

Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 232 (2004) 83–94

www.elsevier.com/locate/iims

Application of MC-ICPMS to the precise determination of tellurium isotope compositions in chondrites, iron meteorites and sulfides

Manuela A. Fehr∗, Mark Rehkämper, Alex N. Halliday

ETH Zürich, Institute of Isotope Geology and Mineral Resources, Sonneggstr. 5, CH-8092 Zürich, Switzerland

Received 8 September 2003; accepted 17 November 2003

Abstract

New mass spectrometric techniques have been developed for the precise and accurate determination of Te isotope compositions. The methods are suitable for the analysis of stony and iron meteorites as well as sulfide mineral separates, such that they can be applied to search for Te isotope anomalies in various solar system materials.

Tellurium is first separated from its matrix with a two-stage liquid chromatographic procedure. For iron meteorites, solvent-extraction is used to isolate Te from Fe prior to the column separation. The isotope composition of Te is then determined by multiple-collector inductively coupled plasma-mass spectrometry (MC-ICPMS). Tellurium has a very high first ionization potential and thus MC-ICPMS is much more suitable for the isotopic analyses than positive ion thermal ionization mass spectrometry (TIMS). Only about 100 ng Te are required for a single high precision measurement. Analyses of two terrestrial sulfides, the carbonaceous chondrite Allende and the iron meteorite Canyon Diablo reveal that these have Te isotope compositions that are identical to the terrestrial standard within uncertainty. The Te isotope data acquired for standard solutions as well as meteorites and sulfides display reproducibilities (2σ) of approximately \pm 4500 ppm for ¹²⁰Te/¹²⁸Te, \pm 140 ppm for 122 Te/ 128 Te, ± 100 ppm for 124 Te/ 128 Te, ± 30 ppm for 126 Te/ 128 Te, and ± 60 ppm for 130 Te/ 128 Te. Compared to published results for meteorite samples obtained by TIMS, this represents an improvement in precision of about one to two orders of magnitude for $^{122-130}$ Te/ 128 Te and by a factor of 4 for $120 \text{ Te}/128 \text{ Te}$. A number of experiments furthermore demonstrate that the isotope data acquired by MC-ICPMS are accurate, even for complex geological samples.

© 2003 Elsevier B.V. All rights reserved.

Keywords: MC-ICPMS; Tellurium isotopes; Meteorites

1. Introduction

The nuclide 126 Sn decays to 126 Te (through the intermediate $126Sb$) with a half-life of 234,500 years [\[1\].](#page-10-0) This decay system is of significant interest as a possible chronometer of early solar system development [\[2\].](#page-10-0) The parent 126 Sn is predominately produced by the *r*-process, because the very short half-life of 125Sn (∼9.6 days) hinders *^s*-process production. Therefore, ¹²⁶Sn is most probably formed in super-nova environments [\[3\]. T](#page-10-0)he discovery of 126 Te excesses that correlate with Sn/Te ratios in meteorites would thus provide powerful confirmation of the theory that a supernova injected freshly synthesized nuclides into the molecular cloud from which our solar system formed, providing evidence of a trigger [\[4–6\]. T](#page-10-0)his would be in contrast to some recent models that propose an internal source for short-lived radionuclides through production by protostellar radiation [\[7–9\].](#page-10-0)

Tellurium is of additional interest because it has eight stable nuclides that are ideally suited for the study of nucleosynthetic processes. The isotopes 120 Te, $^{122-124}$ Te, and 128,130 Te are produced exclusively by the *p*-, *s*-, and *r*-process, respectively, whereas ¹²⁵,126Te are produced by both the *r*- and the *s*-process. The search for nucleosynthetic Te isotope anomalies is particularly important, because a number of recent studies identified isotopic heterogeneities for Mo [\[10–12\],](#page-10-0) Ru [\[13\]](#page-10-0) and Zr [\[14,15\]](#page-10-0) in bulk meteorites. At least some of these heterogeneities, however, could not be confirmed by other workers [\[16–19\].](#page-10-0)

Previous investigations, which were conducted by (positive ion) thermal ionization mass spectrometry (TIMS) did not find any Te isotope anomalies in bulk meteorites [\[2,20,21\].](#page-10-0) Early studies on acid etched residues of Allende, which utilized neutron activation analysis, however, identified large (%-level) differences in Te isotope compositions

[∗] Corresponding author. Tel.: +41-1-632-46-43, fax: +41-1-632-18-27. *E-mail addresses:* fehr@erdw.ethz.ch (M.A. Fehr), markr@erdw.ethz.ch (M. Rehkämper), halliday@erdw.ethz.ch (A.N. Halliday).

^{1387-3806/\$ –} see front matter © 2003 Elsevier B.V. All rights reserved. doi:10.1016/j.ijms.2003.11.006

[\[22–24\].](#page-10-0) More recent analyses of presolar grains by TIMS [\[25\]](#page-10-0) and negative ion TIMS (N-TIMS) [\[26\]](#page-11-0) were unable to reproduce these results and found Te isotope anomalies only for 128Te and 130Te.

Tellurium isotope studies by TIMS are very difficult, due to the very high first ionization potential of this element (∼9 eV). Application of the N-TIMS technique appears to provide good sensitivity, but no improvement was reported for the measurement precision [\[27\].](#page-11-0) The most precise Te isotope data have hitherto been obtained by multiple-collector inductively coupled plasma-mass spectrometry (MC-ICPMS). Lee and Halliday [\[28\]](#page-11-0) conducted multiple analyses of Te standard solutions by MC-ICPMS and the isotopic data are about 2–3 times more precise than the best TIMS results. The MC-ICPMS methodology has, however, not yet been adapted for the determination of Te isotope compositions for geological samples or meteorites.

Multiple collector-ICPMS is, in general, more suitable than TIMS for the acquisition of precise isotope ratio data for elements with high first ionization potentials. Analytical studies that aim to resolve small radiogenic or nucleosynthetic isotope anomalies of elements such as Zr [\[29,30\], M](#page-11-0)o [\[11\],](#page-10-0) Ru [\[17\], H](#page-10-0)f [\[31\], o](#page-11-0)r W [\[32\]](#page-11-0) therefore constitute one of the most important applications of this mass spectrometric technique. In addition, MC-ICPMS is also used to analyze the isotopic compositions of Sr, Nd [\[33\],](#page-11-0) and Pb [\[34\],](#page-11-0) which are the three "traditional" isotope systems of geochemistry. These analyses were performed routinely (and exclusively) by TIMS in the past but in comparison, MC-ICPMS provides superior sample throughput and data of comparable precision. A particularly novel application of MC-ICPMS is the determination of mass dependant variations in the stable isotope compositions of "heavy" elements such as Fe [\[35\],](#page-11-0) Cu [\[36\],](#page-11-0) Mo [\[37\],](#page-11-0) Cd [\[38\]](#page-11-0) or Tl [\[39\],](#page-11-0) amongst others. Regardless of the application, MC-ICPMS can provide isotopic data that is precise to about $\pm 0.01\%$ (∼100 ppm) or better. Given these capabilities, it is not surprising that MC-ICPMS not only finds broad application in geo- and cosmochemistry [\[40,41\]](#page-11-0) but also in other research fields such as environmental and medical studies [\[42,43\].](#page-11-0)

In this study, we have developed new chemical separation methods and MC-ICPMS measurement protocols that permit the precise determination of Te isotope compositions for bulk meteorites and sulfides. Special emphasis was placed on the precise measurement of 126 Te, because isotope anomalies from the decay of 126 Sn are expected to be extremely small.

2. Experimental procedures

2.1. Sample preparation

2.1.1. General

All critical laboratory work was carried out in Class 10 laminar flow hoods using purified reagents. Mineral acids and ethanol were purified once or twice (HCl) by sub-boiling distillation in quartz or Teflon stills and $18 \text{ M}\Omega$ -grade water from a Millipore system was used throughout. Saturated bromine water was prepared as described by Rehkämper and Halliday [\[44\].](#page-11-0) The MIBK (methyl-isobutyl-ketone, 4-methyl-2-pentanone) was cleaned just prior to use, by extracting a blank acid sample.

Two Te standards, with identical isotope compositions, were used in the present study. The first was prepared by dissolving pure elemental Te (obtained from Johnson Matthey Chemicals, USA) in $HNO₃$. From this we prepared a solution with ∼100 μ g/ml Te in 2 M HNO₃ by dilution. The second was an ICP standard solution with $1000 \mu g/ml$ Te from Alfa Aesar (Germany). These solutions were used as terrestrial reference standards in this study, because a standard reference material with a certified Te isotope composition was not available.

2.1.2. Sample digestion

Chondrite samples of up to 0.5 g were first digested in a high-pressure asher (HPA-S, Anton Paar, Austria) for 3 h at about 100 bar and 220 $°C$, with 5 ml aqua regia in 90 ml quartz glass vessels. Larger samples of up to 1 g were treated with 8 ml of aqua regia. The samples were then transferred to 60 ml Savillex beakers, evaporated to dryness and digested with 6 ml 28 M HF on a hotplate overnight. After dry-down, they were re-dissolved in 15 ml 6 M HCl and dried again.

Most of the terrestrial rock samples were digested using the chondrite procedure. Alternatively, they were successively treated on a hotplate with 8 ml 28 M HF plus 1 ml $14 M HNO₃$ and 20 ml 6 M HCl. Pyrrhotite and pyrite samples of less than 0.5 g were dissolved on a hotplate in Savillex beakers using $15 \text{ ml } 2.7 \text{ M HNO}_3$ plus 5 ml bromine water and 6 ml aqua regia, respectively.

About 5 g of iron meteorite was first cleaned with ethanol and then leached twice to remove any surface contamination with 16 ml of 50% aqua regia at room temperature. The residues after leaching were digested on a hotplate with 40 ml of aqua regia.

2.1.3. Solvent extraction

A solvent extraction procedure was the first step for the separation of Te from iron meteorites. The procedure was modified from methods previously published by Kawamura et al. [\[45\]](#page-11-0) and Terashima [\[46\]. A](#page-11-0)fter digestion, the iron meteorites were dissolved on a hotplate in 20 ml 6 M HCl. Following cooling to room temperature, the samples were treated with 2 ml of an aqueous $KMnO₄$ solution (1%). After 5 min, an additional 20 ml of 6 M HCl were added, followed by 60 ml MIBK. The beakers were then shaken for 1 min. The majority of the Fe partitions into the organic (MIBK) phase, and this overlies the denser aqueous 6 M HCl, which concentrates Ni and Te. After removal of the MIBK by pipette, the extraction procedure (starting with the addition of MIBK) was repeated five times. Following this, the aqueous solution was dried down, re-dissolved in 9 ml 2 M HCl

Table 1 Elution sequence of the anion-exchange and the Tru-SpecTM resin chromatography

Eluent	Volume (ml)	Eluted				
2 ml BioRad AG1 X 8 anion-exchange resin (200–400 mesh)						
"HF-method"						
1 M HNO ₃	10	Resin cleaning				
5 M HF	10	Resin conditioning				
5 M HF (sample solution)	6	Matrix				
5 M HF	13.5	Matrix				
15 M HF	6	Matrix				
6M HCl	12	Matrix				
1 M HNO ₃	10	Sn, Te				
"HCl-method"						
1 M HNO ₃	10	Resin cleaning				
$2M$ HCl	10	Resin conditioning				
2 M HCl (sample solution)	15	Matrix				
$2M$ HCl	10	Matrix				
12 M HCl	4	Matrix				
$5M$ HF	4	Matrix				
1 M HNO ₃	10	Sn, Te				
200 μl Eichrom Tru-Spec TM resin						
$0.5M$ HCl	10	Resin cleaning				
		and conditioning				
0.5 M HCl (sample solution)	1	Te				
$0.5M$ HCl	5	Te				

and then further purified by ion-exchange chromatography ("HCl-method") as described below.

2.1.4. Separation of Te by liquid chromatography

A two-stage liquid chromatographic procedure was used for the isolation and purification of Te (Table 1). The first step serves to separate Sn and Te from matrix elements, whereas the second isolates Te from Sn.

The first step utilized either the so-called "HF-method" or the "HCl-method". Both procedures were performed with BioRad Poly Prep® chromatography columns and 2 ml of anion-exchange resin (AG1 X 8, 200-400 mesh). A fresh resin bed (0.8 cm diameter, 4 cm length) was prepared for each separation. These columns were used for sample sizes of up to 0.5 g and larger samples were split over several columns.

For the "HF-method" (Table 1), the digested samples were dried down three times with several drops of 28 M HF and then taken up in 3 ml 5 M HF and refluxed on a hotplate overnight. These solutions were centrifuged and the fluoride precipitates were washed twice for 2 h with 1.5 ml of 5 M HF. Following cleaning and equilibration of the resin beds (with $10 \text{ ml } 1 \text{ M HNO}_3$ and $10 \text{ ml } 5 \text{ M HF}$ the sample and the wash solutions were loaded onto the ion-exchange columns. Matrix elements were eluted with 13.5 ml 5 M HF, 6 ml 15 M HF, and 12 ml 6 M HCl. Finally, Te and Sn were collected by elution with $10 \text{ ml } 1 \text{ M HNO}_3$.

For the "HCl-method", which was modified from Smith et al. [\[47\],](#page-11-0) the digested samples were first dried down three times with a few drops of 12 M HCl and then dissolved

in 9 ml 2 M HCl (Table 1). After refluxing overnight, the solutions were centrifuged, and any precipitate was treated twice for 2 h with 3 ml of 2 M HCl. The combined 2 M HCl fractions were loaded onto the resin bed, which had been pre-treated with 10 ml each of $1 M HNO₃$ and $2 M HCl$. Following loading, the column was rinsed with 10 ml 2 M HCl. Elution of matrix elements was completed by addition of 4 ml 12 M HCl and 4 ml 5 M HF. Tellurium and Sn were then collected with $10 \text{ ml} 1 \text{ M HNO}_3$.

The Te fractions from the first column were evaporated to dryness and then dried down, first with a drop of 14 M $HNO₃$, and then three times with a drop of $12 M$ HCl. Following this, they were re-dissolved in 1 ml 0.5 M HCl on a hotplate overnight. The second separation step was adapted from Yi et al. [\[48\]](#page-11-0) and utilized 2.2 cm long Teflon columns filled with 200 μ l Eichrom Tru-SpecTM resin (Table 1). A fresh resin bed was prepared for each sample, which was cleaned and equilibrated with 10 ml 0.5 M HCl. Collection of Te commenced with loading of the 0.5 M HCl sample solution. Tellurium was then further eluted with 5 ml 0.5 M HCl, whereas Sn remained on the Tru-SpecTM resin.

2.2. Mass spectrometry

2.2.1. Instrumentation and measurement protocols

Sample solutions were introduced into the mass spectrometer by free aspiration with a Cetac MCN 6000 desolvating nebulizer. The Te isotope measurements were performed with a Nu Plasma MC-ICPMS by simultaneous collection of the ion beams of $^{118}Sn^+, {^{120}Te^+}, {^{122}Te^+}, {^{123}Te^+}, {^{124}Te^+},$ 125 Te⁺, 126 Te⁺, 128 Te⁺, 129 Xe⁺ and 130 Te⁺ with Faraday cups. Prior to each measurement session, the instrument was carefully tuned to maximize the Te signal intensity by adjusting the torch position, gas flows, acceleration potential, lens voltages and deflector-settings. Typical operating parameters are listed in [Table 2](#page-3-0) and total ion beam intensities of \sim 4 × 10⁻¹³ A/ppb (2500 Mcps/ppm) were routinely achieved for Te. This is equivalent to a transmission efficiency of about 3×10^{-4} , assuming a solution uptake rate of 120μ l/min.

The Te fractions from the chromatographic separation were dried down three times with a drop of 14 M HNO₃ and then re-dissolved in an appropriate volume of $0.1 M HNO₃$, such that the final sample solutions yielded total Te ion beam intensities of about $3-6 \times 10^{-11}$ A. All samples were analyzed together with (and relative to) standard solutions that had very similar Te concentrations (∼100 ng/ml Te).

The isotope ratio measurements for both sample and standard solutions comprised the collection of 80 ratios (5 s integrations), in blocks of 20, which required ∼10 min. "On-peak" baselines were measured for 15 s prior to each block, while the ion beam was deflected by the electrostatic analyzer. On each measurement session, the samples were only analyzed after repeated runs of Te standard solutions had confirmed the absence of any drift in the measured isotopic data or other problems. The sample measurements

Table 2 Instrument parameters

RF power (W)	1350
Acceleration potential (V)	\sim 4000
Gas flow rates	
Ar coolant (l/min)	13
Ar auxiliary (l/min)	$1 - 1.3$
MCN 6000	
Nebulizer pressure (bar)	6
Ar sweep gas setting	3.5
N_2 setting	$0 - 0.01$
Solution uptake rate $(\mu l/min)$	\sim 120
Spray chamber temperature $(^{\circ}C)$	75
Desolvator temperature $(^{\circ}C)$	160
Vacuum	
Expansion chamber (mbar)	$1.7 - 2.3$
Analyzer (mbar)	\sim 2 × 10 ⁻⁹
Sensitivity (A/ppb)	\sim 4 × 10 ⁻¹³
Transmission efficiency	3×10^{-4}
Abundance sensitivity ^a	\sim 2 × 10 ⁻⁶
Mass resolution ^b	\sim 400

^a Measured at mass 237 relative to 238 U.

 b *M*/ ΔM , 10% valley definition [\[49\].](#page-11-0)

were interspersed between analyses of Te standards. Prior to each analysis, the sample delivery system was flushed with $0.1 M HNO₃$ to ensure that the results were not biased by memory effects. Washout of Te usually required 5–10 min.

Table 3 Isobaric and molecular interferences for Te isotopes

$$
\varepsilon^{1XX} \text{Te} = \left(\frac{R_{\text{Sam}} - R_{\text{Std}}}{R_{\text{Std}}}\right) \times 10^4 \tag{1}
$$

Each sample is expressed relative to the standard data obtained on the same measurement session.

2.2.2. Mass spectral interferences

Isobaric interferences on the masses of Te can be generated either by isobars or molecular species (Table 3). These interferences cannot be resolved by the mass spectrometer because the NuPlasma MC-ICPMS operates at a mass resolution of about 400. All sample solutions were therefore carefully checked for the potential presence of elements that can generate such interferences. For critical elements, the maximum element/Te ratios that can be tolerated were furthermore determined, by analyzing Te solutions that contained known contaminant levels. Samples that displayed element/Te ratios that were too large, were further purified by ion-exchange chromatography. In this case, the "HF-method" was applied if too much Cd was present, but otherwise the samples were cleaned using the "HCl-method".

The numbers are the abundances of the respective isotopes in percent.

^a M denotes the isotopes listed.

Isobaric interferences on Te isotopes can be generated by Sn, Xe, Ba, and Sb ([Table 3\).](#page-3-0) Interference corrections were applied for Sn and Xe, based on the measured ion currents for 118Sn^+ and $129\text{X}e^+$ and the isotopic abundances given by Lee and Halliday [\[28\]](#page-11-0) and Basford et al. [\[50\].](#page-11-0) Standard solutions typically displayed Sn/Te concentration ratios of about $1-3 \times 10^{-4}$ and Sn/Te ratios of up to 1.5×10^{-3} could be tolerated for samples without compromising the accuracy of the analytical data. The Sn corrections for samples were typically 7–35% for 120 Te/ 128 Te, but less than 2.5‰ for 122 Te/¹²⁸Te and 124 Te/¹²⁸Te. Such large corrections for samples, however, are only accurate if the interference term is adjusted for the instrumental mass bias. Xenon is present in the Ar plasma gas and therefore both samples and standards typically yielded Xe/Te ratios of $4–9 \times 10^{-3}$. The Xe corrections are negligible or very small ($\langle 15 \text{ ppm} \rangle$ for $120 \text{ Te}/128 \text{ Te}$, $126,130$ Te/ 128 Te and <70 ppm for $122-124$ Te/ 128 Te.

The development of an analytical protocol for very small meteorite samples required that data acquisition was performed by static multicollection of all ion beams in a single measurement sequence. Consequently, interference corrections for $130Ba⁺$ and $123Sb⁺$ were not applied online during the analyses, because the collector set up did not permit the simultaneous measurement of the interference monitors $135Ba⁺$ and $121Sb⁺$. However, due to the low abundance of ¹³⁰Ba⁺, Ba/Te ratios as high as 7.5×10^{-3} could be tolerated without compromising the data quality. At this level, the contribution of $130Ba⁺$ to the $130Te⁺$ ion beam is insignificant (given the analytical precision) at less then 25 ppm. Tellurium standard solutions typically yielded Sb/Te ratios of 4×10^{-5} such that the presence of Sb did not significantly affect the accuracy of the ¹²³Te data. The Sb correction was typically about 1.5% for 123 Te/ 128 Te and was applied offline. For samples, however, the Sb corrections would be much larger and the 123Te/128Te data were therefore considered to be unreliable.

A particular problem of Te isotopic measurements by MC-ICPMS are the interferences from molecular ions $(MH^+, MN^+, MO^+$ or MAr^+ with $M =$ Se, Kr, Rb, Sr, Zr, Ru, Pd, Ag, Cd, Sn, Sb, I, Te and Xe) which can be produced in the plasma source [\(Table 3\).](#page-3-0) Use of a desolvating nebulizer greatly reduces the formation of oxides, nitrides, and hydrides. The MCN 6000 nebulizer was furthermore operated without or with very low N_2 flow [\(Table 2\),](#page-3-0) because this also resulted in maximum sensitivity for Te. No other measures were taken to further reduce the production of molecular ions, such as the use of a shielded torch or lowering RF power.

The hydrides of Te, Xe and I can interfere with Te iso-topes [\(Table 3\).](#page-3-0) Interferences from TeH $^+$ ions on Te masses will not be problematic, however, if they affect samples and standards to (nearly) the same extent and/or if the hydride production rates are low. The present analyses fulfil both conditions. First, differences in the isotopic compositions of samples and standards are expected to be less than 0.1% and second, the desolvating nebulizer limits the production of hydrides to TeH⁺/Te⁺ < 5 × 10⁻⁵ (this upper limit results from the instability of the Xe background at mass 131). This indicates that Te-hydrides do not compromise the accuracy of the present Te isotope data. If the formation of 127 IH⁺ and $XeH⁺$ with I and Xe from the plasma gas was important, this would generate relatively constant interference levels. Such interferences were not significant, however, because identical Te isotope compositions were obtained for standard solutions with Te concentrations between 50 and 400 ppb. Hydride interferences from Sn and Sb could be a more severe problem, as many samples solutions displayed elevated Sn/Te and Sb/Te concentration ratios. However, the maximum tolerable level of Sn determined for the sample solutions (see above) also accounts for the potential effects of Sn-hydrides. For Sb, even Sb/Te ratios of 0.6 did not compromise the measured 124Te/128Te data and all samples had $Sb/Te < 0.02$.

The presence of Cd in sample solutions was a particular problem for the present study, because this element can produce oxide- and nitride-based interferences for nearly every Te isotope [\(Table 3\).](#page-3-0) The highest tolerable Cd/Te ratio is 0.25 but many sample solutions were found to have higher Cd contents if the Te was separated using the "HCl-method". This problem can be readily circumvented, however, because the Te fractions obtained from the "HF-method" are virtually free of Cd.

Regardless of which column separation is used, sample solutions typically contain Rb, Sr, and Zr, but at levels that cannot bias the results. The maximum tolerable concentration ratios for these elements are Rb/Te \lt 0.13, Sr/Te \lt 0.12, and Zr/Te < 0.06. The presence of Ru can be a problem if iron meteorites are analyzed but concentration ratios of Ru/Te < 0.1 are acceptable for sample solutions. Krypton is introduced into the mass spectrometer with the Ar plasma gas, but insufficient $KrAr^+$ is formed to bias the Te isotope data. The identical Te isotope compositions measured for solutions with different Te concentrations support this conclusion. Any bias would furthermore affect both samples and standards to a similar extent. The elements Se, Pd, and Ag were also only present at very low concentrations that did not compromise the isotopic analyses of Te.

Doubly charged $^{238}U^{2+}$ can produce an interference on 119Sn^+ . This problem was avoided by using 118Sn^+ to monitor the Sn levels during the measurements. In addition, we found that large amounts of Fe in the sample solutions can generate erroneous Te isotope data, presumably due to a matrix effect. As a result, sample solutions must display Fe/Te ratios of 5 or less, to be suitable for isotopic analysis.

3. Results and discussion

3.1. Yields and blanks of the sample preparation method

The main advantages of the "HCl-method" compared to the "HF-method" are the superior Te yields (∼100% versus

 $~\sim$ 85%) and the higher capacity of the columns for Fe-rich samples. The "HF-method", however, appears to produce cleaner sample solutions in general, which are free of residual Cd. The "HF-method" was therefore preferred for the separation of Te from Cd-rich samples, such as chondritic meteorites.

The Te yield of the second chromatographic separation (with Tru-SpecTM resin columns) was about 80%. The biggest problem of this step was obtaining a complete dissolution of the sample in 0.5 M HCl. For iron meteorites, where the isolation of Te comprises solvent extraction, the "HCl-method" and Tru-SpecTM resin chromatography, the total Te yield was about 55% on average. The solvent extraction procedure alone had a yield of ∼75%.

To optimize the yield of the column separations (especially the "HF-method"), it is advantageous to hold the use of $HNO₃$ during the sample dissolution to a minimum. The yields were furthermore significantly improved by leaching of the precipitates that formed in the final sample solutions before loading of the ion-exchange columns. Although Te can be highly volatile under some conditions, we did not observe any evaporative loss of Te in the present study.

Total procedural blanks were routinely determined on blank solutions using Cd as an internal standard. For iron meteorites, the blanks were $\leq 300 \text{ pg}$ Te, but for all other samples the contamination was significantly lower at <30 pg Te. Given that our analyses of natural samples typically utilized >50 ng of Te, these blank levels are insignificant.

3.2. Precision and accuracy of isotope ratio measurements for standard solutions

The reproducibility (2σ) of isotopic measurements conducted on a single measurement session (8–12 h) using 100–150 ng/ml Te solutions was typically ±4500 ppm for 120 Te/ 128 Te, ± 140 ppm for 122 Te/ 128 Te, ± 100 ppm for 124 Te/ 128 Te, ± 30 ppm for 126 Te/ 128 Te and ± 60 ppm for 130 Te/ 128 Te. Any single run generally displayed within-run errors (2σ mean) that were equal to or better (by up to a factor of 2) than the within-day precision.

The long-term reproducibility (2σ) was evaluated from the data collected over a period of 10 months (October 2001–July 2002) on 32 measurement sessions, each comprising 6–30 individual runs (Fig. 1). For 126 Te/ 128 Te, the long-term reproducibility is about ± 100 ppm. If only the results of the last 4 months (April 2002–July 2002) are considered, the reproducibility is significantly better at about \pm 30 ppm, which is identical to the precision achievable on a single day (Fig. 1). During this latter 4-month period, all measurements utilized the same skimmer cone and particular care was taken to ensure that the sample introduction system and the torch were clean, whereas four different skimmer cones (of the same design) were used in the previous measurement sessions. These results indicate that proper attention to such "details" can significantly improve the quality of the analytical data.

Fig. 1. Mean 126 Te/ 128 Te ratios obtained on different measurement sessions, plotted in chronological order. Each data point represents the average of 6–30 individual analyses of a Te standard solution. Errors bars (2σ) denote the external reproducibility. Results are shown for a total of 32 measurement sessions. The data on the left-hand side were collected from October 2001 to March 2002 with four different skimmer cones, whereas the results on the right were obtained with a single skimmer from April 2002 to July 2002.

Previous Te isotope studies applied various internal normalization schemes to correct for the instrumental mass fractionation and a direct comparison of the data is therefore not possible. The results of this study were originally normalized to 125 Te/ 128 Te = 0.22204 [\[28\]](#page-11-0) with the exponential law, because this produces data for 126 Te without requiring a Sn interference correction. For comparison, we renormalized our results to 124 Te/ 128 Te = 0.14853 [\[28,51\]](#page-11-0) and the same normalization was also applied to six previously published datasets [\(Table 4\).](#page-6-0) The measured Te isotope compositions of this study are identical, within error, to the results of Smith and De Laeter [\[21\]](#page-10-0) and Wachsmann and Heumann [\[27\],](#page-11-0) which were obtained by TIMS and N-TIMS, respectively. This agreement is not very conclusive, however, due to the large uncertainties of the latter results. The relatively precise MC-ICPMS and TIMS data of Lee and Halliday [\[28\]](#page-11-0) and De Laeter [\[51\]](#page-11-0) also show good agreement with the present results, but there exist small differences (e.g. for 122Te , 128Te or 130Te , 128Te). The data of Loss et al. [\[52\]](#page-11-0) differ significantly from our results. This discrepancy is probably an artifact of the mass discrimination correction, because Loss et al. [\[52\]](#page-11-0) obtained results that are consistently lower than our data for ratios where the lighter isotopes are numerators and vice versa [\(Table 4\).](#page-6-0)

For our purposes, the measurement of 126 Te is of primary importance. Our results for this isotope have a precision that is a factor of two better than the MC-ICPMS data of Lee and Halliday [\[28\].](#page-11-0) For the other isotopes both studies achieve a similar reproducibility. It must be noted, however, that our precision is based on data collected over a period of 4 months (Fig. 1), whereas Lee and Halliday [\[28\]](#page-11-0) evaluated only the results of a few measurement sessions. Compared to TIMS and N-TIMS, the MC-ICPMS data have a precision for 126 Te that is generally better by a factor of at least 5.

Based on the results summarized in [Table 4, w](#page-6-0)e have made a new estimate of the isotopic abundances and the atomic

^a Mean values of 12 measurement sessions (291 runs) conducted from April 2002 to July 2002.

b Uncertainities are 2σ standard deviations.

^c Isotopic abundances and uncertainties are calculated by [\[28\]](#page-11-0) from the data listed in [\[51\].](#page-11-0)

weight of Te (Table 5). Our results show good agreement with the data of De Laeter [\[51\]](#page-11-0) and Lee and Halliday [\[28\]](#page-11-0) but the isotopic abundances recommended by IUPAC [\[53\]](#page-11-0) differ significantly from our values. The IUPAC data, however, appear to be based mainly on the results of Smith et al. [\[20\],](#page-10-0) and the latter study used a different method for the correction of the instrumental mass fractionation.

The atomic weight of Te that was calculated from our results is identical, within error, to the values estimated by Lee and Halliday [\[28\]](#page-11-0) and IUPAC [\[53\].](#page-11-0) In the latter case, the agreement is not conclusive, due to the large uncertainty of the IUPAC estimate. Significant differences are apparent in comparison to the values published by De Laeter [\[51\]](#page-11-0) and Smith et al. [\[20\],](#page-10-0) and these are mainly due to variations in the calculated abundances of 130 Te.

3.3. Precision and accuracy of isotope ratio measurements for geological samples doped with Te

Three different types of synthetic samples were used to test and evaluate the accuracy of the isotopic measurements. A number of analyses utilized a terrestrial igneous rock (a diorite), which was doped with various amounts of Te. Further measurements were conducted with a Te-free chondrite matrix that was doped with Te. The chondrite matrix was obtained by the collection of all Te-free matrix fractions, which were eluted whilst solutions of the meteorites Allende and Murchison were processed through the primary anion-exchange separation. These matrix fractions were dried down, doped with Te and then further processed as normal samples. In addition, we also analyzed a synthetic iron meteorite, which was made up from 4.6 g Fe and 0.4 g Ni, which were doped with 0.8μ g Te. Because the synthetic samples have no Te of extraterrestrial origin, their Te isotope compositions should display ε^{1XX} Te = 0 for all isotopes. The Te/matrix ratios of these synthetic samples are similar to those of natural meteorite samples $(3.3 \times 10^{-7} - 2.7 \times 10^{-6})$.

The doped diorite samples were processed using both the "HF-method" and "HCl-method". For some additional samples, the isolation of Te utilized an ion-exchange procedure that is also used in our laboratory for the separation of W and Zr from meteorites ("W–Zr-method") [\[30,54\].](#page-11-0) In this case, Te was eluted from the primary anion-exchange column of the "W–Zr-method" with $1 M HNO₃$, following the elution of the other transition metals.

With one exception all individual analyses of the Te-doped diorite vielded ε^{1XX} Te values that are indistinguishable. within error, from the expected result, ε^{1XX} Te = 0 and this is also true for the mean values (Fig. 2, [Table 6\).](#page-8-0) Only a

Fig. 2. Results obtained for ε^{126} Te for the different synthetic samples (Te-doped diorite, Te-doped chondrite matrix, and a synthetic iron meteorite doped with Te). Error bars (2σ) denote the external reproducibility of the standard for a particular measurement session. Different symbols represent individual digestions.

Table 6 Mean Te isotope compositions of synthetic samples (doped with Te)

Sample	Te/matrix	ε^{120} Te $\pm 2\sigma$	ε^{122} Te + 2σ	ε^{124} Te + 2σ	ε^{126} Te + 2σ	ε^{130} Te + 2σ
Te standard		0.0 ± 45.0	0.00 ± 1.40	0.00 ± 1.00	0.00 ± 0.30	0.00 ± 0.60
Iron-meteorite matrix	1.6×10^{-7}	$-1.8 + 24.7$	-0.93 ± 1.18	-0.36 ± 0.54	-0.10 ± 0.25	0.30 ± 0.91
Chondrite matrix	1.2×10^{-6} to 1.7×10^{-6}	$-0.2 + 14.4$	-0.47 ± 0.50	-0.24 ± 0.74	-0.07 ± 0.20	0.46 ± 0.88
Diorite matrix	3.3×10^{-7} to 2.7×10^{-6}	$-42+652$	$-0.85 + 1.37$	-0.76 ± 1.21	-0.16 ± 0.38	$0.90 \pm 0.61^{\circ}$

^a Mean of two measurements, 2σ error of the single measurements is shown.

single 124 Te/ 128 Te result for a doped diorite differs significantly from the standard. It could be argued that some of the results have slightly negative $\varepsilon^{122-126}$ Te and positive ε^{130} Te values, but this is not clearly resolvable given the analytical errors ([Fig. 2,](#page-7-0) Table 6). The samples that were processed with the "W-Zr-method" display results identical to those obtained with the "HF-method" and the "HCl-method", but the chemical yield of the former separation technique was not reproducible.

The ^{1XX}Te/¹²⁸Te ratios measured for the Te-doped chondrite matrix samples were also identical to the Te standard solution in all cases [\(Fig. 2,](#page-7-0) Table 6). The same result was obtained for the simulated iron meteorite, from which the Te was isolated by solvent extraction and the "HCl-method" ([Fig. 2,](#page-7-0) Table 6). Most ε^{130} Te values again show a slight positive trend, but this is not significant given the analytical errors (Table 6). These results clearly indicate that our chemical and mass spectrometric methods can provide accurate isotope data for all Te isotopes, even following separation of Te from complex natural samples.

3.4. Results for chondrites, iron meteorites and terrestrial sulfides

The accuracy and precision of our methods was further verified by repeated analyses of the Allende chondrite, the iron meteorite Canyon Diablo, and two terrestrial sulfides, pyrrhotite and pyrite (Figs. 3 and 4 and Table 7). Pyrrhotite was chosen for these measurements because of its chemical similarity to the troilite of iron meteorites. Most Allende samples were processed with the "HF-method", but the "HCl-method" was applied in some cases. Isolation of Te from the sulfides utilized the "HCl-method" and the Canyon Diablo sample (5 g of metal with small amounts of sul-

-2 -1 0 1 2 Te Standard ε 126 Te (metal + sulfide) pyrite pyrrhoti te terrestrial sulfides Canyon Diablo (IA) "HCl-method" "HFmethod" Allende (CV)

Fig. 3. Results obtained for ε^{126} Te for the Allende chondrite, the Canyon Diablo iron meteorite and terrestrial sulfides. Error bars (2σ) represent the external reproducibility of the standard for a particular measurement session. Different symbols denote individual digestions. Open squares are used for mean values $\pm 2\sigma$ reproducibility, whereas open circles are for averages $\pm 2\sigma$ mean uncertainties. The 2σ mean errors were only calculated for datasets with more than six individual measurements.

Table 7 Mean Te isotopic compositions of samples

Sample Allende (CV)		Canyon Diablo (IA)	Pyrrhotite	Pyrite	
ε^{120} Te $\pm 2\sigma$	0.1 ± 29.5	-4.7 ± 34.7	-28.8 ± 34.3	-6.1 ± 46.3	
ε^{122} Te $\pm 2\sigma$	-0.58 ± 1.40	-0.31 ± 1.41	-0.86 ± 1.56	-0.07 ± 2.05	
ε^{124} Te + 2σ	-0.27 ± 0.87	0.34 ± 0.62	-0.34 ± 0.60	-0.10 ± 1.43	
ε^{126} Te $\pm 2\sigma$	-0.01 ± 0.38	0.01 ± 0.13	0.14 ± 0.79	0.07 ± 0.54	
ε^{130} Te $\pm 2\sigma$	0.44 ± 0.70	0.35 ± 0.66	0.24 ± 0.41	0.49 ± 0.75	
# measurements	17 (16 for $120,122$ Te)			13	
# digestions					

Fig. 4. Results obtained for ε^{120} Te, ε^{122} Te, ε^{124} Te, and ε^{130} Te for the Allende chondrite, the Canyon Diablo iron meteorite and terrestrial sulfides. All symbols are used as in [Fig. 3.](#page-8-0)

fides) was processed by solvent extraction followed by the "HCl-method".

All average Te isotope compositions that were determined for these three samples and the overwhelming majority of the individual results are identical, within the 2σ errors, to the results obtained for the Te standard ([Figs. 3 and 4](#page-8-0) and [Table 7\).](#page-8-0) Some very minor offsets are nonetheless apparent: the ε^{122} Te values of Allende and the pyrrhotite are on the low side, whereas ε^{130} Te is slightly too high for all samples. It is possible that the low ε^{122} Te results are an artifact of residual uncorrected mass discrimination, because 125 Te/ 128 Te was used for internal normalization. The slight positive offset in ε^{130} Te could be due to isobaric interferences from 130 Ba. The measured Ba/Te ratios of all samples, however, were sufficiently low, such that the accuracy of the data should not be compromised by the interference. Given these small deviations, any interpretation of Te isotope compositions should consider the 2σ rather than the 2σ mean uncertainties, to avoid the identification of small isotopic anomalies that may be artifacts of very minor spectral interferences and/or matrix effects.

It is particularly noteworthy that the reproducibility of the sample data is similar to that obtained for pure standard solution ([Table 7\).](#page-8-0) The comparison of the present results with TIMS literature data demonstrates the superiority of the new methods for precise Te isotopic measurements of bulk meteorites. For the determination of ε^{126} Te, the MC-ICPMS techniques achieve reproducibilities that are about two orders of magnitude better than results obtained by TIMS. The present analyses are furthermore about 15 times more precise for the determination of ε^{122} Te, ε^{124} Te, and ε^{130} Te and circa 4 times more precise for the measurement of ε^{120} Te [\[2,20,21\].](#page-10-0)

The data demonstrate that terrestrial Te standards, terrestrial sulfides, the Allende carbonaceous chondrite and the iron meteorite Canyon Diablo have identical Te isotope compositions. This suggests that most solar system materials may be homogeneous in terms of Te isotopes, which is in agreement with the results of previous isotopic studies conducted by TIMS [\[2,20,21\]. T](#page-10-0)he agreement between the standards and the terrestrial sulfides furthermore confirms that the new techniques also generate accurate Te isotope compositions for such samples.

All of the data discussed above was collected with "standard" skimmer cones, which feature a relatively narrow exit angle (NA-type Ni cones, Nu Instruments part #319 284). A few additional measurements were performed to investigate whether an alternative skimmer cone, which has a much wider exit angle (WA-type Ni cone, Nu Instruments part #319 497), could be used instead. The main advantage of the WA-type skimmers is their superior transmission efficiency. As a test, we analyzed solutions of two chondrites and a pyrrhotite with both skimmer cones. The results obtained with the NA skimmers display no or only small deviations from ε^{126} Te = 0 ([Fig. 5\).](#page-10-0) When the interface was fitted with a WA cone, the same sample solutions, however, displayed positive deviations in ε^{126} Te values for Allende (ε^{126} Te = 0.66 ± 0.23), Murchison (ε^{126} Te = 0.77 ± 0.23) and the terrestrial pyrrhotite (ε^{126} Te = 1.28 ± 0.23) [\(Fig. 5\).](#page-10-0) Very similar results were obtained if different normalization schemes were used for the mass bias correction.

Fig. 5. Results obtained for ε^{126} Te for the chondrites Allende and Murchison and a terrestrial sulfide (pyrrhotite) using either a normal narrow-angle (open squares) or a wide-angle skimmer cone (filled squares), which provides better sensitivity. Error bars (2σ) denote the external reproducibility of the standard.

The reason why the WA skimmers appear to be associated with slightly higher ε^{126} Te values that are likely to be erroneous, is unclear at present. It is possible, that the data are biased by enhanced interferences from oxides, nitrides and argides or more severe matrix effects. Clearly, these results indicate (1) that NA-type skimmer cones should be used for high-precision Te isotopic measurements and (2) that extreme care is required in the development and application of very precise and accurate isotopic measurement techniques that utilize MC-ICPMS.

4. Conclusions

A new MC-ICPMS technique for high-precision Te isotope ratio measurements is reported. This technique permits isotopic analyses of small quantities of Te (100–150 ng) isolated from bulk meteorites and sulfide mineral separates with reproducibilities (2 σ) of about \pm 4500 ppm for ¹²⁰Te/¹²⁸Te, ± 140 ppm for 122 Te/ 128 Te, ± 100 ppm for 124 Te/ 128 Te, \pm 30 ppm for ¹²⁶Te/¹²⁸Te, and \pm 60 ppm for ¹³⁰Te/¹²⁸Te. Compared to previous TIMS studies, the method therefore achieves a reproducibility for the determination of 126 Te anomalies in natural samples that is improved by about two orders of magnitude. For other Te isotopes, the MC-ICPMS data are more precise by factors of about 4–15.

With its excellent reproducibility, the new technique provides unparallel analytical capabilities for the resolution of extremely small differences in the abundance of ¹²⁶Te in meteorites, which could reflect radiogenic ingrowth from the decay of 126 Sn. In addition, it also permits the identification of small and previously unresolvable nucleosynthetic

Te isotope anomalies. As such, it paves the way for new cosmochemical investigations of Te isotope compositions in various extraterrestrial materials. Bulk samples of two terrestrial sulfides, the carbonaceous chondrite Allende, and the iron meteorite Canyon Diablo were analyzed and found to display Te isotope compositions that are identical, within error, to the terrestrial standard.

Acknowledgements

We thank Der-Chuen Lee, Maria Schönbächler, Sarah Woodland and Don Porcelli for many helpful discussions and Glen L. MacPherson for providing samples from the collection of the Smithsonian Institution of Washington. The two anonymous referees are thanked for their helpful comments and suggestions. Financial support was provided by the ETH Forschungskomission and the Schweizerische Nationalfonds (SNF).

References

- [1] F. Oberli, P. Gartenmann, M. Meier, W. Kutschera, M. Suter, G. Winkler, Int. J. Mass. Spectrom. 184 (1999) 145.
- [2] J.R. De Laeter, K.J.R. Rosman, Meteorit. Planet. Sci. 19 (1984) 217.
- [3] Y.-Z. Qian, P. Vogel, G.J. Wasserburg, Astrophys. J. 506 (1998) 868.
- [4] A.G.W. Cameron, J.W. Truran, Icarus 30 (1977) 447.
- [5] A.P. Boss, H.A.T. Vanhala, Phil. Trans. R. Soc. Lond. A 359 (2001) 2005.
- [6] H.A.T. Vanhala, A.P. Boss, Astrophys. J. 575 (2002) 1144.
- [7] F.H. Shu, H. Shang, A.E. Glassgold, T. Lee, Science 277 (1997) 1475.
- [8] T. Lee, F.H. Shu, H. Shang, A.E. Glassgold, K.E. Rehm, Astrophys. J. 506 (1998) 898.
- [9] H. Shang, F.H. Shu, T. Lee, A.E. Glassgold, Space Sci. Rev. 92 (2000) 153.
- [10] A. Masuda, O. Lu, Meteorit. Planet Sci. 33 (1998) A99.
- [11] N. Dauphas, B. Marty, L. Reisberg, Astrophys. J. 565 (2002) 640.
- [12] Q. Yin, S.B. Jacobsen, K. Yamashita, Nature 415 (2002) 881.
- [13] J.H. Chen, D.A. Papanastassiou, G.J. Wasserburg, Lunar Planet. Sci. Conf. 34 (2003) 1789.
- [14] C. Sanloup, J. Blichert-Toft, P. Télouk, P. Gillet, F. Albarède, Earth Planet. Sci. Lett. 184 (2000) 75.
- [15] Q. Yin, S.B. Jacobsen, J. Blichert-Toft, P. Télouk, F. Albarède, Lunar Planet. Sci. Conf. 32 (2001) 2128.
- [16] D.-C. Lee, A.N. Halliday, Meteorit. Planet. Sci. 37 (2002) A85.
- [17] H. Becker, R.J. Walker, Chem. Geol. 196 (2003) 43.
- [18] H. Becker, R.J. Walker, Nature 425 (2003) 152.
- [19] M. Schönbächler, D.-C. Lee, A.N. Halliday, M. Rehkämper, M.A. Fehr, B. Hattendorf, D. Günther, Earth Planet, Sci. Lett. 216 (2003) 467.
- [20] C.L. Smith, K.J.R. Rosman, J.R. De Laeter, Int. J. Mass. Spectrom. Ion Phys. 28 (1978) 7.
- [21] C.L. Smith, J.R. De Laeter, Meteorit. Planet. Sci. 21 (1986) 133.
- [22] R.V. Ballad, L.L. Oliver, R.G. Downing, O.K. Manuel, Nature 277 (1979) 615.
- [23] L.L. Oliver, R.V. Ballad, J.F. Richardson, O.K. Manuel, Meteorit. Planet. Sci. 14 (1979) 503.
- [24] L.L. Oliver, R.V. Ballad, J.F. Richardson, O.K. Manuel, J. Inorg. Nucl. Chem. 43 (1981) 2207.
- [25] R. Maas, R.D. Loss, K.J.R. Rosman, J.R. De Laeter, R.S. Lewis, G.R. Huss, G.W. Lugmair, Meteorit. Planet. Sci. 36 (2001) 846.
- [26] S. Richter, U. Ott, F. Begemann, Nature 391 (1998) 261.
- [27] M. Wachsmann, K.G. Heumann, Int. J. Mass. Spectrom. Ion Process. 114 (1992) 209.
- [28] D.-C. Lee, A.N. Halliday, Int. J. Mass. Spectrom. Ion Process. 146/147 (1995) 35.
- [29] C. Münker, S. Weyer, K. Mezger, M. Rehkämper, F. Wombacher, A. Bischoff, Science 289 (2000) 1538.
- [30] M. Schönbächler, M. Rehkämper, A.N. Halliday, D.-C. Lee, M. Bourot-Denise, B. Zanda, B. Hattendorf, D. Günther, Science 295 (2002) 1705.
- [31] J. Blichert-Toft, M. Boyet, P. Télouk, F. Albarède, Earth Planet. Sci. Lett. 204 (2002) 167.
- [32] D.-C. Lee, A.N. Halliday, Nature 378 (1995) 771.
- [33] B. Luais, P. Télouk, F. Albarède, Geochim. Cosmochim. Acta 61 (1997) 4847.
- [34] T. Hirata, Analyst 121 (1996) 1407.
- [35] N.S. Belshaw, X.K. Zhu, Y. Guo, R.K. O'Nions, Int. J. Mass. Spec. 197 (2000) 191.
- [36] C.N. Maréchal, P. Télouk, F. Albarède, Chem. Geol. 156 (1999) 251.
- [37] A.D. Anbar, K.A. Knab, J. Barling, Anal. Chem. 73 (2001) 1425.
- [38] F. Wombacher, M. Rehkämper, K. Mezger, C. Münker, Geochim. Cosmochim. Acta 67 (2003) 4639.
- [39] M. Rehkämper, M. Frank, J.R. Hein, D. Porcelli, A. Halliday, J. Ingri, V. Liebetrau, Earth Planet. Sci. Lett. 197 (2002) 65.
- [40] A.N. Halliday, D.-C. Lee, J.N. Christensen, M. Rehkämper, W. Yi, X. Luo, C.M. Hall, C.J. Ballentine, T. Pettke, C. Stirling, Geochim. Cosmochim. Acta 62 (1998) 919.
- [41] M. Rehkämper, M. Schönbächler, C.H. Stirling, Geostand. Newslett. 25 (2001) 23.
- [42] T. Walczyk, F. von Blanckenburg, Science 295 (2002) 2065.
- [43] A.S. Ellis, T.M. Johnson, T.D. Bullen, Science 295 (2002) 2060.
- [44] M. Rehkämper, A.N. Halliday, Geochim. Cosmochim. Acta 63 (1999) 935.
- [45] K. Kawamura, H. Ito, T. Tanabe, Jpn. Analyst 19 (1970) 824.
- [46] S. Terashima, Geostand. Newslett. 25 (2001) 127.
- [47] C.L. Smith, J.R. De Laeter, K.J.R. Rosman, Geochim. Cosmochim. Acta 41 (1977) 676.
- [48] W. Yi, A.N. Halliday, D.-C. Lee, J.N. Christensen, Geochim. Cosmochim. Acta 59 (1995) 5081.
- [49] K. Habfast, in: I.T. Platzner (Ed.), Modern Isotope Ratio Mass Spectrometry, Wiley, Chichester, UK, 1997, p. 11.
- [50] J.R. Basford, J.C. Dragon, R.O. Pepin, M.R. Coscio Jr., V.R. Murthy, Geochim. Cosmochim. Acta Suppl. 4 (1973) 1915.
- [51] J.R. De Laeter, Astrophys. J. 434 (1994) 695.
- [52] R.D. Loss, J.R. De Laeter, K.J.R. Rosman, T.M. Benjamin, D.B. Curtis, A.J. Gancarz, J.E. Delmore, W.J. Maeck, Earth Planet. Sci. Lett. 89 (1988) 193.
- [53] K.J.R. Rosman, P.D.P. Taylor, J. Anal. At. Spectrom. 13 (1998) N45.
- [54] D.-C. Lee, A.N. Halliday, Chem. Geol. 169 (2000) 35.