Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 242 (2005) 251–255

www.elsevier.com/locate/ijms

# Determination of the $^{87}Sr/^{86}Sr$ isotope ratio in USGS silicate reference materials by multi-collector ICP–mass spectrometry

Lieve Balcaen, Isabel De Schrijver, Luc Moens, Frank Vanhaecke*

*Ghent University, Laboratory of Analytical Chemistry, Institute for Nuclear Sciences, Proeftuinstraat 86, B-9000 Ghent, Belgium*

Received 9 August 2004; accepted 18 October 2004

## Abstract

Multi-collector ICP–mass spectrometry (MC-ICP–MS) was used for $^{87}Sr/^{86}Sr$ isotope ratio determination in newly introduced silicate reference materials from the US Geological Survey (USGS): granite G-3, andesite AGV-2, and basalt BCR-2. Next to the $SrCO_3$ isotopic standard NIST SRM 987, also analogous USGS reference materials from the previous generation, and for which reference $^{87}Sr/^{86}Sr$ data obtained by TIMS are available, were analysed for validation purposes. Sample preparation consisted of acid digestion and subsequent isolation of Sr by means of a dedicated and commercially available crown ether-based resin. The Sr fractions thus obtained were analysed via MC-ICP–MS whereby mass discrimination was corrected for internally, while the isobaric interference at a mass-to-charge ratio of 86 caused by Kr impurities in the Ar gas was mathematically corrected for by using the signal for a Kr isotope free from spectral overlap. Finally, also the effect of the small amount of Rb that may still be present in the Sr fraction was corrected for mathematically on the basis of the signal intensity for $^{85}Rb$. The MC-ICP–MS results for G-2, AGV-1 and BCR-1 showed an excellent agreement with the corresponding TIMS values (<0.003% bias in all cases), such that it can be assumed that also the $^{87}Sr/^{86}Sr$ isotope ratio results obtained for the new reference materials are reliable.

*Keywords:* $^{87}Sr/^{86}Sr$ isotope ratio determination; USGS; Silicate reference materials; Multi-collector ICP–mass spectrometry; Sr resin

## 1. Introduction

Reference materials (RMs) that display a known – preferably even a certified – isotopic composition are of interest for validation purposes in isotopic analysis. For a number of silicate reference materials that can be obtained from the US Geological Survey (USGS), information on both the elemental composition and the $^{87}Sr/^{86}Sr$ isotope ratio, as determined by TIMS, is available. Although these materials are no certified isotopic reference materials, they have been widely used for normalisation and validation purposes in isotopic analysis. Due to their huge success, these reference materials are running out of stock and therefore, a 'new generation' was launched recently. For the production of this new generation of reference materials, material from the same quarry that was sampled for the previous generation(s) of the corresponding RM was taken in every instance. Only those boulders for which preliminary analysis showed a close compositional match with the reference materials from the previous generation were used in the production of each new RM [1].

Traditionally, thermal ionisation mass spectrometry (TIMS) is used for determination of $^{87}Sr/^{86}Sr$ isotope ratios because of the high precision and accuracy attainable [2]. As a result of the straightforward sample introduction (continuous nebulisation of the sample solution in an ion source operated at atmospheric pressure), the higher ionisation efficiency of the ICP ion source and the higher sample throughput, multi-collector ICP–mass spectrometry (MC-ICP–MS) is replacing TIMS for an increasing number of applications [3,4]. Although it was originally assumed that for ICP–MS, isolation of the analyte element from the matrix was not re-

---

* Corresponding author. Tel.: +32 92646625; fax: +32 92646699.
*E-mail address:* Frank.Vanhaecke@UGent.be (F. Vanhaecke).

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.10.025

quired, it was soon established that also for MC-ICP–MS the analyte element had to be separated from the matrix in order to be able to successfully correct for mass discrimination, at least when optimum precision and accuracy are aimed at. Nevertheless, the sample pre-treatment for MC-ICP–MS is still less demanding than that for TIMS [5].

In this work, MC-ICP–MS was used for $^{87}$Sr/$^{86}$Sr isotope ratio determination in USGS silicate reference materials. For Sr isotope ratio determination however, MC-ICP–MS shows the disadvantage of isobaric overlap of some of the Sr$^+$ signals with those of the isobaric Kr$^+$ isotopes (at mass-to-charge ratios of 84 and 86). Correction for these interferences is mandatory to obtain accurate results.

## 2. Experimental

### 2.1. Reagents and samples

Only high purity reagents were used in the preparation of the sample solutions. Water of 18 MΩ cm was obtained by purifying doubly distilled water in a Milli-Q system (Millipore, Bedford, MA, USA). 14 mol l$^{-1}$ HNO$_3$ was purified in-house by subboiling distillation in quartz equipment. 28 mol l$^{-1}$ HF (analytical grade) was purchased from Merck (Darmstadt, Germany).

The USGS provided us with three ‘pairs’ of silicate RMs, each consisting of the ‘old’ and the ‘new’ generation of the reference material: granite G-2 and G-3, andesite AGV-1 and AGV-2 and basalt BCR-1 and BCR-2. For G-2, AGV-1 and BCR-1, provisional TIMS $^{87}$Sr/$^{86}$Sr values and the corresponding uncertainties are available from Ref. [6].

Hence, these materials were analysed for validation purposes. To the best of the authors’ knowledge, only Mahoney et al. [7] and Raczek et al. [8] determined $^{87}$Sr/$^{86}$Sr in some of the new generation materials using TIMS after isolation of Sr by means of ion exchange procedures.

### 2.2. Sample pretreatment

The USGS reference materials (available in powdered form) were taken into solution by open vessel acid digestion on a hotplate. Approximately 0.1–0.2 g of powdered sample was dissolved using 10 ml of 28 mol l$^{-1}$ HF and 3 ml of 14 mol l$^{-1}$ HNO$_3$ in a PTFE vessel. After evaporation to dryness, the residue was taken up in 10 ml 3 mol l$^{-1}$ HNO$_3$ and filtered through a Whatman 541 filter paper. Subsequently, Sr was isolated from the matrix components and from Rb. The latter is required to avoid isobaric overlap of the signals of $^{87}$Sr$^+$ and $^{87}$Rb$^+$. Often, cation-exchange chromatography [9] is used for this purpose. In this work however, Sr was isolated using a dedicated and commercially available crown ether-based Sr resin [10,11]. Columns loaded with this Sr resin material were purchased from Eichrom Technologies Inc. (Bruz, France). The resin is based on the crown ether di-tert-butylcyclohexano-18-crown-6, dissolved in octan-1-ol and sorbed onto an inert polymethacrylate, with a particle size between 100 and 150 μm. The maximum column load is 2 ml. The method involves passage of the sample solution in 3 mol l$^{-1}$ HNO$_3$ medium through the extraction column, which retains Sr. Rubidium and other matrix elements are washed from the column leaving a pure Sr fraction on-column. The Sr may then be stripped from the column with a small volume of diluted nitric acid (0.05 mol l$^{-1}$).

The behaviour of Sr and Rb on the Sr resin column was studied using a matrix-matched standard solution, showing a bulk composition similar to that of the digests of the USGS standards (10 mg l$^{-1}$ Al and 5 mg l$^{-1}$ Ba, Ca, Fe, K, Mg and Na were added to mimic the matrix of these reference material digests).

The sample solution (in 3 mol l$^{-1}$ HNO$_3$ medium) was loaded on the column. After rinsing the column with 1 ml of 3 mol l$^{-1}$ HNO$_3$, 20 ml of 3 mol l$^{-1}$ HNO$_3$ were passed through the column and each individual 1 ml fraction was analysed by quadrupole-based ICP–MS. The Sr concentration in all of these fractions was negligible. Rb on the other hand was present at a high concentration level in the first five fractions. Subsequently, the column was rinsed with 1 ml of 0.05 mol l$^{-1}$ HNO$_3$ followed by 20 ml of 0.05 mol l$^{-1}$ HNO$_3$. Analysis of each individual 1 ml fraction demonstrated that Sr was eluted within the first 5 ml. A typical elution curve for Rb and Sr thus obtained is given in Fig. 1.

For each actual analysis, the USGS reference material digest in 3 mol l$^{-1}$ HNO$_3$ was loaded onto the column, which was subsequently rinsed with 20 ml 3 mol l$^{-1}$ HNO$_3$. Next, the Sr was stripped from the column with a small volume of diluted nitric acid (0.05 mol l$^{-1}$). The first ml was discarded and the next 5 ml were collected for final analysis. The solutions thus obtained were further diluted with 0.14 mol l$^{-1}$ HNO$_3$ to a Sr concentration of 0.2–0.3 mg l$^{-1}$ for mass spectrometric analysis. Procedure blanks were prepared in exactly the same way, but without sample intake.

For method validation, the SRM 987 SrCO$_3$ isotope standard (NIST) was used. To check for possible changes in the Sr isotope ratio induced by the column extraction procedure, a sample of SRM 987 was also subjected to this sample pretreatment (similar conditions as for the USGS samples).

### 2.3. Instrumentation

A ThermoFinnigan Neptune double-focusing MC-ICP–MS instrument, equipped with 10 Faraday collectors was used (ThermoFinnigan, Bremen, Germany). This instrument can be operated at higher mass resolution, but for all measurements carried out in this work, low mass resolution sufficed. The solutions were introduced into the plasma by means of a low flow PFA-nebuliser mounted onto a stable introduction system (SIS), which is a combination of a cyclonic spray chamber and a Scott-type spray chamber. The instrument settings and the data acquisition parameters used are summarised in Table 1. Before each block of measurements, the potential of the electrostatic analyser was adapted

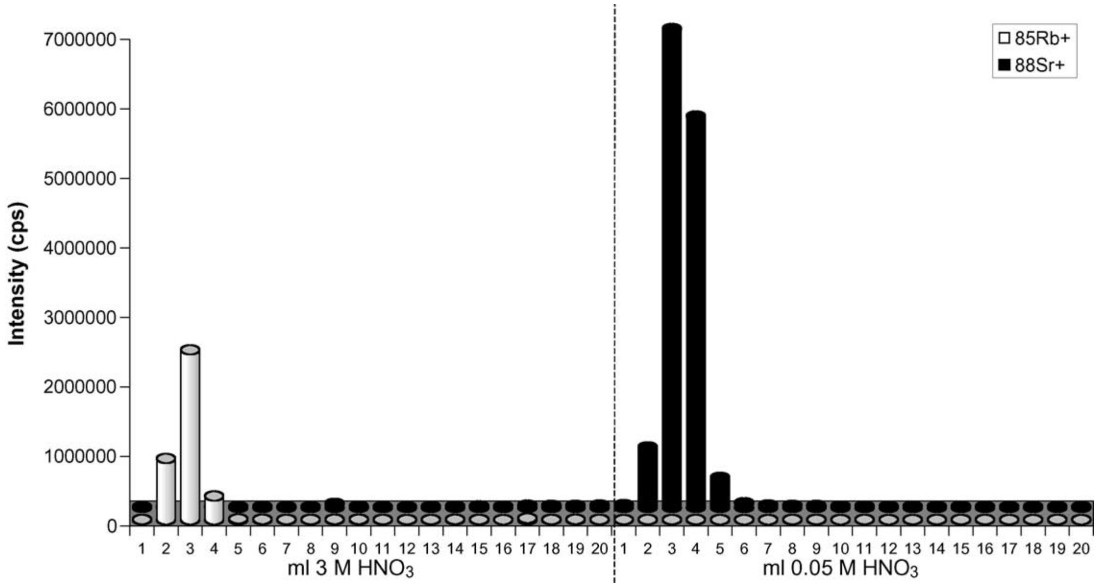

Fig. 1. Typical elution curves for Rb (white) and Sr (black) from the crown ether-based Sr resin – signal intensities measured by means of quadrupole-based ICP–MS.

to deflect the ion beams in order to simultaneously reset the zero reference points for all measured masses.

### 2.4. Measurements and data processing

The raw data obtained were first corrected for the procedure blank. Subsequently, the signal intensities were ratioed and mass discrimination was corrected for internally, which necessitated monitoring of the $^{88}$Sr/$^{86}$Sr isotope ratio, which is constant in nature. The use of internal normalisation for mass discrimination correction applying the exponential law is a common practice in MC-ICP–MS [12].

$$R_{\mathrm{corr}} = R_{\mathrm{obs}} \times \left(\frac{m_{87}}{m_{86}}\right)^{\beta}$$

where $R_{\mathrm{obs}}$ is the measured ratio, $m_{86}$ and $m_{87}$ are the exact masses for $^{86}$Sr and $^{87}$Sr isotopes, respectively and $R_{\mathrm{corr}}$ is the 'true' ratio. The mass fractionation coefficient $\beta$ is obtained by:

$$\beta = \frac{\ln[(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{cert}}/(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{obs}}]}{\ln(m_{88}/m_{86})}$$

where $(^{88}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{cert}} = 8.375209$ (the value conventionally accepted by the International Union of Geosciences (IUGS) – Subcommission on Geochronology [13]).

Although Sr was isolated from the matrix components and from Rb by means of crown ether-based Sr resins, the signal for $^{85}$Rb$^{+}$ signal was measured simultaneously with the Sr$^{+}$ signals, to allow a mathematical correction for the remaining Rb. In this way, the $^{87}$Sr$^{+}$ signal intensity was corrected for the

Table 1
ThermoFinnigan Neptune instrument settings and data acquisition parameters

| | |
|---|---|
| Instrument settings | |
| Sample uptake rate (μl min$^{-1}$) | 50 |
| Guard electrode | Connected |
| Rf power | 1200 W |
| Plasma gas flow rate (l min$^{-1}$) | 15 |
| Auxiliary gas flow rate (l min$^{-1}$) | 0.7–0.8 |
| Nebuliser gas flow rate (l min$^{-1}$) | 1.1–1.2 |
| Sampling cone | Ni, 1.1 mm aperture diameter |
| Skimmer | Ni, 0.8 mm aperture diameter |
| Lens settings | Optimised for maximum analyte signal intensity |
| Data acquisition parameters | |
| Scan type | Static multi-collection |
| Cup configuration | L4: $^{82}$Kr, L3: $^{83}$Kr, L2: $^{84}$Sr, L1: $^{85}$Rb<br>C: $^{86}$Sr, H1: $^{87}$Sr, H2: $^{88}$Sr |
| Resolution | ∼300 |
| Typical $^{88}$Sr sensitivity (V ppm$^{-1}$) | 30 |
| Sampling time | Four blocks consisting of 10 measurements of 10 s integration each |

Table 2
Experimental $^{87}Sr/^{86}Sr$ isotope ratio results for the SRM 987 Isotopic Standard and the USGS RMs and the corresponding reference values

| | Reference value | Uncertainty | ThermoFinnigan Neptune MC-ICP–MS | Uncertainty (2S.E.) |
|---|---|---|---|---|
| SRM 987 | 0.71034 (certificate); *0.71026 (commonly accepted value)* | 0.00026 | 0.710251 | 0.000015 |
| SRM 987 – after column extraction | 0.71034 (certificate); *0.71026 (commonly accepted value)* | 0.00026 | 0.710250 | 0.000010 |
| G-2 | 0.709833 | 0.000058 | 0.709832 | 0.000014 |
| G-3 | | | 0.710019 | 0.000012 |
| AGV-1 | 0.704062 | 0.000048 | 0.704081 | 0.000014 |
| AGV-2 | | | 0.704079 | 0.000007 |
| BCR-1 | 0.70501 | 0.00008 | 0.705007 | 0.000011 |
| BCR-2 | | | 0.705015 | 0.000013 |

contribution from $^{87}Rb^+$ on the basis of the signal intensity for $^{85}Rb^+$ and using a $^{85}Rb/^{87}Rb$ value of 2.59265 [13]. For this correction, mass discrimination was taken into account and corrected for by using the exponential law and assuming that for Rb the mass discrimination coefficient is the same as for Sr. Depending on the initial Rb/Sr ratio in the samples and the efficiency of the separation on the columns, the $^{85}Rb/^{88}Sr$ ratio in the final samples varied between $10^{-4}$ and $10^{-5}$. Also the contribution of $Kr^+$ at a mass-to-charge ratio of 86 has to be corrected for, as Kr is present as a contaminant in the Ar plasma gas. Mathematical correction was based on the signal intensity for $^{83}Kr^+$ and a $^{83}Kr/^{86}Kr$ ratio of 0.664533 [14]. Also in this correction, the mass discrimination was taken into account appropriately. Typically, the $^{83}Kr/^{88}Sr$ ratio was in the order of $10^{-5}$.

It is self-evident that the occurrence of these interferences also affected the correction for mass discrimination, executed as described above (overestimation of $\beta$). To overcome this problem, $\beta$ was recalculated using the signals obtained after correction for the isobaric interferences. This iteration process was repeated four times.

## 3. Results and discussion

For method validation and interlaboratory comparison, a strontium carbonate isotopic standard (NIST SRM 987 Isotope Standard) was measured five times and all results were subjected to the data processing procedure as described above. For each replicate analysis, an internal precision (2 × standard error on the mean or 2S.E.) of ~0.0015% could be obtained. The average value ($n = 5$) for the $^{87}Sr/^{86}Sr$ ratio in this standard was $0.710251 \pm 0.000013$, where the uncertainty is given as a 95% confidence interval ($n = 5$) and can be interpreted as the short term stability of the instrument for Sr isotopic analysis, because the five individual measurements of the SRM 987 standard were spread over one working day. The average value obtained for the $^{87}Sr/^{86}Sr$ ratio is in good agreement with the certified value of $0.71034 \pm 0.00026$ (NIST certificate) and in excellent agreement with the commonly accepted high-precision value of 0.71026 [15].

The effect of the column extraction procedure (in terms of fractionation effects and blank levels) on the Sr isotopic ratio was studied by comparison of the results for a pure SRM 987 standard with those of a similar standard solution that was subjected to the total extraction procedure. From Table 2, it can be seen that both values are almost identical, from which it can be concluded that the column extraction does not induce measurable differences in the isotopic composition of the samples.

After the evaluation of the precision and accuracy of the method proposed for Sr isotopic analysis, six USGS samples were analysed and the MC-ICP–MS results as well as the corresponding reference values are given in Table 2. As can be seen, the precision attainable using MC-ICP–MS (2S.E.) is of the same order of magnitude as that stated for TIMS. Although each value is only the result of a single analysis of a given solution, the deviation between MC-ICP–MS results and the reference values for G-2, AGV-1 and BCR-1 is <0.003% in every instance. Given the excellent results for the 'older' generation RMs, the results obtained for the new generation RMs can be assumed to be reliable. Additionally, our MC-ICP–MS result also shows a good agreement with the TIMS value reported by Mahoney et al. for BCR-2 ($0.705024 \pm 0.000005$) [7]. Comparison with the recent TIMS data of Raczek et al. [8] for AGV-1 (0.703931), AGV-2 (0.703931), BCR-1 (0.704960) and BCR-2 (0.704958) reveals small systematic differences. However, also the value obtained for the SRM 987 (0.710203) by Raczek is slightly different to the one obtained by MC-ICP–MS in the present study. Presumably, these differences can be attributed to machine bias. Therefore (to be able to compare both datasets), all results can be normalised to an agreed value of SRM 987 (e.g., 0.71026). From these normalised data sets it can be concluded that there is also a good agreement between the results of Raczek and those obtained by MC-ICP–MS in the present study.

## 4. Conclusions

In this study, it was shown that the use of multi-collector ICP–mass spectrometry (MC-ICP–MS) permits highly precise and accurate $^{87}$Sr/$^{86}$Sr data for silicate reference materials to be obtained. The MC-ICP–MS results for the old generation RMs (G-2, AGV-1 and BCR-1) showed an excellent agreement with the corresponding TIMS values (<0.003% bias in all cases), such that it can be assumed that also the $^{87}$Sr/$^{86}$Sr isotope ratio results obtained for the new reference materials are reliable. Due to the huge similarity between the isotopic data of the ‘old’ and the ‘new’ generation RMs, G-3, AGV-2 and BCR-2 can replace G-2, AGV-1 and BCR-1 for normalisation purposes in isotopic analysis.

## Acknowledgements

The authors are grateful to ThermoFinnigan and in particular to Claudia Bouman for the MC-ICP–MS measurements. Lieve Balcaen is a research assistant of the Fund for Scientific Research (FWO-Vlaanderen), which is also acknowledged for financial support (FWO research project G.0037.01).

## References

[1] Wilson S.A., USGS, personal communication.
[2] D.H. Smith, in: C.M. Barshick, D.C. Duckworth, D.H. Smith (Eds.), Inorganic Mass Spectrometry – Fundamentals and Applications, Marcel Dekker, New York, 2000, p. 1.
[3] M. Rehkamper, M. Schonbachler, C.H. Stirling, Geostandard Newslett. 25 (2001) 23.
[4] T. Walczyk, Anal. Bioanal. Chem. 378 (2004) 229.
[5] F. Vanhaecke, L. Moens, Anal. Bioanal. Chem. 378 (2004) 232.
[6] http://www.geostandards.lanl.gov.
[7] J.B. Mahoney, D. Weis, B. Kieffer, R. Friedman, W. Pretorius, K. Scoates, A. Goolaerts, C. Maerschalk, Abstract GSA Seattle, 2003.
[8] I. Raczek, K.P. Jochum, A.W. Hofmann, Geostandard Newslett. 27 (2003) 173.
[9] F. Vanhaecke, G. De Wannemacker, L. Moens, P. Van den Haute, Fresenius J. Anal. Chem. 371 (2001) 915.
[10] E.P.H. Horwitz, M.L. Dietz, R. Chiarizia, J. Radioanal. Nucl. Chem. 161 (1992) 575.
[11] C. Pin, C. Bassin, Anal. Chim. Acta 269 (1992) 249.
[12] C.P. Ingle, B.L. Sharp, M.S.A. Horstwood, R.R. Parrish, D.J. Lewis, J. Anal. Atom. Spectr. 18 (2003) 219.
[13] R.H. Steiger, E. Jager, Earth Planet. Sci. Lett. 36 (1977) 359.
[14] K.J.R. Rosman, P.D.P. Taylor, J. Anal. Atom. Spectr. 14 (1999) 5N.
[15] M. Stein, A. Starinsky, A. Katz, S.L. Goldstein, M. Machlus, A. Schramm, Geochim. Cosmochim. Acta 61 (1997) 3975.