

Short communication

# Reassessment of the NBS SRM-607 K-feldspar as a high precision Rb/Sr and Sr isotope reference

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## Abstract

We report high precision Rb/Sr and Sr isotope analyses for the NBS SRM-607 standard feldspar, which is widely used as a reference material for Rb–Sr ratios as well as Sr isotope compositions. The Rb–Sr ratios of different aliquots of the standard were obtained by isotope dilution using MC-ICPMS for Rb isotope analyses with admixed Zr for mass bias correction and TIMS for Sr isotope measurements. Different ~ 10 mg sample aliquots show variations in Rb/Sr ( $\pm 0.74\%$ ) and Sr isotopes ( $\pm 0.33\%$ ) that are outside the certified values and far outside analytical uncertainties. Age related correlation of Rb/Sr with Sr isotope composition indicates that sample heterogeneity is a major reason for large inter-laboratory differences reported for this standard. Nevertheless, the standard can be used as a high precision reference for Rb–Sr calibration, if Rb/Sr and Sr isotope composition are referenced to a Rb–Sr model isochron. In this case the uncertainty on the Rb/Sr of the standard is  $\pm 0.24\%$ .

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## 1. Introduction

With the introduction of multi-collector mass spectrometers that are equipped with an inductively coupled plasma source (MC-ICPMS), analytical precisions of isotope ratio determinations of many elements were improved significantly (Halliday et al., 1995; Rehkämper et al., 2001). The plasma source provides a higher ionization potential compared to conventional thermal ionization mass spectrometry (TIMS), which enables the analysis of small amounts of sample material even for elements with high ionization potentials (e.g., Hf, Rehkämper et al., 2001). Even though the simultaneous ionization of all elements in the plasma generates

isobaric interferences of different elements and therefore lead to instrumental pitfalls of isotope ratio determinations, as e.g., for Sr isotopes (e.g., Ramos et al., 2004), it allows for precise isotope measurements of elements with only two isotopes using the method of external normalization. The latter technique can be applied to such elements with only two isotopes, where the instrumental mass bias in MC-ICPMS can be corrected by monitoring an element in a neighbouring mass range with a known isotopic composition (Maréchal et al., 1999). Although, the assumption that two elements show identical mass bias effects is not necessarily absolutely correct (Albarède et al., 2004), this technique achieves an external reproducibility of  $\pm 0.1\%$  of the desired isotope ratio for most elements (e.g., Ag for Cd, Wombacher et al., 2003, or Zn for Cu isotope measurements Maréchal et al., 1999). Such a reproducibility of isotope ratios is needed for isotope dilution analyses

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in order to obtain satisfactory age resolutions (e.g., isochron ages).

For Rb–Sr analyses, the inability to control fractionation effects during TIMS measurements limits the precision of Rb concentration determinations by isotope dilution and, as a consequence, Rb/Sr in natural materials can only be determined with uncertainties that are typically  $\sim \pm 1\%$  (e.g., [Waight et al., 2002](#)). Hence, the quality of this widely used dating tool is limited by the precision obtainable for Rb/Sr and can yield ages that are not much better than  $\pm 1\%$ . This is in stark contrast to other chronometers, such as U–Pb, Lu–Hf and Sm–Nd systems, where parent–daughter elemental ratios can potentially be reproduced to  $\pm 0.1\%$ . Using Zr for mass bias correction during MC-ICPMS measurement of  $^{87}\text{Rb}/^{85}\text{Rb}$  has proven suitable for Rb isotope analyses and provides a reproducibility of  $\pm 0.02\%$  (2 s.d.) for unspiked Rb isotope compositions ([Waight et al., 2002](#); [Nebel et al., 2005](#)). Isotope dilution analyses of Rb/Sr, which are the limiting factor for age determinations with the Rb–Sr isotope system, are an order of magnitude worse than Rb isotope ratios and are potentially precise to  $\pm 0.2\%$  (2 s.d.) for Rb/Sr using isotope dilution ([Waight et al., 2002](#); [Willigers et al., 2004](#)), as deduced by replicate analyses of whole rock samples. Accordingly, using the same technique of Rb analyses by MC-ICPMS, [Willigers et al. \(2004\)](#) reported corresponding Rb–Sr ages with an uncertainty of  $< 0.3\%$  (2 s.d.). This technique therefore potentially enables Rb–Sr age determinations to be as precise as e.g., U–Pb and Lu–Hf ages. The improved uncertainty of Rb–Sr ratios, compared to Rb or Sr isotope ratio analyses, results from the combined uncertainties of the individual Rb and Sr isotope measurements, which might be affected by isobaric interferences during mass spectrometric runs (e.g., [Waight et al., 2002](#); [Ramos et al., 2004](#)). Sample heterogeneity or possible uncertainties from data reduction (e.g., from spike subtraction) may also have an effect on Rb/Sr. The achieved uncertainty of  $< 0.3\%$  for Rb–Sr age determinations, however, is a significant improvement over previous techniques.

Another potential source of error in accurate age determinations results from inadequate spike calibration, which results mostly from the difficulty in producing accurate standard solutions for Rb. Metal cannot be used as a standard because of its enormous exothermal reaction when exposed to air. Conventionally, Rb salts (i.e., carbonate or chloride) are used, but they are extremely hygroscopic, which makes it difficult to determine their exact weight. Other Rb salts as e.g., sulphates are less suitable as these may not be stoichiometric, i.e. these occur to some extent as sulphites. Hence, isotope enriched tracers that are calibrated

against standard solutions made from Rb salts should ideally be cross calibrated against a reference, preferably an international standard. However, at present, there are only limited Rb–Sr reference materials available that can be used for inter-laboratory comparisons and non taking advantage of the precision possible using these new MC-ICPMS techniques. Presently, the accepted standard reference material for Rb/Sr and subsequently Sr isotope compositions is a powdered potassium feldspar (NBS SRM-607). The NBS SRM-607 has a certified Sr isotope composition of  $1.2004 \pm 0.0002$  ( $\pm 0.02\%$ ) and a Rb/Sr weighted mean of  $8.000 \pm 0.042$  ( $\pm 0.53\%$ ) as calculated from Rb and Sr concentrations. Both values are outside the analytical uncertainty when compared to the potentials of combined Rb isotope analyses using MC-ICPMS and Sr isotope analyses using TIMS.

## 2. Standard K-feldspar NBS SRM-607

The standard K-feldspar NBS SRM-607 originates from the Kingman Feldspar mine in Arizona, USA, and was first described by [Heinrich \(1960\)](#). The standard material comes from one feldspar crystal (powdered to 200–325 mesh, corresponding to roughly 45–75  $\mu\text{m}$ ) and was initially distributed under the label NBS SRM-70a. The material has since been widely used as a standard for major and minor elements in K-feldspars. [Compston et al. \(1969\)](#) introduced the feldspar as a potential reference material for Rb–Sr geochronology and the NBS SRM-70a can now be purchased as NBS SRM-607 from the National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards, NBS, USA) with certified concentrations of Rb, Sr and Sr isotopic composition (see [Table 1](#)). The corresponding certified variation in the  $^{87}\text{Rb}/^{86}\text{Sr}$  is  $\pm 1.36\%$ , or  $\pm 0.53\%$  as the weighted mean on Rb/Sr calculated from Rb and Sr concentrations. Although this uncertainty in Rb/Sr roughly matches the requirements of the conventional Rb–Sr dating technique using TIMS, it does not meet the current needs of the MC-ICPMS method, especially with respect to low sample amounts, i.e.,  $\sim 10$  mg. Additionally, several authors reported Rb and Sr concentrations and Rb/Sr for this standard that vary outside the conventional analytical uncertainty for TIMS analyses (i.e.,  $> 1\%$ ). This was attributed to inter-laboratory deviation due to different spike calibrations ([DeLaeter and Abercrom, 1970](#)), sample inhomogeneity or blank contribution ([Pankhurst and O’Nions, 1973](#)). More recent analyses of the standard ([Amelin and Zaitsev, 2002](#); [Waight et al., 2002](#)) even suggest variations in the Sr isotope composition of  $> 0.5\%$ .

Table 1

| Sample/comments                    | $^{87}\text{Rb}/^{86}\text{Sr}$ | $\pm 2$ s.d. | $^{87}\text{Sr}/^{86}\text{Sr}$ | $\pm 2$ s.e. | Model age <sup>a</sup> in Ma  |
|------------------------------------|---------------------------------|--------------|---------------------------------|--------------|-------------------------------|
| <i>Data from MC-ICPMS analyses</i> |                                 |              |                                 |              |                               |
| This study                         |                                 |              |                                 |              | 1418.8 $\pm$ 7.8              |
| SRM-607-A                          | 23.99                           | 0.05         | 1.19798                         | 0.00028      |                               |
| SRM-607-B                          | 24.18                           | 0.05         | 1.20138                         | 0.00011      |                               |
| SRM-607-C                          | 24.22                           | 0.05         | 1.20145                         | 0.00003      |                               |
| SRM-607-D                          | 24.20                           | 0.05         | 1.20270                         | 0.00014      |                               |
| SRM-607-E                          | 24.15                           | 0.05         | 1.20029                         | 0.00002      |                               |
| SRM-607-F                          | 24.09                           | 0.05         | 1.20202                         | 0.00024      |                               |
| SRM-607-G                          | 24.06                           | 0.05         | 1.20046                         | 0.00010      |                               |
| SRM-607-H                          | 24.29                           | 0.05         | 1.20536                         | 0.00004      |                               |
| SRM-607-I <sup>b</sup>             | 24.08                           | 0.05         | 1.20062                         | 0.00002      |                               |
| SRM-607-J <sup>b</sup>             | 24.18                           | 0.05         | 1.20149                         | 0.00002      |                               |
| Waight et al.                      |                                 |              |                                 |              | 1412 $\pm$ 30                 |
|                                    | 24.34                           | 0.05         | 1.20032                         | 0.00004      | 1415.2 $\pm$ 1.9 <sup>c</sup> |
|                                    | 24.24                           | 0.05         | 1.20219                         | 0.00004      |                               |
|                                    | 24.27                           | 0.05         | 1.20263                         | 0.00004      |                               |
| <i>Data from TIMS analyses</i>     |                                 |              |                                 |              |                               |
| Amelin and Zaitsev                 |                                 |              |                                 |              | 1410.3 $\pm$ 5.4              |
|                                    | 24.30                           | 0.23         | 1.20125                         | 0.00001      |                               |
|                                    | 24.19                           | 0.30         | 1.20249                         | 0.00001      |                               |
|                                    | 24.47                           | 0.14         | 1.20342                         | 0.00001      |                               |
|                                    | 24.14                           | 0.19         | 1.20016                         | 0.00001      |                               |
| Foland and Allen                   |                                 |              |                                 |              | 1419 $\pm$ 5.7                |
|                                    | 23.98                           | 0.20         | 1.20053                         | 0.00001      |                               |
|                                    | 24.21                           | 0.20         | 1.20109                         | 0.00001      |                               |
|                                    | 24.13                           | 0.20         | 1.20116                         | 0.00001      |                               |
|                                    | 24.17                           | 0.20         | 1.20119                         | 0.00002      |                               |
| Patchett and Ruiz                  |                                 |              |                                 |              | 1415 $\pm$ 14                 |
|                                    | 24.20                           | 0.24         | 1.20112                         | 0.00002      |                               |
| Lambert et al.                     |                                 |              |                                 |              | 1422 $\pm$ 14                 |
|                                    | 24.04                           | 0.24         | 1.20039                         | 0.00026      |                               |
| Pankhurst and O'Nions              |                                 |              |                                 |              | 1388 $\pm$ 14                 |
|                                    | 24.56                           | 0.25         | 1.19890                         | 0.00040      |                               |
| NIST certified value               |                                 |              |                                 |              | 1409 $\pm$ 14 <sup>d</sup>    |
|                                    | 24.26                           | 0.24         | 1.20039                         | 0.00020      |                               |

Errors on Sr isotope compositions are within-run statistics, errors on Rb/Sr are  $\pm 0.2\%$  external errors; a) calculated using  $y=0.02035x+0.71$  and  $1.42 \times 10^{-11}/a$  for  $\lambda^{87}\text{Rb}$ ; b) aliquots analyzed with Rb–Sr-16 spike; which was calibrated by TIMS analyses only c) excluding one outlier; d) assumed error on the  $^{87}\text{Rb}/^{86}\text{Sr}=1\%$ .

Taking the possible analytical reproducibility of  $\pm 0.004\%$  (2 s.d.) for  $^{87}\text{Sr}/^{86}\text{Sr}$  (Waight et al., 2002, this study) with modern TIMS, an inter-laboratory difference in measured Sr isotope compositions of NBS SRM-607 orders of magnitudes larger than the potential reproducibility of  $^{87}\text{Sr}/^{86}\text{Sr}$  (e.g., for the NBS SRM-987 standard) strongly limiting the use of this standard as a reference material. Furthermore, the immense inter-laboratory spread in reported Rb/Sr requires a detailed study of the standard reference material. Therefore, before its use can become more widespread, especially with respect to the Rb-MC-ICPMS technique, a study of NBS SRM-607 is essential, because this feldspar is the most widely distributed standard material for the calibration and inter-laboratory comparison of the Rb–Sr system. To

improve its potential use, different 10 mg batches of NBS SRM-607 were analyzed to constrain the  $^{87}\text{Sr}/^{86}\text{Sr}$  and the Rb–Sr ratio precisely.

### 3. Analytical procedures

#### 3.1. Mass spectrometry

Strontium isotopes were determined with a TIMS (Finnigan Triton), by loading the separated sample Sr in 6 M HCl on W single filaments embedded between TaF<sub>5</sub> (Birck, 1986). All measurements were made in static mode with rotating amplifiers to negate relative cup efficiencies. Runs of the NBS-987 standard from each session were normalized to a  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.710243 to

correct for the instrumental drift between analytical sessions and cup biases. The observed difference in day-to-day instrumental drifts was between  $\sim 10$  and 40 ppm. Mass fractionation during TIMS analyses was corrected using a  $^{86}\text{Sr}/^{88}\text{Sr}$  of 0.1194. The mean  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{84}\text{Sr}/^{86}\text{Sr}$  obtained from 20 replicate analyses for the NBS-987 during the course of this study were  $0.710248 \pm 28$  and  $0.056487 \pm 14$  (both 2 s.d.). This corresponds to a reproducibility from different analytical sessions of  $\pm 0.004\%$  for the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\pm 0.03\%$  for the  $^{84}\text{Sr}/^{86}\text{Sr}$  (both 2 s.d.). Rubidium measurements were performed on a MC-ICPMS (Micromass *IsoProbe*). Natural Zr ALPHA AESAR standard solution was used to correct for mass bias effects. Instrumental parameters, Zr isotope ratios and running conditions are described in detail elsewhere (Nebel et al., 2005). Differing to the method of Nebel et al. (2005), weak HF (0.12 M) is added to standard and sample solutions so that Zr washouts are improved, which results in short washout times with no detectable Zr backgrounds after about 1/2 min. Rubidium isotope ratios are all reported relative to a  $^{87}\text{Rb}/^{85}\text{Rb}$  of 0.3857 (Catanzaro et al., 1969; Bohlke et al., 2005).

### 3.2. Spike calibration

To obtain Rb and Sr concentrations and consequently Rb–Sr ratios, samples were doped with an isotopically enriched tracer for isotope dilution analyses. All reagents used in this study were ultraclean (i.e., all acids were distilled two times in quartz or Teflon® vessels) and Millipore® de-ionized water was used (18.2 M  $\Omega$  cm). The  $^{87}\text{Rb}$  spike was purchased from Oak Ridge Laboratories, Tennessee, USA (batch no. R40-2878); NBS SRM-988 reference material was used as Sr spike. The mixed isotope tracer was designed to keep the error magnification between 1 and 3 for a Rb–Sr ratio that corresponds to that of the NBS SRM-607 and similar geologic materials. It was calibrated against three individual standard solutions prepared from ultrapure ALFA AESAR salts. Only equivalent Rb and Sr salts were mixed, i.e.,  $\text{Rb}_2\text{CO}_3$  (99.975% purity) and  $\text{SrCO}_3$  (99.99% purity),  $\text{RbI}$  (99.975% purity) and  $\text{SrI}_2$  (99.99% purity), and  $\text{RbCl}$  (99.975% purity) and  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  (99.9965% purity), to avoid precipitation of salts after mixing of two different solutions. All salts were dried at  $\sim 200$  °C for one day in an oven to remove adsorbed water and subsequently sealed before cooling to room temperature. For weighing at least 1 g of each salt was taken to minimize weighing errors. All salts were dissolved in 0.75 M HCl. After mixing the Rb–Sr standard solutions with the spike, the mixed solutions were placed in closed vials on a hot plate for 1 h to achieve equilibrium between spike and standard

solution. Note, however that for sample dissolution procedures, presumably extended equilibration time between spike and sample is required. Subsequently, the material was evaporated to dryness and then re-dissolved in 1 ml 2.5 M HCl. Rubidium and Sr were separated from the matrix using a conventional cation exchange resin (Dowex AG-50X8) and Eichrom® Sr-Spec to clean the Rb cut. A detailed description of the procedure is given in Nebel et al. (2005).

The spike was calibrated against each of the three salt-based standard solution, two of which (carbonate and iodide basis) yield average Rb/Sr that differ by 0.17% from each other. Individual means of replicate analyses ( $n=5$ ) from the each of the carbonate and iodide standard solutions provided mean uncertainties on Rb/Sr ratios of  $\pm 0.09\%$  and  $\pm 0.08\%$ , respectively, from which we calculate a weighted mean spike concentration with an uncertainty of  $\pm 0.15\%$ , which is averaged from the two solutions (Fig. 1). The third solution (chloride basis) shows unrealistic Sr concentration and consequently Rb/Sr, which is most likely due to the strongly hygroscopic nature of the salt that resulted in an inadequately known stoichiometry, despite drying the salt at 200 °C.

### 3.3. Uncertainties of Rb–Sr ratios and Rb concentrations

A minimum error on the  $^{87}\text{Rb}/^{86}\text{Sr}$  is given by the uncertainties from the individual isotope ratio analyses of the  $^{87}\text{Rb}/^{85}\text{Rb}$  ( $\pm 0.05\%$ ) and the  $^{84}\text{Sr}/^{86}\text{Sr}$  ( $\pm 0.03\%$ ), which results in a combined error of at least  $\pm 0.06\%$  in the Rb–Sr ratio. If individual in-run statistics from the mass spectrometric measurement show larger errors than the external reproducibility calculated from standards,

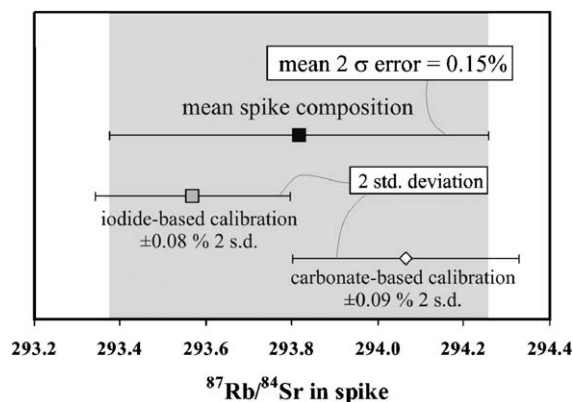


Fig. 1. Calculated  $^{87}\text{Rb}/^{84}\text{Sr}$  of the spike used for calibrations against standard solutions prepared from iodide and carbonate salts. Final spike composition is averaged from the two individual calibrations including errors.

this value must be used. Another error source for the Rb/Sr is the addition of spike to the sample. Depending on the spike–sample ratio, an error magnification factor that results from spike subtraction has to be multiplied with the error from the isotope analyses, which is close to 1 for well-spiked samples. Repeated runs of spiked standard solutions that were used for spike calibrations yielded  $^{87}\text{Rb}/^{86}\text{Sr}$  with an averaged error of  $\pm 0.08\%$  and  $\pm 0.09\%$  (Fig. 1).

The spike concentration is the average from two individual calibrations of the spike against solutions made from iodide and carbonate salts. Taking into account that both calibrations from individual standard solutions represent a mean of repeated runs with total analytical uncertainties for the Rb/Sr of  $\pm 0.08\%$  and  $\pm 0.09\%$ , respectively, the averaged spike calibration has a mean uncertainty on the Rb/Sr of  $\pm 0.15\%$  (2 s.d.; Fig. 1). This is the a priori uncertainty on Rb/Sr, which arises from the uncertainty of the spike composition and thus has to be added to total age determinations when using this method for geochronology. Note that for relative comparison of the individual NBS SRM-607 analyses, this effect must not be incorporated. However, the technique presented here yields a combined total uncertainty of  $\pm 0.18\%$  (2 s.d.) for absolute comparisons of geologic samples, calculated from the analytical Rb/Sr reproducibility of  $\pm 0.09\%$  and the uncertainty of the spike calibrations of  $\pm 0.15\%$ . This reproducibility is in general agreement with the previously reported uncertainty on Rb–Sr ratios by Waight et al. (2002) using a different MC-ICPMS for Rb analyses. The analytical uncertainty in Rb concentration determinations is also estimated from the spike calibration procedure. Replicate analyses ( $n=5$ ) of three individual standard solutions used for spike calibration provide three mean Rb concentrations that have individual two standard deviations of  $\pm 0.21\%$ ,  $\pm 0.23\%$  and  $\pm 0.26\%$ , respectively. However, the three mean values vary within  $\pm 0.5\%$ , which is the reproducibility on Rb concentration determinations.

### 3.4. Analyses of NBS SRM-607

To identify a possible sample heterogeneity, multiple batches ( $n=8$ ) of small amounts of NBS SRM-607 (i.e.,  $\sim 10$  mg each) were analyzed. After doping with the newly calibrated isotope tracer enriched in  $^{87}\text{Rb}$  and  $^{84}\text{Sr}$ , each sample batch was dissolved in a HF/HNO<sub>3</sub> (5:1) acid mixture in 7.5 ml Teflon® beakers and placed on a hotplate at  $\sim 120$  °C for one day. After the sample was evaporated to dryness, an additional uptake in small amounts of 2.5 M HCl was performed to obtain a chloride form. Rubidium and Sr were separated from the mineral matrix using the same technique as for the spike cali-

bration procedure. Total blank determinations that were run with the samples yielded Sr blank contributions of less than 20 pg and Rb blanks less than 150 pg, rendering blank corrections insignificant. Data reduction was performed using an in-house calculation spread sheet, model ages were calculated with Isoplot (Ludwig, 2001). The uncertainty on each analysis of the eight NBS SRM-607 separates was calculated using the method described above and multiplied with the error magnification factor that results from individual spike additions. For Sr, this factor was between 1 and 1.05. For Rb, the error magnification effect increased up to a factor of 2.4, depending on individual spiked samples. Uncertainties for each run are presented in Table 1.

## 4. Results

The certified uncertainty of  $\pm 1.36\%$  for the  $^{87}\text{Rb}/^{86}\text{Sr}$  reflects the poor knowledge of the ‘true’ Rb/Sr of the standard. The large range in published Rb/Sr for this standard is probably not only due to different spike calibrations, but also caused by inhomogeneity of the powdered standard material. Results from this study for the multiple analyses ( $n=8$ ) of NBS SRM-607 are listed in Table 1 and presented in Fig. 2. The average from all eight analyses of the  $^{87}\text{Rb}/^{86}\text{Sr}$  has an uncertainty of  $\pm 0.69\%$  (2 s.d.), and  $\pm 0.35\%$  (2 s.d.) for the  $^{87}\text{Sr}/^{86}\text{Sr}$ , which is outside the external reproducibility estimated from repeated standard analyses for both ratios. This range reflects the largest spread of data published so far for this standard and is highly indicative of sample inhomogeneity at the scale of sampling, i.e., approximately 10 mg. In a Nicolaysen diagram of  $^{87}\text{Rb}/^{86}\text{Sr}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$ , the data points are correlated (Fig. 2) and lie along a reference line with a slope corresponding to a middle Proterozoic age.

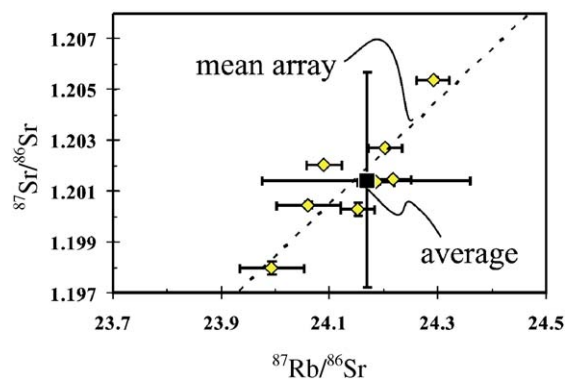


Fig. 2. Eight different batches from NBS SRM-607 were analyzed for Rb/Sr and Sr isotope compositions. The black cube represents the mean value from all analyses with 2 standard deviation errorbars. The dashed line shows the apparent correlation of the data.

This age of 1.4 Ga is in agreement with ages reported from the source area of the standard feldspar (Bennet and DePaolo, 1987; Ferguson et al., 2004; Miller et al., 2004). The amount of sample used for a single Rb–Sr isotope analysis in earlier studies was generally larger than 100 mg or only averages from multiple analyses is reported. However, the observation that  $^{87}\text{Sr}/^{86}\text{Sr}$  correlates with Rb/Sr has also been reported by other authors (Foland and Allen, 1991; Amelin and Zaitsev, 2002; Waight et al., 2002). Amelin and Zaitsev (2002) suggested a  $^{87}\text{Sr}/^{86}\text{Sr}$  heterogeneity of the standard from four  $\sim 10$  mg analyses but all analyses overlap within the reported analytical uncertainties in the Rb/Sr of  $\pm 1\%$ , because the data was obtained by conventional TIMS measurements. Hence the observed apparent variation in the  $^{87}\text{Rb}/^{86}\text{Sr}$  could not be resolved in their study.

## 5. Discussion

For international standards, large amounts of material are required to supply numerous laboratories, and a homogeneous standard of an appropriate size is difficult to produce. Simple homogenization by milling is obviously not adequate to achieve powder homogeneity that enables the generation of reproducible data, when analysing amounts of material that are commonly used in modern geochemistry. The heterogeneity of the  $^{87}\text{Rb}/^{86}\text{Sr}$  revealed by the improved precision of MC-ICPMS analyses therefore strongly limits the use of the standard as an inter-laboratory reference material for Rb–Sr studies. Reproducible results within the achievable analytical precision can, if at all, only be obtained from relatively large batches of the standard, i.e.  $> 100$  mg. Notably such an amount is suggested in the NBS certificate to obtain reproducible values. However, the spread in Rb/Sr and Sr isotope compositions of published data suggests that even such sample amounts not necessarily result in sample homogeneity with respect to Rb/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$ . Nevertheless, the standard is still useful for inter-laboratory calibration purposes because Rb/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  are correlated, thus the quality of any single analysis has to be judged with respect to the correlation line and not to the average concentrations and isotope ratios of the standard.

A regression line drawn through the analyzed aliquots in Rb/Sr vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  suggests that the observed correlation has geologic and not analytical reasons. Incomplete spike–sample equilibration cannot cause this enormous scatter in the Sr isotope composition. The initial  $^{87}\text{Sr}/^{86}\text{Sr}$  obtained from the correlation line in Fig. 2 is  $0.72 \pm 0.28$ . Although highly imprecise, this ratio is in the range expected for initial Sr of the greater

source area of the feldspar (Ferguson et al., 2004). The time related correlation indicates that the original feldspar crystal was not homogeneous and that significant variations in Rb/Sr are natural. The true nature of the variation remains unclear. However, such zoning or banding with varying element concentrations are also reported from other giant crystals that are used as geologic reference materials (e.g., for Lu–Hf and to a lesser extent for U–Pb in the 91500 standard zircon, Nebel-Jacobsen et al., 2005). The present day variability in  $^{87}\text{Sr}/^{86}\text{Sr}$  of the NBS SRM-607 is almost certainly due to decay of Rb in a crystal with zoned Rb/Sr. Thus, all analyses are expected to plot on a reference model age isochron assuming that all feldspar aliquots share a homogeneous initial  $^{87}\text{Sr}/^{86}\text{Sr}$ . With an assumed, but also geologically reasonable initial Sr value of 0.71, as first suggested by Amelin and Zaitsev (2002) and indistinguishable from the calculated initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of  $0.72 \pm 0.28$ , a Rb–Sr isochron yields a mean model age from eight analyses of  $1418.8 \pm 7.8$  Ma (Fig. 3) using a Rb decay constant of  $1.42 \times 10^{-11}/\text{a}$  (Steiger and Jäger, 1977). This absolute age is calculated with the chosen initial  $^{87}\text{Sr}/^{86}\text{Sr}$  value by Amelin and Zaitsev (2002) of 0.71 and yields an age that is in general agreement with ages obtained from the greater sample area of the feldspar (Bennet and DePaolo, 1987; Ferguson et al., 2004). Furthermore, the age obtained from NBS SRM-607 in this study is in excellent agreement with earlier analyses from five different laboratories, re-calculated with the same initial  $^{87}\text{Sr}/^{86}\text{Sr}$  (Table 1). It has to be noted, however, that the assumed initial (with a forced error of zero) can be used for inter-laboratory comparison of the standard data only. A change in the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.01 changes the absolute age obtained from an aliquot of NBS SRM-607 by  $\sim 28$  Ma. In contrast,

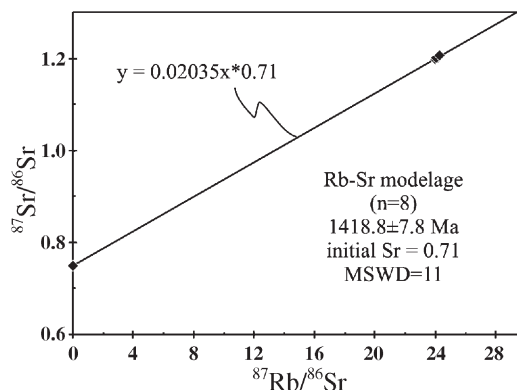


Fig. 3. Reference isochron with an initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.71 in a Nicolaysen plot corresponds to a model age of  $1418.8 \pm 7.8$  Ma. With an uncertainty of  $\pm 0.24\%$  on the  $^{87}\text{Rb}/^{86}\text{Sr}$ , the MSWD is reduced to 3.5. The scatter may be caused by internal variations.

relative ages calculated with an identical initial isotope ratio can be used for comparisons. Absolute ages calculated with the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  of 0.71 may be geologically insignificant, but, however, should yield model ages similar to 1418.8 Ma within the given uncertainty of  $\pm 8$  Ma. A compilation of published values of the standard is shown in Fig. 4A. Although it is probably easier to compare relative ages, we prefer the deviation from a proposed reference isochron to compare different results from the standard in only one dimension. The reference isochron can be expressed with the equation:

$$y = 0.02035x + 0.71 \quad (1)$$

where 0.02035 is the slope  $m$  of the isochron,  $y$  is the  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $x$  the  $^{87}\text{Rb}/^{86}\text{Sr}$  of the sample. The deviation from this model-age isochron can be expressed with a  $\Delta_{\text{MA}}$ , which can be calculated using the term:

$$\Delta_{\text{MA}} = \sin\alpha * ^{87}\text{Rb}/^{86}\text{Sr} - \frac{\sin\alpha}{m} * ^{87}\text{Sr}/^{86}\text{Sr} + 0.71 \quad (2)$$

Here,  $\alpha$  is calculated from the inverse tangent function from the slope  $m$  of the isochron. Absolute errors  $\delta_{\Delta}$  on  $\Delta_{\text{MA}}$  are calculated (with %-errors on isotope ratios) using the equation:

$$\delta_{\Delta} = \sqrt{(\sin\alpha * \text{error}^{87}\text{Rb}/^{86}\text{Sr})^2 + \left(-\frac{\sin\alpha}{m} * \text{error}^{87}\text{Sr}/^{86}\text{Sr}\right)^2} \quad (3)$$

With this expression, it can be demonstrated that nearly all published analyses of the standard measured by TIMS agree within their respective analytical uncertainties with the proposed reference isochron, which is defined as  $\Delta_{\text{MA}}=0$  in Fig. 4B.

The MC-ICPMS data of Waight et al. (2002) and few data points from this study do not plot on the reference line. The offset of two data points (excluding one outlier) from the study of Waight et al. (2002) agree, however, with the  $\Delta_{\text{MA}}$  within the uncertainty of our spike calibration (Table 1, Fig. 4). Hence, a systematic offset due to differences in spike calibration may have to be considered. In contrast, all individual runs from this study were doped with the same isotope tracer and spike calibration effects cancel as a possible cause for the offset from the reference isochron. The difference in individual analysis of our data suggest that either there are geologic reasons for this spread in Rb/Sr in the different sample batches, as e.g., fluid inclusions or different degrees of alteration in zones of the feldspar crystal. This, however, cannot be tested. A second possibility is the underestimation of the uncertainties on the Rb/Sr. The standard

deviation of the mean  $\Delta_{\text{MA}}$  value from the eight analyses yields a  $\delta_{\Delta}=1.06$ , which corresponds to an uncertainty on the  $^{87}\text{Rb}/^{86}\text{Sr}$  of  $\pm 0.24\%$ . Because calculated minimum errors on the Rb/Sr are as low as  $\pm 0.06\%$  (2 s.d.) for standard runs, or at least  $\pm 0.09\%$  for well-spiked samples as demonstrated by repeated analyses of standard solutions, we suggest that variations of  $\pm 0.24\%$  of the standard, outside the external reproducibility, may reflect geologic scatter rather than analytical errors. Consequently, the NBS SRM-607, can be used as a reliable standard and as an inter-laboratory reference for the calibration of the Rb–Sr system within a minimum uncertainty of  $\pm 0.24\%$  (2 s.d.) for Rb/Sr.

### 5.1. Testing the model age expression

To investigate the suggested reference method, we analyzed two additional aliquots of the NBS SRM-607 using an already existing Münster spike (Rb–Sr-16). This spike was calibrated using TIMS against different standard solution than those used in this study. For the calibration, Rb standard solutions were prepared from the NBS SRM-984 reference material and Sr solutions from ultrapure salts comparable to those used in this study (J.Glodny, pers. com.). The two  $\sim 10$  mg samples of NBS SRM-607 were analyzed for Rb using MC-ICPMS and TIMS for Sr with the same method as used for the newly calibrated spike. Uncertainties on the measurements are reported with  $\pm 0.18\%$  (2 s.d.) on the Rb/Sr and in-run statistics for unspiked Sr isotope compositions (Table 1). Results are plotted in Fig. 4B. Both analyses overlap within error and plot on the reference isochron for which we assigned an uncertainty of  $\pm 0.24\%$  (2 s.d.). Accordingly, the accuracy of the older spike calibration can be demonstrated.

## 6. Conclusions

Multiple analyses from 10 mg batches of Rb concentrations by isotope dilution of the NBS SRM-607 using MC-ICPMS reveal sample heterogeneity in Rb/Sr of the standard powder that is significantly outside analytical uncertainties. The observed variation of  $\pm 0.35\%$  (2 s.d.) in  $^{87}\text{Sr}/^{86}\text{Sr}$  is also in stark contrast to the external analytical precision, which is typically  $\leq 40$  ppm. The variation in Rb/Sr shows a strong correlation with  $^{87}\text{Sr}/^{86}\text{Sr}$  that is due to heterogeneities in the feldspar crystal that were generated during the crystal growth. Hence, the demonstrated Rb/Sr heterogeneity of the NBS SRM-607, even within pulverized batches, limits the use of the feldspar as an inter-laboratory standard reference material. Because the

correlation of  $^{87}\text{Rb}/^{86}\text{Sr}$  and Sr isotopes is caused by initial variations in Rb/Sr during the time the feldspar crystallized in its host rock, a reference isochron can be used to evaluate the quality of measurements, including spike–sample equilibrium and spike calibrations. If Rb/Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  of the NBS SRM-607 are reported relative to this reference model isochron, the standard material can be used as a high precision standard. Data referring to this isochron should be reported in the

model age expression  $\Delta_{\text{MA}}$  from the general form in Eq. (2) that is:

$$\Delta_{\text{MA}} = 0.02035 \cdot ^{87}\text{Rb}/^{86}\text{Sr} - 0.9997937 \cdot ^{87}\text{Sr}/^{86}\text{Sr} + 0.71 \quad (4)$$

Inter-laboratory comparisons of spike compositions are thus possible to within  $\pm 0.24\%$  in the Rb–Sr ratio, which is defined by the observed variation in the standard material. Consequently, this tool potentially compensates

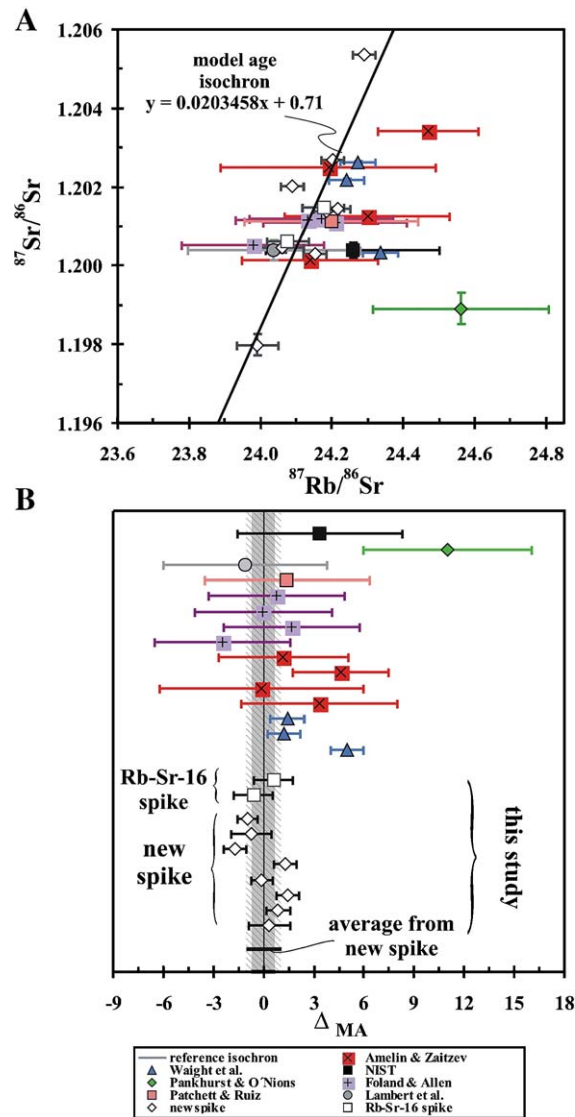


Fig. 4. A) Compilation of published Rb/Sr and Sr isotope compositions for NBS SRM-607 in comparison with the array (black line) obtained from eight analyses in this study with an assumed initial Sr of 0.71. Errors in  $^{87}\text{Sr}/^{86}\text{Sr}$  are 2 s.e. within-run precisions of single analysis; note external reproducibility is 0.004% (2 s.d.) from repeated runs of the NBS-987 standard. Errors in Rb/Sr of Rb isotope dilution analyses by MC-ICPMS are reported in Table 1; errors on Rb analyses from TIMS measurements are assumed to 1% (Pankhurst and O'Nions, 1973; Lambert et al., 1988), if not stated differently (Patchett and Ruiz, 1987; Foland and Allen, 1991; Amelin and Zaitsev, 2002). B) Is the relative deviations of NBS SRM-607 analyses from the isochron expressed as  $\Delta_{\text{MA}}$  for calculations see text. Error on average from new spike is 2 s.d.



for a significant parameter for systematic errors, i.e., variations resulting from spike calibration, on absolute age determinations with the Rb–Sr system. However, compared to the potential precision of the method of  $\pm 0.18\%$  on Rb/Sr as deduced from standard runs, further investigations on homogeneous standards is desirable.

In summary, by using MC-ICPMS for Rb analyses with admixed Zr for mass bias correction, we obtain accuracy in Rb/Sr of  $\pm 0.18\%$  (2 s.d.) and consequently, a similar potential precision for Rb–Sr ages is feasible (e.g., Willigers et al., 2004), non-geologic scatter provided. These results demonstrate the high precision obtainable by Rb analyses with MC-ICPMS in comparison to TIMS for Rb–Sr geochronology, but also underline the accuracy of earlier Rb–Sr analyses from different laboratories, i.e., earlier spike calibrations.

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