

## LECTURE

K. P. Jochum · H.-J. Laue · H. M. Seufert  
C. Dienemann · B. Stoll · J. Pfänder · M. Flanz  
H. Achtermann · A. W. Hofmann

## Multi-ion counting-spark source mass spectrometry (MIC-SSMS): A new multielement technique in geo- and cosmochemistry

Received: 22 November 1996 / Revised: 21 February 1997 / Accepted: 1 March 1997

**Abstract** The photoplate detection system of a spark source mass spectrometer has been recently replaced by a detector array consisting of 20 separate small channeltrons for simultaneous ion counting of up to 20 trace elements. The new multi-ion counting – spark source mass spectrometry (MIC-SSMS) technique combines the advantages of conventional SSMS with modern on-line detection of elements. It has important analytical features, such as simple and fast solid-state sample preparation, high precision (about 1–2%) and accuracy (4%) using multielement isotope dilution, high sensitivity which leads to short measuring times (10–50 min) and low detection limits (about 0.001–0.01 µg/g).

### Introduction

Mass spectrometric multielement techniques are important analytical tools in geo- and cosmochemistry. Spark source mass spectrometry (SSMS) has been a powerful multielement method in these fields for more than 30 years [1]; however, it is only used now in a few laboratories [2, 3]. The main features of this method are simultaneous determination of 30–40 trace elements, low detection limits (about 0.01 µg/g), low sample amounts (10–100 mg), and high precision and accuracy using multi-element isotope dilution (ID) [3]. One of the most important advantages is the simple solid-state sample preparation: rock powder and graphite are mixed together and briquetted to rod-shaped electrodes. SSMS does not involve chemical treatment of samples; therefore uncertainties regarding stability of solutions, equilibration with spike and contamination during chemical dissolution pro-

cesses are eliminated. However, there are some disadvantages with the conventional SSMS which uses photographic plates for ion detection, such as long measuring times (about 1–2 days for a 3-photoplate analysis), complex evaluation techniques and a precision limited to 3–15 %.

The advent of small channeltrons as detectors opens a new method of compensating for the drawbacks of the photoplate detection system. We have therefore equipped a spark source mass spectrometer with a multi-ion counting (MIC) system consisting of a channeltron array for ion counting measurements [4, 5]. In the initial experiments, we tested MIC-SSMS mainly for the analysis of Th, U, Re, Os, Ir, Pt, Au, Zr, Hf, Nb, Ta of international geostandards, oceanic basalts and stony meteorites [5–9]. The final MIC system now consists of 20 separate channeltrons for ion detection. In this paper, the new technique is described, analytical data are presented and the results are compared with those obtained by other modern analytical techniques.

### Multi-ion counting

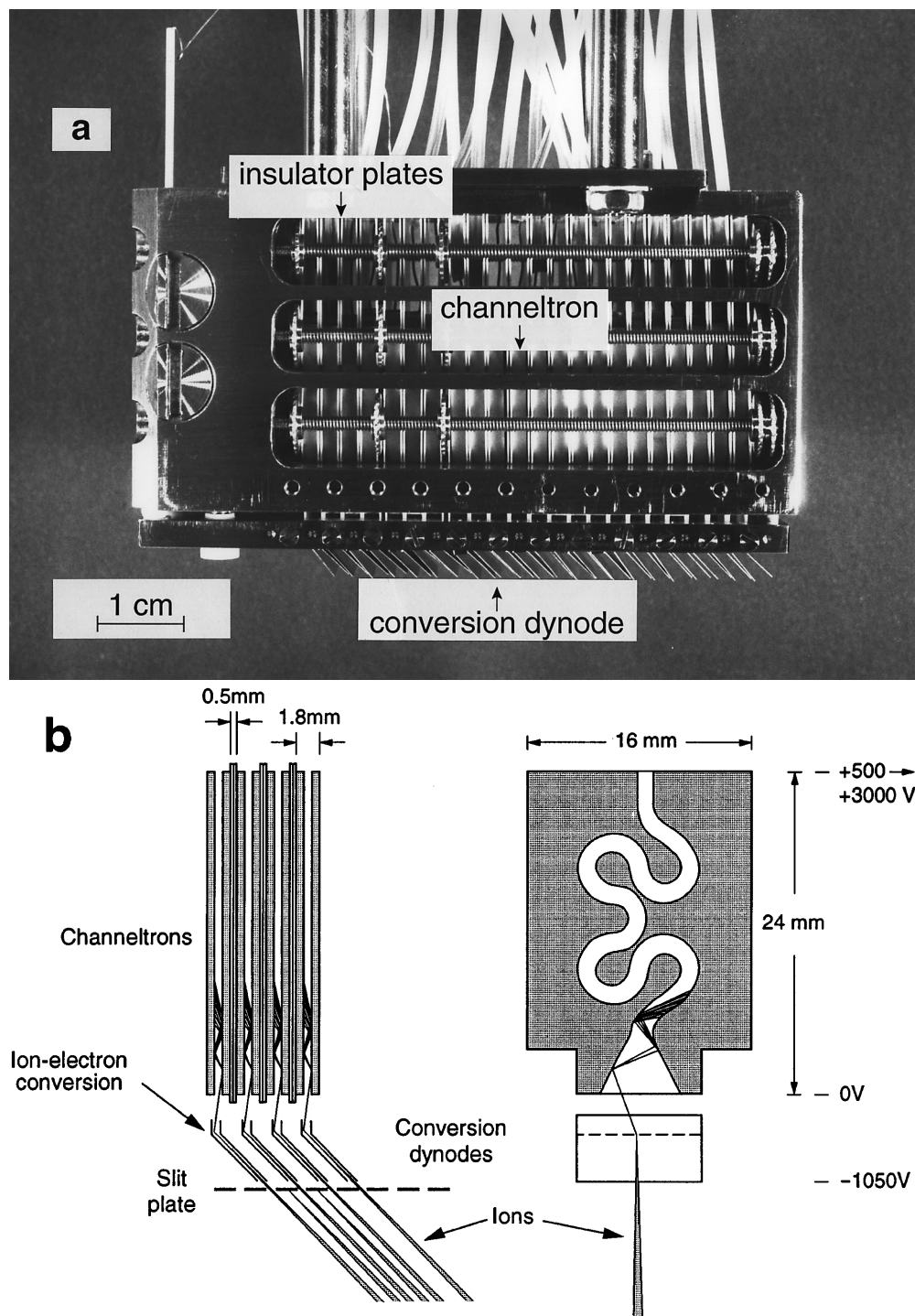
#### Channeltron array

The MIC system consists of a 8 cm long box which is equipped with 20 channeltrons (Fig. 1). The box is situated at the high mass end of the straight image plane of a commercial AEI-MS 702R spark source mass spectrometer with Mattauch-Herzog geometry [1]. Each channeltron (Dr. Sjuts Optotechnik, Katlenburg-Lindau, Germany) has a thin (only 1.8 mm wide) ceramic body. The exit of each channeltron is connected to its individual high positive voltage power source (from +500 V to +3000 V), a separate preamplifier, and a pulse counter (Fig. 2). The entrance is connected to ground. To protect the channeltrons from high voltage arcs, the channeltrons are insulated with 0.25 mm wide Al<sub>2</sub>O<sub>3</sub> plates. A conversion plate (Fig. 1) which is connected to a negative high voltage of 1050 V is incorporated in front of each channeltron. An ion striking the conversion plate is converted into electrons which enter the channeltron and generate an avalanche of electrons along the channel. Typical preamplifier output pulses have a size of 700–1000 mV. They are then registered by the counting electronics. The thresholds for the preamplifiers have been set at 300 mV to suppress the counting of spurious pulses which usually have smaller amplitudes than the real ones. A computer serves for the regulation of the magnetic field (using a hall probe), channeltron

K. P. Jochum (✉) · H. M. Seufert · C. Dienemann · B. Stoll  
J. Pfänder · M. Flanz · H. Achtermann · A. W. Hofmann  
Max-Planck-Institut für Chemie, Postfach 3060,  
D-55020 Mainz, Germany

H.-J. Laue  
Spectromat GmbH, Bevenser Straße 8, 28329 Bremen, Germany

**Fig. 1** a) Channeltron box consisting of small channeltrons and insulator plates for ion counting measurements. A conversion dynode is incorporated in front of each channeltron. b) Sketch of channeltrons (Dr. Sjuts Optotechnik). Ions striking the conversion plates are converted into electrons. These electrons generate an avalanche of electrons along the channel. A slit plate separates the masses of interest from neighboring masses



voltages, thresholds, ion beam suppression, and for the measurement of total ion charge, count rates and measuring time [10].

Channeltrons have to be independently calibrated because they vary in their gain characteristics. Generally, voltages ranging between 2300 V and 2800 V were used. In this range the count rates are nearly independent of the voltages applied which is most favorable for ion counting measurements. A multiple slit plate is placed before the collector array to separate the masses of interest from neighboring masses. Various slit combinations having slit widths between 0.6 and 0.02 mm are available for the measurement of different element combinations at different mass resolutions (300–3000).

#### Measuring procedure

The MIC system allows the measurement of up to 20 trace elements at the same time, for example the simultaneous determination of the 15 isotopes  $^{174}\text{Yb}$ ,  $^{177}\text{Hf}$ ,  $^{182}\text{W}$ ,  $^{185}\text{Re}$ ,  $^{188}\text{Os}$ ,  $^{191}\text{Ir}$ ,  $^{194}\text{Pt}$ ,  $^{197}\text{Au}$ ,  $^{200}\text{Hg}$ ,  $^{203}\text{Tl}$ ,  $^{206}\text{Pb}$ ,  $^{209}\text{Bi}$ ,  $^{232}\text{Th}$ ,  $^{235}\text{U}$ ,  $^{238}\text{U}$ , and the background. Trace element abundances of other mass ranges can be determined by changing the magnetic field. Simultaneous measurement is only possible if all mass lines of interest can be measured in the flat region of the peak. Figure 3 shows a magnetic field scan of 7 isotopes which are measured simultaneously by 7 different channeltrons. In this example, a magnetic field strength of 1.0211 T

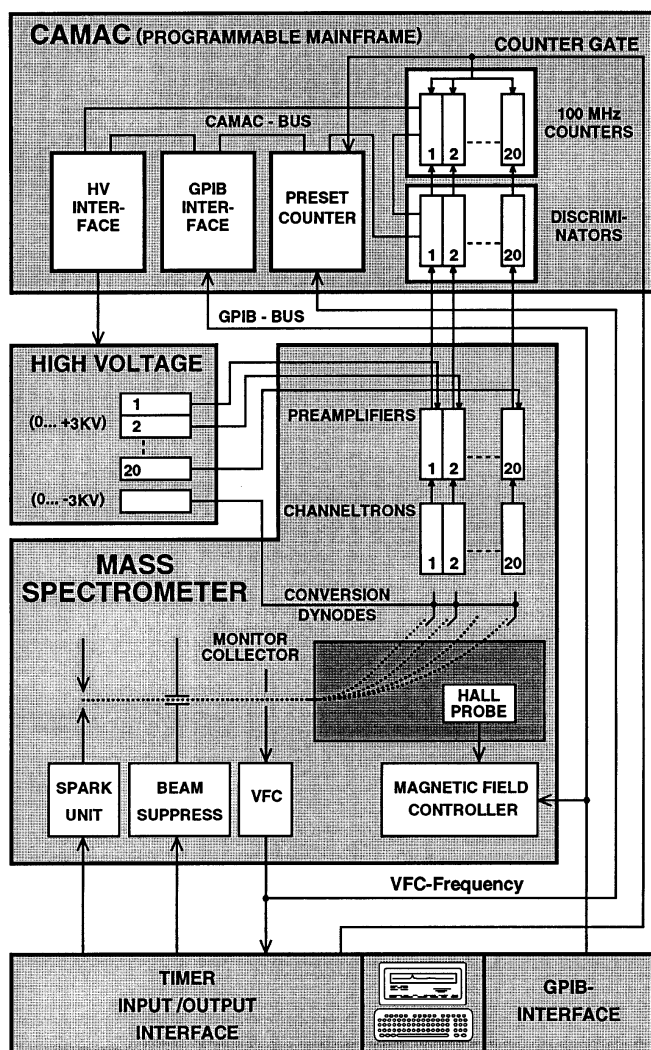


Fig. 2 Scheme of the multi-ion counting system for a spark source mass spectrometer

is used for the analysis which corresponds to the peak flat of all mass lines. Because of the width of the channeltrons and the fixed mass dispersion of the mass spectrometer, isotopes having mass differences of less than 2–3 amu cannot be measured simultaneously. Therefore such experiments are done sequentially by peak jumping using a single channeltron. This technique is especially useful for isotope dilution (ID) analyses (when unspiked and spiked isotopes differ by 1 or 2 amu) and/or for the measurement of highly resolved small mass peaks (where a simultaneous measurement in the flat region of each mass line is difficult to achieve). In practice, a combination of simultaneous and sequential measurements is performed using special control software [10]. A monitor intercepting a fixed fraction of the total ion beam (Fig. 2) provides a measure of the total ion charge accumulated in the course of a measurement. Generally, 1–30 nC are used which corresponds to measuring times of about 4–120 s.

The measurement of low trace element abundances less than about 0.05  $\mu\text{g/g}$  is limited by the background (0.02–0.2 counts/s depending on the mass range) produced by charge exchange between ions and molecules. The dark current of the channeltrons is extremely low and < 0.005 counts/s. The determination of high trace element abundances (> about 300  $\mu\text{g/g}$ ) is influenced by the dead time of the channeltrons. We therefore reduce the ion beam

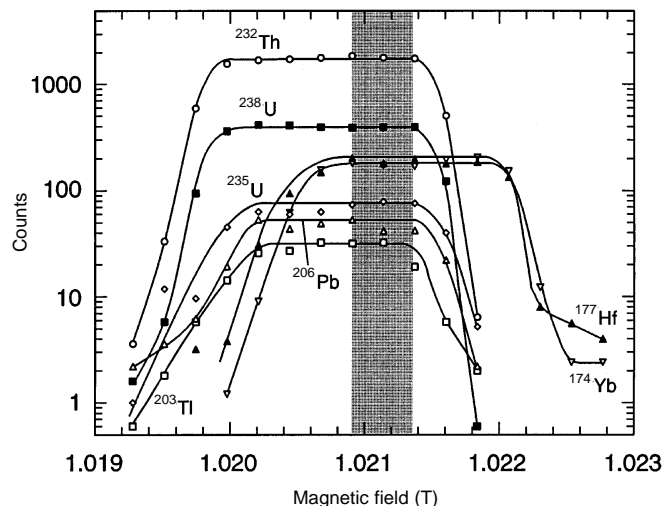


Fig. 3 Magnetic field scan of 7 isotopes ( $^{235}\text{U}$  is spiked) which are measured simultaneously by 7 different channeltrons. Sample is the BEN standard rock; trace element abundances vary between 0.04  $\mu\text{g/g}$  (Tl) and 10  $\mu\text{g/g}$  (Th). Analysis is performed at a magnetic field strength of 1.0211 T which corresponds to the peak flat of all mass lines (grey bar). Measuring time is about 4 s. Slit widths used are 0.6 mm (U, Th isotopes) and 0.5 mm (other isotopes), respectively

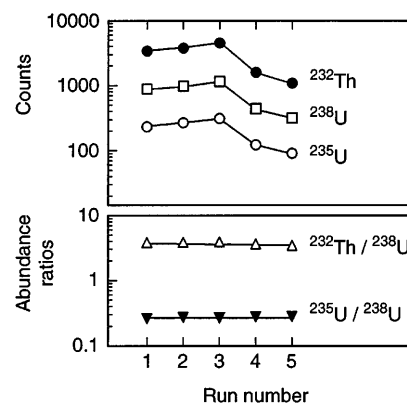


Fig. 4 Count rates and abundance ratios determined during one analysis of the BEN geostandard. Each value represents 45 nC total ion charge (corresponding to a measuring time of 3 min). Abundance ratios remain nearly uniform during the analysis

by using an adjustable slit at the exit of the ion source for the measurement of high concentrations.

Reproducibility of count measurements is relatively poor because spark position, gap width and electrode shape change during operation and can affect the analytical results. Because these parameters influence the measurements of different elements in nearly the same way, isotope and element ratios remain uniform. Figure 4 shows that count rates can vary during one analysis by a factor of 4, whereas abundance ratios differ by a few percent. Therefore, we use the procedure of multi-element ID [3] where elements measurable by ID are determined by precise measuring the ratios of spiked to unspiked isotopes (e.g.,  $^{235}\text{U}/^{238}\text{U}$ , Fig. 4) and other – mainly monoisotopic – elements are determined by measuring element ratios (e.g.,  $^{232}\text{Th}/^{238}\text{U}$ ), using the ID values (e.g., U) for internal standardization and calibrating with relative sensitivity factors [3].

**Table 1** Trace element concentrations ( $\mu\text{g/g}$ ) and trace element ratios in the reference materials BHVO-2 and BHVO-1. The MIC-SSMS data are compared with literature values

	BHVO-2			BHVO-2	BHVO-1	BHVO-1	BHVO-1	BHVO-1	BHVO-1
	Split 1193 MIC-SSMS	Split 3351 MIC-SSMS	Split 2005 MIC-SSMS	mean MIC-SSMS	MIC-SSMS	MIC-SSMS [6]	Ref. values [12]	ID-TIMS [13]	ID-ICPMS [13]
Zr	170	175	175	173 $\pm 3$	177		179		
Hf	4.08	4.55	4.23	4.29 $\pm 0.24$	4.14		4.38		
Nb	18.4	18.6	18.0	18.3 $\pm 0.3$	18.3		19.0		
Ta	1.13	1.19	1.18	1.17 $\pm 0.03$	1.15		1.23		
Th	1.23	1.20	1.20	1.21 $\pm 0.02$	1.21	1.21 $\pm 0.02$	1.08	1.25	1.23
U	0.393	0.401	0.398	0.397 $\pm 0.004$	0.404	0.403 $\pm 0.007$	0.420	0.408	0.409
Zr/Hf	41.7	38.5	41.4	40.5 $\pm 1.8$	42.8		40.9		
Nb/Ta	16.3	15.6	15.3	15.7 $\pm 0.5$	15.9		15.4		
Th/U	3.13	2.99	3.02	3.05 $\pm 0.07$	3.00	3.00 $\pm 0.01$	2.57	3.06	3.01

## Results

In the following important analytical features are discussed using trace element analyses of geostandards, oceanic basalts and stony meteorites. The MIC-SSMS data are compared with recently published data obtained by other laboratories using modern analytical techniques.

### Precision

The precision (defined as  $1 \sigma$  relative standard deviation) depends on several factors, such as ion statistics, electrode and sample heterogeneities and spark fluctuations. To determine the overall precision we analyzed 3 different batches of the BHVO-2 geostandard. Table 1 shows our results obtained from 3 independent analyses. The data represent the mean of 75 measurements using a total ion charge of 3 nC for each experiment. Zr, Hf, U were analyzed by ID, whereas Nb, Th and Ta concentrations were determined using the ID values of Zr, U and Hf, respectively, as internal standards. The analyses indicate that overall precision is about 2%. This value is typical for trace element concentrations higher than about  $0.1 \mu\text{g/g}$ . Very low concentrations in the ng/g range can be determined with a precision of about 4% [11]. The precision may be poorer in the analysis of coarse grained rocks, such as granites, where random fluctuations in Zr and Hf abundances may be due to heterogeneous distribution of zircon grains.

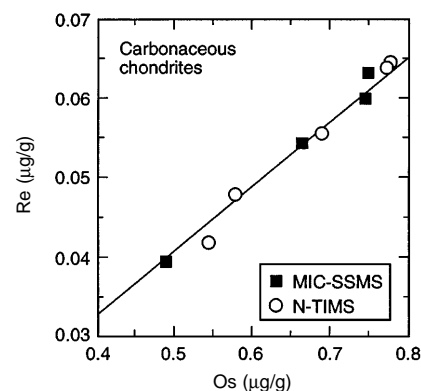
In geo- and cosmochemistry, trace element ratios are of particular importance. MIC-SSMS can determine such ratios with high precision (Table 1), especially if simultaneous measurement is possible (e.g., Th/U, Re/Os). Expanding the total measuring time to about 50 min for one analysis gives even better results (precision  $< 0.5\%$ ). This has been shown by Jochum and Hofmann [6] who analyzed recent Kilauea and Mauna Loa lavas from Hawaii. The Th/U ratio of the Hawaiian geostandard BHVO-1

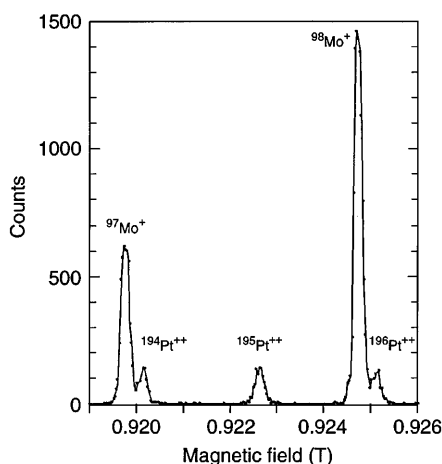
(Table 1) and that of other Hawaiian samples could be determined with such a high precision. MIC-SSMS was therefore able to determine a small but significant 3% difference in Th/U between the lavas of the two volcanoes.

### Accuracy

The accuracy of the analyses can be estimated by comparison with compiled values [12] and recent published high precision data, mainly ID using ICP-MS and TIMS. Our values for BHVO-1 (Table 1) agree within about 4% with the compiled values. Exceptions are Th and U, however, our values for these elements in BHVO-1 (Table 1) and in the low abundant geostandard BIR-1 (Th = 0.033 ppm, U = 0.0098 ppm [11]) agree within 5% with ID-TIMS and ID-ICP-MS measurements [13]. Table 1 also shows that the new USGS reference material BHVO-2 is within error limits identical to BHVO-1.

Figure 5 shows a comparison of recently published data for Re and Os in carbonaceous chondrites by MIC-

**Fig. 5** Comparison of Re and Os analyses of carbonaceous chondrites by MIC-SSMS [8] and N-TIMS [14]. MIC-SSMS measurements were performed by simultaneous measurement of  $^{185}\text{Re}$  and  $^{188}\text{Os}$  isotopes



**Fig. 6** Mass spectra of  $\text{Mo}^+$  and  $\text{Pt}^{++}$  obtained from a standard sample containing 50  $\mu\text{g/g}$  Mo and Pt using a single channeltron detector. At a mass resolution of 2600, the Mo isotopes 97 and 98 are interference-free

SSMS [8] and by high precision NTIMS [14]. Rhenium and Os correlate well. The mean Re/Os ratios obtained by MIC-SSMS ( $0.0821 \pm 0.0019$ ) and by NTIMS ( $0.0807 \pm 0.0020$ ) are identical within about the same error limits.

#### Detection limits

Detection limits (defined as  $3\sigma$  background noise) of the trace elements vary between  $< 0.001$  and  $0.01 \mu\text{g/g}$  mainly due to different ion yields and element-specific isotopic abundances. They are a factor of 10 lower than those obtained with the conventional SSMS. Interferences of molecules and clusters can disturb the determination of some low abundant trace element contents. However, in many cases interferences can be avoided by using highly resolved mass spectra. This is shown in Fig. 6, where at a mass resolution of 2600 the Mo mass lines are separated from doubly charged Pt ions.

#### Measuring time

One of the main advantages of the MIC system is the short measuring time which is only dependent on the element concentration and the precision. Assuming 25–75 repeated measurements and reproducibilities of better than 3% the total measuring time of simultaneous measurements is between 10 and 50 min for trace element analysis at the  $0.3\text{--}300 \mu\text{g/g}$  level. Compared to the conventional photoplate detection system this means an improvement by more than a factor of 20. Total analysis time is about 2 h including mass spectrometer time as well as the time for electrode preparation (about 2 samples in 1 h) and data reduction (about 15 min). Sequential measure-

ments, which are often useful for ID and ng/g trace element analysis, lengthen the measuring time depending on the number of magnetic field jumps.

#### Sample amount

Generally 50–100 mg sample are needed for the preparation of 2 electrodes. MIC-SSMS also permits the analysis of small (1–10 mg) samples situated on the tips of the electrodes. Because of the high sensitivity of the MIC system, sample consumption is very low. It is about  $2 \mu\text{g}$  for each measurement using a total ion charge of 3 nC.

#### Conclusions

MIC-SSMS is a new sensitive technique for multielement analysis of geological and extraterrestrial samples. Moreover, it is also possible to analyze a variety of other solid samples by MIC-SSMS, such as high-purity materials, technical alloys, and biological samples. Applications of MIC-SSMS in geo- and cosmochemistry are precise determination of geochemically interesting elements (such as Nb, Ta, Th, U, Zr, Hf, Pb, Ba, Re, noble metals, all rare earth elements), and trace element ratios (such as Th/U, Nb/Ta, Zr/Hf) and analysis of samples where only small amounts are available (such as basalt glasses, minerals, meteorites, lunar samples).

**Acknowledgements** Comments by J. Snow and the reviewers are gratefully acknowledged.

#### References

1. Taylor SR (1965) *Geochim Cosmochim Acta* 29: 1243–1261
2. Taylor SR, Gorton MP (1977) *Geochim Cosmochim Acta* 41: 1375–1380
3. Jochum KP, Seufert HM, Midinet-Best S, Rettmann E, Schönbberger K, Zimmer M (1988) *Fresenius Z Anal Chem* 331:104–110
4. Laue H-J, Seufert HM, Jochum KP (1994) *Verh DPG* 4: 523 (abstract)
5. Jochum KP, Laue H-J, Seufert HM, Hofmann AW (1994) *Fresenius J Anal Chem* 350:642–644
6. Jochum KP, Hofmann AW (1995) In: Rhodes JM, Lockwood JP (eds) *Mauna Loa Revealed*. AGU Washington, pp 307–314
7. Hofmann AW, Jochum KP (1996) *J Geophys Res* 101:11831–11839
8. Jochum KP (1996) *Geochim Cosmochim Acta* 60:3353–3357
9. Dreibus G, Spettel B, Wlotzka F, Schultz L, Weber HW, Jochum KP, Wänke H (1996) *Meteoritics* 31 Suppl.:A39–A40 (abstract)
10. Flanz M, Achtermann H, Stoll B, Jochum KP (1997) In: *Festkörperanalytik*. PTB Braunschweig (in press)
11. Jochum KP, Laue H-J, Seufert HM, Hofmann AW (1997) *Proc 30th Int'l Geol Congress* (in press)
12. Govindaraju K (1994) *Geostandards Newsletter* 18:1–158
13. White WM (1993) *Earth Planet Sci Lett* 115:211–226
14. Meisel T, Walker RJ, Morgan JW (1996) *Nature* 383:517–520