Available online at www.sciencedirect.com

ScienceDirect

International Journal of Mass Spectrometry 261 (2007) 183–191

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

High precision Ag isotope measurements in geologic materials by multiple-collector ICPMS: An evaluation of dry versus wet plasma

Maria Schönbächler[a,b,*], Richard W. Carlson[a], Mary F. Horan[a],
Timothy D. Mock[a], Erik H. Hauri[a]

[a] Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Road, NW, Washington, DC 20015, USA
[b] Department of Earth Sciences and Engineering, Imperial College, London SW7 2AZ, UK

Received 12 July 2006; received in revised form 8 September 2006; accepted 8 September 2006
Available online 27 October 2006

Abstract

This paper presents an improved technique for the precise and accurate determination of Ag isotopic composition in geologic samples. Following the separation of Ag from the rock matrix with a three-stage ion exchange procedure, the isotopic composition is measured by MC-ICPMS. Instrumental mass bias is corrected externally using a Pd standard, which was added to each sample, and sample-standard bracketing. The use of wet plasma significantly improves the analytical precision by eliminating variations in fractionation between Pd and Ag. A virtually identical behavior of the mass bias for Pd and Ag during the analyses is a prerequisite for the external correction method. Replicate dissolutions of the carbonaceous chondrite Allende with <100 ng Ag yield an external reproducibility (2 S.D.) of 53 ppm for ^{107}Ag/^{109}Ag. Since the ion exchange procedure provides a good separation from matrix elements such as Ti and Fe, the method is suitable for the analysis of stony and iron meteorites as well as sulfide minerals and terrestrial basalts. The technique thus can be applied to investigate Ag isotopic variations in a large variety of solar system materials.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Silver isotopes; MC-ICPMS; Stable isotope fractionation; Meteorite; Extinct radionuclide

---

1. Introduction

The isotopic composition of Ag has received special attention in the past because of its ability to date and trace processes that took place very early in the solar system. This potential is based on the decay of the extinct radionuclide ^{107}Pd to ^{107}Ag with a half-life of 6.5 My, which can produce variation in the Ag isotopic composition. Silver is a moderately volatile and mainly chalcophile element, while Pd is more refractory and siderophile. This renders the system particularly useful for dating core formation processes and volatile loss. Only one other radionuclide system (^{205}Pb–^{205}Tl [1]) has similar abilities while the short-lived ^{182}Hf–^{182}W system [2] and the long-lived chronometers Pt–Re–Os [3,4] can be used to study core formation, but not volatile loss. Early Ag isotopic studies successfully provided evidence for the former presence of ^{107}Pd and established a chronology for volatile depleted iron meteorites [5–9]. These Ag isotopic analyses were performed by thermal ionization mass spectrometry (TIMS) and report a precision of ∼1–2 permil. This limited the useful application of the Pd–Ag system to volatile depleted meteorites that exhibit extremely high Pd/Ag ratios (up to 1.2×10^5), because large Pd/Ag fractionations are required to produce measurable Ag isotope differences in the permil range.

More recent studies have taken advantage of the development in the field of multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) and have been able to improve the analytical precision for Ag isotopic analyses by an order of magnitude [10,11]. This is desirable because many meteorites have low Pd/Ag ratios and are expected to show Ag isotopic variations at the ε level only (ε is the deviation from the standard in parts per 10^4). Such precision is also required to search for

---

[*] Corresponding author. Tel.: +44 20 7594 6547; fax: +44 20 7594 7444.
E-mail address: marias@imperial.ac.uk (M. Schönbächler).

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2006.09.016

decay products of the short-lived radionuclide ^{107}Pd in terrestrial samples with the ultimate goal to trace a core signature and/or date terrestrial core formation. The improvement in precision afforded by MC-ICPMS analysis has already led to the discovery of Ag isotopic variation in native Ag ore samples, which are probably due to stable Ag isotope fractionation during natural chemical processing [12]. This opens up a whole new field of applications of Ag isotope variation in economic geology and hydrothermal geochemistry studies.

The precision of TIMS measurements is limited by the fact that Ag has only two isotopes (^{107}Ag and ^{109}Ag) and thus no internal correction is possible for the mass fractionation induced during thermal evaporation in mass spectrometers. Although the instrumental mass bias observed during MC-ICPMS measurements is about 10 times larger than for TIMS, MC-ICPMS offers several ways to monitor the mass bias. One method is sample-standard bracketing, where samples are measured interspersed with standards. This method is commonly used to monitor the mass bias during measurements of a variety of stable isotopes including those of Fe [13]. With the MC-ICPMS, the mass bias is to first-order related only to mass and thus the instrumental mass discrimination can be monitored by doping the sample solution with an element of similar mass and using the simultaneously measured isotopic composition of the added element to correct for the mass bias. This external normalization method is usually applied in conjunction with standard-sample bracketing and has found wide applications in stable isotope measurements of many elements such as Zn, Cu, Mo, Cd and Tl [14–17]. Although these approaches for mass bias correction have some shortcomings (e.g., [18]), they led to a significant improvement in the precision for Ag isotopic composition. Carlson and Hauri [10] combined standard-sample bracketing and external normalization to Pd for Ag isotopic measurements and were able to improve the uncertainty by a factor of ~10. Woodland et al. [11] improved on this further and reported an external reproducibility of $\pm 2\varepsilon$ for geologic samples passed through ion exchange chemistry, while the uncertainty of synthetic Ag standard solutions was in the range of $\pm 0.5\varepsilon$. The reason for this discrepancy was not clear and leaves space for improvement.

The goal of this study is to develop an optimized analytical procedure for high precision Ag isotopic analyses to study Ag in terrestrial samples including basalts and low Pd/Ag meteorites. This new procedure consists of a three-stage ion exchange chemistry, which assures a good separation of Ag from matrix elements including Ti, which strongly affects ICP-MS behavior. The so far reported chemical separation procedure for Ag for high precision MC-ICPMS analysis is based on [19] and was further developed by other groups [10,11]. It is, however, optimized for iron meteorites and thus does not provide an efficient separation of Ti from Ag. Titantium removal is required for samples such as terrestrial basalts, because they contain larger amounts of Ti, which can compromise the Ag isotopic analyses. Furthermore, we achieved a superior precision for geologic samples ($\pm 0.5\varepsilon$) compared to previous studies, which is crucial for specific cosmochemical and geochemical applications. The improvement of the uncertainty is mainly due to the use of wet plasma, which allows a more reliable correction for the instrumental mass discrimination.

2. Sample preparation

2.1. Dissolution

About 1–2 g of the carbonaceous chondrite Allende and up to 10 g of terrestrial basalt sample powders were digested in a 2:1 mixture of HF:HNO_3 in a closed Savillex teflon beaker on a hotplate at 110 °C for 2 days. After drying down, 6 M HNO_3 was added, left on a hot plate and gently dried down the next day. Subsequently, 6 M HCl was added and heated overnight. If complete dissolution was not achieved after these steps, the sample was centrifuged and the supernatant decanted. The residue was treated with 6 M HCl and small amounts of boric acid. This usually resulted in a clear solution. The different sample fractions were recombined and a 10% aliquot was taken at this point for the determination of Pd and Ag concentration by isotope dilution. The isotope dilution analyses were conducted following the procedure described by Woodland et al. [11], and will not be further discussed here.

In contrast to the basalt samples, Allende contains a considerable amount of organic materials, which are difficult to dissolve in mineral acids, so an aqua-regia step was added to assist in the dissolution of organic material. Complete dissolution, however, was not achieved and a black residue remained that probably consisted of graphite and organic material.

2.2. Ion exchange chromatography

A three-stage ion exchange procedure was used for the isolation and purification of Ag (Table 1). The procedure represents a further development from that described by Woodland et al. [11], which is adapted from previous procedures for high precision Ag isotopic analyses [19,7,10].

The first step was performed with 9.5 ml AG1-X8 resin (100–200 mesh, chloride form) in a column having 1 cm diameter and a 12 cm resin bed height. Up to 10 g of basalt can be loaded onto a single column of this size. The dissolved samples were dried down and taken up in 30 ml 2.6 M HCl. Within 120 ml Savillex® digestion vessels, the samples were kept at 140 °C overnight in an oven. The next morning, the samples were diluted to 160 ml with ultra-pure H_2O, which resulted in a final concentration of ~0.5 M HCl. The samples were centrifuged shortly before loading onto the column. Cleaning and preconditioning of the resin was performed with 100 ml of 9 M HCl followed by 250 ml of 0.5 M HCl. After sample loading, the columns were washed sequentially with 190 ml 0.1 HCl, 80 ml 0.001 M HCl and 20 ml 0.5 M HNO_3. Subsequently, Ag was eluted with 50 ml 0.5 M HNO_3 and dried down on a hotplate. The elution peak of Ag slightly varied. These small variations were possibly due to the presence of varying amounts of matrix elements that influenced the conversion of the resin from its Cl^- to the NO_3^- form. The problem could have been circumvented by the collection of a larger Ag fraction but this would also have

Table 1
Ag ion exchange chromatography

Volume (ml)	Acid	Step
Resin: 9.5 ml AG1-X8, 100–200 mesh, chloride form (wet volume) silicate samples <10 g		
100	9 M HCl	Resin cleaning
250	0.5 M HCl	Preconditioning
160	0.5 M HCl	Load sample
190	0.1 M HCl	Rinse matrix
80	0.001 M HCl	Rinse matrix
20	0.5 M HNO_3	Rinse matrix
50	0.5 M HNO_3	Elute Ag
Resin: 1.25 ml AG1-X8, 100–200 mesh, chloride form (wet volume) silicate samples <1.5 g[a] and cleanup		
20	9 M HCl	Resin cleaning
30	0.5 M HCl + 0.15% H_2O_2	Preconditioning
10	0.5 M HCl + 0.15% H_2O_2	Load sample
30	0.1 M HCl + 0.15% H_2O_2	Rinse matrix
10	0.001 M HCl	Rinse matrix
4	0.5 M HNO_3	Rinse matrix
10	0.5 M HNO_3	Elute Ag
Resin: 1 ml AG50W-X8, 200-400 mesh, hydrogen form (wet volume), all samples		
180	0.5 M HNO_3	Cleaning/preconditioning
0.5	0.5 M HNO_3	Load sample
16	0.5 M HNO_3	Rinse matrix
14	0.5 M HNO_3	Elute Ag

[a] For silicate samples <1.5 g this column is applied without the use H_2O_2 and then repeated with H_2O_2.

increased the contamination with matrix elements such as Ti and was thus avoided if possible. In order to assure that no Ag was lost due to these small shifts, about 20 ml of the eluant before and after the Ag cut was collected and analyzed for Ag content. High Ag yields are important to avoid possible isotopic fractionation of Ag on the column. If the fractions collected before and after the silver cuts contained more than 1% of the total Ag in the sample, which occurred rarely, all fractions containing Ag were recombined and processed together through the further ion exchange procedure.

The second separation step was designed to achieve a better separation of Ti from Ag. It utilized 1.25 ml AG1-X8 resin (100–200 mesh, chloride form) in a 6 mm by 45 mm column, that was cleaned and preconditioned with 20 ml 9 M HCl and 30 ml freshly prepared 0.5 M HCl–0.15% H_2O_2. The samples were taken up in 10 ml 0.5 M HCl and refluxed at 140 °C over night. Before loading onto the pretreated columns, H_2O_2 was added to the samples until a 0.5 M HCl–0.15% H_2O_2 mixture was obtained. The matrix elements including Ti were eluted with 30 ml 0.1 M HCl–0.15% H_2O_2, 10 ml 0.001 M HCl and 4 ml 0.5 M HNO_3. Subsequently, Ag was collected with 10 ml 0.5 M HNO_3. This second column resembles the first described above except for the use of H_2O_2, which controls the oxidation state of Ti, and thus eliminates Ti in the Ag cut. As for the first column, the elution of Ag varied to some extent and was checked accordingly. For silicate samples <1.5 g (e.g., Allende), the first large column was unnecessary and the preliminary separation of Ag was performed on the second column described above without the addition of H_2O_2.

Prior to the third column, the samples were dried down, taken up in 0.5 ml 0.5 M HNO_3 and refluxed at 140° overnight. The samples were then loaded onto a pre-cleaned column that held 1 ml AG50W-X8 cation exchange resin (200–400 mesh in a 4 mm by 80 mm column). After sample loading, the columns were rinsed with 16 ml 0.5 M HNO_3 and the Ag stripped from the resin with additional 14 ml 0.5 M HNO_3.

This three-stage ion exchange procedure efficiently separated Ag from major elements like Ti and Fe and achieved a very good separation from Pd, Cd and Ru. Cadmium and Ru introduce isobaric interferences on Pd that compromise the use of Pd for mass bias correction. Elements such as Cu, Zn, Ga, Ge, Sr, Y, Zr, Nb and Mo, which may create molecular interferences on Pd and Ag, were either not detectable or only present in sample solutions at low concentrations (element/Ag $\ll 0.1$). The yield of the three-stage procedure was usually ∼99%. Total procedural chemistry blanks, including sample dissolution and ion exchange chemistry were <250 pg.

2.3. *Preparation of Ag sample and standard solution for analysis*

After ion exchange chemistry, the Ag solutions were dried down and taken up in 0.5 M HNO_3. A small aliquot (4%) was taken and checked for Ti, Cr, Fe, Ni, Cu, Zn. Ge, Ga, Sr, Y, Zr, Nb, Mo and Pd to assure that these elements are below the level that could influence the precise and accurate measurement of the Ag isotopic composition. Thereafter, NIST SRM3138 Pd was added to the sample solution shortly before the isotopic measurement in order to obtain $^{106}Pd/^{107}Ag$ signal intensity ratios of 1. The Pd/Ag ratios and concentrations of sample and standard solution were matched within 20%. For the Ag standard solution, Pd was always admixed the same day as the isotopic analysis, because longer storage of mixed Pd–Ag solutions influences the measured Ag isotope composition [20]. In addition, the solutions should be virtually HCl free, because small traces of HCl can compromise the Ag analyses [20]. Exposure of Ag solutions to light could possibly result in photo-oxidation of Ag and influence the Ag isotopic composition. However, we have found that a pure NIST SRM978a Ag standard solution in HNO_3 stored over a 3-year period in a clear bottle exposed to light yielded the same isotopic composition as a freshly prepared Ag standard solution kept in an opaque container, and thus we do not consider light exposure of the Ag solutions a problem.

3. Mass spectrometry

3.1. *Instrumentation and data collection protocol*

The analyses were performed on the VG Axiom multicollector ICPMS at the Department of Terrestrial Magnetism (DTM). Detailed instrumental-type descriptions are given elsewhere [21,22]. Before analyzing samples, the performance of the instrument was checked with several runs of Ag standard solutions. Samples were always measured interspersed between Ag standards.

The measurements were conducted in static mode acquiring the masses 102, 104–111 amu (atomic mass unit) with Faraday cups and 10^{11} Ω resistor. In each measurement, 60 ratios (10 s integrations) were collected in blocks of 30. Baselines for each faraday cup were measured at half-mass below the actual mass for 15 s prior to each block. A measurement required about 10 min. Two sample introduction systems were used: (1) a low-uptake Teflon nebulizer (Elemental Scientific, USA) combined with a MCN-6000 desolvating system (CETAC, USA), which is referred to as dry plasma and (2) a low-uptake Teflon nebulizer (Elemental Scientific, USA) combined with a water-cooled glass cyclonic and impact bead spraychamber referred to as wet plasma. In a strict sense, the use of the MCN-6000 desolvating system does not result in a completely dry plasma, however, it is estimated that the desolvation process reduces the water content by two orders of magnitude [23] therefore leaving behind only minor traces of water. The solution uptake rate using the MCN-6000 desolvating system (dry plasma) was about 50 μl per minute resulting in a sensitivity of about 29 V/ppm Ag, while analyses in the wet plasma mode consumed about 110 μl per minute and yielded 22 V/ppm Ag. Hence, about three times more Ag was aspirated for wet plasma analyses. The nebulizer system was washed with 0.5 M HNO_3 between the analyses. Washout times of Ag were relatively rapid whereas the time interval to reduce Pd memories to an insignificant level required ≥15 min using the MCN. In wet plasma mode, this washout time was reduced to <5 min. Complete washout for Pd is not critical because the same NIST SRM3138 Pd standard was added to each sample including the Ag standard and the residual Pd did not fractionate during the washout procedure.

3.2. Data processing

For all isotopic measurements on the Axiom, the ^{108}Pd/^{105}Pd ratio was used for instrumental mass fractionation correction of ^{107}Ag/^{109}Ag based on the reference value of ^{108}Pd/^{105}Pd = 1.18899 [5] and applying the exponential mass-fractionation law. This correction was chosen because it yielded the best precision, but a similar precision was achieved with the empirical mass fractionation corrections as described by Maréchal et al. [14]. The mass bias was also monitored by means of ^{110}Pd/^{105}Pd and ^{106}Pd/^{105}Pd for quality check purposes. The data reported here all yielded identical results within the uncertainties for the different mass bias corrections. The overall mass fractionation was about 1.7% per amu in the dry plasma mode, while it was 1.4% under wet plasma condition. The Ag isotopic composition of each sample is expressed in ε (parts per 10^4) relative to the mean value of the NIST SRM 978a Ag standard, by which the sample was bracketed. The value chosen for the normalization ratios (^{108}Pd/^{105}Pd = 1.18899 [5]) has no influence on data expressed in ε ^{107}Ag.

Silver isotopes do not suffer from isobaric interferences. The isobaric Cd interferences on ^{106}Pd, ^{108}Pd and ^{110}Pd were corrected using the interference free ^{111}Cd as a monitor and the instrumental mass bias for Cd isotopes was taken into account for the correction procedure.

4. Results and discussion

4.1. Accuracy and precision of Ag isotope ratio measurements

The long-term average ^{107}Ag/^{109}Ag = 1.07911 ± 0.00027 (2 S.D. = standard deviation of the population) was obtained for the NIST SRM 978a Ag standard solution using the Axiom in dry plasma mode. The analyses were conducted over 21 separate measurement sessions within a period of 9 months. This value is identical within uncertainty to the ratio previously obtained on the Plasma-54 at DTM (1.07916 ± 0.00052) [10] and the TIMS value (1.0811 ± 0.0017) reported by Chen and Wasserburg [6]. It is only slightly lower than ^{107}Ag/^{109}Ag = 1.08048 ± 0.00042 determined by Woodland et al. [11] on a Nu Plasma MC-ICPMS. The long-term average established on the Axiom using wet plasma over a 9-month period (18 measurement sessions) is 1.07976 ± 0.00016. This value is the most precise so far reported and falls into the range defined by the previous data. However, the wet plasma value does not overlap with the dry plasma ratio obtained on the same instrument over a similar time span. This hints at the possibility that the sample introduction system influences the mass bias introduced during the measurements and the ability to correct for it. Our data indicate that this is only true for external normalization because the long-term averages for ^{106}Pd/^{105}Pd internally mass bias corrected relative to ^{108}Pd/^{105}Pd are identical for dry and wet plasma conditions (1.22288 ± 0.00007 and 1.22295 ± 0.00005, respectively).

The reproducibility of isotopic measurements for 100 ppb Ag solutions was typically 0.35ε (2 S.D.) for ^{107}Ag/^{109}Ag over one measurement session. This value does not depend on the use of wet or dry plasma. It is superior to the reproducibility obtained on the Plasma-54, which is 1.30ε [10].

4.1.1. Dry plasma experiments

Absolute values of ^{107}Ag/^{109}Ag can vary due to instrument setting and measuring conditions. Important for the application of Ag isotopic analyses is the precision and accuracy of sample measurements relative to the standard. Carlson and Hauri [10] reported offsets in the range of 3ε for the NIST SRM 978a Ag standard that was processed through ion exchange chemistry relative to the same standard solution *not* subjected to chemistry. Their experiment was performed on the Plasma-54 using dry plasma. In this study, the experiment was repeated on the Axiom and similar observations were made (Fig. 1a). The column treated standards display positive and negative deviations in the range of 3ε. Fig. 1b illustrates the natural logarithms of the measured ^{107}Ag/^{109}Ag ratio plotted against ^{108}Pd/^{105}Pd for the same data. Standards with identical isotopic composition should fall on a straight line in this graph, given that the ratio of the mass fractionation factors of Ag (β_{Ag}) and Pd (β_{Pd}) remained constant [14]. This is a prerequisite for the use of Pd to monitor the instrumental mass discrimination of Ag because it implies that changes in the mass bias similarly affect Ag and Pd isotopes. It does not necessarily mean that the mass fractionation factors are identical ($\beta_{Ag} = \beta_{Pd}$). In fact, this has been shown not to be the case for several element pairs including Pb–Tl [24], Cu–Zn

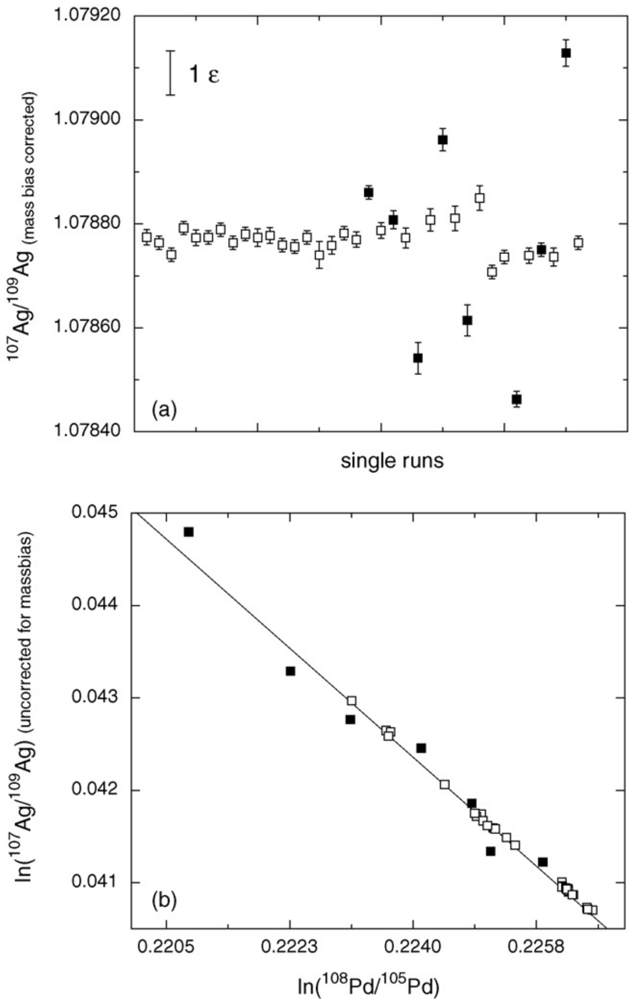

Fig. 1. (a) Consecutively measured ^{107}Ag/^{109}Ag ratios obtained over one measurement session obtained by dry plasma. The instrumental mass bias is corrected relative to ^{108}Pd/^{105}Pd. The within-run precisions are shown (2 S.D.$_{\text{mean}}$; which represents the standard deviation of the mean). Filled square: Ag standards passed through ion exchange chemistry; open square: untreated Ag standard solution. (b) The natural logarithm of ^{108}Pd/^{105}Pd relative to ln(^{107}Ag/^{109}Ag) uncorrected for mass bias, but corrected for a minor Cd interference on ^{108}Pd. The slope defined by the untreated Ag standards is 0.6638 ($R = 0.99$) which deviates from the predicted slope (−0.6575 [20]) based on the assumption $\beta\text{Pd} = \beta\text{Ag}$. β is the fractionation coefficient derived from the exponential law.

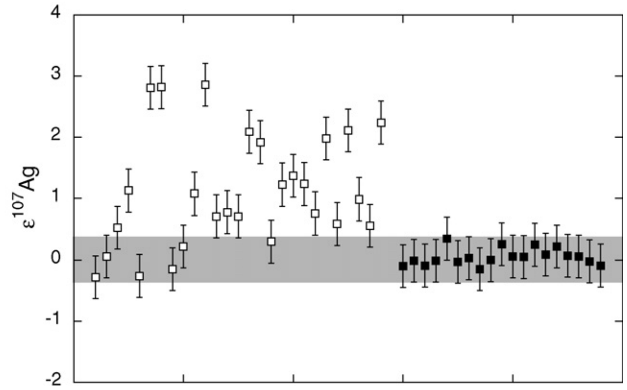

Fig. 2. The ε ^{107}Ag values for standard solutions that were spiked with small amounts of Zn and Cd (Zn/Ag = 0.025–0.1; Cd/Ag = 0.0005–0.01). Open symbol: data obtained under dry plasma conditions; filled symbol: data acquired with wet plasma. The uncertainties represent the external reproducibility (2 S.D.) obtained on standard solution on the same day. The gray bar denotes average including external reproducibility (±0.3ε; 2 S.D.) of the samples shown analyzed under wet plasma conditions. $\varepsilon\,^{107}\text{Ag} = [(^{107}\text{Ag}/^{109}\text{Ag})_{\text{sample}}/(^{107}\text{Ag}/^{109}\text{Ag})_{\text{standard}} - 1] \times 10^4$.

[14], Mo–Ru and Mo–Zr [15], Fe–Cu and Fe–Ni [25] and Pd–Ag [20]. Fig. 1b demonstrates that the analyses of the unprocessed Ag standard solution define a straight line, while the processed standards scatter around the line reflecting the deviations shown in Fig. 1a.

Interestingly, the addition of small amounts of Cd or Zn to the Pd–Ag standard solution also led to offsets ($\leq$+3ε) in Ag isotopic composition compared to the pure Ag standard solution (Fig. 2). The solutions added to the Ag standard did not contain HCl and this is confirmed by the results shown in Fig. 2 because the presence of HCl would lead to negative ε ^{107}Ag values [20], probably due to precipitation of AgCl during the desolvation process. Carlson et al. [26] reported that the addition of Ir, Sm and Nd also resulted in higher measured ^{107}Ag/^{109}Ag compared to the pure Ag standard. They showed that these offsets were accompanied by systematic offsets in the measured Pd isotopic ratios for solutions containing Ir and that these offsets propagated through the mass bias correction to the Ag isotope data. The experiments with Cd and Zn reported here agree with this interpretation. For pure Ag standard solution passed through chemistry, however, the mass bias seems to change drastically for both Ag and Pd. Archer and Vance [27] observed a similar behavior for Zn isotopes normalized to Cu. However, in their case the shifts could be circumvented by measuring column treated sample and standards relative to each other. In the case of Pd–Ag, the shifts remain.

4.1.2. Wet plasma experiments

All the above-described experiments were carried out with Ag standard solutions by means of dry plasma. However, when the Ag standard solutions with admixed Zn or Cd were analyzed under wet plasma condition, the shifts disappeared (Fig. 2) and this is also the case for the shifts observed for Ag standard solutions passed through chemistry. The external reproducibility (2 S.D.) was reduced to that of pure Ag solutions ($\leq$0.5ε). Accordingly, the raw ratio of ^{107}Ag/^{109}Ag and ^{108}Pd/^{105}Pd falls on the same fractionation line as standards with Cd added (Fig. 3). With the use of wet plasma, the sensitivity for Ag decreases by a factor of 3 as stated above, while the measured Pd/Ag ratios of the solutions increase by ~30% compared to dry plasma conditions. The concentrations of the employed Pd and Ag standard solutions were determined by isotope dilution and interestingly, the Pd/Ag ratios obtained by wet plasma reflect the true Pd/Ag ratios of the solutions. Moreover, the actual instrumental mass fractionation is about 20% lower using wet plasma and the mass bias of Ag relative to Pd remains constant even in the presence of solutions that contain impurities (Fig. 3). This is crucial for the mass bias correction by means of Pd. These observations suggest that erroneous data obtained by dry plasma are probably either due to (1) different behavior of Ag and Pd during the desolvation process (e.g., unequal adsorption onto the desolvat-

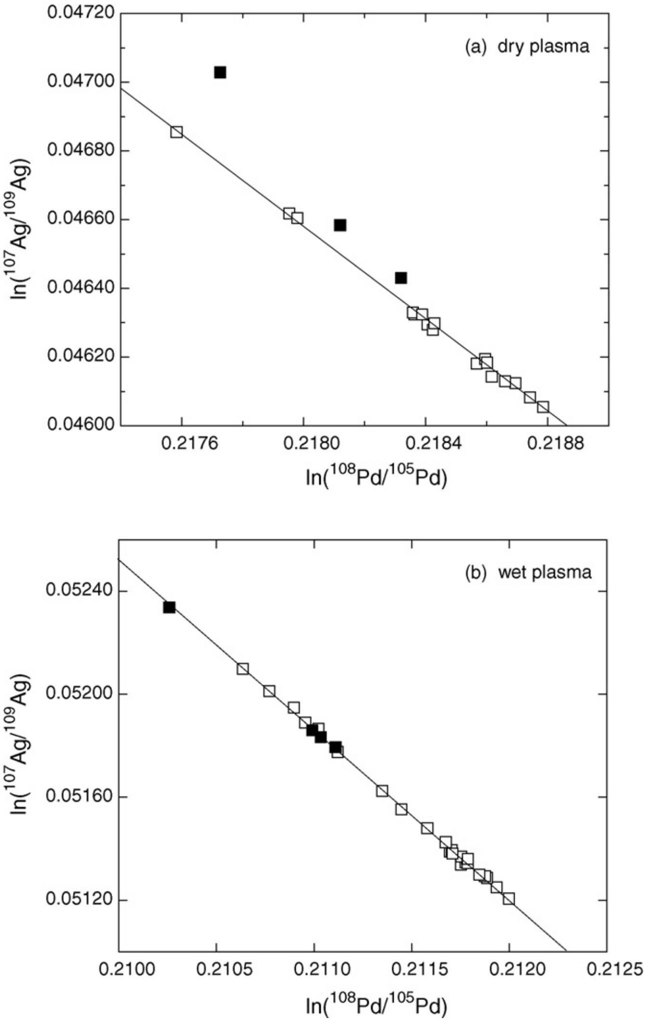

Fig. 3. The natural logarithms of $^{108}Pd/^{105}Pd$ and $^{107}Ag/^{109}Ag$ for Ag standard solutions obtained by (a) dry plasma and (b) wet plasma. The data are corrected for a minor Cd interference. The open symbols represent data for pure Ag–Pd standard solutions while the closed symbols are data that were acquired for Ag–Pd solutions with traces of Cd added (Cd/Ag ∼ 0.001).

ing membrane) that is dependent on the matrix element present or (2) the different size distribution of particulates and greater amount of water entering the plasma that changed the ionization condition in the plasma. The results obtained during this study do not provide unequivocal evidence for either interpretation. However, the first is favored for the following reasons: (A) the washout time for Pd is more than 10× longer than for Ag using the MCN-6000, but it is about equal under wet plasma conditions. This suggests that Pd may be adsorbed on surfaces of the MCN and only slowly released, while Ag is not adsorbed or is adsorbed to a much lesser extent. In addition, the washout times depend upon the matrix element present, which suggests that these reactions are sensitive to matrix elements. This is also true for the observed mass bias changes. (B) The conditions prevailing in the plasma seem to be more ideal during dry-rather than wet plasma operation. For example, in dry plasma mode, the size distribution of the aerosol entering the plasma is narrower [28], and the plasma load is significantly lower leaving more energy for the ionization of Pd and Ag. In line with this, the observed ionization efficiencies of Ag and Pd are generally higher during dry plasma operation. Hence, these plasma properties would suggest that different, and varying, mass discriminations would be more prevalent under wet than dry plasma conditions, but the opposite is observed.

Kamenov et al. [29] analyzed mixtures of Tl and Pb solution under wet and dry plasma conditions. They observed a scatter for Tl^{3+} bearing solution (but not Tl^{+} solutions) analyzed with dry plasma compared to wet plasma results. This is similar to the reported behavior for Ag–Pd solution doped with Zn, Cd, Sm, Nd or Ir. They also suggested that the desolvating process might have introduced variable mass bias. Although the reason for the data scatter in both studies may not be identical, Kamenov et al. [29] also observed a prolonged washout time for Tl^{3+} solution with their desolvating system as has been observed for Pd this study [10,11].

If indeed the desolvation process introduces an element- and matrix-dependent mass bias, it is generally not seen in single element isotope analyses that apply internal normalization because the mass discrimination seems to be identical within a single element and can be corrected with a mass fractionation law. The variations introduced due to the membrane desolvator are furthermore much smaller (ε-level) than the overall mass bias (percent level), which is thought to be caused mainly by the plasma source and the extraction mechanism of the ions from the plasma [14,21].

4.2. Spectral interferences and matrix effects

Spectral interferences and matrix effects can introduce analytical artifacts. External normalization techniques are more vulnerable to matrix effects than those that apply internal normalization and therefore such effects have to be investigated carefully. All Ag solutions were doped with NIST SRM 3138 Pd and possible matrix effects due to the Pd addition were investigated. Woodland et al. [20] reported that Ag isotopic ratios were unaltered as long as $^{106}Pd/^{107}Ag$ was within the range of 0.25–4 for their dry plasma measurements. To investigate possible effects for our wet plasma analyses, synthetic standard solutions of Ag and Pd were mixed in proportion such that their $^{106}Pd/^{107}Ag$ intensity ratio varied within ±20%. For this range of $^{106}Pd/^{107}Ag$, no variations in the measured Ag isotopic composition were observed. Therefore, all our samples and standards were analyzed at constant $^{106}Pd/^{107}Ag = 1$ (within 20%). In addition, the Ag and Pd concentrations of sample and standards were also matched to avoid artifacts due to concentrations differences.

A major concern of wet plasma analyses is possible interferences due to hydride formation. In this study, no hints of such interferences were observed. Due to the sample-standard matching procedure, all isotopes from 105 to 109 had comparable intensities; therefore similar interferences from hydrides on the masses 106–109 are expected assuming an identical hydride formation rate for Pd and Ag. Since only ratios are considered in this study, such interferences would cancel each other out. Moreover, the external reproducibilities of the $^{106}Pd/^{105}Pd$ ratio (internally normalized to $^{108}Pd/^{105}Pd$) are identical during wet and dry plasma analyses. The hydride formation rate for dry plasma analyses is very low and in general not considered a problem, thus the identical ^{106}Pd/^{105}Pd values strongly suggest that interferences from hydrides during wet plasma analyses are insignificant for the presented analytical procedure.

The mass bias correction also can be influenced by the isobaric interferences of Cd on ^{106}Pd, ^{108}Pd and ^{110}Pd. Although the chemical separation procedure assures a very good separation of Cd (Cd/Ag ratio < 0.001; the upper limit of the actual Cd/Ag concentration ratio of the solution is given), the reliability of the correction was checked by means of mixed synthetic solutions containing various amounts of Cd added to the Pd–Ag standard solution. For solutions with Cd/Ag concentrations above 0.01, the Pd isotopic composition started to show small shifts just distinguishable outside the analytical precision, but these shifts only became visible in the Pd-corrected Ag isotopic composition at Cd/Ag greater than 0.1, which is far above the Cd level detected in our sample solutions.

Elements such as Cu, Zn, Ga, Ge, Sr, Y, Zr, Nb and Mo can form molecular interferences with Ar, O, N and C that fall in the mass range of Pd and Ag isotopes. Moreover, major elements like Fe and Ti can potentially introduce matrix effects, if present at higher concentration levels. A small aliquot (4%) of each sample was taken before the addition of Pd and investigated for these elements (including Ti, Fe and Cr). Gadolinium, Ge, Sr, Y, Zr, Nb and Mo were below detection limit for all samples studied and have proven to be of no concern for sample measurements. Signal sizes of less than 10 mV of Ti, Fe, Cu and Zn were occasionally detected in the Ag fraction. Mixtures of synthetic solution were analyzed to investigate the influence of these elements. Titanium/Ag, Fe/Ag and Zn/Ag ratios up to 1 do not affect the Ag isotopic measurements. An elemental ratio of Cu/Ag = 1 does result in negative shifts of about 2ε in ^{107}Ag/^{109}Ag, but the measured Ag isotopic composition is the same as the clean standard when Cu/Ag is 0.025 or lower. All samples measured here had Cu/Ag well below 0.025. In iron meteorites, the elements Ru and Ir are very abundant and a clean separation through ion exchange chemistry is more difficult. Analyses of mixed synthetic solutions showed that the Ir/Ag ratios greater than 1 cause both shifts in measured Ag isotopic composition and prolonged washout times for Ag. No effects from Ru/Ag up to 0.1 have been observed. If higher abundances of Ir and Ru are detected in the Ag fraction, the solutions have to be reprocessed through ion exchange chemistry.

4.3. Reproducibility and accuracy of sample measurements for chondrites and terrestrial basalts

A major goal of this study was to develop a procedure for high precision isotopic measurement adapted to the sample matrices of stony meteorites and terrestrial basalts. For the assessment of the reproducibility and accuracy of the method, the Hawaiian basalt KOO49, the USGS standard rock Cody Shale (SCO-1) and the carbonaceous chondrite Allende were chosen. Given the number and complexity of the problems that can influence Ag isotopic analyses, a meaningful precision of the analytical technique can only be evaluated on replicate analyses of geological samples that were treated separately from dissolution to measurement. Therefore, three different aliquots of powder from the Hawaiian basalt KOO49 were dissolved and passed through the chemical separation procedure. The KOO49-1 aliquot was measured during seven different measurement sessions and an average of $\varepsilon\ ^{107}\text{Ag} = -10.46 \pm 0.25$ (2 S.D.) was obtained (Fig. 4). This excellent external reproducibility obtained for a single sample solution over different measurement sessions is identical to that of standard solutions. These results demonstrate that the use of wet plasma circumvents many of the mass bias correction problems observed under dry plasma conditions and thus leads to a significant improvement in precision. The two other aliquots of KOO49 (KOO49-2 and -3) were similarly processed through ion exchange chromatography and they yielded an average $\varepsilon\ ^{107}\text{Ag} = -9.35 \pm 0.68$ (2 S.D.). The isotopic composition obtained for these two separate dissolutions is different from, and more variable than, the KOO49-1 repeat measurements. This indicates that samples passed through chemistry have a slightly worse external reproducibility than a sample solution that is measured several times during different measurement sessions. Thus, the chemical separation procedure introduces a further uncertainty. There is furthermore a distinct difference of 1.1 ε-units between the average obtained for KOO49-1 and the dissolutions of KOO49-2 and -3. This is significant and emphasizes the importance of high yields. KOO49-1 was processed in early stages of this study, prior to a well-adapted calibration of the Ag elution peak, and 30% Ag was lost during the separation procedure. The other KOO49 dissolutions were not hampered by a poor calibration and had recoveries around 99%.

To verify that the poor yield for KOO49-1 may have influenced these data, the following experiment was performed: an Allende sample was dissolved and processed through the first anion column, where the initial 70% of the Ag elution was collected and further passed through ion exchange chemistry.

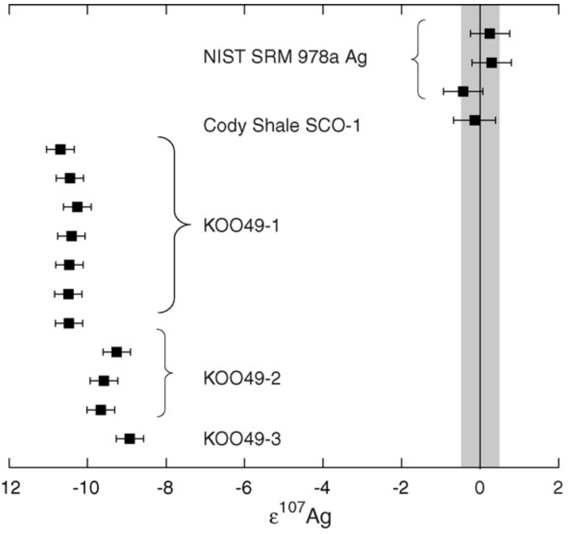

Fig. 4. The Ag isotopic composition for the NIST SRM 978a Ag standard passed through ion exchange chemistry, Cody Shale and the Hawaiian basalt KOO49. The terms KOO49-1, -2 and -3 denote different dissolutions of the basalt sample. The with-in run errors (2 S.D.$_{\text{mean}}$) are shown except for the Ag standards and Cody shale where an external reproducibility (2 S.D.) of $\pm 0.5\varepsilon$ was adopted. The gray bar indicates the external reproducibility of Ag standard solutions ($\pm 0.5\varepsilon$).

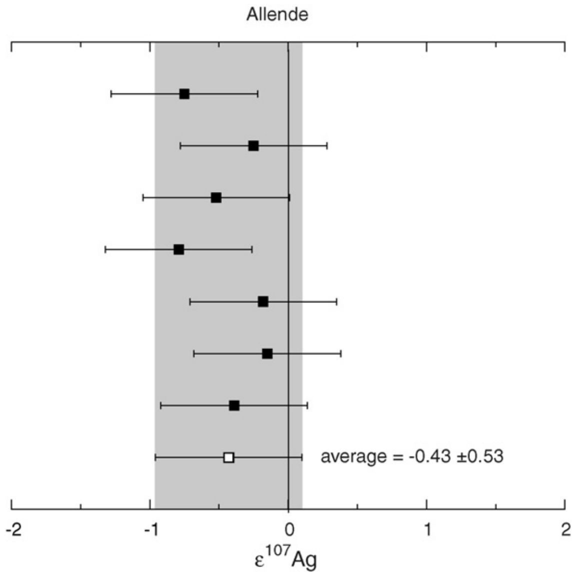

Fig. 5. The Ag isotopic composition for seven different dissolutions of the carbonaceous chondrite Allende (closed symbol). They yield an average $\varepsilon\ ^{107}$Ag of -0.43 ± 0.53 (2 S.D.) (open symbol). The grey bar highlights the uncertainty of the average.

This initial fraction yielded an $\varepsilon\ ^{107}\mathrm{Ag} = 0.96$. The latter 30% of the Ag was collected and treated independently and an $\varepsilon\ ^{107}\mathrm{Ag} = -4.11$ was obtained. Mathematically recombining both fractions results in an average $\varepsilon\ ^{107}$Ag of -0.56 for Allende, which is identical with the average value of -0.46 ± 0.53 (2 S.D.) found from seven different dissolutions of Allende (Fig. 5). Therefore, it is likely that the observed shift of 1.1ε for KOO49-1 is the result of the low Ag yield (~70%) obtained for this sample. This observation provides evidence that Ag isotope fractionation takes places during ion exchange chemistry. Isotope fractionation on ion exchanges columns has been reported earlier for other elements such as Ca, Fe, Cu, Zn, Mo and Cd [14,15,17,30–32]. All these studies observed that the first fractions eluted were enriched in the heavy isotopes, however, the opposite is observed for Ag. Losing the last 30% Ag results in about $+1\varepsilon$ shift in the Ag isotopic composition. It is therefore essential for accurate Ag isotopic determinations to assure Ag recoveries close to 100%. Significant losses of Ag were not observed during the parts of the analytical procedure that employ HCl, while caution has to be taken when HNO_3 is employed. As already mentioned, the elution peak of Ag can slightly vary for unknown reasons. Although the collected fractions were adjusted to optimize the yield, the eluants just before and after the Ag cut were checked for Ag and the yield of each sample was verified.

The reliability of our procedure is demonstrated by seven different dissolutions of Allende sample powder, which display an average $\varepsilon\ ^{107}\mathrm{Ag} = -0.43 \pm 0.53$ (2 S.D.) (Fig. 5). The external reproducibility of ±0.53 (2 S.D.; standard deviation of the population) estimated this way provides a good estimate for the total uncertainty introduced through sample digestion, ion exchange chemistry and mass spectrometry.

The verification of the accuracy is complicated by the fact that there is no geological reference material available for which the Ag isotopic composition is known to sufficient precision. The accuracy is supported by the fact that Ag standards passed through ion exchange chemistry yielded results identical to the untreated standard (Fig. 4). The $\varepsilon\ ^{107}$Ag value of -0.43 ± 0.53 for Allende is furthermore in agreement with the previous result of -1.1 ± 1.8 obtained by Woodland et al. [11], as is the Ag isotopic composition reported here for the Cody shale ($\varepsilon\ ^{107}\mathrm{Ag} = -0.14 \pm 0.50$; Fig. 4), which overlaps with the value given by Woodland et al. [11] ($\varepsilon\ ^{107}\mathrm{Ag} = -1.0 \pm 2.1$).

5. Conclusion

An improved MC-ICPMS technique is presented for high-precision Ag measurements, which permits isotopic analyses of small quantities of Ag (<100 ng). This technique is suitable for terrestrial basalts and stony meteorites, for which an external reproducibility of $\pm 0.5\varepsilon$ for $^{107}\mathrm{Ag}/^{109}\mathrm{Ag}$ is usually obtained. This represents an improvement in precision of more than an order of magnitude compared to TIMS analyses and a factor of four compared to previous MC-ICPMS studies. More precise data were obtained through the application of wet plasma. It appears that small random differences in the mass bias of Ag and Pd relative to each other are introduced during the desolvation process in the presence of matrix elements. Under wet plasma conditions, these effects disappear and the correction for instrumental mass discrimination is more reliable. Moreover, it has been shown that Ag isotopes can be fractionated during ion exchange chromatography and therefore high yields are mandatory for accurate Ag isotopic determinations.

With its excellent reproducibility, this new technique provides the foundation for the resolution of very small differences in Ag isotopic compositions and therefore the study of Ag isotopes in volatile-rich meteorites and the Earth. The precision now achievable opens up the investigation of the Pd–Ag chronometer for the timing of terrestrial core formation. Several bulk samples of a Hawaiian basalt (KOO49) were analyzed and yielded an Ag isotopic composition of -9.35ε for $^{107}\mathrm{Ag}/^{109}\mathrm{Ag}$. This result cannot be explained by the decay of the short-lived radionuclide ^{107}Pd and thus indicates that larger Ag isotopic variations due to stable isotope fractionation occurred in specific terrestrial environments. Further investigations are required to understand the Ag isotopic composition of the Earth.

Acknowledgments

This work was supported by National Science Foundation grant #EAR-0229417. Samples of Allende derive from the meteorite collection donated to DTM by George Tilton, which we gratefully acknowledge. Sample KOO-49 was provided by Fred Frey. We would also like to thank Fouad Tera, Sarah Woodland and Maud Boyet for helpful discussions and Steve Shirey for his assistance in Axiom repair.

References

[1] S.G. Nielsen, M. Rehkämper, A.N. Halliday, Geochim. Cosmochim. Acta 70 (2006) 2643.

[2] A.N. Halliday, T. Kleine, in: D.S. Lauretta, H.Y. McSween Jr. (Eds.), Meteorites and the Early Solar System II, University of Arizona, Tucson, 2006, p. 775.
[3] N.L. Chabot, H. Haack, in: D.S. Lauretta, H.Y. McSween Jr. (Eds.), Meteorites and the Early Solar System II, University of Arizona, Tucson, 2006, p. 747.
[4] M. Wadhwa, G. Srinivasan, R.W. Carlson, in: D.S. Lauretta, H.Y. McSween Jr. (Eds.), Meteorites and the Early Solar System II, University of Arizona, Tucson, 2006, p. 715.
[5] W.R. Kelly, G.J. Wasserburg, Geophys. Res. Lett. 5 (1978) 1079.
[6] J.H. Chen, G.J. Wasserburg, Geochim. Cosmochim. Acta 47 (1983) 1725.
[7] T. Kaiser, G.J. Wasserburg, Geochim. Cosmochim. Acta 47 (1983) 43.
[8] J.H. Chen, G.J. Wasserburg, Geochim. Cosmochim. Acta 54 (1990) 1729.
[9] J.H. Chen, G.J. Wasserburg, in: A. Basu, S.R. Hart (Eds.), Earth Processes: Reading the Isotopic Code, Geophysical Monograph 95, American Geophysical Union, 1996, p. 1.
[10] R.W. Carlson, E.H. Hauri, Geochim. Cosmochim. Acta 65 (2001) 1839.
[11] S.J. Woodland, M. Rehkämper, A.N. Halliday, D.-C. Lee, B. Hattendorf, D. Günther, Geochim. Cosmochim. Acta 69 (2005) 2153.
[12] E.H. Hauri, R.W. Carlson, J. Bauer, Lunar Planet. Sci. 31 (2000) 1812.
[13] N.S. Belshaw, X.K. Zhu, Y. Guo, R.K. O'Nions, Int. J. Mass. Spec. 197 (2000) 191.
[14] C.N. Maréchal, P. Télouk, F. Albarède, Chem. Geol. 156 (1999) 251.
[15] A.D. Anbar, K.A. Knab, J. Barling, Anal. Chem. 73 (2001) 1425.
[16] M. Rehkämper, M. Frank, J.R. Hein, D. Porcelli, A.N. Halliday, Earth Planet. Sci. Lett. 197 (2002) 65.
[17] F. Wombacher, M. Rehkämper, K. Mezger, C. Münker, Geochim. Cosmochim. Acta 67 (2003) 4639.
[18] T.F.D. Mason, D.J. Weiss, M. Horstwood, R.R. Parrish, S.S. Russell, E. Mullane, B.J. Coles, J. Anal. At. Spectrom. 19 (2004) 218.
[19] W.R. Kelly, F. Tera, G.J. Wasserburg, Anal. Chem. 50 (1978) 1279.
[20] S.J. Woodland, M. Rehkämper, D.-C. Lee, A.N. Halliday, in: G.P. Holland, S.D. Tanner (Eds.), Plasma Source Mass Spectrometry: Applications and Emerging Technologies, Royal Society of Chemistry, Cambridge, 2003, p. 338.
[21] M. Rehkämper, M. Schönbächler, C.H. Stirling, Geostand. News. 25 (2001) 23.
[22] P.J. le Roux, S.B. Shirey, L. Benton, E.H. Hauri, T. Mock, Chem. Geol. 203 (2004) 123.
[23] B. Hattendorf, D. Günther, J. Anal. At. Spectrom. 15 (2000) 1125.
[24] W.M. White, F. Albarède, P. Télouk, Chem. Geol. 167 (2000) 257.
[25] B.L. Beard, C.M. Johnson, J.L. Skulan, K.H. Nealson, L. Cox, H. Sun, Chem. Geol. 105 (2003) 87.
[26] R.W. Carlson, E.H. Hauri, C.M.O.D. Alexander, in: G.P. Holland, S.D. Tanner (Eds.), Plasma Source Mass Spectrometry: The New Millenium, Royal Society of Chemistry, Cambridge, 2001, p. 288.
[27] C. Archer, D. Vance, J. Anal. At. Spectrom. 19 (2004) 656.
[28] J.W. Olesik, I.I. Steward, J.A. Hartshome, C.E. Hensmann, in: G.P. Holland, S.D. Tanner (Eds.), Plasma Source Spectrometry: New Developments and Applications, Royal Society of Chemistry, Cambridge, 1999, p. 3.
[29] G.D. Kamenov, P.A. Mueller, M.R. Perfit, J. Anal. At. Spectrom. 19 (2004) 1262.
[30] W.A. Russell, D.A. Papanastassiou, Anal. Chem. 50 (1978) 1151.
[31] A.D. Anbar, J.E. Roe, J. Barling, K.H. Nealson, Science 288 (2000) 126.
[32] C.N. Maréchal, F. Albarède, Geochim. Cosmochim. Acta 66 (2002) 1499.