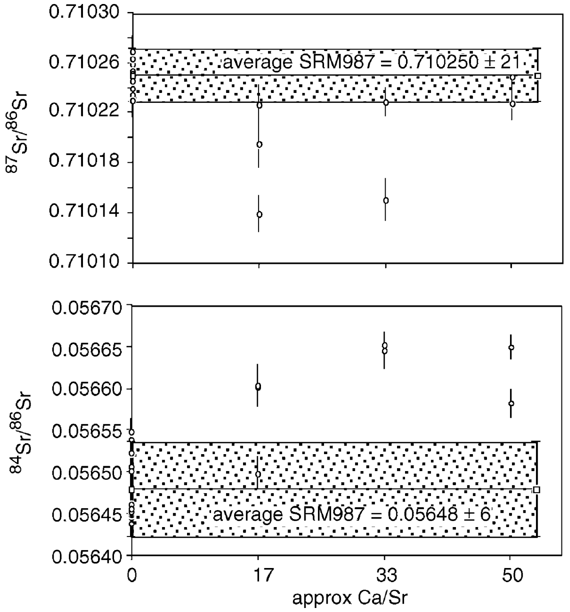

Fig. 7. Variations in measured ^{87}Sr/^{86}Sr, ^{84}Sr/^{86}Sr and ^{86}Sr/^{88}Sr ratios on a series of SRM987/Ca mixtures.

than those expected in feldspar (∼140) and carbonate (∼500).

In a further test of possible interference problems, we also analysed bulk dissolutions of the sphene and apatite used in LA-MC-ICPMS experiments (Table 4). Two separate bulk dissolutions of the sphene gave consistently higher $^{87}Sr/^{86}Sr$ than the separated Sr and LA-MC-ICPMS analyses, whereas apatite dissolutions were more similar to conventional and LA-MC-ICPMS analyses. In both cases, $^{84}Sr/^{86}Sr$ values are incorrect, but yield both higher and lower values than the accepted ratio.

These experiments (Fig. 7) clearly show that the presence of even relatively small (compared with most materials suitable for LA-MC-ICPMS studies) amounts of Ca cause significant shifts in all Sr isotope ratios. This likely reflects not only the presence of Ca argide and dimer interferences on mass 84, disrupting the $^{84}Sr/^{86}Sr$ ratio, but also interferences on mass 88 which result in incorrect mass fractionation corrections. However, the observed shifts in ratios in bulk sample dissolutions and LA-MC-ICPMS analyses are not always in the same direction as observed in the simplistic Ca/Sr experiment and illustrates that Ca dimers and argides are not the sole explanation for the discrepant stable and radiogenic Sr isotope ratios of these analyses.

Several other possible causes can be considered for inaccurate LA-MC-ICPMS Sr isotopic analyses. As shown for imperfectly separated whole rock samples, the presence of doubly charged REE interferences will also result in an additional suite of isobaric interferences that will be most problematic in REE-rich material such as sphene and apatite (Table 5). Other more complex molecules, such as $^{27}Al + ^{40}Ca$ oxides interfering on mass 83 and higher, and $^{56}Fe^{16}O_2$ interfering on ^{88}Sr may also be present, although these are likely to be negligible in most material suitable for LA studies. Another possibility is that the ‘wet’ plasma used during the Sr/Ca experiment may cause a different suite of interferences from the ‘dry’ plasma typical of LA-MC-ICPMS analysis, although we consider that the experiment represents a reasonable first order approximation.

It is now also becoming apparent that the variation in mass bias with mass is non-standard and not entirely accurately corrected for by the exponential mass fractionation law and magnified by the greater mass fractionation inherent in MC-ICPMS [25]. It is, therefore, possible that the very different plasma conditions created by aspirating purified Sr aqueous solutions (300 ppb dissolved solids) and Sr/Ca mixtures (up 50 ppm dissolved solids) and ablating bulk material may cause greater deviations in mass bias behaviour away from the exponential law. For Sr it is more difficult to correct for these effects empirically as can be done for Nd [25], as it is not possible to normalise to an isotope ratio that has an average mass identical to that of the ratio being measured and the $^{84}Sr/^{86}Sr$ ratio cannot be measured precisely enough to allow normalisation based on correlations between the different ratios. Variations in the condition of the plasma as it adjusts from baselines measured in 0.2% HNO_3 with 0 ppb dissolved solids to a solution with 50 ppm dissolved solids may explain in part the poor reproducibility of Sr/Ca mixtures even when analysed in sequence, and the drift in mass fractionation observed during the analysis. Such changes in plasma conditions would also be expected between the gas blank OPZ measured prior to ablation and the addition of large amounts of material during ablation.

4.3. Comparison with previous LA studies on different instruments

In situ Sr isotopic analyses have been carried out on a number of quite different MC-ICPMS instruments and as a final observation it is interesting to compare our observations with those of other workers. Davidson et al. [15] achieved reasonable agreement between LA and conventional MC-ICPMS $^{87}Sr/^{86}Sr$ ratio determinations of feldspar using a Micromass Isoprobe. This instrument differs significantly from the Axiom in having a hexapole collision cell designed to break down polyatomic species. Such instrumentation could potentially reduce the formation of Ca dimers and argides, although Davidson et al. [15] do not present $^{84}Sr/^{86}Sr$ data, making it difficult to assess whether isobaric interferences were present. Some fluctuations in $^{84}\text{Sr}/^{86}\text{Sr}$ were observed during data acquisition but no systematic offsets were noted (Davidson, personal communication, 2002). Using a similar instrument, Bizzarro et al. [26] carried out Sr isotopic analyses on carbonates and apatites and noted a correlation between $^{84}\text{Sr}/^{86}\text{Sr}$ (values up to 0.06) and $^{87}\text{Sr}/^{86}\text{Sr}$ for some carbonate samples. Considerable scatter is also evident in $^{84}\text{Sr}/^{86}\text{Sr}$ for most other samples and their reproducibility on this ratio (∼0.7%) is considerably worse than for conventional MC-ICPMS data, in contrast to their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting possible interference problems on mass 84. Ehrlich et al. [19] report good agreement between $^{87}\text{Sr}/^{86}\text{Sr}$ MC-ICPMS analyses of water and carbonates without chemical separation using an NU Plasma MC-ICPMS (no collision cell), and TIMS analyses of the same material. However, these authors report no stable ratio data to assess if Ca argide or dimer interferences were present. Although it is difficult to assess the relative performances of the different instruments given the lack of presented stable ratio data, it is possible that interferences caused by Ca dimers, Ca argides and doubly charged REE are reduced on instruments fitted with collision cells. Further work is required to determine if different MC-ICPMS instruments are more effective at determining reliable in situ Sr isotope ratios, however, we are at present unconvinced that accurate ratios can be determined using our double-focusing MC-ICPMS.

5. Conclusions

A technique has been developed that allows for analysis of Sr isotopic compositions in a range of materials by MC-ICPMS. Replicate analyses of unspiked standards and aqueous solutions indicate that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be reproduced to 0.003% (2 S.D.), comparable to reproducibilities typically given for TIMS analyses. Replicate isotope dilution analyses of rock powders show that Sr concentrations can be reproduced to <0.5% and that Rb/Sr ratios can be reproduced to ∼0.2% (2 S.D.) providing efficient separation of Rb and Sr is achieved. Reproducibilities of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in isotope dilution samples are considerably poorer than for unspiked samples. In most cases this is the direct consequence of imperfect correction for the isobaric interference of ^{87}Rb on ^{87}Sr. Given these complications, it may remain advantageous to analyse spiked Sr samples by TIMS where interfering Rb is effectively removed during low temperature ionisation, or to aliquot solutions following dissolution and prior to spiking.

LA-MC-ICPMS Sr isotope investigations carried out during this study reveal consistently incorrect $^{84}\text{Sr}/^{86}\text{Sr}$ ratios, which should not deviate from a natural ratio of 0.0565. Where $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have been checked by solution analysis, the two data sets are also consistently discrepant. Tests suggest that these results are in part a consequence of isobaric interferences from Ca dimers and argides as both Ca and Ar are present in large quantities in the material being ablated and the plasma, respectively. However, other results suggest that isobaric interferences from doubly charged REE and disruption of mass bias behaviour due to differential plasma loading may also play a role in producing inaccurate LA-MC-ICPMS Sr isotope analyses. We urge caution, by monitoring of stable ratios and cross-checking of LA-MC-ICPMS analyses with conventional MC-ICPMS or TIMS analyses, to ensure that in situ techniques are yielding accurate Sr isotope ratios.

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