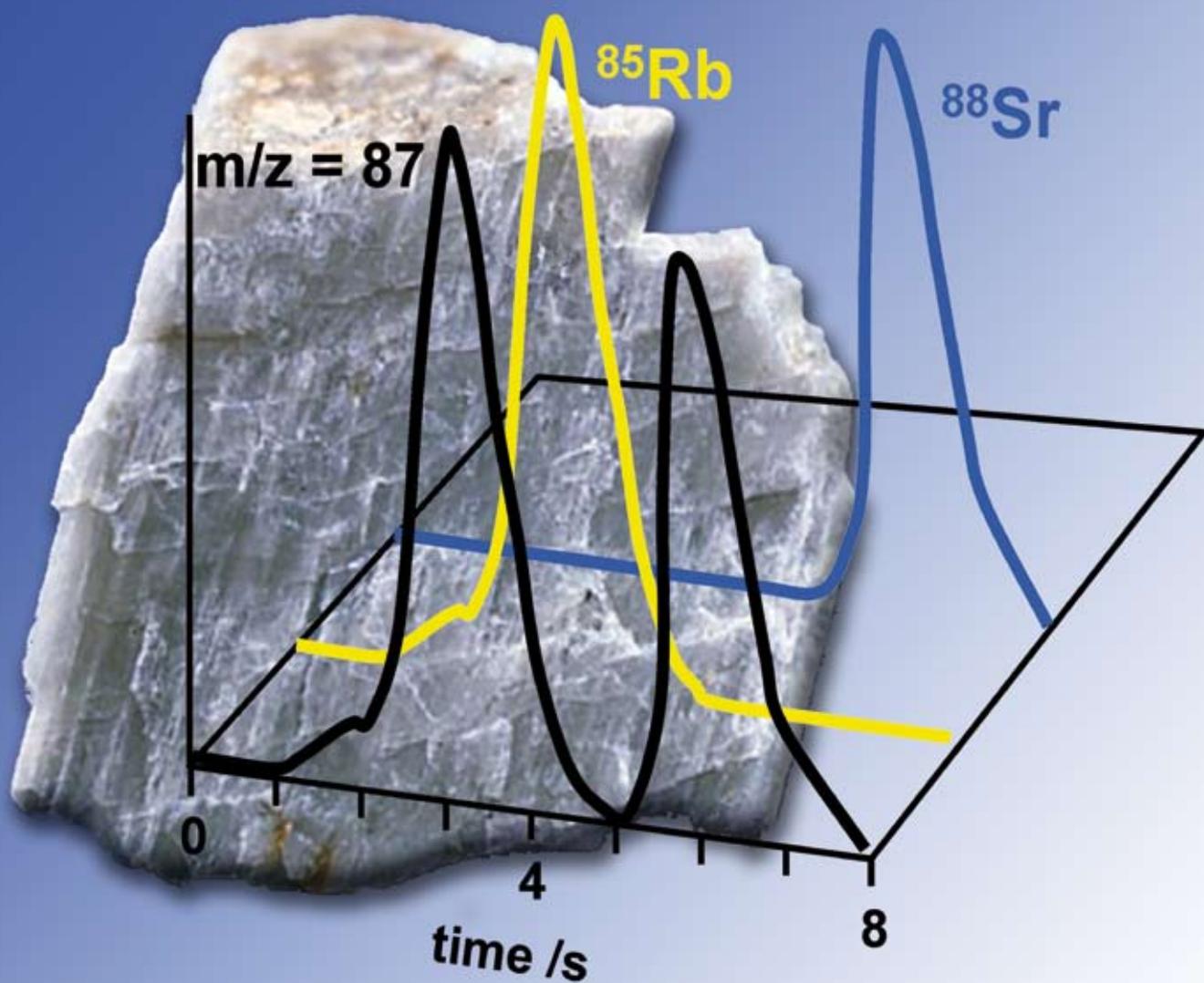


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Use of electrothermal vaporization for volatility-based separation of Rb–Sr isobars for determination of isotopic ratios by ICP-MS†

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A new method of separating Rb and Sr by ETV-ICP-MS is demonstrated. An electrothermal vaporizer (ETV) is used for sample introduction and control of the ETV heating cycle provides temporal separation of the isobars at m/z 87, allowing ^{87}Rb and ^{87}Sr determination within the same sample. The method utilizes an inductively coupled plasma mass spectrometer (ICP-MS) for ionization and detection. A one or two vaporization stage heating method is used for the ETV separation, and initial methodology and feasibility experiments were conducted on an ETV-ICP-TOFMS. Final measurements were made using a MC-ICP-MS for data collection. The method uses minimal sample preparation and no front end chromatographic separation of Rb and Sr prior to analysis. The technique is applied to the analysis of a potassium feldspar sample (NIST SRM 607) and is demonstrated to be viable as a means of determining isotopic data for the Rb–Sr geochronological technique. The standard was determined to have a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 1.1876 ± 0.011 , a Sr concentration of $64.1 \pm 4.7 \mu\text{g g}^{-1}$, and a Rb concentration of $557 \pm 6 \mu\text{g g}^{-1}$ (95% CI). This corresponds to a model age of 1266 ± 186 million years, statistically similar to the certified value of 1409 ± 14 for the standard. Error analysis is presented for several key calculations and a discussion is presented regarding approaches to improve precision.

Introduction

Isotope ratio measurements for the purpose of dating have traditionally employed thermal ionization mass spectrometry (TIMS), unless the elements of interest are convertible to a gas (*e.g.*, ^{40}Ar or ^{14}C dating).^{1,2} This frequently requires separation of the elements of interest to avoid alteration of the ionization efficiency as a result of surface contamination by the sample matrix. In some instances, separation is also required because isobars are present (*e.g.*, Sm–Nd or Rb–Sr dating). For Rb–Sr geochronology, both ^{87}Rb and ^{87}Sr must be determined. A resolving power of 286 000 is needed to spectrally isolate these two isobars, which is beyond the capabilities of most mass spectrometers.

A more recent trend in isotope ratio studies of geological samples is the use of inductively coupled plasma mass spectrometry (ICP-MS), which has been recently reviewed.³ Generally, multicollector (MC-ICP-MS) systems are preferred over other mass spectrometer designs (*e.g.*, single collector or quadrupoles), due to the improved precision of isotope ratio measurements.⁴ There has also been increasing interest in the potential of ICP time-of-flight mass spectrometers (ICP-TOFMS) as a means of measuring isotopic ratios. ICP-TOFMS systems can provide multimass detection of fast transient signals and retain a fixed duty cycle, regardless of the number of masses analyzed.⁵ The TOF design is ideal for

working with rapid transient peaks, while delivering good precision and sensitivity in isotopic ratio determinations, due to relative insensitivity to spectral skew and plasma flicker noise.^{6–8} The MC-ICP-MS provides significantly better precision on isotope ratios than an ICP-TOFMS, but the TOF is considerably less expensive and better suited to time resolved analysis of fast transients. Regardless, isobars remain a problem with both of these instruments.

Electrothermal vaporization (ETV) sample introduction into ICP-MS has the demonstrated ability to temporally (*viz.*, thermally) separate interfering isobars from each other, due to differences in volatility.^{9–12} In a recent paper, factors that contributed to improved temporal resolution using ETV were explored, and several examples of elemental isobaric separation were demonstrated.¹² An additional benefit of ETV, with respect to geological samples, is the ability to easily accommodate complex matrices that may perform poorly in nebulizers, such as those with high levels of dissolved salts and even hydrofluoric acid.¹³ It is also a micro-analytical technique, capable of working with microlitre sample volumes or even solid samples. This paper will examine the exploitation of the volatility differences for Rb and Sr for the determination of the $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios needed for Rb–Sr geochronology. The concept will be applied to a digested potassium feldspar sample.

It is well known that ^{87}Rb decays to ^{87}Sr , and that the age of a suite of cogenetic samples can be determined, assuming that there is a sufficient variance in their Rb/Sr ratios and the system has remain closed.^{1,14} This can be done based on a standard equation:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right) = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)(e^{\lambda t} - 1) \quad (1)$$

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where t is the age since formation and λ is the decay constant of the system ($1.42 \times 10^{-11} \text{ yr}^{-1}$).¹⁵ The ratios $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ and $\frac{^{87}\text{Rb}}{^{86}\text{Sr}}$ are the present day values, while $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0$ is the ratio at the time of formation. When a rock is formed (*e.g.*, by crystallization from a magma or recrystallization during metamorphism), the Rb or Sr concentrations of the constituent minerals are variable. Thus, by graphing $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$ vs. $\frac{^{87}\text{Rb}}{^{86}\text{Sr}}$ for minerals from a rock, or alternatively from a suite of cogenetic rocks assumed to have originated at the same time, the value of t (*i.e.*, age of the formation) can be determined from the slope of the resulting line (*i.e.*, isochron).

Previous methods have relied on ion exchange chromatography to separate the ^{87}Rb and ^{87}Sr isobars.¹ While effective, this approach can be time consuming, tedious, and presents opportunities for sample contamination. This study explores the feasibility of using the thermal ramp of an ETV to temporally separate the more volatile Rb from Sr, thereby minimizing sample preparation by eliminating the traditional chromatographic separation. The accuracy and precision of the approach will be evaluated on a digested potassium feldspar sample, and routes to improved precision will be explored with error propagation and Poisson statistics.

Experimental

Reagents

Distilled water was deionized on two mixed bed resin columns prior to use. All materials were stored in polyethylene or polypropylene screw capped bottles and vials that had been acid washed in 4 M HNO_3 for at least 24 h, prior to rinsing with deionized water. 1% HNO_3 was prepared from concentrated (70%) redistilled 99.999% pure HNO_3 (Aldrich). Concentrated (49%) trace metal grade HF was used in digestions (Fisher Scientific). Metal standard solutions were prepared from ICP grade standards (SCP Science). For modifier experiments, concentrated HCl (Fisher, trace metal grade) and a Pd standard (Acros) diluted in 1% HNO_3 were used. Ar was used as the carrier gas for the ETV and the plasma gas for the ICP-MS (Praxair or Airgas). NIST SRM 607, a potassium feldspar, was used for the measurement of Rb and Sr. For isotope dilution mass spectrometry (IDMS) studies, the ^{87}Rb spike was made from NIST SRM 984, while the ^{84}Sr spike was obtained from Oak Ridge National Laboratory. These spikes have been mixed and calibrated at The University of Texas at Austin.

Instrumentation

Initial development of the ETV-ICP-MS protocol (*e.g.*, heating programs, diagnostic data, *etc.*) employed a time-of-flight ICP-MS instrument (Optimass 8000; GBC Scientific; Hampshire, IL, USA), while the isotopic analysis of the feldspar was done on a multicollector system (MC-ICP-MS, IsoProbe, GV Instruments, Manchester). For the ICP-TOFMS, the ion optics were tuned prior to use with a nebulizer and a 100 ng mL^{-1} multi-element tuning solution (Ba, Be, Ce, Co, In, Mg, Pb, Tl, Th; Solutions Plus, Inc.). The same tuning solution at 1 ng mL^{-1} was used to optimize the response of the detector.

For optimal sensitivity with the dry plasma, the forward power was 700 W and the sample gas flow was 1.15 L min^{-1} . The MC-ICP-MS was tuned using a mixed Rb–Sr solution to set the Faraday cup positions and to tune the sensitivity. It was run at 1400 W with a sample gas flow of 1.0 L min^{-1} .

The ICP-MS was coupled to an ETV constructed from a modified graphite furnace atomizer and autosampler (GTA-95; Varian, Inc.), which has been described previously.¹⁶ The specifics of the materials, valve system, and triggering have also been previously described.¹⁷ Due to the ability of the plasma of the MC-ICP-MS to tolerate changes in gas flow rates related to ETV usage, the valve system was not utilized with this instrument.

For the ICP-TOFMS, data were acquired in the instrument's analog mode, generally using a 15 s data collection period accumulating 150 spectra and producing a time resolution of 100 ms. Data were first acquired in the Optimass software (version 1.2) and then exported to Microsoft[®] Excel for more detailed analysis. With the MC-ICP-MS, a blank was collected as a single cycle that was then subtracted from all sample data. The samples were collected as sets of 0.3 s cycles, in order to allow for the transients to be viewed after collection. Data was again exported to and analyzed in Microsoft[®] Excel. Analytical data are presented with 95% confidence intervals (CI).

ETV heating program

For some of the analyses, the ETV was operated with only one vaporization stage. 10 μL of sample was dosed into the furnace and the heating program shown in Table 1 was employed. In order to improve the temporal resolution of the peaks, the heating rate during the vaporization stage ($\sim 350 \text{ }^\circ\text{C s}^{-1}$) was significantly slower than the 1000–2000 $^\circ\text{C s}^{-1}$ rate typically employed with an ETV. Similarly, the 1 m length of transport tubing between the ETV and the ICP-TOFMS had a small diameter (1.7 mm i.d.) to minimize laminar flow broadening and improve resolution of the transient peaks.^{12,18}

In a second approach, the ETV was operated using two separate vaporization stages with two different final temperatures. The two-step vaporization heating program is also given in Table 1. A 10 μL aliquot was dosed into the ETV, and 1 m of more conventional 6 mm i.d. tubing was used for transport

Table 1 ETV heating program. Steps labeled with an asterisk (*) were not employed in the one step heating program. The ramp time for Vaporize 2 was 8 s in the one step method and 3 s in the two step method

Step	Temperature/ $^\circ\text{C}$	Ramp time/s	Hold time/s	Dosing hole closed
Dry	100	5	10	No
Char	300	20	20	No
Pause 1	50	3	15	Yes
Vaporize 1*	2000	3	5	Yes
Cool 1*	50	14	2	Yes
Pause*	50	0	2	No
Pause 2*	50	0	15	Yes
Vaporize 2	2800	8/3	5	Yes
Cool 2	50	14	0	Yes
Clean	2800	1.3	3	No
Cool	50	14	0	No

to the ICP-MS. The larger diameter gave a small, expected improvement in transport efficiency.¹²

SRM 607 analysis

A sample of potassium feldspar was obtained from the National Institute for Standards and Technology (NIST SRM 607, previously known as NBS 607). A 9.8 mg aliquot was digested using 1 mL of concentrated HF and 0.2 mL concentrated HNO₃ at 120 °C. This was then heated at 120 °C to dryness, and the residue was taken up in 1 mL of 1% HNO₃ and heated at 100 °C until all material dissolved. The solution was then diluted to 12 mL with 1% HNO₃ for analysis on the MC-ICP-MS. The concentration of ⁸⁸Sr yielded <10⁻¹⁰ amps, which was sufficient to avoid amplifier saturation in the detection circuit.

For determining the $\frac{87\text{Sr}}{86\text{Sr}}$ ratio, a 10 μL aliquot of the digested sample was dosed into the ETV and analyzed by the two-step vaporization method on the MC-ICP-MS. The original heating program was created with the ETV coupled to the ICP-TOFMS. As a similar ETV system was used with the MC-ICP-MS, fine tuning of the method caused the nominal setting of the first vaporization stage temperature to be changed to 2100 °C and the hold time after the first ramp was slightly longer (8 s). Analysis was performed for five replicates. Since the information on the first, low volatility peak was not needed for this measurement, the Ar flowing through the ETV during the first heating stage was vented and not introduced to the ICP. The ratio of $\frac{88\text{Sr}}{86\text{Sr}}$ was used to correct for mass bias by a standard exponential law,¹⁹ and the ⁸⁵Rb signal was used with the mass fractionated ratio of $\frac{87\text{Rb}}{85\text{Rb}}$ to correct for the ⁸⁷Rb isobaric interference on ⁸⁷Sr.

Analysis of the $\frac{87\text{Rb}}{86\text{Sr}}$ ratio was carried out using isotope dilution mass spectrometry. The digested sample was spiked with a mix of Sr (enriched to contain 97% ⁸⁴Sr) and Rb (enriched to contain 99% ⁸⁷Rb). The spike had been previously analyzed and calibrated with the MC-ICP-MS and was designed for solutions containing more Rb than Sr. The Rb determination was carried out after diluting the sample 1 : 20, to prevent saturation of the amplifiers of the Faraday cups measuring Rb. A 50 ng mL⁻¹ solution of natural abundance Rb was run in order to provide a Rb mass bias factor by external bracketing. Five replicates were obtained using 10 μL aliquots of the solutions.

The method blank was analyzed for both Rb and Sr contamination using IDMS and sample nebulization with previously calibrated spikes designed for blank analysis. Analysis of the method blank suggested a significant level of contamination. This was corrected by assuming the standard $\frac{87\text{Sr}}{86\text{Sr}}$ ratio of 0.71.

Results and discussion

One-step vaporization stage method

As described previously by Ertas and Holcombe,¹² temporal resolution of species vaporized in an ETV with different volatilities can be improved with slower heating rates. Fig. 1 shows that by using a 100 ng mL⁻¹ mixed solution of Rb and Sr, a clear separation of Rb and Sr can be achieved with an

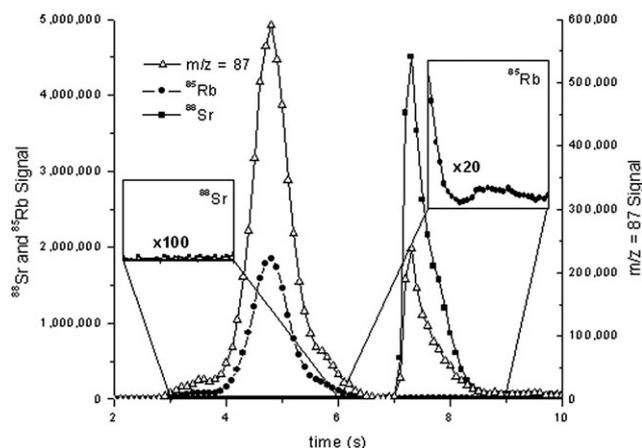


Fig. 1 ETV transient signals from the one-step vaporization method, collected by ICP-TOFMS with 100 ms time resolution. Over the course of the 8 s ramp, the more volatile Rb is vaporized before the more refractory Sr. ⁸⁵Rb and ⁸⁸Sr have no interferences, but the signal at m/z 87 is a combination of ⁸⁷Rb in the first peak and mostly ⁸⁷Sr in the second peak. Expanded scales of ⁸⁵Rb and ⁸⁸Sr are also shown.

ETV heating rate of ~ 350 °C s⁻¹. ⁸⁵Rb and ⁸⁸Sr were monitored since they have no isobaric interferences with other Sr or Rb isotopes. The signal at m/z = 87 was also monitored since it is the isobaric interference of interest. As can be seen, there is baseline separation for the two peaks.

However, Fig. 1 also shows that a small amount of Rb vaporizes late in time and nearly coincident with Sr. Variations in ramp rates or charring temperatures failed to remove this second Rb peak, and the size of the second peak increased with the Rb concentration in the sample. Since this later peak was still observed even in the absence of the Sr, it is probable that interaction with the ETV furnace, rather than occlusion in Sr crystals may be the source of the delayed vaporization.²⁰

There is a large body of literature for electrothermal atomization atomic absorption spectrophotometry (ETAAS) that is frequently useful in selecting a chemical modifier to better separate two different elements. However, in this instance there is little information on modifiers that might be useful in delaying the Sr peak or increasing the volatility of the Rb. Chemical modifiers of Cl (*via* HCl), F (*via* HF), and PdNO₃ (all with thermal pretreatments at 300 and 800 °C) were used in an attempt to further enhance the separation, but no significant improvement in the separation was observed.

Two-step vaporization method

Having determined that reasonably good thermal separation of the Rb and Sr was possible, a method based on using two separate ETV vaporization stages was explored using the ICP-TOFMS. If successful, this would permit separate data collection triggering of the ICP-MS data collection software. This method takes advantage of the integration capabilities of the ICP-TOFMS software to get a direct readout of the peak areas of Rb and Sr signals without exporting the data to a spreadsheet.

The first vaporization step of the method uses a nominal temperature of 2000 °C. It was found that this temperature was high enough to vaporize only the Rb portion of the

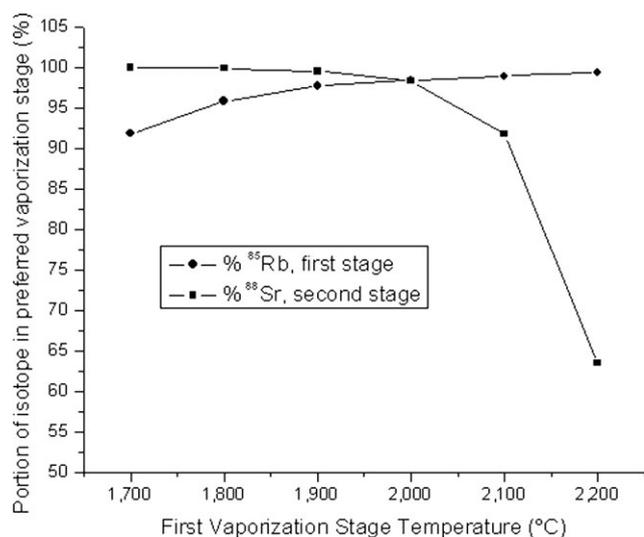


Fig. 2 Results from first vaporization stage temperature variation studies on 100 ng mL⁻¹ Rb and Sr solution using the two-step vaporization method. For ⁸⁵Rb, the portion plotted refers to the fraction of the signal obtained in the first vaporization relative to the total amount observed when the two vaporizations were summed. The quantity shown is similar for ⁸⁸Sr, but refers to the portion in the second vaporization stage.

sample. After vaporizing the Rb, the heating program cooled the furnace, the ICP-TOFMS software was reset for a second data collection, and the ETV was heated a second time to a higher temperature (2800 °C) to vaporize the Sr. The cool down between vaporization stages was used to promote more uniform longitudinal heating of the ETV tube²¹ to insure complete Sr vaporization in the second heating if some Sr movement toward the cooler ends of the furnace occurred during the first vaporization stage. The cooling cycle also provided the time needed for the resetting of the instrument for a second data collection, without leaving the furnace at a high temperature for an extended period of time. Although time-resolved spectra were collected at each vaporization step, time resolved data is not necessary to obtain peak areas and isotopic data.

Various vaporization temperatures were investigated for the first vaporization stage using a 100 ng mL⁻¹ solution of admixed Rb and Sr. The results were analyzed based on the total integrated areas of the ⁸⁵Rb and ⁸⁸Sr signals (neither of which has isobaric interferences) in both vaporization stages as shown in Fig. 2. It can be seen that >98% of the Rb was observed in the first vaporization step and >98% of the Sr was seen in the second vaporization step, when the first vaporization stage was set to a nominal vaporization temperature of 2000 °C. Variations by as much as ±100 °C in the first vaporization step produced similar separation quality.

This separation method was tested with various relative concentrations of Rb and Sr. With the Sr fixed at 100 ng mL⁻¹, the Rb was mixed at 50, 100, 200, 500, and 1000 ng mL⁻¹. In all cases, >98% of the Rb was removed in the first vaporization stage while the behavior of the Sr was unaffected.

It should be emphasized that 2000 °C was the nominal temperature setting on the GTA-95 ETV system. Previous work suggests that this furnace used as an ETV may be about 200 °C lower than that set point.²² This is to be expected because of the added heat sink imposed by the dosing hole plug and possible heat loss to the Ar gas flowing through the tube.

SRM 607 analysis

Potassium feldspar (SRM 607) was obtained and analyzed (Table 2). Potassium feldspars are popular for Rb–Sr dating, since they frequently have a much higher concentration of Rb than Sr. This results in relatively large changes in the ⁸⁷Sr/⁸⁶Sr ratio over time, which helps define more precise ages for geochronological studies. However, the large Rb to Sr ratio can challenge some analyses, since the large amount of Rb must be separated from the Sr to avoid excessive isobaric interference.

The ratio of ⁸⁷Sr/⁸⁶Sr was determined using the two step vaporization method. In the absence of any separation, the molar ratio of ⁸⁵Rb/⁸⁶Sr in this SRM is 63. With the 2-step heating, this ratio under the second peak was observed as an average 0.14, suggesting that ~99.8% of the Rb was removed in the first heating cycle.

Over five replicates, the average value for the ⁸⁷Sr/⁸⁶Sr ratio was determined as 1.188 ± 0.011, which is about 1% lower than the certified value of 1.2004 ± 0.0002 but nearly within the limits of measurement precision.

There appears to be a systematic error in the determination, but a cause of the inaccuracy has not been determined. The challenge may lie in the ratio of Rb isotopes used in the isobar correction. For this analysis, it was assumed that the mass bias in the ratio of ⁸⁷Rb/⁸⁵Rb was the same as the ⁸⁸Sr/⁸⁶Sr ratio. While a good first approximation, this may not be entirely correct. The vaporization of the Rb in the first heating stage could be expected to produce an isotopic fraction, the same as is observed when vaporizing materials off of a TIMS filament. This would lead one to generally conclude that the small amount of remaining Rb (observed in the second vaporization stage) would be enriched in the heavy component, since the lighter isotope would preferentially vaporize during the first vaporization stage. However, analysis of a transient peak produced on the MC-ICP-MS of a 50 ng mL⁻¹ solution of Rb with a natural abundance indicates otherwise, as shown in Fig. 3. The plot of the ⁸⁷Rb/⁸⁵Rb ratio decreases over the life of the transient, suggesting that the heavy isotope is being vaporized preferentially earlier in time. This would tend to indicate that

Table 2 Results from analysis of the feldspar sample (NIST SRM 607) with 95% CI

	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Rb/ ⁸⁶ Sr	Age/Ma
Standard value from NIST	1.2004 ± 0.0002	24.3 ± 0.2	1409 ± 14
Value from ETV-MC-ICP-MS	1.1876 ± 0.0041	25.7 ± 1.9	1266 ± 186
RSD of ETV-MC-ICP-MS	0.34%	2.6%	5%
Statistical limit for ETV-MC-ICP-MS (as RSD)	0.023%		

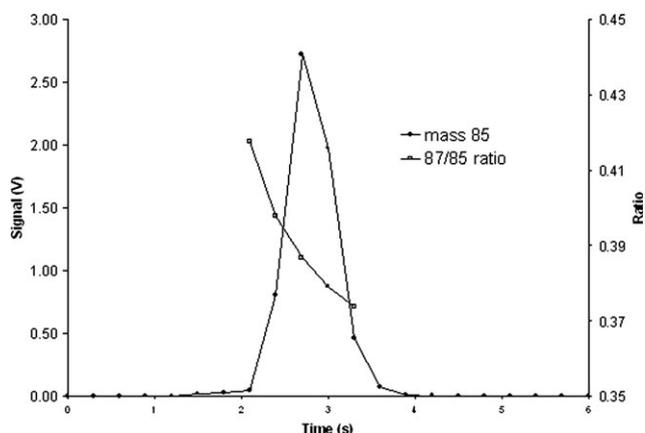


Fig. 3 Transient signals from the MC-ICP-MS for the first heating stage (in a two stage method) for a 50 ng mL⁻¹ solution of Rb. The second axis plots the observed ratio of ⁸⁷Rb/⁸⁵Rb, corrected with the exponential mass bias law, based on the mass bias of the integrated area of the Rb signal. This serves to leave only thermal fractionation effects in the data, removing the effects of plasma mass bias. It is useful to note that the ratio has a true value of 0.385.

the Rb observed during the second vaporization cycle would be enriched in the lighter component. This counter intuitive result is challenging to explain, and merits further exploration. However, with the current ETV approach, the very small amount of Rb remaining in the ETV at the start of the second vaporization stage leaves very little material to analyze to obtain an isotope ratio. At any rate, if it is the case that the ⁸⁷Rb/⁸⁵Rb ratio used was too large, that could reasonably explain the systematic bias observed.

The ⁸⁷Rb/⁸⁶Sr ratio was analyzed by IDMS. The concentration of Rb in the sample was determined to be 557 ± 6 μg g⁻¹, which is about 6% higher than the NIST value of 524 ± 1 μg g⁻¹. There is no statistically significant difference between the determined concentration for Sr of 64.1 ± 4.7 μg g⁻¹ and the NIST value of 65.5 ± 0.3 μg g⁻¹, owing in part to the precision of the determined concentrations. This analysis also gave an ⁸⁷Rb/⁸⁶Sr ratio of 26.4 ± 1.9, which is about 9% higher than the NIST value of 24.3 ± 0.2. However, the ~10 mg used in this study was well below the 100 mg minimum amount recommended by NIST. This may account for some (but likely not all) of the apparent differences in the results for ⁸⁷Rb/⁸⁶Sr, as well as concentrations of Rb and Sr, since previous studies have indicated that inhomogeneity in this material may have a geologic basis.²³ However, this small amount was used to demonstrate the ease with which ETV can deal with extremely small sample sizes, including the possibility of single microscopic mineral particles.

Table 3 Variables used in statistical analysis

Term	Description	Value
I_{85Rb}	Intensity of mass 85 (Rb only), as a number of ions	4 731 895
I_{86Sr}	Intensity of mass 86 (Sr only), as a number of ions	36 464 408
I_{87}	Intensity of mass 87 (containing Rb and Sr), as a number of ions	46 283 339
I_{88}	Intensity of mass 88 (Sr only), as a number of ions	326 221 496
R	Value of the observed isotope ratio for ⁸⁷ Sr/ ⁸⁶ Sr	1.1876
R_{Rb}	Applied value of the Rb isotope ratio, 87/85	0.412

Finally, these determined ratios can be used as an indicator of the age of the material analyzed. Although this generally requires multiple samples to define an isochron, a “model age” can be calculated using a typical intercept value of 0.71 for $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0$ in eqn (1). If this is done, the sample predicts an age of 1266 ± 186 million years. While the age appears to be 10% lower than the NIST value of 1409 ± 14 million years, the two values are not statistically different (95% CI). It should be noted that the inaccuracies associated with both of the experimentally determined isotopic ratios contribute to an underestimation of the age of the feldspar. Depending on the application, this level of precision may or may not be justified by the savings in analysis time.

Statistical limits on precision

The voltage output from the MC-ICP-MS can be converted to the number of ions detected, based on the current-to-voltage amplification. Assuming Poisson statistics limit the possible precision, it is then possible to use standard error propagation techniques to model the effect of variables on the precision that could be obtained. This is described fully in the ESI†.

Table 3 details the variables used in the subsequent discussion. In brief, the relative standard deviation of the observed ⁸⁷Sr/⁸⁶Sr ratio (denoted as R) is predicted to be

$$\frac{\sigma_R}{R} = \frac{\sqrt{I_{87} + I_{85Rb}^2 \sigma_{R_{Rb}}^2 + R_{Rb}^2 I_{85Rb} + \frac{(I_{87} - R_{Rb} I_{85Rb})^2}{I_{86Sr}}}}{I_{86Sr} R} \quad (2)$$

Amounts of ions produced by the sample are also shown in Table 3. The small contribution to error from the uncertainty in the applied Rb isotope ratio can also be calculated, as described in the ESI†. Utilizing these values predicts a statistically limited RSD of 0.023% for the ⁸⁷Sr/⁸⁶Sr isotope ratio, which is about an order of magnitude different from the observed precision of 0.34% RSD. The reason for difference is not known. Still, based on eqn (2) (derived in the ESI†) there are some interesting suggestions on parameters that could be important in improving precision with the present system.

It is interesting to note that if all the detected signals that were used in eqn (2) were increased by a factor n , the error would be reduced by approximately \sqrt{n} . More concentrated sample solutions or pre-concentration in the ETV would be two ways of realizing this improvement. However, a more concentrated sample was avoided in this analysis in order to ensure that no transient analyte signals saturated the amplifiers of the Faraday cups. Slightly larger amounts of material could be used successfully by creating a longer transient, which might be achieved through lowered heating rates or simple

attachments, like a transient extension flask²⁴ or single bead string reactor.²⁵

Eqn (2) also addresses the impact of the Rb signal present during the Sr determination in the second ETV vaporization peak. For example, 100% Rb removal would produce a theoretical limit of about 0.0227% RSD, which is a negligible improvement compared to 0.023% predicted with the separation actually achieved in the method addressed in this paper. At the other extreme, having no separation (*e.g.*, nebulizer introduction) and simply using correction equations degrades precision by more than an order of magnitude, *i.e.*, an RSD of $\sim 0.4\%$ for $\frac{87\text{Sr}}{86\text{Sr}}$. Leaving more than 7% of the Rb behind in the second vaporization step would make the Rb correction the dominant factor in the error budget, assuming all other factors remain constant. In short, the separation is adequate and precision improvements are best addressed by enhancing the signal magnitude.

Finally, it is of interest to consider the number of ions observed in the analyses as compared to the number of atoms put into the ETV furnace based on the certified concentrations. This calculation shows that from the furnace to the detector, the system had an efficiency of around 90 ppm, or observing about 1 in every 10 000 atoms provided to the system. This is partially attributable to using the MC system in a lower resolution mode with a large slit width.

Conclusions

Using the thermal program of an ETV to achieve Rb–Sr separation is considerably faster than the traditional pre-analysis separation by ion exchange chromatography. Currently there is systematic bias present in the procedure that produces an estimated age that is $\sim 10\%$ too small. The source of this error is not known at this time. While the isotopic precision of 0.3% RSD is encouraging, it still remains significantly larger than the theoretical limit based on quantum noise.

As is commonly true, whether the analytical speed justifies the loss in precision becomes a matter of the question being addressed by the results from the analysis. Even with the current precision, it is possible that the analytical throughput may allow the approach to serve as a useful screening tool for isolating a subset of samples for more precise measurements. This method also allows for the analysis of very small quantities of material, with future possibilities for the analysis of single microscopic crystals. It is also obvious that this method

suggests the feasibility of using this approach for other isotopic ratio measurements where throughput, isobaric separations, and/or small samples are the primary analytical concerns.

Acknowledgements

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