

Determination of ultra-low Nb, Ta, Zr and Hf concentrations and the chondritic Zr/Hf and Nb/Ta ratios by isotope dilution analyses with multiple collector ICP-MS

Stefan Weyer^{a,b}, Carsten Münker^{a,*}, Mark Rehkämper^{a,c}, Klaus Mezger^a

^a*Institut für Mineralogie, Zentrallabor für Geochronologie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 24, D-48149, Münster, Germany*

^b*Max-Planck-Institut für Chemie, Postfach 3060, 55020, Mainz, Germany*

^c*ETH Zürich, Institute of Isotope Geology and Mineral Resources, NO C61, CH-8092, Zurich Switzerland*

Received 14 August 2001; accepted 12 June 2002

Abstract

This study presents a new technique for the determination of precise and accurate concentrations of the high field strength elements (HFSE) Zr, Hf, Nb and Ta. The Ta concentration was determined for the first time by the isotope dilution (ID) technique using an isotopic tracer enriched in ¹⁸⁰Ta. Zirconium and hafnium concentrations were also determined by ID, whereas the concentration of the mono-isotopic Nb was measured relative to Zr, after quantitative separation of the HFSE from the matrix. The analyses were performed on a Micromass Isoprobe multiple collector (MC) inductively coupled plasma source mass spectrometer (ICP-MS). Only about 0.5 ng of Zr, Hf and Ta are necessary to perform an ID analysis with an external reproducibility of better than 1% on the MC-ICP-MS using Faraday collectors. This new technique enables the precise and accurate determination of the HFSE concentrations even in ultra-depleted rocks like peridotites. The absolute uncertainties for ultra-depleted rocks, particular for Ta concentrations at the sub-ng level are limited by blanks and sample heterogeneities and not by the precision of the measurement.

New and more precise Zr, Hf, Nb and Ta concentration data for the geological standard reference materials BHVO-2, BCR-2, BE-N, BIR-1 and the ultra-depleted standards PCC-1 and DTS-1 are presented. External reproducibilities of the concentration measurements are 0.4–5% for basalts and 2–10% for depleted peridotite samples (2 RSD), depending on element and concentration. The Zr/Hf and Nb/Ta ratio of the solar system was determined based on new data for two chondrites and six achondrites. The chondritic Nb/Ta of 17.6 ± 1.0 determined in this study agrees with previous predicted values from the literature. However, the chondritic Zr/Hf of 34.2 ± 0.3 determined in this study differs from previous literature values.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: High field strength elements; Niobium; Tantalum; Multiple collector ICP-MS; Isotope dilution; Chondritic ratio

1. Introduction

The cations of the elements Zr, Hf, Nb and Ta are relatively small and highly charged and are grouped as high field strength elements (HFSE). The iso-valent element pairs Zr–Hf and Nb–Ta have very

* Corresponding author. Fax: +49-251-83-38397.

E-mail address: muenker@nwz.uni-muenster.de (C. Münker).

similar ionic radii and display, like other “geochemical twins” (e.g., Y and Ho or Sm and Hf), a very coherent behaviour during igneous processes. Their ratios in mantle-derived rocks have long been regarded as constant and indistinguishable from the chondritic values of $Zr/Hf = 36.3 \pm 3$ and $Nb/Ta = 17.6 \pm 2$ (Jochum et al., 1986). More recent studies employing improved analytical techniques indicate that mantle-derived magmas in certain geochemical environments and tectonic settings are characterised by distinct variations in Zr/Hf (e.g., Xie and Kerrich, 1995; Niu and Batiza, 1997; David and Schiano, 2000) and Nb/Ta ratios (e.g., Plank and White, 1995; Stolz et al., 1996; Niu and Batiza, 1997; Münker, 1998). These observations led to an increased interest in using Zr/Hf and Nb/Ta ratios as tools for the study of geochemical processes in the Earth’s mantle.

Mantle-derived melts usually show only small variations in Nb/Ta or Zr/Hf , which reflect different processes related to the source, melt generation and contamination. The mantle source itself, sampled by orogenic peridotites and mantle xenoliths may give a more direct view into mantle processes, but trace element concentrations are very low and therefore difficult to measure accurately. Due to their extremely low concentrations in mantle rocks, the concentrations of the HFSE, particularly Nb and Ta, are virtually impossible to measure precisely with conventional methods. The most precise Nb and Ta concentrations of samples with low concentrations of these elements (e.g., meteorites and mantle rocks) were determined using INAA and SSMS (Jochum et al., 1986, 1989, 2000a) or using inductively coupled plasma source mass spectrometer (ICP-MS) (Ionov et al., 1993, 1994; Eggins et al., 1997; Niu and Hekinian, 1997; Makishima et al., 1999; Yu et al., 2000). However, existing Nb and Ta data for peridotites are not precise enough (e.g., uncertainties for Ta are often $\sim 100\%$) to resolve differences in Nb/Ta ratios.

Here, the first isotope dilution (ID) data for Ta using an isotopic tracer enriched in ^{180}Ta are presented. Natural Ta has two stable isotopes, ^{180}Ta and ^{181}Ta . With an abundance of only 0.012 (2)% (De Bièvre and Taylor, 1993), ^{180}Ta is the rarest primordial nuclide of the solar system. Tantalum measurements were performed using a multiple collector inductively coupled plasma source mass spectrometer

(MC-ICP-MS), which is particularly suitable for measuring low concentrations, because of its high sensitivity. This technique produces much more precise and accurate Ta data than conventional methods and is even applicable for peridotites with very low Ta concentrations. Zirconium and Hf have been measured previously by isotope dilution using ID-ICPMS (Xie and Kerrich, 1995; David et al., 1999) or thermal ionisation mass spectrometry (TIMS) (Boswell and Elderfield, 1988). Since Nb is mono-isotopic and no Nb spike is available, it is presently impossible to analyse Nb by ID. Therefore, Nb concentrations were determined by measuring the Zr/Nb of the samples and using the well-determined Zr concentration for internal standardisation.

Possible applications of the new method are the precise determination of Nb/Ta , Zr/Hf and Zr/Nb ratios of the Earth’s different reservoirs, including depleted mantle rocks. A more precise and accurate knowledge of the ratios will contribute to the understanding of crust and mantle evolution. A further application that requires precise Zr/Nb ratios in low-concentration samples is the $^{92}\text{Nb}/^{92}\text{Zr}$ extinct nuclide system, which has become an interesting tool for constraining very early differentiation processes in the solar system (Münker et al., 2000; Sanloup et al., 2000; Yin et al., 2002). This isotope system has become accessible due to progress with new instrumental techniques that allow precise and accurate measurements of the Zr isotope composition even in small amounts of low concentration samples. The determination of precise Zr/Nb ratios together with the Zr isotope composition in extraterrestrial rocks and minerals opens the possibility to date early silicate fractionation processes on meteorite parent bodies and planets.

This study presents precise and accurate HFSE concentration data for low-concentration geological standard reference material and their Zr/Hf and Nb/Ta ratios together with new and more precise chondritic Zr/Hf and Nb/Ta ratios.

2. Analytical techniques

2.1. Sample digestion

For the depleted peridotites, ~ 1 g of sample powder was spiked with a mixed isotopic tracer

(HFSE-II, see below) and digested in a high-pressure asher system (HAP-S[®]) overnight in sealed quartz glass vessels using inverse aqua regia (5 ml HNO₃–3 ml HCl). At about 100 bar and 300 °C, the sample powder is converted to a gelatinous slurry with most of the silica bonds already cracked and spinel and sulphide phases dissolved. The slurry-like samples are then quantitatively transferred into a 90-ml Savillex[®] beakers, where they are evaporated and digested with a HF–HClO₄ (3:1) mixture on a hot plate (120 °C) overnight. At this stage, total sample spike equilibration is achieved. In order to get rid of insoluble fluorides, additional HClO₄ is added before the sample is evaporated to dryness. The sample is treated twice with 6 M HCl and traces of HF (~ 0.06 M, to avoid hydrolysis of Nb and Ta) to fume off all remaining HClO₄ as Cl₂. Subsequently, the samples are dissolved in 4 ml of 6 M HCl. About 1.2 ml of 0.5 M ascorbic acid is added to the clear solution, to reduce all Fe³⁺ to Fe²⁺, which changes the colour of the solution from greenish-yellow to pale bluish-green. Addition of ascorbic acid is necessary for large samples to avoid overloading the column with Fe³⁺, which has high partition coefficients on column 1 as compared to Fe²⁺. Prior to loading onto ion exchange columns, the samples are diluted with deionised water

to 12 ml of solution to obtain a mixture of 2 M HCl–0.05 M ascorbic acid.

Meteorite samples were digested for 24 h at 200° in Savillex[®] beakers placed inside Parr[®] bombs using a 1:1 mixture of HNO₃ and HF. All basaltic geological standards as well as the standard reference glasses were digested in 15 ml Savillex[®] beakers on a hot plate using 3 ml of conc. HF and 1 ml of HClO₄ per 100 mg of sample. The samples were evaporated twice with 6 M HCl and traces of HF before they were finally dissolved in 4 ml of 3 M HCl prior to loading onto ion exchange columns.

2.2. Chemical separation procedure

The chemical separation procedure that was used for the peridotite samples in this study is shown in Table 1. Basaltic samples and glass standards are loaded in 4 ml of 3 M HCl on column 1 and the matrix is separated with 10 ml of 3 M HCl. The separation is based on the new separation procedure developed by Münker et al. (2001). In the first step, the HFSEs including Zr, Hf, Nb, Ta and Ti are separated from the whole rock matrix on Eichrom Ln spec[®] columns (column 1). Lutetium can be separated (together with other HREE) from the sample

Table 1
HFSE (Zr, Hf, Nb, Ta) and Lu separation scheme for peridotite samples

Digestion of ca. 1 g of rock powder		
<i>Column 1 (5 × 0.5 cm = 1 cm³) Eichrom Ln-spec resin (100–200 mesh)</i>		
load	bulk sample	12 ml 2 M HCl/0.05 M ascorbic acid
rinse	matrix + LREE (Sm, Nd)	12 ml 2 M HCl
collect	Lu (HREE)	10 ml 6 M HCl
collect	HFSEs (Ti, Zr, Nb, Hf, Ta)	12 ml 2 M HF
<i>Column 2 (6 × 0.8 cm = 3 cm³) anion resin, Biorad AG1-X8 (100–200 mesh)</i>		
load	HFSEs	10 ml 2 M HF
collect	Ti, Zr, Nb and Hf	12 ml 6 M HNO ₃ /0.2 M HF
rinse	remaining Hf	12 ml 6 M HNO ₃ /0.2 M HF
collect	Ta	12 ml 6 M HNO ₃ /0.2 M HF/1% H ₂ O ₂
<i>Column 3 (identical to column 1) Eichrom Ln-spec resin (100–200 mesh)</i>		
load	HFSEs (without Ta)	4 ml 3 M HCl
rinse	rest of matrix	10 ml 3 M HCl, 10 ml 6 M HCl, 2 ml H ₂ O
rinse	Ti	~ 20–100 ml (depending on amount of Ti)
collect	Zr	0.45 M HNO ₃ /0.09 M citric acid/1% H ₂ O ₂
collect	Hf	50 ml 6 M HCl/0.06 M HF
		12 ml 2 M HF

matrix on this column. A small aliquot (5–10%) of the HFSE fraction is used for the Zr ID analysis and the measurement of the $^{93}\text{Nb}/^{90}\text{Zr}$ ratio. Since the $^{93}\text{Nb}/^{90}\text{Zr}$ ratio is used for the determination of the Nb concentration, any fractionation of Zr and Nb in the first column step has to be avoided. However, recovery after column 1 is usually >90% for both elements, even for 1 g of peridotite and >95% for smaller amounts of basaltic samples (see below).

The HFSE fraction from column 1 (minus the aliquot for the Nb/Zr analysis) is loaded on a 3-ml Biorad® AG 1X8 (100–200 mesh) anion resin (column 2) in order to separate Ta from the rest of the HFSE fraction. A quantitative separation of Ta from Hf is essential in this step, because ^{180}Hf causes an isobaric interference on the spiked ^{180}Ta . This is particularly critical in this study, because a ^{180}Hf spike was used for the Hf ID analyses. In this case, the $^{180}\text{Hf}/^{177}\text{Hf}$ ratio of the spiked sample must be known in order to apply a Hf interference correction to the measured $^{180}\text{Ta}/^{181}\text{Ta}$. However, even for natural Hf, the abundance of ^{180}Hf is 35%. Given the range of common Hf/Ta ratios in basalts and peridotites (ca. 5 to 100), the $^{180}\text{Hf}/^{180}\text{Ta}$ ratio in a sample that is spiked adequately with ^{180}Ta might be as high as 2000. However, the separation of Hf from Ta that is achieved on column 2 reduced the $^{180}\text{Hf}/^{180}\text{Ta}$ ratio to <0.01 in all investigated samples and therefore the Hf interference correction is minor. The separation of W from Ta is less critical, since the abundance of ^{180}W is only 0.12%. The $^{180}\text{W}/^{180}\text{Ta}$ ratios in spiked samples are usually <0.1, without any chemical separation and they are reduced on column 2 to values of <0.001. The effects of insufficient chemical separation and interference corrections are shown below.

After column 2, the remaining HFSEs (minus the Ta fraction) are reloaded onto the Ln spec® column (column 3, which is identical to column 1) in order to separate Hf from Ti and Zr. This step is crucial if the isotope composition of Hf is measured together with the concentration, because large amounts of Ti (e.g., 100 ppm, assuming a Ti/Hf ratio of ca. 2000 in the sample) can lower the transmission of Hf in the mass spectrometer by a factor of 10, cause irreproducible variations in the mass bias, and shift the measured isotope ratio by several epsilon units off the true value (Blichert-Toft et al., 1997; Münker et al., 2001).

The separation of Zr from Hf is not essential for Hf IC measurements by MC-ICP-MS, because Zr does not change the measured Hf isotope ratios. Nevertheless, Zr was separated from Hf to avoid contamination of the mass spectrometer with large amounts of Zr. Zirconium recovered from column 3 was collected and used to check the Zr ID measurement determined from the initial HFSE fraction from column 1. In all samples, the difference between Zr concentrations determined from the two different Zr cuts was less than 0.3%. Since natural Ti/Zr ratios are much lower (by a factor of 10–70) than Ti/Hf ratios, the concentration of Ti in the HFSE fraction of column 1 is usually not higher than 10 ppm and does not affect the Zr ID measurement. The pure Zr fraction from column 3 cannot be used for the determination of the Zr/Nb ratio and the Nb concentration, because Nb is lost during the Ti separation. For this reason, the separation of Hf from matrix, HREE, Ti and Zr cannot be achieved in one separation step on column 1 (Münker et al., 2001) if the Nb concentration is desired as well. Concerning Ta, a one-step separation on column 1 would be possible, because most of the Ta (>80%) would remain on the column and could be collected together with Hf. Tantalum could even be separated from Hf on column 1 with 6 M HCl–0.2 M HF. However, this procedure results in a Ta loss of up to 50% and the Ta–Hf separation is insufficient for the Ta measurement, requiring an additional separation step on column 2.

2.3. Reagents and blanks

Determining trace element abundances in low-concentration samples makes it absolutely necessary to decrease blanks from all possible sources in order to achieve lower pg levels for the total procedure. Particularly for Ta, a low blank is essential, since the Ta concentration in peridotites can be at the sub-ppb level. Since Ta sticks to Teflon® beakers, an extensive cleaning procedure is necessary and reagent blanks have to be reduced for the analysis of Ta.

For sample dissolution and Ta separation, the following reagents were used: quartz-distilled 6 M HCl, quartz-distilled conc. HNO_3 , double Teflon®-distilled conc. HF, Suprapure® HClO_4 , analytical grade H_2O_2 , analytical grade ascorbic acid and deionised water ($>10^{18}$ M Ω /cm). Additionally, analytical

grade citric acid is used for the separation of Hf from Ti and Zr, but not for the separation of Ta. All reagents that are used for the Ta separation have Ta blanks lower than 10 pg per amount of reagent used for one sample. Other possible blank sources are the quartz glass vessels of the HPA-S, the Savillex[®] beakers used for the final digestion and the collection of the Ta fraction from the column, centrifuge tubes, columns and resins. All equipment was cleaned carefully in several steps, always using HF as a cleaning reagent, since HF complexes Ta. The most effective cleaning procedure for the Savillex[®] beakers was heating first with aqua regia and then with 22 M HF–1 M HNO₃.

The total Ta blank was determined several times during the course of this study and varied from 70 to 110 pg. Therefore, the uncertainty of blank correction is a major limiting factor for sub-ng Ta samples. Total blanks for the other HFSE are 10–50 pg for Nb, 1–2 ng for Zr and 120–200 pg for Hf. The uncertainty in the measured Nb concentration due to the blank correction is <1% for all investigated samples. The uncertainties in the Zr and Hf concentrations due to the blank corrections are only significant for the samples PCC-1 and DTS-1 where they are about 1% for Zr and 2% for Hf.

2.4. Spike and standard solutions

Isotopically enriched tracers used for the isotope dilution analysis of Ta, Zr and Hf were purchased as Ta₂O₅, ZrO₂ and HfO₂ powders from Oak Ridge National Laboratories (USA) and they are enriched in the nuclides ¹⁸⁰Ta, ⁹⁴Zr and ¹⁸⁰Hf. The oxide powders were dissolved in 24 M distilled HF and a few drops conc. HNO₃ in 15 ml Savillex[®] beakers. These stock solutions were used to create a mixed spike solution (HFSE-I), which includes the isotopically enriched tracers of Ta, Zr and Hf in proportions that are suitable for isotope dilution analysis of a variety of rocks including basalts and peridotites. The mixed spike also contains an isotopic tracer enriched in ¹⁷⁶Lu, allowing the spike to be used for the application of the Lu–Hf isotope system. Since Lu is not stable in a strong HF solution, but all HFSEs and particularly Ta require some HF to remain in solution, a 2 M HNO₃–0.1 M HF solution was chosen for the final mixed spike. For low-concen-

tration samples like peridotites, a second, low-concentration mixed spike (HFSE II) was prepared by diluting HFSE-I by about a factor of 10. Additionally, two pure Ta spikes (Ta-I and Ta-II) with different concentration were produced from the stock ¹⁸⁰Ta spike.

In order to calibrate the mixed spike solutions, metal solutions of natural Ta, Zr and Hf were prepared gravimetrically from about 1 g each of the pure metals (>99.9% Ta, Zr and Hf, respectively) acquired from Ames Laboratory. The metal ingots were dissolved in a conc. HF–HNO₃ mixture.

A gravimetrically diluted mixed standard solution (HFSE-Std1) was prepared from the concentrated stock solutions. This diluted solution was used for spike calibration. The element concentrations of HFSE Std-1 are known within 0.1%. The mixed Zr–Nb solutions, which were used as standard solutions for the measurement of the ⁹³Nb/⁹⁰Zr ratio, were prepared in the same way from the concentrated metal solutions. The metal solutions were also used as isotopic standards.

2.5. Mass spectrometry

All measurements were performed on a multiple collector ICP-MS, the Micromass Isoprobe in Münster. The first multiple collector ICP-MS, the VG Elemental Plasma 54 and its fundamental features are described in numerous publications (Walder and Freedman, 1992; Walder et al., 1993; Blichert-Toft et al., 1997; Halliday et al., 1998). A multiple collector ICP-MS combines the ICP-source with a magnetic sector analyser and a multiple Faraday cup array that have been previously used in thermal ionisation mass spectrometry. The ICP source provides excellent ionisation efficiency (>80% for most elements), which makes the instrument ideal for analysing elements that have a high first ionisation energy and are difficult or impossible to analyse by TIMS (e.g., Ta, Zr and Hf). Additionally, the simultaneous ionisation allows the application of an external mass discrimination correction (Blichert-Toft et al., 1997; Maréchal et al., 1999; Scherer et al., 1999), which leads to higher precision and accuracy of measured isotopic ratios for elements that have only two isotopes like Ta.

The Micromass Isoprobe is a single focussing multiple collector ICP-MS, and it is equipped with a

hexapole collision cell, where sample ions collide with a neutral gas (Ar for elements with an atomic mass >40 amu), reducing the energy spread to 1–2 V. The instrument in Münster is also equipped with a Cetac[®] MCN 6000 desolvating microconcentric nebulizer. The hexapole collision cell, together with the MCN 6000 nebulizer, leads to a high sensitivity. A total ion beam intensity of ca. 0.1 nA is routinely generated from a 50-ppb solution of Ta or Hf, corresponding to 6.25×10^9 cps/ppm. For Zr, an ion beam of about 0.08 nA is obtained for a 50-ppb solution. The uptake rate is usually about 60 μ l/min, resulting in a transmission efficiency of about 3800 ppm for Ta and Hf. For most heavy elements (atomic mass >80 amu), 0.5 ng is enough to obtain a sufficiently precise ID analysis with an external run reproducibility of <0.5% (2 RSD).

The multiple collector block is equipped with nine faraday cups, four channeltrons and a Daly detector. Thus, ID analyses of extremely low-concentration samples (sub-ppb) can in principle be performed using the channeltrons or the Daly detector. However, sensitivity of the instrument was sufficient to perform all analyses, including the Ta ID analyses of the peridotite samples, by using only the faraday collectors.

The collector configurations and other detailed procedures of the Ta IC and ID, the Zr ID and Nb measurements are described below. The Hf ID (and IC) analyses were performed as described in M \ddot{u} nker et al. (2001).

2.6. Ta IC and ID measurements

The collector configuration for Ta measurements is shown schematically in Table 2a. Since adequately spiked samples have $^{180}\text{Ta}/^{181}\text{Ta}$ ratios of 0.03–0.003, isotope dilution analyses can be easily performed by

measuring both isotopes on faraday collectors (^{180}Ta on H2 and ^{181}Ta on H3). Because of the high dynamic range of the faraday cups, even natural Ta with an isotope ratio of ~ 0.00012 can be measured with this collector configuration. The isobaric interferences on ^{180}Ta from Hf and W are corrected by simultaneously measuring ^{178}Hf (Axial) and ^{182}W (H4), respectively.

The amount of Hf in the Ta fraction is monitored with the ratio $^{178}\text{Hf}/^{180}\text{total}$, where $^{180}\text{total} = ^{180}\text{Ta} + ^{180}\text{Hf} + ^{180}\text{W}$ (which is usually $\sim ^{180}\text{Ta} + ^{180}\text{Hf}$, because ^{180}W is negligible). Since the abundance of ^{178}Hf is lower than that of the interfering ^{180}Hf (by a factor of 1.32 for natural Hf and 1.8–3.0 for spiked samples), $^{178}\text{Hf}/^{181}\text{Ta}$ and $^{178}\text{Hf}/^{180}\text{Hf}$, which are used for the interference correction, have to be determined precisely if the Hf/Ta ratio is higher than about 0.1. Fig. 1a demonstrates this relationship. For a Hf monitor value of about 0.5, which corresponds to $^{180}\text{Hf}/^{180}\text{Ta}$ of 2, the uncertainty of the measured $^{178}\text{Hf}/^{181}\text{Ta}$ must be lower than 1% to get a <2% uncertainty on the $^{180}\text{Ta}/^{181}\text{Ta}$ ratio. This assumes that the $^{178}\text{Hf}/^{180}\text{Hf}$ is well known (either natural or spiked and determined prior to the Ta ID measurement). This precision can be attained in principle, but may be critical for low-abundance samples with low ion beams on the faraday detector. To ensure an accurate interference correction, both $^{180}\text{Ta}/^{181}\text{Ta}$ and $^{178}\text{Hf}/^{181}\text{Ta}$ were corrected for mass bias before the interference correction was applied. However, typical Hf monitor values of the Ta ID measurements were usually <0.01. Therefore, even a 100% error in the interference correction or no interference correction would produce an error <1.3–3% (depending on $^{178}\text{Hf}/^{180}\text{Hf}$ of the sample). A more precise Hf interference correction could be achieved by using an ion counter to monitor ^{178}Hf .

The very minor W interference is monitored with $^{182}\text{W}/^{180}\text{total}$. For a $^{182}\text{W}/^{180}\text{total}$ monitor of <1,

Table 2a
Collector configuration for Ta IC and ID analyses

Mass	177	178	180	181	182	185	187
Measured elements			Ta	Ta		Re	Re
Natural abundance (%)			0.012	99.99		37.40	62.60
Spike abundance (%)			4.3	95.7			
Interfering elements (natural abundance in %)	Hf (18.6)	Hf (27.3)	Hf (35.1)		W (26.3)		
Cup-configuration	L2 faraday	Ax faraday	H2 faraday	H3 faraday	H4 faraday	H5 faraday	H6 faraday

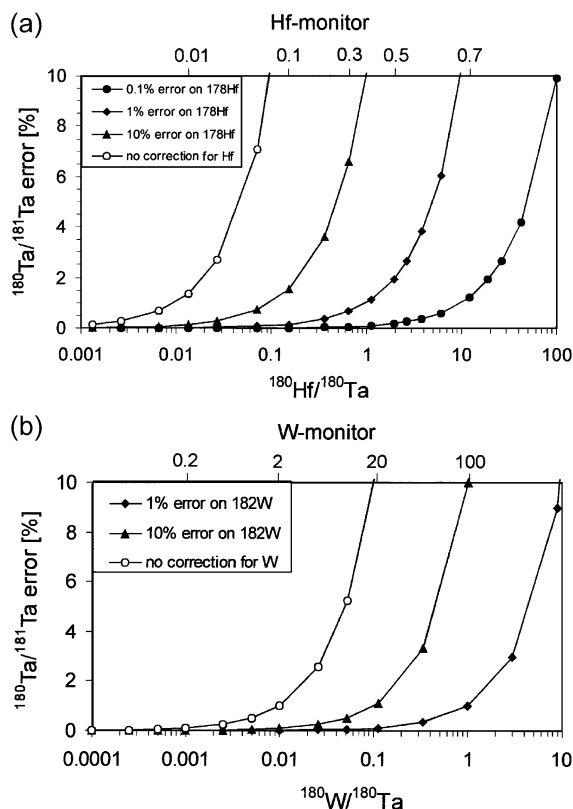


Fig. 1. (a) Effect of wrong Hf interference correction on the measured $^{180}\text{Ta}/^{181}\text{Ta}$ ratio. As long as the Hf monitor [$^{178}\text{Hf}/(^{180}\text{Ta} + ^{180}\text{Hf} + ^{180}\text{W})$] is < 0.01 , the Hf interference does not have a strong effect on the measured Ta isotope ratio, even if no correction is done. If the Hf monitor is > 0.1 , interference correction has to be done precisely. (b) Effect of wrong W interference correction on the measured $^{180}\text{Ta}/^{181}\text{Ta}$ ratio. For a small W monitor [$^{182}\text{W}/(^{180}\text{Ta} + ^{180}\text{Hf} + ^{180}\text{W}) < 1$], the W interference does not have a strong effect on the measured Ta isotope ratio, even if no correction is done. If the W monitor is > 1 , a precise interference correction can easily be performed, since the signal on the W monitor is high enough to be measured precisely on a Faraday detector.

which was the case for most samples in this study, the interference correction is $< 0.5\%$ of the measured $^{180}\text{Ta}/^{181}\text{Ta}$ ratio (Fig. 1b). Even higher amounts of W can be corrected accurately, since the natural $^{180}\text{W}/^{182}\text{W}$ is well known and $^{182}\text{W}/^{181}\text{Ta}$ can be measured very precisely for high W concentrations. Note that the calculated values for the Hf and W monitor in Fig. 1a and b are maximum values, since it is assumed that $^{180}\text{W} = 0$, for calculating the Hf monitor and $^{180}\text{Hf} = 0$, for calculating the W monitor.

The mass discrimination for all elements is corrected externally by simultaneously measuring $^{185}\text{Re}/^{187}\text{Re}$ (^{185}Re on faraday cup H5 and ^{187}Re on H6,) which is added to each sample prior to analysis and whose isotopic composition is well known. For the external mass bias correction, the exponential law of Russel et al. (1978) and a $^{185}\text{Re}/^{187}\text{Re}$ ratio of 1.6738 were used.

2.7. Zr ID measurements and the determination of the Nb concentration

The collector configuration for the Zr ID and Nb measurements is shown schematically in Table 2b. All isotopes including ^{93}Nb are measured on faraday collectors. The mixed spike solutions (HFSE I and HFSE II) are enriched in ^{94}Zr and the measured $^{94}\text{Zr}/^{90}\text{Zr}$ ratio is used to calculate the Zr concentration. An internal mass bias correction was applied by measuring the $^{92}\text{Zr}/^{90}\text{Zr}$ ratio and using the exponential law (Russel et al., 1978). In addition, an external mass bias correction was made by simultaneously measuring the $^{88}\text{Sr}/^{87}\text{Sr}$ of admixed NBS-987 Sr standard (using the exponential law and $^{88}\text{Sr}/^{87}\text{Sr}_{\text{true}} = 11.797$). The results of both correction procedures agree to within 0.1%, if the Mo concentration in the sample solution is low ($\text{Mo}/\text{Zr} < 0.1$).

Two Zr isotopes (^{92}Zr and ^{94}Zr) have isobaric interferences from Mo that need to be corrected by simultaneously measuring $^{95}\text{Mo}/^{90}\text{Zr}$. Since $^{95}\text{Mo}/^{90}\text{Zr}$ was not mass bias corrected before it was used for the interference correction, the interference correction on ^{92}Zr was only precise enough if Mo/Zr was below 0.1. Higher Mo/Zr ratios result in a $^{92}\text{Zr}/^{90}\text{Zr}$ ratio that is too low. If this value is used for the mass bias correction of the Zr ID ratio ($^{94}\text{Zr}/^{90}\text{Zr}$), the mass bias is undercorrected, resulting in erroneously high $^{94}\text{Zr}/^{90}\text{Zr}$ ratios and low Zr concentrations. Since Mo was not completely separated from Zr before the Zr ID measurement (a weak, but unpredictable separation is achieved on column I), the Mo/Zr ratios were too high in many peridotite and meteorite sample solutions, and an internal mass bias correction could not be applied. For these samples, the external (Sr) mass bias correction was used. Alternatively a different Zr isotope ratio ($^{91}\text{Zr}/^{90}\text{Zr}$) that is not affected by isobaric interferences can be

Table 2b

Collector configuration for Zr ID and Nb analyses

Mass	87	88	90	91	92	93	94	95	96
Measured elements	Sr	Sr	Zr	Zr	Zr	Nb	Zr		Zr
Natural abundance (%)	7.00	82.6	51.5	11.2	17.2	100	17.4		2.80
Spike abundance (%)			0.725	0.235	0.383		98.45		
Interfering elements	Rb				Mo		Mo	Mo	
Natural abundance in %	27.8				14.8		9.25	15.9	
Cup-configuration	L3 faraday	L2 faraday	Ax faraday	H1 faraday	H2 faraday	H3 faraday	H4 faraday	H5 faraday	H6 faraday

used for an internal mass bias correction (Münker et al., 2000).

The Nb concentration is calculated from the measured $^{93}\text{Nb}/^{90}\text{Zr}$ ratio and the Zr concentration determined by isotope dilution. The fractionation of $^{93}\text{Nb}/^{90}\text{Zr}$ within the interface of an ICP-MS includes two components: the elemental fractionation of Nb/Zr, which is mainly caused by different ionisation behaviour of the two elements, and the mass-dependent fractionation. The mass-dependent fractionation could be corrected in theory using $^{92}\text{Zr}/^{90}\text{Zr}$, but it varies slightly between different elements. Variations of the plasma conditions can change both the mass-dependent fractionation and the elemental fractionation, although variations of the latter are typically much more significant. A correction factor that considers both is determined before and after sample analysis by measuring $^{93}\text{Nb}/^{90}\text{Zr}$ standard solutions that have Nb/Zr ratios known to be better than 0.1%. Because the behaviour of both elements within the plasma interface seems to be slightly dependent on the Nb/Zr ratio, two different Nb/Zr standard solutions are used, covering the range of Nb/Zr for most samples (Fig. 2). The Nb concentration is calculated using the raw $^{93}\text{Nb}/^{90}\text{Zr}$ and not the mass bias-corrected ratio, since mass bias correction did not improve the stability of the measured $^{93}\text{Nb}/^{90}\text{Zr}$ during the course of the analyses. The determination of the sensitivity factor before and after each set of samples (or every 2–3 h) is sufficient, since $^{93}\text{Nb}/^{90}\text{Zr}$ stays constant to within 0.5% during the course of a day.

2.8. Spike calibration

The isotopic compositions of the pure Ta, Zr and Hf spikes, as well as the isotopic composition of Ta, Hf and Zr in the mixed spike (after chemical separa-

tion of the elements) were determined by multiple measurements of each spike solution (Table 3). In the case of Hf and Ta, there is a distinct difference between the isotopic composition measured in the mixed spike and the pure spike.

The isotope ratio of Ta in the pure spike, $(^{180}\text{Ta}/^{181}\text{Ta})_{\text{pure spike}}$, is 0.045197 (4), whereas in HFSE I, $(^{180}\text{Ta}/^{181}\text{Ta})_{\text{mixed spike}}$ is 0.044608 (17). For Hf, the difference was even bigger: $(^{180}\text{Hf}/^{177}\text{Hf})_{\text{pure spike}} = 382.4 \pm 0.3$ and $(^{180}\text{Hf}/^{177}\text{Hf})_{\text{mixed spike}} = 315.7 \pm 0.2$ (uncertainties are 2SE). The isotopic composition of Zr agrees between pure and mixed spike within analytical error and $(^{94}\text{Zr}/^{90}\text{Zr})_{\text{mixed spike}}$ was determined to be 135.7 ± 0.3 . The difference between mixed and pure spike for Hf and Ta is caused by the Zr spike, which contains about 150 ppm natural Hf and 50 ppm natural Ta. Therefore, it was important to determine not only

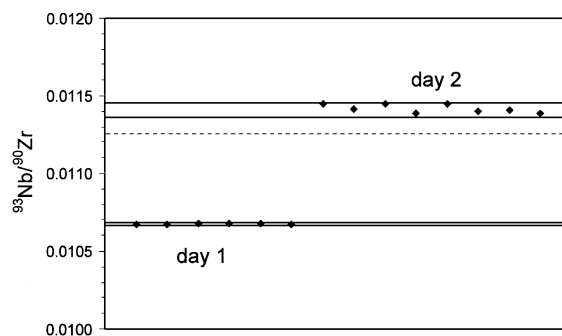


Fig. 2. Multiple analyses of $^{93}\text{Nb}/^{90}\text{Zr}$ in a standard solution (Zr/Nb = 172.7) used for the determination of a correction factor for the Zr–Nb analysis of high Zr/Nb samples. Reproducibility during 1 day (solid lines) can be as good as 0.025% (day 1) and is always better than 0.5%. The selected 2 days represent the maximum and the minimum value observed for the measured $^{93}\text{Nb}/^{90}\text{Zr}$ ratios (not mass bias corrected) of this solution. The total variation is about 6.5%. The dashed line represents the $^{93}\text{Nb}/^{90}\text{Zr}$ molar ratio in the solution. The in-run uncertainties are within the size of the symbols.

Table 3
Isotope compositions and concentrations of spikes used in this study

	Mixed spikes			Pure Ta-spikes		
	HFSE-I	HFSE-II		Ta-I	Ta-II	
	Spike ratio	Concentration ($\mu\text{g/g}$)	Concentration ($\mu\text{g/g}$)	Spike ratio	Concentration ($\mu\text{g/g}$)	Concentration ($\mu\text{g/g}$)
$^{180}\text{Ta}/^{181}\text{Ta}$	0.044608 (17)	0.09527 (13)	0.009424 (18)	0.045197 (8)	0.12281 (10)	0.01262 (2)
$^{94}\text{Zr}/^{90}\text{Zr}$	135.77 (17)	20.05 (2)	1.983 (3)			
$^{180}\text{Hf}/^{177}\text{Hf}$	315.84 (12)	1.0140 (12)	0.1003 (2)			
$^{176}\text{Lu}/^{175}\text{Lu}$	2.5224 (15)	0.3891 (8)	0.03849 (12)			

the elemental concentrations, but also the isotopic composition of the mixed spike.

In order to determine the concentration of each element in the mixed spike HFSE-I, various mixtures of the spike and the diluted Ames metal solution (HFSE Std1, described above) were prepared and analysed after chemical separation. The total amount of impurities in each metal used for the calibration is $<0.1\%$. Therefore, the uncertainty of elemental concentrations in the pure metal solutions is $<0.1\%$. However, the Zr metal contains 102 ppm Hf and 25 ppm Ta (measured in a 10 ppm Zr metal solution), requiring a correction of 0.2% for the Hf concentration and 0.4% for the Ta concentration of the HFSE-Std1 solution. The concentrations of Ta, Zr and Hf in mixed spike HFSE-I, together with the concentrations in mixed spike HFSE-II, which are calculated from the gravimetric dilution, are given in Table 3. Also shown are isotope compositions and concentrations for the pure Ta spikes Ta-I (calibrated against a pure Ta metal solution, Ta-Std1) and Ta-II (calculated from the gravimetric dilution). The stability of all spikes was frequently tested with metal solutions and geological standards.

2.9. The isotopic composition of natural Ta

A reference value of 0.00012 (2) for the $^{180}\text{Ta}/^{181}\text{Ta}$ isotope ratio of natural Ta is recommended by De Bièvre and Taylor (1993). The uncertainty of this ratio is ca. 17%, which means that the abundance of ^{180}Ta is one of the least constrained values of any isotope. The best measurement from a single source was done by White et al. (1956), who determined a value of 0.000123 (3) for the $^{180}\text{Ta}/^{181}\text{Ta}$ ratio with TIMS and a single ion counter [it is not clear whether the 2.5% uncertainty is a 1 or 2 σ in run precision

(RSE) or the external reproducibility of replicate analyses (RSD)].

Due to these large uncertainties, it was considered necessary to obtain a more precise value for the abundance of ^{180}Ta in natural materials. Therefore, the isotope composition of natural Ta was determined by multiple measurements of a 50-ppb standard solution using the same collector configuration as for the spiked samples (Fig. 3). The signal on the mass 181 was usually tuned to 7–8 V, resulting in a mass 180 signal of about 1 mV. The long-term value for $^{180}\text{Ta}/^{181}\text{Ta}$, which was obtained over a period of about 7 months, is 0.0001198 ppm. In Fig. 4, the two stable Ta isotopes, ^{180}Ta and ^{181}Ta , are shown on a mass scan that was obtained using the axial faraday detector. The mass scan was performed with the 50-ppb Ta standard solution, which was also used for the determination of the isotopic composition of Ta.

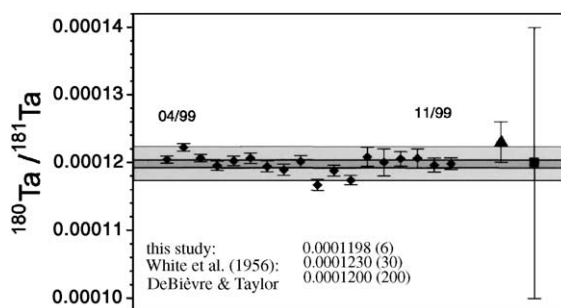


Fig. 3. Multiple analyses of a 50-ppb solution of natural Ta (diamonds) measured over a time period of ca. 7 months to determine the isotope composition of natural Ta. The triangle is the best measurement from a single source from the literature (White et al., 1956) and the square represents the recommended value of De Bièvre and Taylor (1993). Light gray field represents 2 RSD (=2%) and the dark gray field 2 RSE (=0.5%) of the $^{180}\text{Ta}/^{181}\text{Ta}$ ratio.

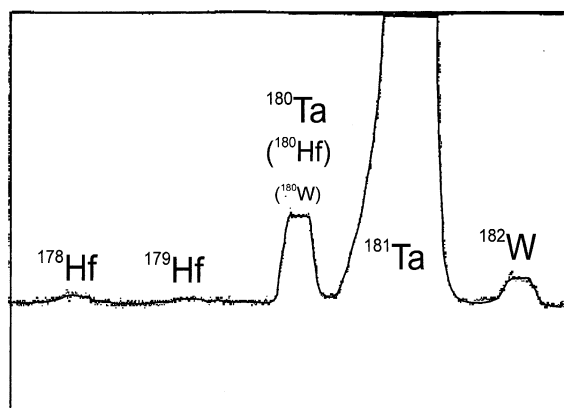


Fig. 4. Mass scan over the Ta and the neighbouring masses (Hf and W) of a natural Ta solution using the Axial Faraday detector: The small ^{180}Ta (+ ^{180}Hf + ^{180}W) peak is only about 1 mV, but has nevertheless a good peak shape allowing to measure precise $^{180}\text{Ta}/^{181}\text{Ta}$ ratios.

A limiting factor for the accuracy of the isotope ratio is the abundance sensitivity of the MC-ICP-MS, which can be expressed by a 10–15-ppm interference on mass 237 from the tail of ^{238}U . For that reason, the baseline for ^{180}Ta was only measured at mass 179.5, and not between ^{180}Ta and ^{181}Ta at mass 180.5. The interference of the ^{181}Ta tail on ^{180}Ta is estimated to be about 6–8 ppm, assuming that the tail on ^{181}Ta is similar in shape to that of ^{238}U . The interference at mass 179.5, where the baseline was measured, is probably still about 2–3 ppm. Since this baseline is subtracted from ^{180}Ta , the total uncorrected interference from the ^{181}Ta tail is ca. 5 ppm. This would result in a measured $^{180}\text{Ta}/^{181}\text{Ta}$ that is 4% too high. Therefore, abundance sensitivity is probably the major limiting factor of natural $^{180}\text{Ta}/^{181}\text{Ta}$ measurements with MC-ICP-MS using faraday collectors only. Correcting for abundance sensitivity by using the estimations above gives a lower $^{180}\text{Ta}/^{181}\text{Ta}$ of 0.000115.

In spite of the small signal on ^{180}Ta , the uncertainty from the abundance sensitivity and the Hf interference correction, the external reproducibility of the $^{180}\text{Ta}/^{181}\text{Ta}$ ratio determined with the faraday cup configuration is very good (2% 2 RSD). The long-term mean value (uncorrected) of 0.0001198 for $^{180}\text{Ta}/^{181}\text{Ta}$ agrees very well with the recommended value of 0.00012 from De Bièvre and Taylor (1993). It is even lower than, but within analytical uncertainty of, the ratio of 0.000123 reported by White et al.

(1956). Either the uncertainty caused by the abundance sensitivity on Ta measurements is overestimated, or more likely, White et al. (1956) and other workers had similar problems.

2.10. Reproducibility of Ta analyses for low-concentration samples

Since samples with very low Ta concentrations were analysed, it is important to evaluate the external reproducibility of the Ta measurements using low concentration Ta solutions with similar isotopic compositions to those of spiked samples. For this experiment, a low-concentration (1 ppb) spike solution was used as in-house standard, because its isotopic composition is well known and approximates more closely the compositions of spiked samples than natural Ta. In contrast to the measurement of natural Ta, the abundance sensitivity is negligible for the measurement of spiked samples with $^{180}\text{Ta}/^{181}\text{Ta}$ ratios between 0.003 and 0.03. The signal on ^{180}Ta for this diluted spike solution was 8–10 mV, which is similar to the signals obtained during the ID analyses of the depleted peridotites.

Fig. 5 shows multiple analyses of the 1-ppb spike solution over ca. 1 year. The (2 RSD) uncertainty is about 0.8% and the $^{180}\text{Ta}/^{181}\text{Ta}$ of 0.04514(37) agrees with the value of 0.045197(4) that was determined for the concentrated spike. The internal precision varies

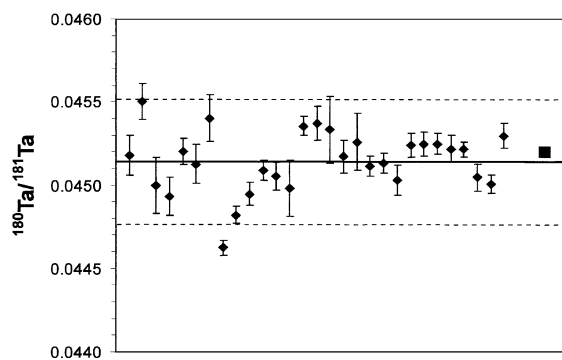


Fig. 5. Multiple measurements of a 1-ppb Ta spike solution over a time period of more than 1 year (diamonds, error bars are in-run uncertainties). The mean value (solid line) of 0.04514 agrees within 0.13% with the value determined for a concentrated (50 ppb) spike solution (square). The external (2 RSD) reproducibility of the 1 ppb spike measurements are 0.8% (dashed lines).

between 0.06 and 0.3%. The last 11 values of Fig. 5 are more constant than the values at the beginning, because the sensitivity of the mass spectrometer was improved by a factor of two using a new nebulizer. The 1-ppb spike solution was measured regularly as a standard solution between samples in order to identify potential problems with interference corrections, or machine memory.

2.11. Recoveries

Since Ta, Zr and Hf are spiked, a 100% chemical recovery is not necessary for the acquisition of accurate concentration data as long as complete sample–spike equilibration is achieved. However, due to the low Ta concentration in the peridotite samples, the best possible recovery is desired. Since Nb is not spiked and the $^{93}\text{Nb}/^{90}\text{Zr}$ ratio is used to determine the Nb concentration, it is essential to have almost complete recovery for both Zr and Nb in the HFSE fraction of column 1. The fractionation of Zr/Nb on the Ln spec column 1, tested by measuring a Zr/Nb standard solution before and after passing through the columns, is negligible (Table 4). However, sample matrices of geologic materials may cause significantly different behaviour of Zr/Nb on the columns. Additionally, the concentration of an element in the sample

solution can be reduced by incomplete digestion, invisible precipitation or hydrolysis.

Therefore, yield tests (including sample digestion and column separation) were performed with two different sample matrices (peridotite and basalt), doped with Zr, Nb, Ta and Hf (Table 4). The composition of the peridotite is known to within $\pm 10\%$ for Nb and Ta, and to within $\pm 3\%$ for Zr and Hf. The composition of BIR1 is known to within $\pm 5\%$ for Nb and Ta, and to within $\pm 2\%$ for Zr and Hf (see results below). The shelf solutions used for doping the samples were prepared from pure Ames metal ingots (see above) and their elemental concentrations are known within $\pm 0.1\%$. Since the amount of Zr, Hf, Nb and Ta added was always more than 10 times the natural amounts in the samples, the compositions of the doped samples were known to within $\pm 1\%$ for all elements.

The total recoveries of Ta were 84% and 91%, depending on the matrix. For the peridotite matrix, the recovery of Zr and Nb in the HFSE fraction of the first column was 93% and 89%, respectively. The uncertainty in Nb concentration determined from the post-chemistry Zr/Nb ratio and the Zr concentration (measured by ID) was only 4%. Zr and Nb yields for a basaltic matrix are about 100% and the resulting error for the calculated Nb concentration is about 3%. The

Table 4
Recovery of Zr, Hf, Nb and Ta for a basaltic and a peridotitic matrix

BIR 1					
	Sample weight: 0.1008 g				
	In sample (μg)	Doped (μg)	Total (μg)	Yield (μg)	Yield (%)
Zr	1.41	10.9	12.31	12.1	98
Hf	0.0583	1.047	1.1053	1.006	91
Nb	0.0548	1.269	1.3238	1.34	101
Ta	0.00353	0.0446	0.04813	0.0437	91
BP7-Pe					
	Sample weight: 0.9358 g				
	In sample (μg)	Doped (μg)	Total (μg)	Yield (μg)	Yield (%)
Zr	1.22	10.99	12.21	11.4	93
Hf	0.0889	1.027	1.1159	0.892	80
Nb	0.0065	0.1229	0.1294	0.115	89
Ta	0.00065	0.0520	0.05265	0.0443	84
Zr/Nb	Original	After column separation	Error of Nb concentration (%)		
Mix shelf	8.795	8.868	1		
BIR-1 doped	9.3	9.0	3		
BP7-Pe doped	95	99	4		

Hf yield was about 80% for the peridotite and 91% for the basalt matrix for the complete three-stage chemical separation.

3. Results

3.1. Isotope dilution analyses of geological samples

Different types of geological standard reference material were measured to evaluate the method developed in this study (Tables 5a–5c, Figs. 6 and 7). The selected standards include samples that have low to very low HFSE concentrations, such as BIR-1 (basalt), PCC-1 (peridotite) and DTS-1 (dunite). Table 5b shows Zr, Hf, Nb and Ta concentration data obtained for seven geological reference glasses, which

were produced as reference material for in situ micro-analysis (Jochum et al., 2000b). These reference glasses (which were received as powders) were analysed with different methods in many laboratories, including the laboratory at Münster, to obtain preliminary reference values. Two of the glasses (GOR128-G and GOR 132-G) have very low HFSE concentrations, particularly for Ta, which limits the possibility of other methods to obtain accurate concentration data.

The concentrations obtained for the basaltic standard reference material agree very well with values obtained in other laboratories (Table 5a). Two basalts (BB and BIR-1) were analysed several times over a period of ca. 1 year to test the external reproducibility (including sample digestion and column separation) of the concentration determination and long-term spike

Table 5a
Concentrations of Zr, Hf, Nb and Ta in basaltic reference materials

	Zr (ppm)		Nb (ppm)		Hf (ppm)		Ta (ppm)		Zr/Hf		Nb/Ta	
	This study	Reference values	This study	Reference values	This study	Reference values	This study	Reference values	This study	Reference values	This study	Reference values
BHVO-2	166	173 ^a	–	18.3 ^a	4.50	4.29 ^a	1.11	1.17 ^a	36.9	40.3 ^a	–	15.6 ^a
BCR-2	184		13.0		5.00		0.738		36.8		17.6	
BE-N	261.6	260 ^b ; 278.45 ^c	–	105 ^b	5.80	5.6 ^b ; 5.841 ^c	5.96	5.7 ^b	45.1	44.8 ^b ; 47.7 ^c	–	18.4 ^b
BB (1) ^d	193.0		–		4.817		3.383		40.1		–	
BB (2) ^d	192.6		–		4.837		3.394		39.8		–	
BB (3) ^d	193.3		–		4.832		3.470		40.0		–	
BB (4) ^d	192.0		60.8		4.821		3.442		39.8		17.7	
BB (5) ^d	193.7		59.6		4.834		3.450		40.1		17.3	
BB (mean)	192.92	192 ^c	60.2	64 ^c	4.828	4.5 ^c	3.428	3.6 ^c	40.0	42.7 ^c	17.5	17.8 ^c
BB (2 RSD [%])	0.7		2.7		0.4		2.2		0.6		3.1	
BIR-1 (1)	13.90		0.532		0.584		0.0355		23.8		15.0	
BIR-1 (2)	13.87		0.552		0.581		0.0353		23.9		15.6	
BIR-1 (3)	13.99		0.565		0.578		0.0361		24.2		15.7	
BIR-1 (4)	14.01		0.538		0.587		0.0359		23.9		15.0	
BIR-1 (5)	14.03		0.554		0.579		0.0350		24.2		15.8	
BIR-1 (mean)	13.96	15.6 ^a ; 15.5 ^b ; 14.9 ^f ; 14.5 ^g	0.548	0.53 ^a ; 0.6 ^b ; 0.51 ^f	0.582	0.57 ^a ; 0.6 ^b ; 0.53 ^f ; 0.63 ^g	0.0356	0.036 ^a ; 0.04 ^b ; 0.031 ^f	24.0	27.4 ^a ; 26 ^b ; 28.1 ^f ; 23.0 ^g	15.4	14.9 ^a ; 15 ^b ; 16.5 ^f
BIR-1 (2 RSD [%])	1.01		4.815		1.233		2.5027		1.7		5.21	

^a Jochum et al. (2000a).

^b Govindaraju (1994).

^c David and Schiano (2000).

^d In house standard from Geochemisches Institut, Universität Göttingen, Germany.

^e Münker et al. (2000).

^f Yu et al. (2000).

^g Xie and Kerrich (1995).

Table 5b
Concentrations of Zr, Hf, Nb and Ta in seven geological reference glasses

	Zr (ppm)		Hf (ppm)		Zr/Hf	
	MC-ICPMS	Reference value ^a	MC-ICPMS	Reference value ^a	MC-ICPMS	Reference value ^a
GOR128-G	10.1	10.2	0.362	0.351	27.8	29.1
GOR132-G	10.2	10.3	0.360	0.370	28.4	27.8
T1-G	154	147	4.32	3.90	35.6	37.7
St.Hs 6/80-6-G	125	120	3.31	3.16	37.7	38.0
ML3B-G	125	126	3.43	3.32	36.5	38.0
KL2-G	154	159	4.18	4.14	36.8	38.4
ATHOG	509	524	13.6	13.6	37.4	38.5
	Nb		Ta		Nb/Ta	
	MCICPMS	Reference value ^a	MC-ICPMS	Reference value ^a	MC-ICPMS	Reference value ^a
GOR128-G	0.106	0.11	0.0238	0.028	4.5	3.9
GOR132-G	0.072	0.071	0.0371	0.034	1.9	2.1
T1-G	8.76	9.10	0.439	0.45	19.9	20.2
St.Hs 6/80-6-G	6.62	7.1	0.405	0.418	16.4	17.0
ML3B-G	8.96	9.0	0.532	0.55	16.8	16.3
KL2-G	15.8	15.8	0.923	0.97	17.2	16.3
ATHO-G	56.0	61.9	3.59	3.8	15.6	16.2

^a Reference values from Jochum et al. (2000b).

Table 5c
Concentrations of Zr, Hf, Nb and Ta in peridotites

	Zr (ppm)		Hf (ppm)		Zr/Hf	
	This study	Reference values	This study	Reference values	This study	Reference values
DTS-1	0.131	0.11 ^a ; 0.253 ^b ; 0.13 ^c ; 0.17 ^d	0.0046	0.0046 ^a ; 0.0069 ^b ; 0.0052 ^c ; 0.0056 ^d	28	24 ^a ; 37 ^b ; 25 ^c ; 30 ^d
PCC-1	0.105	0.13 ^a ; 0.191 ^b ; 0.149 ^c ; 0.145 ^d	0.0039	0.0071 ^a ; 0.0054 ^b ; 0.0047 ^c ; 0.0038 ^d	27	18 ^a ; 35 ^b ; 32 ^c ; 38 ^d
BP-7PeW (1) ^e	1.31	1.3 (MIC-SSMS) ^f	0.096	–	13.6	–
BP-7PeW (2) ^e	1.29		0.093		13.9	
BP-7PeW (3) ^e	1.34		0.096		14.0	
BP-5Pe (1) ^e	0.53	0.66 (MIC-SSMS) ^f	0.051	–	10.4	–
BP-5Pe (2) ^e	0.50		0.047		10.6	
	Nb (ppb)		Ta (ppb)		Nb/Ta	
	This study	Reference values	This study	Reference values	This study	Reference values
DTS-1	9.6	32 ^a ; 12 ^b ; 9.6 ^c ; 32 ^d	1.1	2.1 ^a ; 2 ^b ; 1.3 ^c ; 1.3 ^d	8.7	15 ^a ; 6 ^b ; 7 ^c ; 25 ^d
PCC-1	8.5	38 ^a ; 11 ^b ; 8.9 ^c ; 24 ^d	0.64	3 ^a ; 2 ^b ; 19 ^c ; 0.5 ^d	13.3	13 ^a ; 6 ^b ; 0.5 ^c ; 48 ^d
BP7-PeW (1) ^e	–	11 (MIC-SSMS) ^f	–	–	–	–
BP7-PeW (2) ^e	6.3		0.64		9.8	
BP7-PeW (3) ^e	7.1		0.67		10.6	
BP5-Pe (1) ^e	–	7.4 (MIC-SSMS) ^f	0.48	–	–	–
BP5-Pe (2) ^e	4.0		0.52		7.7	

^a Ionov et al. (1993).

^b Eggins et al. (1997).

^c Makishima et al. (1999).

^d Yu et al. (2000).

^e Iherzolite samples from the Balmuccia peridotite complex, Ivrea Zone, Italian Alps.

^f Multi-ion counting-spark source mass spectrometry analyses determined in this study at the Max Planck Institut für Chemie in Mainz, Germany (for analytical techniques see Jochum et al. (2000a) and references therein).

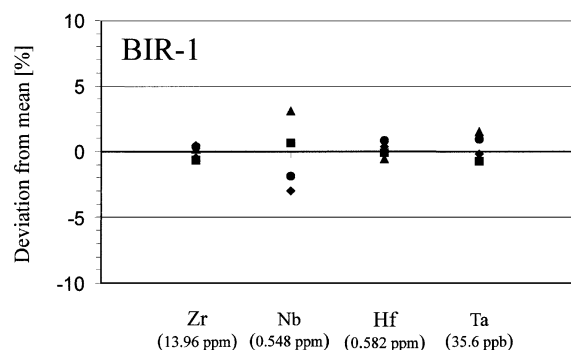


Fig. 6. External reproducibility of the concentration determinations (MC-ICP-MS) of the geological standard BIR-1 (depleted basalt).

stability. The Zr and Hf concentrations of replicate analyses can be reproduced within 0.7% and 0.4% (2 RSD) for high-HFSE basalts, and about 1% for low-HFSE basalts like BIR-1 (Fig. 6). Niobium, which was not measured by isotope dilution, has the highest uncertainty (2.7% and 4.8%, respectively) and the uncertainty in the Ta concentration is better than 3% for all basalts.

The Zr, Hf, Nb and Ta concentrations of the geological reference glasses agree within $\pm 5\%$ (for most samples) with the reference values that were calculated from the concentration data of all methods (Table 5b). In particular, the Ta concentrations determined by isotope dilution are much more precise than those determined by conventional methods (Fig. 7). For all glass standards, the MC-ICP-MS results agree within error with most of the other methods. The Ta concentration of the low-HFSE samples (such as GOR128-G) are determined by isotope dilution with an uncertainty $< 5\%$, but are poorly determined by conventional methods ($> 20\%$ uncertainty).

Major progress in HFSE concentration measurements has been achieved for ultra-depleted rocks like peridotites and dunites (Table 5c). Although the quality of conventional ICP-MS analyses of ultra-depleted rocks has also improved significantly in the last few years, Nb and Ta abundances are still poorly known in most natural samples, with uncertainties of up to $> 100\%$. Therefore, Nb/Ta and Zr/Hf ratios in mantle rocks are poorly constrained at present. In this study, new and more precise Zr, Hf, Nb and Ta concentrations of the geological reference standard materials PCC-1, DTS-1 are presented. The external

reproducibility of low-HFSE samples is tested on two peridotite samples (BP7-PeW and BP5-Pe) from the Balmuccia peridotite complex (Northern Italy). Niobium concentrations of 4–10 ppb and Ta concentrations of < 1 ppb were reproduced to within $\pm 5\%$. The external reproducibility of the Zr/Hf ratios of the Balmuccia peridotite samples is ca. 2% (2 RSD). To get reference values for these samples, they were also analysed for Zr and Nb by multiple ion counting spark source mass spectrometry (MIC-SSMS) at the Max-Planck-Institut für Chemie in Mainz following the method described in Jochum et al. (2000a) and references therein. The Zr concentration agrees very well with the concentration determined with MC-ICP-MS. The Nb concentrations deviate significantly. However, the uncertainty of Nb concentrations determined by SSMS at this concentration level is very large, because of molecular interferences that are difficult to correct for.

3.2. Isotope dilution analyses of meteorites

It is generally assumed that Zr, Hf, Nb and Ta behave as lithophile elements during core formation and that their ratios in the bulk silicate Earth (BSE) agree with the chondritic ratios, although Wade and Wood (2001) recently reported that some Nb ($\sim 20\%$) might be in the core. In order to compare Zr/Hf and Nb/Ta of various geochemical reservoirs

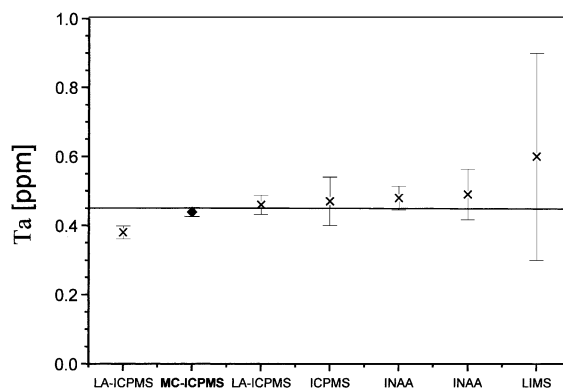


Fig. 7. The Ta concentration of the standard reference glass T1-G determined by isotope dilution on the MC-ICP-MS in Münster compared with the results of other methods. Error bars are “absolute uncertainties”. The Ta ID value agrees within error with the mean value of all methods and has the smallest uncertainty.

and estimates of the BSE with the chondritic ratios, a precise and accurate knowledge of these ratios is essential. So far, the most precise analyses of these elements in meteorites were performed using (ID) SSMS and RNAA for Ta (Jochum et al., 1986, 2000a) and very recently also MC-ICP-MS (David and Schiano, 2000). Since it is generally only possible to evaluate the precision, but not the accuracy of a single method, it is important to compare the results of different methods to cancel out systematic errors, which might be due to matrix effects or uncertainties in spike calibration. There are very few published meteorite Zr/Hf ratios. Jochum et al. (1986) assumed that the chondritic Zr/Hf is well constrained by the value measured in oceanic basalts. However, recent analyses showed that there is a large variation in Zr/Hf among oceanic basalts (Niu and Batiza, 1997; David and Schiano, 2000). Furthermore, Weyer et al. (submitted for publication) demonstrated that Zr/Hf is highly fractionated during partial melting in the mantle. Therefore, oceanic basalts are unsuitable for determining the chondritic Zr/Hf.

In this study, two chondrites and six achondrites were analysed for Zr, Hf, Nb and Ta (Table 6). The element ratios Zr/Hf, Nb/Ta and Zr/Nb of the chondrites and the eucrites all agree within analytical uncertainties, implying that no fractionation process (including core formation and igneous processes) on the parent body of the achondrites fractionated these elements. This is particularly remarkable for Zr/Nb, which is highly fractionated during partial melting processes at low degrees of melting on Earth. However, the flat REE patterns of eucrites (e.g., Hsu and Crozaz, 1996 and references therein) indicate that incompatible elements are not strongly fractionated in these meteorites. Only the angrite Sahara-99555 has a slightly higher Zr/Nb, which might be due to a partial melting process on the parent body. This sample is quite a new find and additional information about other trace elements is still very scarce. The data for Sahara-99555 is therefore excluded in the calculation of solar system trace element ratios.

The mean Nb/Ta value of all investigated chondrites and eucrites in this study is 17.6 and agrees with the Nb/Ta ratio of Jochum et al. (1986, 2000a). There is some scatter in Nb/Ta among the various samples, especially in the chondrites. This scatter is higher than the expected analytical uncertainty, which is based on

the reproducibility of samples that have HFSE contents similar to those of chondrites (e.g., BIR-1, Table 5a and Fig. 6). At present, it is not known whether the scatter is due to a real heterogeneity of the chondritic reservoir, a small-scale heterogeneity within the various meteorite samples from which the powder was prepared, or heterogeneity within the powder.

The Zr/Nb ratios of all investigated chondrites and eucrites are significantly lower than the reference values of Jochum et al. (2000a). The variation of Zr/Nb among the individual samples is about as high as the variation of Nb/Ta. The mean value for Zr/Nb of 13.3 ± 0.6 (2 RSE) obtained in this study differs significantly from the value of 15.5 determined by Jochum et al. (2000a). More analyses, of chondrites in particular, are necessary to determine the precise solar system Zr/Nb value, because small fractionation effects on the parent body of the eucrites cannot be ruled out at present.

For the first time, precise Zr/Hf ratios have been determined for a large number of meteorites. In all chondrites and eucrites, Zr/Hf was lower than the previously suggested chondritic value of 36.6 (Jochum et al., 1986). The Zr/Hf ratios determined for Allende and Murchison are also significantly lower than the ID values from David and Schiano (2000) (Table 6). Since the Zr/Hf value, obtained for BE-N in this study is also lower than the value of David and Schiano (2000), the differences among the studies may be due to uncertainties in the spike calibration. It has to be emphasised that in the present study, solutions prepared from pure metals, with concentrations that are known to about 0.1%, have been used for spike calibration, whereas David and Schiano (2000) used commercial metal solutions and determined the concentration using a titration method. As in this study, David and Schiano (2000) also observed ca. 3% variations in Zr/Hf among various chondrites as well as in different analyses of the same meteorite. They proposed to use the value of Orgueil as a representative value for the Bulk Earth. However, solar system trace element ratios of refractory lithophile elements, such as Zr and Hf, are best determined by the analyses of many different chondrites, because the effects of powder heterogeneities and small-scale heterogeneities within the meteorite should average out. Since the condensation temperatures of Zr and Hf are very similar (Jochum et al., 1986), it is most

Table 6
Concentrations of Zr, Hf, Nb and Ta in meteorites

Sample	Type	Zr (ppm)		Nb (ppm)		Hf (ppm)		Ta (ppm)		Zr/Hf		Nb/Ta		Zr/Nb	
		This study	Reference	This study	Reference	This study	Reference	This study	Reference	This study	Reference	This study	Reference	This study	Reference
<i>Chondrites</i>															
Allende-MS ^a	CV	7.43		0.563		0.222		0.0342		33.5		16.5		13.2	
	CV	6.88		0.575		0.199		0.0328		34.6		17.5		12.0	
	CV	6.63		0.485		0.192		–		34.6		–		13.7	
Allende-MPI ^b	CV	6.44	7.04 ^c	0.474	0.452 ^c	0.185		0.0323	0.027 ^c	34.8		14.7	16.7 ^c	13.6	15.6 ^c
Allende			6.36 ^d				0.1797 ^d ; 0.2109 ^c ; 0.0192 ^e				35.4 ^d				
Murchison	CM	4.95	5.41 ^c 5.192 ^d	0.425	0.343 ^c	0.149	0.1458 ^d ; 0.1285 ^e	0.0206	0.02 ^c	33.2	35.6 ^d	20.6	17.2 ^c	11.6	15.8 ^c
<i>Achondrites</i>															
Sahara-99555	angrite	45.8		2.78		1.29		0.1431		35.5		19.4		16.5	
Juvinas	euclite	41.1	51.0 ^c	3.34	3.46 ^c	1.20	1.42 ^c	0.1743	0.203 ^c	34.2	35.9 ^c	19.2	17 ^c	12.3	14.7 ^c
Millbillillie	euclite	30.2		2.09		0.89		0.1211		34.0		17.3		14.5	
Stannern	euclite	39.4		2.82		1.15		0.156		34.3		18.1		14.0	
HH-059	euclite	76.4		5.52		2.20		0.3175		34.7		17.4		13.8	
Pasamonte	euclite	47.7	58.6 ^c	3.44	3.68 ^c	1.39	1.58 ^c	0.2004	0.211 ^c	34.2	37.1 ^c	17.2	17.4 ^c	13.9	15.9 ^c
Mean value ^f										34.2		17.6		13.3	
2 SE ^f										0.3		1.0		0.6	

^a Allende-MS= about 10 g of powder produced from a fragment of the Allende meteorite (produced in Münster).

^b Allende-MPI= Allende powder from the Max Planck-Institut in Mainz.

^c Jochum et al. (2000a).

^d David and Schiano (2000).

^e Blichert-Toft and Albarède (1997).

^f The sample Sahara-99555 is excluded from the calculation of the mean and the 2 SE values, since the relatively high Zr/Nb indicates a fractionation process.

unlikely that variations in Zr/Hf of various chondrites reflect variations among different parent bodies. The mean Zr/Hf of all chondrites and eucrites investigated in this study is 34.2 ± 0.3 (2 RSE) and is indistinguishable from the chondrite-only mean value, which is 34.1 ± 0.6 . Therefore, Zr and Hf are apparently not fractionated in the investigated eucrites and the mean Zr/Hf value of chondrites and eucrites is representative for the solar system.

4. Conclusions

The absolute uncertainties in HFSE concentrations determined with the presented method are estimated to be $\pm 2\%$ for Zr and Hf in basalts, $\pm 4\%$ for Zr and Hf in ultra-depleted rocks, $\pm 3\%$ for Ta in basalts, $\pm 5\%$ for Ta in ultra-depleted rocks, $\pm 5\%$ for Nb in basalts and $\pm 8\%$ for Nb in ultra-depleted rocks. These uncertainties include any systematic uncertainties, such as uncertainties in spike compositions.

Compared to other methods, the Zr and Hf ID concentration data acquired with the MC-ICP-MS are more precise and accurate for low-HFSE (<1 ppm) rocks. For samples with higher HFSE concentrations, ID-TIMS and ID-MIC-SSMS analyses can achieve a similar precision. For basalts, volcanic or synthetic glass, variations of $>2\%$ in the Zr/Hf ratio can be readily identified with the procedure outlined here. For ultra-depleted samples such as peridotites, Zr/Hf can be determined precisely enough to identify deviations of $>4\%$ from the chondritic value.

Niobium in basalts can be measured by MC-ICP-MS with a precision similar to that of SSMS (Jochum et al., 1990, 2000a) or a well-calibrated conventional ICP-MS without separation of Nb from the matrix. However, the Nb concentrations of ultra-depleted samples (<100 ppb) can be determined more accurately using the method described in this study. For such samples, the errors due to Zr/Nb fractionation during the chemical treatment appear to be less severe than the matrix and interference effects that are encountered by other techniques (e.g., ICP-MS and SSMS) when they are applied to concentration measurements close to the detection limit.

Tantalum concentrations determined by isotope dilution with a MC-ICP-MS are the most precise and accurate data for all types of investigated rocks,

when compared to conventional methods. Even ultra-depleted rocks that have Ta concentrations in the sub-ppb level can be analysed with good precision, which was not possible before. Nb/Ta in peridotites can be determined with a precision of $\pm 10\%$, and Nb/Ta in higher concentration samples with a precision of $\pm 5\%$.

A new and more precise chondritic Zr/Hf ratio of 34.2 ± 0.3 was determined, that is significantly different from the previously assumed value (Jochum et al., 1986). The chondritic Nb/Ta of 17.6 determined in this study confirms the value of Jochum et al. (2000a). Furthermore, the new analytical technique presented here opens new possibilities for the study of Nb and Ta abundances in mantle rocks. The results will contribute to the discussion concerning the global budget of these elements and their ratios in the different reservoirs of the Earth.

Acknowledgements

We are grateful to the Max-Planck-Institut für Chemie in Mainz, Germany, for providing a Tantalum isotopic tracer, which led to the major progress of the present study. We thank the Institut für Planetologie, Münster, Germany and the Max-Planck-Institut für Chemie in Mainz, Germany for providing meteorite samples and geological standard reference material. We are grateful to E. S. Scherer (Münster) for critical reading of the manuscript. S. Weyer thanks A. Hofmann (Max-Planck-Institut für Chemie,) for financial support during the course of this study. J. Blichert-Toft and T.E. Jeffries provided helpful reviews. [RR]

References

- Blichert-Toft, J., Albarède, F., 1997. The Lu–Hf isotope geochemistry of chondrites and the evolution of the mantle–crust system. *Earth Planet. Sci. Lett.* 148, 243–258.
- Blichert-Toft, J., Chauvel, C., Albarède, F., 1997. Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS. *Contrib. Mineral. Petrol.* 127, 248–260.
- Boswell, S.M., Elderfield, H., 1988. The determination of zirconium and hafnium in natural waters by isotope dilution mass spectrometry. *Mar. Chem.* 25, 197–209.
- David, K., Schiano, P.A., 2000. Assessment of Zr/Hf fractionation

- in oceanic basalts and continental materials during petrogenetic processes. *Earth Planet. Sci. Lett.* 178, 285–301.
- David, K., Birck, J.L., Telouk, P., Allegre, C.J., 1999. Application of isotope dilution for precise measurement of Zr/Hf and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios by mass spectrometry (ID-TIMS/ID-MC-ICP-MS). *Chem. Geol.* 157, 1–12.
- De Bièvre, P., Taylor, P.D.P., 1993. Table of the isotopic composition of the elements. *Int. J. Mass Spectrom. Ion Process.* 123, 149–166.
- Eggins, S.M., Woodhead, J.D., Kinsley, L.P.J., Mortimer, G.E., Sylvester, P., McCulloch, M.T., Hergt, J.M., Handler, M.R., 1997. A simple method for the precise determination of >40 trace elements in geological samples by ICPMS using enriched isotope internal standardisation. *Chem. Geol.* 134, 311–326.
- Govindaraju, K., 1994. 1994 compilation of working values and sample description for 383 geostandards. *Geostand. Newsl.* 18, 1–158.
- Halliday, A.N., Lee, D.C., Christensen, J.N., Rehkämper, M., Yi, W., Luo, X.Z., Hall, C.M., Ballentine, C.J., Pettke, T., Stirling, C., 1998. Applications of multiple collector-ICPMS to cosmochemistry, geochemistry, and paleoceanography. *Geochim. Cosmochim. Acta* 62 (6), 919–940.
- Hsu, W., Crozaz, G., 1996. Mineral chemistry and the petrogenesis of eucrites: I. Noncumulate eucrites. *Geochim. Cosmochim. Acta* 60, 4571–4591.
- Ionov, D.A., Dupuy, C., O'Reilly, S.Y., Kopylova, M.G., Genshaft, Y.S., 1993. Carbonated peridotite xenoliths from Spitsbergen: implications for trace element signature of mantle carbonate metasomatism. *Earth Planet. Sci. Lett.* 119, 282–297.
- Ionov, D.A., Hofmann, A.W., Shimizu, N., 1994. Metasomatism-induced melting in mantle xenoliths from Mongolia. *J. Petrol.* 35, 753–785.
- Jochum, K.P., Seufert, H.M., Spettel, B., Palme, H., 1986. The solar system abundances of Nb, Ta and Y, and the relative abundances of refractory lithophile elements in differentiated planetary bodies. *Geochim. Cosmochim. Acta* 50, 1173–1183.
- Jochum, K.P., McDonough, W.F., Palme, H., Spettel, B., 1989. Compositional constraints on the continental lithospheric mantle from trace elements in spinel peridotite xenoliths. *Nature* 340, 548.
- Jochum, K.P., Seufert, H.M., Thirlwall, M.F., 1990. High-sensitivity Nb analysis by spark-source mass spectrometry (SSMS) and calibration of XRF Nb and Zr. *Chem. Geol.* 81, 1–16.
- Jochum, K.P., Stolz, A.J., McOrist, G., 2000a. Niobium and Tantalum in carbonaceous chondrites: constraints on the solar system and primitive mantle niobium/tantalum, zirconium/niobium, and niobium/uranium ratios. *Meteorit. Planet. Sci.* 35, 229–235.
- Jochum, K.P., Dingwell, D.B., Hofmann, A.W., Stoll, B., Raczek, I., Rocholl, A., Becker, S., Besmehn, A., Besesette, D., Dietze, H.-J., Dulski, P., Erzinger, J., Hellebrand, E., Hoppe, P., Horn, I., Janssens, K., Jenner, G., Klein, M., McDonough, W.M., Maetz, M., Mezger, K., Münker, C., Nikogosian, I.K., Pickhart, C., Seufert, H.M., Simakin, S.G., Sobolev, A.V., Spettel, B., Straub, S., Vincze, L., Wallianos, A., Weckwerth, G., Weyer, S., Wolf, D., Zimmer, M., 2000b. The preparation and preliminary characterization of eight geological MPI-DING reference glasses for in situ microanalysis. *Geostand. Newsl.* 24, 87–133.
- Makishima, A., Nakamura, E., Nakano, T., 1999. Determination of Zirconium, Niobium, Hafnium and Tantalum at ng/g levels in geological materials by direct nebulisation of sample HF solution into FI-ICP-MS. *Geostand. Newsl.* 23, 7–20.
- Maréchal, C.N., Telouk, P., Albarede, F., 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. *Chem. Geol.* 156, 251–273.
- Münker, C., 1998. Nb/Ta fractionation in a Cambrian arc/back arc system, New Zealand: source constraints and application of refined ICPMS techniques. *Chem. Geol.* 144, 23–45.
- Münker, C., Weyer, S., Mezger, K., Rehkämper, M., Wombacher, F., Bischoff, A., 2000. ^{92}Nb – ^{92}Zr and the early differentiation history of planetary bodies. *Science* 289, 1538–1542.
- Münker, C., Weyer, S., Scherer, E., Mezger, K., 2001. Separation of high field strength elements (Nb, Ta, Zr, Hf) and Lu from rock samples for MC-ICPMS measurements. G-cubed 2, paper number 2001GC000183, 2001.
- Niu, Y., Batiza, R., 1997. Trace element evidence from seamounts for recycled oceanic crust in the Eastern Pacific mantle. *Earth Planet. Sci. Lett.* 148, 471–483.
- Niu, Y., Hekinian, R., 1997. Basaltic liquids and harzburgitic residues in the Garrett Transform: a case study at fast spreading ridges. *Earth Planet. Sci. Lett.* 146, 243–258.
- Plank, T., White, W.M., 1995. Nb and Ta in arc and Mid Ocean Ridge basalts. *EOS* 76 (46), 655.
- Russel, W.A., Papanastassiou, D.A., Tombrello, T.A., 1978. Ca isotope fractionation on the Earth and other solar system materials. *Geochim. Cosmochim. Acta* 42, 1075–1090.
- Sanloup, C., Blichert Toft, J., Télouk, P., Gillet, P., Albarède, F., 2000. Zirconium isotope anomalies in chondrites and the presence of ^{92}Nb in the early solar system. *Earth Planet. Sci. Lett.* 184, 75–81.
- Scherer, E., Münker, C., Rehkämper, M., Mezger, K., 1999. Improved precision of Lu isotope dilution measurements by MC-ICP-MS and application to Lu–Hf geochronology. *AGU*, 1118 (Fall).
- Stolz, A.J., Jochum, K.P., Spettel, B., Hofmann, A.W., 1996. Fluid and melt-related enrichment in the subarc mantle: evidence from Nb/Ta variations in island arc basalts. *Geology* 24 (7), 587–590.
- Wade, J., Wood, B.J., 2001. The Earth's “missing” niobium may be in the core. *Nature* 409, 75–78.
- Walder, A.J., Freedman, P.A., 1992. Isotopic ratio measurement using a double focusing magnetic sector mass analyser with an inductively coupled plasma as an ion source. *J. Anal. At. Spectrom.* 7, 571–575.
- Walder, A.J., Koller, D., Reed, N.M., Hutton, R.C., Freedman, P.A., 1993. Isotope ratio measurements by inductively coupled plasma multiple collector mass spectrometry incorporating a high efficiency nebulization system. *J. Anal. At. Spectrom.* 8, 1037–1041.
- Weyer, S., Münker, C., Mezger, K., 2002. Nb/Ta, Zr/Hf and REE in the depleted mantle: implications for the differentiation history of the crust–mantle system. *Earth Planet. Sci. Lett.*, submitted for publication.
- White, F.A., Collins, T.L., Rourke, F.M., 1956. Search for possible naturally occurring isotopes of low abundance. *Phys. Rev.* 101, 1786–1791.

- Xie, Q., Kerrich, R., 1995. Application of isotope dilution for precise measurement of Zr and Hf in low-abundance samples and international reference materials by inductively coupled plasma mass spectrometry: implications for Zr (Hf)/REE fractionations in komatiites. *Chem. Geol.* 123, 17–27.
- Yin, Q.Z., Jacobsen, S.B., McDonough, W.F., Horn, I., Petaev, M.I., Zipfel, J., 2002. Supernova sources and the ^{92}Nb - ^{92}Zr p-process chronometer. *Astroph. Jour.* 535, 49–53.
- Yu, Z., Robinson, P., Townsend, T., Münker, C., Crawford, J., 2000. Determination of high field strength elements, Rb, Sr, Mo, Sb, Cs, Tl and Bi at ng/g levels in geological reference materials by magnetic sector ICP-MS after HF/HClO₄ high pressure digestion. *Geostand. Newsl.* 24, 39–50.