

Janne Blichert-Toft · Catherine Chauvel
Francis Albarède

Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS

Received: 12 September 1996 / Accepted: 13 January 1997

Abstract Potential applications of the Lu-Hf isotope system have long been impeded by the analytical difficulties of obtaining data on a wide variety of geological materials. Many of these limitations will now be eliminated because Hf isotopes can be readily measured with high precision and accuracy on small and/or Hf-poor samples using the newly developed magnetic sector-multiple collector ICP-MS, also known as MC-ICP-MS or the 'Plasma 54'. We present here a new method to separate and determine isotopic compositions of both Hf and Lu from various types of geological materials using MC-ICP-MS. The chemical separation of Hf and Lu has been designed to take advantage of the characteristics of this unique instrument. The separation of Hf can be achieved with a straightforward two-step ion-exchange column chemistry, which has a high efficiency (better than 85% recovery) and low blanks (typical total blanks less than 150 pg for the largest samples of 1 g bulk rock). The isolation of Lu is achieved with a single-stage ion-exchange column procedure with near 100% yields and blanks below 20 pg. Hf isotopic compositions can be routinely measured on 50 ng Hf with an internal precision better than 20 ppm in less than 15 min and with an external precision better than 40 ppm. Our value for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of the JMC 475 Hf standard currently is 0.282163 ± 9 (2s). The Lu isotopic ratio is measured rapidly and precisely without isolating Lu from the bulk of Yb, and a mass fractionation correction increases the accuracy of the results compared with TIMS data. Our current reproducibility of the Lu/Hf

ratio is $\approx 1\%$. Selected Lu-Hf isotope analyses of some modern and ancient geological samples validate the technique we have described here and illustrate the new opportunities for Lu-Hf isotope geochemistry that have opened up with the advent of magnetic-sector ICP mass spectrometry.

Introduction

^{176}Lu is radioactive and decays by beta emission to stable ^{176}Hf with a half-life of 35.9 billion years (Sguigna et al. 1982). This is both long enough for a significant amount of the parent isotope still to exist in the present-day Solar System and short enough for considerable variation to have been generated in the isotopic composition of the daughter element, thus allowing the dating of ancient samples and the tracing of ancient parent/daughter chemical fractionations. As such, the Lu-Hf isotope system is an important tool in dating geological events and in understanding planetary accretion processes, core formation, and the chemical evolution of the mantle-crust system throughout Earth history. In addition, it provides a unique complement to the similarly behaved and widely used Sm-Nd isotope system, in that the radioactive parent of the Lu-Hf isotope system, like Sm, belongs to the group of rare earth elements (REE). During primary magmatic events, such as extraction of melts from the mantle, the two isotopic systems behave analogously and form coherent positively correlated arrays in the space of Hf and Nd isotopic compositions (Patchett and Tatsumoto 1980a; Patchett 1983a, b; Stille et al. 1983; Salters and Hart 1991).

Contrary to the Sm-Nd isotope system, however, the radiogenic daughter of the Lu-Hf isotope system is not a REE, but belongs with the IVb group of high field strength elements and, despite principally lithophile behavior, exhibits markedly different chemical properties from those of Lu. Most notably, during metamorphic and magmatic events taking place in the crust, such as granulite facies metamorphism and crustal anatexis, Lu

J. Blichert-Toft (✉)¹ · F. Albarède¹
Ecole Normale Supérieure de Lyon, 46 Allée d'Italie,
69364 Lyon Cedex 07, France

C. Chauvel²
Geosciences Rennes, Université de Rennes, Campus de Beaulieu,
35042 Rennes Cedex, France

¹UMR CNRS 5570

²UPR CNRS 4661

Editorial responsibility: J. Patchett

becomes preferentially hosted by garnet that may form refractory residual assemblages after crustal melting, whereas Hf partitions strongly into zircon. This behavior, over time, has the potential of decoupling the Lu-Hf and Sm-Nd isotope systems and producing reservoirs in the lower crust that are characterized by high $^{176}\text{Hf}/^{177}\text{Hf}$ ratios relative to the corresponding $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. Any surviving correlation between the two isotope systems could place constraints on the respective importance of mantle differentiation and crustal growth mechanisms. In particular, the Lu-Hf isotope system could be used as an independent chronometric system against which the remarkably homogeneous isotopic composition of the early Earth mantle (Blichert-Toft and Albarède 1994), its apparent lack of Nd isotopic evolution (Shirey and Hanson 1986; Chase and Patchett 1988; Galer and Goldstein 1991), and the absence of a widespread ^{142}Nd anomaly in Early Archaean rocks (Harper and Jacobsen 1992; Goldstein and Galer 1992, 1993; Bennett et al. 1993; McCulloch and Bennett 1993) could be tested, thus providing a better understanding of the differentiation of the mantle-crust system (e.g., Vervoort et al. 1996).

Nevertheless, the difficulty associated with the isotopic measurement of Hf has long prevented the widespread application of the Lu-Hf isotope system to studies of terrestrial and extra-terrestrial materials, especially those poor in Hf. Consequently, there has been only modest improvement in our capability of measuring Hf isotopic compositions since Patchett and Tatsumoto (1980b) first introduced Lu-Hf isotope geochemistry to Earth and Planetary Sciences. One of the most significant limitations has been the inability to establish a precise planetary reference for the Lu-Hf isotope system based on chondritic meteorites. If the Lu-Hf system is to reach its full potential as both a geochronometer and a proxy of geological processes, it is essential that this be determined.

Recently, the production of a plasma source mass spectrometer (multiple-collector inductively-coupled plasma mass spectrometer or MC-ICP-MS, also named the "Plasma 54" by VG Elemental, the company that developed and produces it) has brought routine, high-precision, high-efficiency Lu-Hf isotope analysis within reach (Walder and Freedman 1992; Chauvel et al. 1993; Walder et al. 1993). The high sensitivity and precision of this new technology for Hf isotopic measurements promise to expand significantly the field of Lu-Hf chronometry. This paper reports on (a) the chemical separation methods necessary to determine Hf and Lu isotopic compositions by plasma source mass spectrometry, (b) the current performance of the instrument in Lyon for Lu and Hf isotope analysis, and (c) the precision and reproducibility of standards and a variety of modern and ancient natural samples.

Limitations of existing techniques (TIMS and hot-SIMS)

The major analytical limitations that have hindered the routine use of Hf isotopes in geological studies using thermal ionization mass

spectrometry (TIMS) are (a) low yield of Hf ions during mass analysis owing to the high first-ionization potential of Hf which requires extremely high filament currents and, in the case of rocks poor in Hf, chemical processing of undesirably large quantities of sample raising difficulties with blank levels and sample availability, (b) laborious and often imperfect chemical separation procedures for the isolation of Hf from Ti and Zr, and (c) the inability to correct accurately Lu for mass fractionation, because it has only two naturally occurring isotopes. The last point is a limitation only when the parent-daughter ratio is of interest, which is the case for ancient materials or samples with the potential of tracing solid-liquid fractionation processes in the mantle or the crust. Currently, internal precision of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio on a μg -sized Hf separate is at best 35 ppm (Patchett and Tatsumoto 1980a, c; Patchett et al. 1981; Pettingill and Patchett 1981; Tatsumoto et al. 1981; Patchett 1983a, b; Stille et al. 1983, 1986; White and Patchett 1984; Smith et al. 1987; Gruau et al. 1990; Salters and Hart 1991; Corfu and Noble 1992; Beard and Johnson 1993; Johnson and Beard 1993; Vervoort and Patchett 1996; Vervoort et al. 1996), while the $^{176}\text{Lu}/^{177}\text{Hf}$ ratio cannot be determined with a precision better than 1 to 2% due to uncorrected mass discrimination. For both ratios, this is about a factor of five worse than state-of-the-art Sm-Nd isotope measurements by TIMS.

An alternative to conventional thermal ionization for Hf isotope analysis is the hot-SIMS (secondary ionization mass spectrometry) technique having several orders of magnitude better ionization efficiency than ordinary TIMS due to ion beam bombardment of the Hf vapor coming off the filament. This technique was developed on the Lamont Isolab 54 (Salters 1994) and allows the routine analysis of substantially smaller samples than TIMS. Internal precision of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio is currently better than 100 ppm for samples down to 50 ng (Salters 1994; Salters and Zindler 1995; Salters 1996). In order to take full advantage of the high ionization yield of hot-SIMS, however, Hf must be more completely isolated from other elements competing for ionization, such as Zr and Ti. This requires chemical separations that are even more complicated and time-consuming than those used for conventional TIMS. Moreover, the actual mass spectrometric analysis remains a several hour long and delicate procedure, and the problem of not being able to correct Lu for mass discrimination likewise persists for Lu isotope dilution analysis. Nevertheless, hot-SIMS is a major improvement over TIMS and only the lack of development of suitable commercial mass spectrometers has prevented it from becoming the prevailing technique for Hf isotope analysis.

The critical advantage of MC-ICP-MS for Hf isotope measurement is the plasma source, which ionizes elements over the entire mass range with a much greater efficiency than TIMS and hot-SIMS, while keeping the advantages of a conventional mass spectrometer (magnetic sector, multi-collector configuration). This increased efficiency has allowed improved precision, both internal and external, and the ability to analyze much smaller samples than with TIMS. Both of these improvements are achieved with analysis times nearly an order of magnitude less than with TIMS and hot-SIMS. Although the MC-ICP-MS is the main advancement for Hf isotope analysis relative to prior Hf techniques, it has allowed modification of the laborious Lu-Hf separation chemistry to a simpler scheme. In the present work, we will demonstrate the superior internal and external reproducibility of Hf and Lu isotopic measurements with MC-ICP-MS for standards and geological samples and the excellent sensitivity of this new technique.

The Plasma 54

The Plasma 54 developed by VG Elemental over the past six years is a multiple collector double-focusing magnetic sector mass spectrometer with an inductively-coupled plasma (ICP) instead of a solid source (Walder and Freedman 1992; Walder et al. 1993) (Fig. 1). The only part that the Plasma 54 has in common with standard ICP-MS is the plasma source (torch box), while the most important differences are the mass filter, which is a magnetic sector and not a quadrupole, and the multiple collection assembly. These

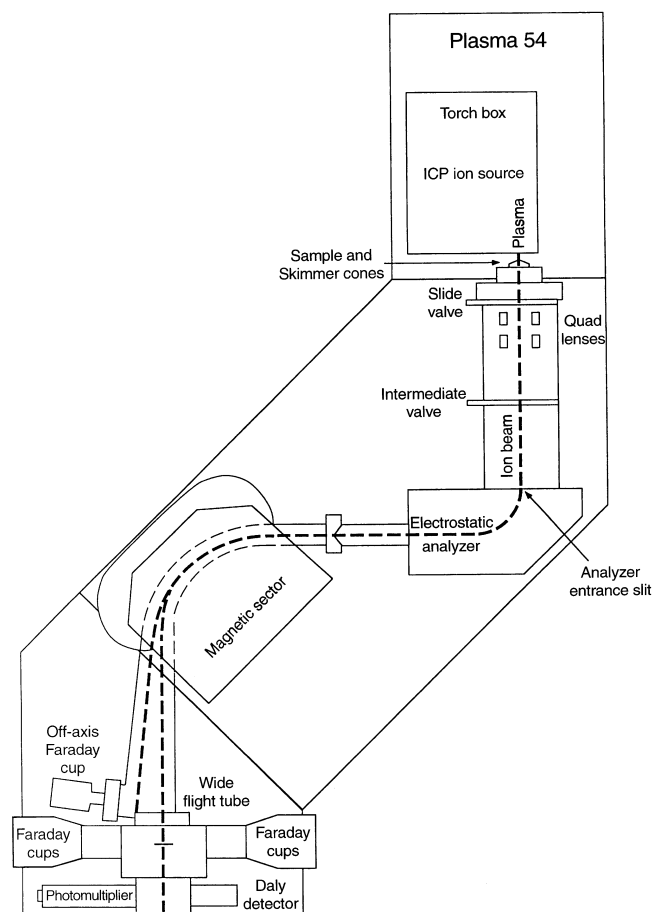


Fig. 1 Schematic outline of the multiple collector ICP-MS 'Plasma 54' manufactured by VG Elemental

differences will be shown to result in improvement in isotope ratio precision of nearly two orders of magnitude compared with ordinary ICP-MS.

The interface of the Plasma 54 differs from that of standard quadrupole ICP-MS by the application to both sample and skimmer cones of a high voltage of about 6000 V that accelerates and extracts ions generated by the plasma. While the high-voltage ion acceleration ensures good transmission, a stack of four quad lenses reshapes the circular plasma ion beam produced by the cones in order to fit the vertical analyzer entrance slit and optimize transmission into the double focusing mass analyzer.

A 10-cm radius electrostatic analyzer between the torch box and the mass spectrometer of the Plasma 54 decelerates and focuses the ion beam in order to match the energy dispersion of the plasma source with that of the magnetic sector analyzer. Good energy focusing has been found to be a critical step in producing precise isotopic ratios. This indicates that there is a substantial energy distribution in the plasma, especially at high temperatures (about 25 eV for a dry plasma).

The part of the Plasma 54 extending from the electrostatic sector closely resembles the standard VG Elemental Sector 54 multicollector mass spectrometer with the exception of a flared flight tube designed to accommodate an off-axis Faraday collector necessary for large mass-dispersion geochemical analyses. The double-focusing mass analyzer is capable of providing the flat-topped peaks essential to high-precision isotope analysis, and a multiple collection assembly deals with the unstable ion beam that usually limits the usefulness of plasma sources for such work. The configuration of the Lyon Plasma 54 has nine Faraday collectors

and a Daly multiplier detector with ion counting. Mass resolution is about 380 at 5% peak height and abundance sensitivity is about 2 ppm at one amu.

Dissolution and chemical separation

Different dissolution schemes must be used for different types of samples. By contrast, identical purification steps can be applied to all types of samples once properly dissolved.

Dissolution of modern samples

For zero age samples, usually only the Hf isotopic composition is of interest. This greatly simplifies the dissolution scheme because spike does not need to be added for Lu/Hf ratio determination. About 50–100 mg of rock powder, or more in the case of Hf-poor samples, is digested for 24–48 h with a 3:1 concentrated HF:HNO₃ mixture in a savillex capsule at about 100–120 °C and evaporated to dryness. Since sample-spike equilibration is not an issue, this dissolution method is adequate for most types of materials, provided they do not contain large amounts of zircons and other refractory minerals.

Dissolution of ancient samples

For ancient samples, the Lu/Hf ratio needs to be measured precisely by isotope dilution, thus requiring the addition of spike to the sample. Determining Lu/Hf ratios on geological samples is a non-trivial problem due to the difficulty of achieving complete sample-spike equilibration simultaneously for both elements. Lu dissolves readily in HCl, but not in HF, and Hf goes into solution easily in HF, but not in HCl. The optimum condition for one element is therefore the inferior condition for the other. Another consequence of this contrasting behavior is that although a mixed Lu-Hf spike is preferable because it helps reducing errors on Lu/Hf ratios, it carries the disadvantage of being potentially unstable in a solution of HF and HCl. Our own experience has shown that if too much HF is present (> 0.1 M HF/1 M HCl), Lu may precipitate from solution as an insoluble fluoride complex. Producing a mixed Lu-Hf spike is therefore a delicate task and the resulting spike should be recalibrated often to verify the stability of Lu in solution.

In order to obtain sample and spike in complete equilibration, the sample must be totally dissolved. This is well known to be best achieved using high-pressure, steel-jacketed teflon bombs as opposed to savillex capsules where resistant phases, such as zircon and some garnets, may not be completely dissolved. In the present work, however, all samples were dissolved in savillex capsules. We therefore emphasize that the uncertainties

associated with this work represent a worst-case-scenario that should be substantially improved by the use of pressure bombs for dissolution of spiked samples.

The dissolution of ancient samples currently involves digestion of sample powder and mixed Lu-Hf spike, added to the powder at the onset of the attack, with a 3:1:0.5 concentrated HF:HNO₃:HClO₄ mixture. The sample-spike dissolution is done in a savillex capsule kept at about 100–120 °C for 24–48 h followed by evaporation to dryness. For large samples, the chemical attack is repeated once. It is essential that HClO₄ is added to the attack solution in order to expel fluorides and ensure complete dissolution of the sample in 6 M HCl for sample-spike equilibration. HCl dissolution and subsequent evaporation is undertaken after the initial attack and is repeated 2–3 times.

Chemical separation of Hf and Lu

Upon adequate dissolution and spike-sample homogenization, concentrated HF is added to the residue and the closed beaker left on a hot plate overnight in order to bring the maximum amount of Hf into solution, while at the same time entraining REE with fluoride salts. The solid is centrifuged out and leached an additional three times with HF. This procedure leaves at least 90% of Hf in solution together with most of some minor and trace elements, such as Ti, Cr, Zr, Nb, Mo, Ta, and W, as well as a fraction of the sample matrix, while the REE as a group partition entirely into the fluoride residue, which

also contains most of the sample matrix. Selected key minor and trace element distributions for one determination between the fluoride salt and the HF supernatant of an ordinary basalt from the Piton de la Fournaise Volcano of Reunion Island tracked quantitatively by conventional ICP-MS are given in Table 1. This particular experiment did not include repeated leaching steps after initial separation of the Hf-bearing HF solution from the REE portion and therefore represents a minimum estimate of the Hf yield. This first-order, virtually complete, separation of REE from Hf eliminates at an early stage in the procedure the potential isobaric interferences from Lu and Yb on the critical radiogenic Hf mass 176 during mass spectrometric analysis. Because this method therefore by design partitions Lu from Hf, it is essential that sample and spike are in complete equilibrium prior to the fluoride precipitation step in order to avoid erroneous Lu/Hf ratios.

The decanted supernatant containing Hf is evaporated to dryness, taken up in a 1:1 mixture of dilute HF and HCl, and loaded on an anion-exchange column (AG1-X8, 100–200 mesh) (Table 2). The sample matrix and any residual trace of REE are removed by dilute 1:1 HF:HCl eluant, while Hf, Zr, and Ti (together with Cr^{VI}, Nb, Mo, Ta, and W) adhere to the resin as fluoride complexes until eluted with 6 M HCl. The efficient separation of the bulk rock from Hf is critical because the presence of either large concentrations of elements easy to ionize or heavy matrix elements would hamper the ionization of Hf.

Table 1 Minor and trace element distributions between fluoride salt and HF supernatant of basalt Q1101 from the Piton de la Fournaise Volcano of Reunion Island

Element ^a	WR Q1101 (ppm)	HF Supernatant (ppm)	Fluoride Salt (ppm)	Fraction in Supernatant (%)	Fraction in Fluoride Salt (%)
Ba	126.3	25.10	101.4	19.8	80.2
Y	23.70	0.10	23.90	0.4	99.6
La	17.26	0.49	16.75	2.8	97.2
Ce	41.89	8.03	33.84	19.2	80.8
Pr	5.24	0.07	5.18	1.3	98.7
Nd	23.44	0.25	23.28	1.1	98.9
Sm	5.46	0.04	5.49	0.7	99.3
Eu	1.80	0.01	1.76	0.6	99.4
Gd	5.54	0.04	5.52	0.7	99.3
Tb	0.81	0.00	0.80	0.0	100.0
Dy	4.68	0.02	4.61	0.4	99.6
Ho	0.86	0.00	0.86	0.0	100.0
Er	2.38	0.01	2.38	0.4	99.6
Tm	0.31	0.00	0.31	0.0	100.0
Yb	1.76	0.01	1.75	0.6	99.4
Lu	0.28	0.00	0.28	0.0	100.0
Ti	14500	14100	32	99.8	0.2
Zr	178	159	19.90	88.9	11.1
Nb	24.90	21.10	1.00	95.5	4.5
Hf	4.31	3.92	0.38	91.2	8.8
Ta	4.23	1.77	0.68	72.2	27.8
Pb	1.36	0.10	1.33	7.0	93.0
Th	1.87	0.06	1.77	3.3	96.7
U	0.57	0.53	0.01	98.1	1.9

^a Determined by ICP-MS (VG Plasma Quad, University of Montpellier II). Analytical precision is ±4–5%.

Table 2 Ion-exchange column specifications and Lu-Hf separation scheme

	Resin bed dimensions h × Ø (cv) ^a	Resin type	Elements eluted	Elements collected
Hf column				
I	4 cm × 0.8 cm (2.0 cm ³)	AG1-X8 100–200 mesh (anion)	Bulk sample in 10 cv 0.5 M HCl/0.5 M HF	Hf, Zr, Ti in 3 cv 6 M HCl
II	12 cm × 0.45 cm (2.0 cm ³)	AG50W-X8 200–400 mesh (cation)	Ti and Cr ^{VI} in 3.5 cv 2.5 M HCl/H ₂ O ₂	Hf, Zr in 2.5 cv 2.5 M HCl/0.3 M HF
Lu column				
I	13.5 cm × 0.75 cm (6.0 cm ³) (max. 0.3 g bulk rock)	AG50W-X12 200–400 mesh (cation)	Bulk sample in 3.3 cv 2 M HNO ₃ /0.5 M C ₂ H ₂ O ₄ and 6.7 cv 2 M HNO ₃	Heavy REE in 3 cv 8 M HNO ₃

^a h height, Ø internal diameter, cv column volume.

Although the elements accompanying Hf after the first elution (Zr, Ti, etc) do not behave as ionization suppressors for Hf, the presence of significant amounts of Ti in the Hf fraction reduces the transmission of Hf significantly during mass spectrometric analysis on the Plasma 54 and causes systematic drift in the measured isotopic ratios. This is due partly to the formation of deposits of refractory Ti on the sample-cone orifice, which creates an interfering electrical shield across the cone aperture, and partly to matrix effects between Ti and Hf in the ion beam itself. The presence of large amounts of Cr in the Hf fraction has a similar effect to that of Ti, but poses a major problem only for chondrites and some komatiites, in which Cr is a major element, and only because these samples are treated with HClO₄ in the initial chemical attack. During evaporation of HClO₄ at about 200 °C, Cr^{III} becomes oxidized to Cr^{VI} (in the form of CrO₃) which, contrary to Cr^{III}, behaves analogously to Hf and sticks to the anion exchange resin while the sample matrix is being washed off and therefore is eventually eluted with Hf. Ti and Cr are separated from Hf on a second-stage cation-exchange column (AG50W-X8, 200–400 mesh) using HCl-H₂O₂-HF mixtures (Salters 1994) (Table 2). Ti is eluted first as an orange to orange-red Ti·(H₂O)_x complex, which is followed within less than one column volume by the CrO⁴⁺ complex appearing as a distinct, narrow brownish-grey band on the column. Because even substantial amounts of Zr in the Hf fraction neither influence Hf ionization or transmission nor interfere isobarically with Hf or form molecules that could interfere isobarically with Hf, it is not necessary (contrary to what is needed for TIMS and hot-SIMS determination of Hf isotopic compositions) to separate Hf from Zr. The Hf-Zr fraction recovered from the second-stage Hf column is therefore the fraction from which the sample Hf isotopic composition is eventually measured on the Plasma 54.

The fluoride salt containing the REE fraction is re-attacked in a concentrated HF:HNO₃:HClO₄ mixture, or simply treated with HClO₄ alone, evaporated to dryness, and taken up in nitric media. The addition of HClO₄ at this stage is again essential in order to expel

the fluorides for full recovery of the REE. Either all of the sample or just an aliquot in the case of large samples, is loaded on a cation-exchange column (AG50W-X12, 200–400 mesh) (Table 2), where washing with a mixture of dilute HNO₃ and oxalic acid (C₂H₂O₄) followed by dilute HNO₃ alone leaves a rather pure REE fraction on the column (Gast et al. 1970; Govindaraju and Mevelle 1987; Cassidy 1988). Further addition of concentrated HNO₃ strips a dominantly heavy REE fraction, which is analyzed directly on the Plasma 54 without further separation. This method allows the processing of a large range of sample sizes without having to resolve to excessively large resin bed volumes, which would increase acid consumption and blank levels. Alternatively, for standard sample sizes not exceeding about 100 mg, conventional cation-exchange techniques (e.g., Hart and Brooks 1977) suffice to isolate the heavy REE fraction from the sample matrix without overloading reasonably sized columns.

The above MC-ICP-MS-compatible chemistry protocol for Hf and Lu purification compares favorably with those associated with TIMS and hot-SIMS techniques. For the purification of Hf, only two relatively simple elution steps are employed instead of three and four, respectively, for TIMS (Patchett and Tatsumoto 1980b; Barovich et al. 1995) and hot-SIMS (Salters 1994) protocols. For Lu separation, a single column is required. A second elution step serving to separate Lu from Yb, such as either cation-exchange with 2-methylacetic acid (Smith and Hoffman 1956; Eugster et al. 1970; Gruau et al. 1988) or reversed-phase partition chromatography using HDEHP coated on teflon beads (Cerrai and Testa 1963; Richard et al. 1976; Vervoort and Patchett 1996), has been found unnecessary.

Recovery and chemistry blanks

All chemistry procedures were carried out in a clean environment with laminar airflow drying boxes and all teflon and polyethylene material cleaned in HF. Throughout the chemistry, only double subboiling distilled acids and ultrapure reagents were used. Total

procedural chemistry blanks currently are less than 150 pg for a 150 ng sample of Hf and 20 pg for a 30–40 ng sample of Lu, or about one permil of the measured sample when attacking 1 g of powder, and substantially less for smaller bulk-rock sample sizes.

Yields of the various ion-exchange columns were measured quantitatively by ICP-MS (quadrupole: VG Plasma Quad, University of Montpellier II; magnetic sector: Plasma 54, Ecole Normale Supérieure de Lyon) using calibration curves and direct comparison of signal intensities between samples and gravimetrically prepared standard solutions. The Hf yield of the dissolution procedure and the first-stage Hf column is consistently in excess of 90%, while Hf recovery for samples through the second-stage Hf column varies from 85 to 95%. The Lu yield of the dissolution procedure and the single-stage Lu column is between 95 and 100%.

Lu and Hf standards and spikes

Mixed ^{176}Lu - and ^{180}Hf -enriched spikes with different Lu/Hf ratios were prepared for the isotope dilution analysis of a variety of geological materials. In order to calibrate the Lu and Hf spike solutions and the various mixed Lu-Hf spikes by both isotope dilution and calibration curves on the Plasma 54, Lu and Hf normal solutions were prepared from one gram chunks of pure Lu and Hf metals provided by the Ames Laboratory. The Lu/Hf ratios and Lu and Hf concentrations of multiple mixed Lu-Hf normals prepared gravimetrically from the Ames stock solutions are known to better than 0.1%. The resulting spike calibrations carried out on the Plasma 54 likewise are known to better than 0.1%. These values were checked against calibrations by TIMS, which yielded Lu and Hf isotopic compositions and concentrations identical within error to those measured on the Plasma 54.

Our Hf spike is enriched in ^{180}Hf to more than 98%, which is sufficiently pure that sample concentration and Hf isotopic composition can be measured on the same aliquot provided the sample is adequately underspiked with respect to Hf. We spike the sample in such a way that the contribution of ^{180}Hf from the spike represents 3% of ^{180}Hf in the sample-spike mixture. This leads to a correction of the measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratio due to the presence of the spike of 4 to 6 on the sixth digit (4–6 ppm). For spiking of the sample with respect to Lu, the optimum spiking criterium is applied. Our mixed Lu-Hf spikes are prepared so as to fulfill these two criteria simultaneously as well as allowing for at least 200 mg of spike to be added in order to minimize weighing error. Incomplete sample-spike isotopic equilibration does not affect the value obtained for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of the sample, but does affect its $^{176}\text{Lu}/^{177}\text{Hf}$ ratio. If different $^{176}\text{Hf}/^{177}\text{Hf}$ ratios are obtained for replicates, incomplete dissolution of a heterogeneous mineral assemblage or powder heterogeneity are therefore to be suspected.

Mass spectrometry

Detailed descriptions of the fundamental features of MC-ICP-MS can be found in Walder and Freedman (1992), Walder et al. (1993), and Halliday et al. (1995), so for brevity only the actual performance of the plasma sector machine in Lyon at the time of writing will be summarized here.

Sensitivity

The sensitivity of the Plasma 54 in Lyon, which is now routinely obtained, currently is about 0.01 nA for a 50 ppb solution of Hf or Lu, translating into a transmission efficiency of about 500 ppm. Although this sensitivity may at times increase by as much as a factor of two, it is still significantly lower than that of conventional sector mass spectrometers and is due primarily to the inefficient sampling of the plasma.

Nebulization system

We have experimented extensively on various configurations of the plasma source (Meinhard, glass-expansion, or the CETAC 100 micro concentric nebulizer in various combinations with the Fassel type spray chamber or the ultra-high efficiency Mistral heating and condensation stages) in order to optimize sample consumption, signal stability, and machine blank. Minimal memory effects and maximum ion beam efficiency and stability are obtained when using the glass-expansion nebulizer in combination with the Fassel type spray chamber and capillary teflon tubing and operating the system in the free aspiration mode (P. Télouk, manuscript in preparation). During free aspiration, the sample uptake tubing is disconnected from the peristaltic pump and sample solution is being aspirated due to an infinitesimal pressure differential between the nebulizer and the atmospheric conditions outside of the torch box. Free aspiration of sample solution is preferable to peristaltic pumping because it avoids the severe memory effects inherent to Tygon tubing, which is mandatory in use with peristaltic pumps, and allows for the smallest possible sample consumption. We also experienced significant grounding problems affecting the stability of the ion beam when the peristaltic pump is used.

Our preferred nebulization system operates reproducibly at a maximum uptake rate of 50 μl per minute, though usually at no more than 25 μl per minute. Typical argon flow rates are 12–14 l min^{-1} for the cooling, 1–2 l min^{-1} for the auxiliary, and 0.7–1.0 l min^{-1} for the nebulizer. The minimum solution volume necessary for adequate free aspiration is about 0.4 ml. The minimum analysis time required to obtain an in-run precision better than 50 ppm for a 50 ppb solution of Hf is about 10 min. The current sensitivity of the Plasma 54 together

Table 3 Analysis data structure of static mode routines for interference and fractionation corrected Hf and Lu isotopic measurements

Faraday cup position	Low 4	Low 3	Low 2	Low 1	Axial	High 1	High 2	High 3	High 4
Hf isotopic analysis									
Nominal amu collected	173	175	176	177	178	179	180	181	182
Elements collected	Yb monitor	Lu monitor	Hf with Lu and Yb interferences	Hf	Hf	Hf	Hf with Ta and W interferences	Ta monitor	W monitor
Lu isotopic analysis									
Nominal amu collected	168	170	171	172	173	174	175	176	177
Elements collected	Yb with Er interference	Yb with Er interference	Yb monitor	Yb monitor	Yb monitor	Yb with Hf interference	Lu	Lu with Yb and Hf interferences	Hf monitor

with the consumption rate of the nebulization system and the analysis time for one sample thus in the worst case amounts to a total Hf signal of about 0.01 nA for a throughput of 2.5 ng of Hf per minute and at times almost twice that. Precise Hf isotopic compositions can therefore now be determined routinely on as little as 25 ng of Hf. In order to determine element concentrations by isotope dilution with a precision better than 1%, the minimum sample size is even smaller, on the order of 5 ng or less.

Hf reference and standard values

Hf and Lu isotopic measurements are generally performed in static mode according to the routines outlined in Table 3. Cup bias factors (to correct for varying collector efficiencies) depend strongly on the alignment of the machine and amount to less than ± 30 ppm for each of the nine Faraday collectors. If efficiency factors necessary to obtain the correct standard values exceed 30 ppm, the machine is re-aligned. Currently, cup efficiency factors for Hf are calculated relative to the values recommended for the isotopic composition of Hf by Stevenson and Patchett (1990) (Table 4). Some of these values were confirmed within error on the Plasma 54 using a multidynamic collection scheme (see Appendix), which cancels differences in collector efficiencies but requires a larger sample size for a given level of precision due to multiple peak switching. The results of repeated multidynamic analyses of the JMC 475 Hf standard are shown for the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in Fig. 2.

Interferences

Because Hf and Lu are not completely purified prior to isotopic analysis, the measured Hf and Lu isotopic ratios must be corrected for isobaric interferences. Potential interferences on Hf are W and Ta at mass 180 and Lu

and Yb at mass 176. These are corrected by monitoring, respectively, the isotopes ^{182}W , ^{181}Ta , ^{175}Lu , and ^{173}Yb (Table 3). The ^{180}W and ^{180}Ta interferences are subtracted using values of 0.004501 for $^{182}\text{W}/^{180}\text{W}$ (Lee and Halliday 1995) and 0.0001200 for $^{180}\text{Ta}/^{181}\text{Ta}$ (DeBièvre et al. 1984), while the ^{176}Lu and ^{176}Yb interferences are subtracted using values of 0.02656 for $^{176}\text{Lu}/^{175}\text{Lu}$ (this study; Table 4) and 0.7876 for $^{176}\text{Yb}/^{173}\text{Yb}$ (McCulloch et al. 1977; Table 4).

Potential interferences on Lu are Hf and Yb, both at mass 176, and are corrected by monitoring the major, interference-free masses 171, 172, or 173 for Yb and mass 177 for Hf (Table 3). The $^{176}\text{Lu}/^{175}\text{Lu}$ ratio is obtained by subtracting the ^{176}Hf and ^{176}Yb interferences using the value of 0.28216 for $^{176}\text{Hf}/^{177}\text{Hf}$ (Stevenson and Patchett 1990; this study; Table 4) and either the value given above for $^{176}\text{Yb}/^{173}\text{Yb}$ or the values for $^{176}\text{Yb}/^{172}\text{Yb}$ or $^{176}\text{Yb}/^{171}\text{Yb}$ (McCulloch et al. 1977;

Table 4 Average best 'true' values (in bold) for the isotopic compositions of Yb, Lu, and Hf as measured by TIMS and reproduced within error by MC-ICP-MS. These values currently are used as reference for isotopic measurements carried out on the Plasma 54. Values recommended by IUPAC are shown for comparison

	TIMS/Plasma 54	IUPAC ^c
$^{168}\text{Yb}/^{171}\text{Yb}^{\text{a,b}}$	0.00951	0.00910
$^{170}\text{Yb}/^{171}\text{Yb}^{\text{a,b}}$	0.2137	0.2133
$^{172}\text{Yb}/^{171}\text{Yb}^{\text{a,b}}$	1.5264	1.5315
$^{173}\text{Yb}/^{171}\text{Yb}^{\text{a,b}}$	1.1248	1.1272
$^{174}\text{Yb}/^{171}\text{Yb}^{\text{a,b}}$	2.2163	2.2237
$^{176}\text{Yb}/^{171}\text{Yb}^{\text{a,b}}$	0.8859	0.8881
$^{176}\text{Lu}/^{175}\text{Lu}$	0.026525 ^c / 0.02656^b	0.02669
$^{176}\text{Hf}/^{177}\text{Hf}^{\text{d,b}}$	0.282160	0.2838
$^{178}\text{Hf}/^{177}\text{Hf}^{\text{d,b}}$	1.467168	1.4794
$^{179}\text{Hf}/^{177}\text{Hf}^{\text{d,b}}$	0.732500	0.7500
$^{180}\text{Hf}/^{177}\text{Hf}^{\text{d,b}}$	1.886666	1.9216

^a McCulloch et al. (1977).

^b This study.

^c Patchett and Tatsumoto (1980b); Patchett (1983b).

^d Stevenson and Patchett (1990).

^e De Bièvre et al. (1984).

Fig. 2 $^{176}\text{Hf}/^{177}\text{Hf}$ values obtained for the JMC 475 Hf standard on the Plasma 54 using a multiple dynamic analysis scheme. The $^{176}\text{Hf}/^{177}\text{Hf}$ ratio of 29 analyses averages 0.282163 (unweighted mean) with a 2 standard deviation of ± 0.000009 (33 ppm). Error bars represent 2s internal run precisions. These analyses represent the performance of the Plasma 54 from January to September 1996

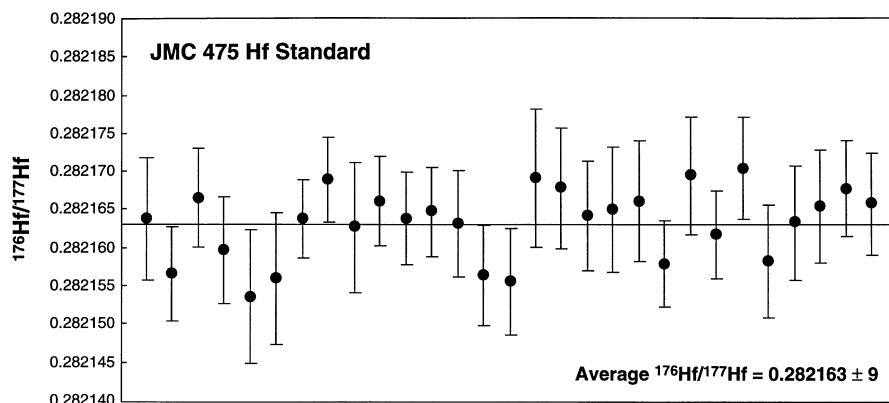


Table 4). The interference and mass-fractionation corrected isotopic composition of Lu was measured on the Plasma 54 and found to be identical within error to that obtained using TIMS (Patchett and Tatsumoto 1980b; Patchett 1983b) and that recommended by IUPAC (De Bièvre et al. 1984) (Table 4).

Although Lu and Yb are always monitored as a matter of precaution during Hf isotope analysis, they are not observed in Hf separates purified according to the separation scheme described here. Likewise, Hf is never observed in the Lu separates, though again always monitored. However, because Lu is measured without previous separation from Yb, the Yb correction of ^{176}Lu is significant but will be showed below to be more precise than the current reproducibility of the Lu/Hf ratio. By contrast, most Hf separates contain natural Ta and W in various amounts, but because the natural abundances of ^{180}Ta and ^{180}W are about 0.01 and 0.1%, respectively, corrections made to ^{180}Hf are negligible relative to the precision in determining the Lu/Hf ratio. For the samples presented here, Ta and W corrections were significant on the fourth digit or less (< 500 ppm). In practice, interferences at mass 180 are only important when samples have been spiked with a ^{180}Hf -enriched spike. In order to restrict Ta and W interferences to those of natural sample abundances, which are usually at trace level, sample preparation should avoid crushing in tungsten-carbide mortars.

Gadolinium-oxide potentially interferes with the masses of Yb as well as mass 176 of Lu but can be accurately corrected for by peak stripping (Albarède 1995) at a high level of precision provided the major masses of Yb are monitored during analysis. Because Lu from geological samples is measured on the Plasma 54 in the presence of Gd, the extent to which GdO forms in the source of the Plasma 54 was investigated. Examination of analyses of both Gd standard solutions prepared from pure AMES metal and total REE fractions from various geological materials showed that GdO is not produced in detectable amounts ($< 0.02\%$). The conspicuous absence of GdO and other molecular species is ascribed to the relative dryness and high temperature of the plasma. Similarly, the extent of hydride

production in the plasma was monitored for various configurations of the nebulization system by measuring the 181/180 ratio of a pure Hf solution and was found to be less than 2 ppm.

Mass fractionation

Halliday et al. (1995), Taylor et al. (1995), and Hirata (in press) propose that mass fractionation on the MC-ICP-MS can be corrected using either power or exponential laws (Russell et al. 1978), but then apply only the power law correction. Both laws are physically acceptable because the ratio of two ratios conserves the same mass fractionation law. Taylor et al.'s (1995) expression for the exponential law, however, is identical to that of the power law. As pointed out by Halliday et al. (1995), the 'fractionation per mass unit' of the power law is constant. This is in contrast to what we observe for a wide range of masses (60–238 amu) and elements. In the present work, all the Hf and Lu isotopic ratios are normalized for mass fractionation using the exponential law of Russell et al. (1978), which can be written

$$R_{\text{true}} = R_{\text{measured}} \left(\frac{M_2}{M_1} \right)^f$$

where R is the ratio of the ion beams at masses M_2 and M_1 . The variable f is the mass discrimination coefficient which, for all the elements determined on the Plasma 54, is equal to -2.0 ± 0.2 . Expanding this expression for small mass differences, we find that the fractionation $\Delta R/R$ per mass unit is $\approx 2/M_1$, i.e., slightly more than 1% per amu in the Hf range. Mass fractionation for MC-ICP-MS is therefore about one order of magnitude larger than for TIMS and hot-SIMS.

The Hf isotopic ratios are normalized internally to $^{179}\text{Hf}/^{177}\text{Hf}$ of 0.7325. Because Lu has only two naturally occurring isotopes, the mass fractionation factor for Lu is obtained externally from Yb, whose mass fractionation factor is common to that of Lu. The $^{176}\text{Lu}/^{175}\text{Lu}$ ratio is normalized to the more precise of the Yb ratios, $^{172}\text{Yb}/^{171}\text{Yb}$, with reference to a value of 1.5264 (McCulloch et al. 1977). Attempts to use

non-interfering Er or W as monitors of mass fractionation for Lu resulted in more variable results, which we ascribe to the larger mass difference between the isotopes of these elements and Lu compared with the mass difference between the isotopes of Lu and Yb. For spiked samples, the fractionation factor is derived by solving iteratively a non-linear equation combining the exponential fractionation law and the spike-natural mixing equation.

Sample analysis and machine blank

The dry separates from the second-stage Hf column and the single-stage Lu column are redissolved in at least 0.4 ml of 0.05 M HNO₃. This acid molarity is sufficient to dissolve the sample and, together with the fluorine traces left in the sample from the last step of Hf purification, stabilize Hf and Lu in solution, but is too weak to attack teflon tubing and glassware. Immediately prior to analysis (in order to avoid adsorption of Hf onto polyethylene walls during prolonged storage), the dissolved sample is transferred to a small conically-shaped polyethylene centrifuge tube from which the sample solution is freely aspirated directly into the plasma through teflon tubing.

The focusing of the Plasma 54 is optimized with our in-house Hf or Lu-Yb standards, depending on which elements are to be determined, and the electronic equipment allowed to stabilize for about an hour before adjusting the final focusing prior to sample analysis. At regular intervals throughout sample analysis, the Hf standard is run to confirm the stability, accuracy, and precision of the instrument. Cross-calibration has shown that our in-house Hf standard (JMC Hf ICP standard solution, batch 301862F) is isotopically indistinguishable from the JMC 475 inter-laboratory Hf standard (Table 4).

Samples are analyzed manually in alternation with cleaning routines. Aspiration of dilute HF, followed by 3% HNO₃, and conditioning with HNO₃ of the same acidity as that of the sample solution has been found to eliminate machine memory for Hf and Lu. The duration of each cleaning step, typically two minutes, is determined by monitoring the signal intensity of the most abundant of the isotopes of the element to be analyzed while cleaning solution is being aspirated. The next sample is analyzed when this signal for the conditioning solution has fallen below the detection limit for at least one minute. The level of sample dilution is sufficient for the pure conditioning solution to provide an accurate estimate of the memory.

Table 5 shows Hf and Lu isotopic compositions of various geological materials analyzed by the Plasma 54 comparing the accuracy, precision, and reproducibility with those of other laboratories using different techniques. Five measurements of the ¹⁷⁶Hf/¹⁷⁷Hf ratio of the Aleutian arc basalt AUG-7 show a reproducibility of 38 ppm (unweighted standard deviation), which com-

pares with 34 ppm obtained on six runs of the same sample by hot-SIMS by Salters (1994). The unweighted averages of this ratio on the Plasma 54 (0.283200) and the Lamont Isolab 54 (0.283267) differ by 0.000067, which compares with a bias of 0.000047 on the JMC 475 Hf standard between the two laboratories. In-run precision, however, is four times better on the Plasma 54 despite shorter analysis time (15–20 min) and smaller sample size [similar amounts of sample prepared (50–100 mg), but only about half consumed during analysis on the Plasma 54 to obtain the reported precision]. Some typical Hf isotope analyses of a few mid-ocean ridge and ocean island basalts are also shown. They fall within the range of Hf isotopic compositions obtained for similar oceanic basalt samples by TIMS and hot-SIMS.

Duplicates done on different powder aliquots of one enstatite chondrite, Pillistfer, three ordinary chondrites, Moorabie, Barratta, and Kramer Creek, and one carbonaceous chondrite, Allende, are within the 2σ internal run precision for the ¹⁷⁶Hf/¹⁷⁷Hf ratio (duplicates are available only for the Hf isotopic composition). In addition, we reproduce within analytical error the ¹⁷⁶Hf/¹⁷⁷Hf ratio of Allende as measured by TIMS (Patchett and Tatsumoto 1981). We reproduce the ¹⁷⁶Lu/¹⁷⁷Hf ratio of these authors, however, to only about 2%, which we estimate is due primarily to powder heterogeneity combined with small sample sizes and not using pressure bombs for dissolution.

The reproducibility of the ¹⁷⁶Lu/¹⁷⁷Hf ratio is difficult to evaluate. Replicate isotope dilution analyses of shelf standard solutions will underestimate the actual dispersion expected from rock samples because the differential resistance of various minerals is not taken into account. By contrast, replicate analyses of a rock powder cannot distinguish powder heterogeneity from analytical problems, such as incomplete dissolution. An objective upper limit for the reproducibility of the ¹⁷⁶Lu/¹⁷⁷Hf ratio can, however, be estimated if reference ¹⁷⁶Lu/¹⁷⁷Hf values are known. For example, eight samples from the same lithological unit of Isua in West Greenland, of which three are listed as examples in Table 5, have been found to define a statistically significant isochron (unpublished data). We conservatively assume in a first step that the misfit of the analytical points in the isochron diagram is due entirely to analytical errors on the ¹⁷⁶Lu/¹⁷⁷Hf ratio and not to initial isotopic heterogeneity. This interpretation is very robust with respect to the mode of linear fitting, i.e., weighted or unweighted, and to the errors selected. The mean-squared deviation from the straight line in the case of the eight-point Isua isochron is 2% for regression along the ¹⁷⁶Lu/¹⁷⁷Hf (horizontal) axis. A similar test has been undertaken for 23 chondrites (Blichert-Toft and Albarède, 1997), of which five are listed in Table 5, assuming that the true measurements form an isochron with an age of 4.56 Ga. Removing three samples signaled as outliers by a 3-sigma filter, the mean-squared deviation upon regression along the horizontal axis is again 2%. This estimate neglects uncertainties on the ¹⁷⁶Hf/¹⁷⁷Hf ratio and therefore is an

Table 5 Precision, reproducibility, and comparison with other laboratories and techniques of Hf and Lu isotope analyses

Sample No.	Rock Type	[Lu] ppm ^b	[Hf] ppm ^b	¹⁷⁶ Lu/ ¹⁷⁷ Hf ^b	¹⁷⁶ Hf/ ¹⁷⁷ Hf ^c	Lab ^d
AUG-7	Aleutian arc basalt				0.283218 ± 5	ENSL
"	"				0.283195 ± 6	"
"	"				0.283196 ± 6	"
"	"				0.283202 ± 5	"
"	"				0.283190 ± 6	"
"	"				0.283270 ± 26	LDEO ^e
"	"				0.283281 ± 24	"
"	"				0.283259 ± 17	"
"	"				0.283259 ± 20	"
"	"				0.283257 ± 23	"
"	"				0.283273 ± 20	"
SO 12-91-D2	Pacific MORB				0.283266 ± 8	ENSL
CYP 78-04-07A	"				0.283183 ± 7	"
CH 77 DR4-106	Atlantic MORB				0.283238 ± 5	"
NAL 36	Iceland tholeiite				0.283200 ± 6	"
NAL 71	"				0.283215 ± 5	"
Pillistfer ^a	Chondrite E6	0.02678	0.1187	0.0320	0.282708 ± 14	ENSL
"	"				0.282719 ± 13	"
Moorabie ^a	Chondrite L3	0.03587	0.1553	0.0328	0.282786 ± 24	"
"	"				0.282761 ± 15	"
Barratta ^a	Chondrite L4	0.03653	0.1587	0.0327	0.282774 ± 11	"
"	"				0.282772 ± 16	"
Kramer Creek ^a	Chondrite L4	0.03901	0.1599	0.0346	0.282802 ± 19	"
"	"				0.282763 ± 24	"
"	"				0.282759 ± 9	"
Allende ^a	Chondrite C3	0.04983	0.2109	0.0335	0.282776 ± 15	"
"	"				0.282775 ± 8	"
Allende 810215	Turbidite within Isua Garbenschiefer	0.0460	0.199	0.0327	0.28280 ± 8	USGS Denver ^f
810348	Greywacke (Isua Formation A6)	0.2083	3.9958	0.00741	0.280878 ± 9	ENSL
810423	Isua Amphibolite	0.1178	1.7457	0.00959	0.281007 ± 6	"
		0.5756	2.8301	0.0289	0.282501 ± 5	"

^a Chondrites provided by the Geological Museum of Copenhagen.

^b 2σ errors for Lu and Hf concentrations and ¹⁷⁶Lu/¹⁷⁷Hf are < 1%.

^c Uncertainties reported on ¹⁷⁶Hf/¹⁷⁷Hf are 2σ/√n analytical errors in last decimal place. All duplicate analyses were carried out on different powder aliquots. Sample sizes were 1 g for chondrites and 50–100 mg for Isua samples and modern basalts. Sample solutions were consumed entirely for the chondrite analyses and about half for the modern basalt and Isua analyses.

^d The average value of the JMC 475 inter-laboratory Hf standard at ENSL during the period of collection of the AUG-7 data (June 1996) was 0.282160, whereas the value of this standard at LDEO from 1990–1994, when the Lamont AUG-7 data were obtained, averaged 0.282207. The value of the JMC 475 Hf standard at USGS Denver at the time of analysis of Allende was 0.28220 compared with 0.282163 at ENSL (Fig. 2) for the period of collection of the chondrite data (January–September 1996).

^e Hot-SIMS data from Salters (1994).

^f TIMS data from Patchett and Tatsumoto (1981).

upper limit of the error on ¹⁷⁶Lu/¹⁷⁷Hf. Introducing the external reproducibility of standards as the error on ¹⁷⁶Hf/¹⁷⁷Hf, we find that estimated and calculated errors on the ¹⁷⁶Lu/¹⁷⁷Hf ratio at the 95% confidence level agree for a value of about 1%.

Table 6 shows the Lu concentration obtained for five different chondrites on the Plasma 54 with and without preceding separation of Lu from Yb. Upon dissolution each chondrite was split into two aliquots both of which were taken through a cation-exchange column where REE fractions were collected. One REE fraction was measured directly on the Plasma 54 for Yb and Lu isotopic composition according to the analysis configuration given in Table 3, while the other REE fraction was loaded on a standard HDEHP column on which Lu was separated from Yb (Cerrai and Testa 1963; Richard et al. 1976; Vervoort and Patchett 1996). The pure Lu

fraction was then analyzed on the Plasma 54 using the same analysis configuration as that used for the REE fraction, but with the Yb in-house standard solution being analyzed both before and after the Lu sample in

Table 6 Lu concentrations obtained on the Plasma 54 with and without foregoing Lu-Yb separation

Chondrite ^a	Type	[Lu] ppb Lu not separated from Yb	[Lu] ppb Lu separated from Yb
Pillistfer	E6	28.70	28.43
Moorabie	L3	37.97	38.36
Tennasilim	L4	36.54	36.92
Heredia	H5	33.50	33.88
Allende	C3	47.80	48.28

^a Chondrites provided by the Geological Museum of Copenhagen.

order to keep track of mass fractionation. The resulting Lu concentrations from the one-stage and two-stage separation procedures agree to within about 1%. We attribute this discrepancy to (1) the rather imprecise isotopic composition of Yb, which is known to no better than 4 digits (McCulloch et al. 1977), (2) the less precise mass fractionation correction in the case of pure Lu fractions, and (3) the low Lu content of chondrites. Nevertheless, this test carried out on some of the more difficult and Lu-poor natural material to analyze, validates the method of measuring Lu in the presence of the bulk of Yb by correcting for the isobaric interference of Yb on mass 176.

Conclusions

The Plasma 54 has been shown to be capable of generating high-precision Lu-Hf isotopic measurements with an internal reproducibility of, respectively, 20 ppm and 1% for the $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{176}\text{Lu}/^{177}\text{Hf}$ ratios on separates of as little as 25–50 ng of Hf and 5 ng of Lu in about 10–20 min per analysis and with an external reproducibility which is better than 40 ppm. This is similar to state-of-the-art Sm-Nd isotope measurements by TIMS, but superior to Lu-Hf isotope measurements by TIMS in terms of both precision and sample size. Relative to hot-SIMS, plasma source mass spectrometry performs only slightly better with respect to external and internal precision and sample size, and is advantageous mainly because of the simpler separation chemistry and the shorter analysis time. Compared with quadrupole ICP-MS, which produces isotopic ratios with a precision no better than one permil, the Plasma 54 represents an improvement in precision by two orders of magnitude owing to its magnetic sector and multiple collection.

The dramatically improved Hf sensitivity of the Plasma 54 despite a very fast sample throughput has lifted the analytical barrier for a wide range of samples. For instance, the precise Hf isotope analysis of chondrites is now possible by processing no more than 1 g of material for each sample versus some unfeasible 10 g required by previous methods. Likewise, a large variety of other Hf-poor natural materials, such as mafic and ultramafic rocks and mineral separates other than zircons, as well as Hf-rich, but precious materials, such as achondrites and manganese nodules, can now be analyzed in significantly smaller quantities and with far better precision and efficiency than before. In addition, the separation chemistry for Hf and Lu is relatively simple compared with those necessary for TIMS and hot-SIMS measurements. The samples presented in this paper have demonstrated the ability of the Plasma 54 to produce high-quality Hf and Lu isotopic data on both modern and ancient material by processing small samples (50–100 mg bulk rock) with minimal chemical preparation (two-stage Hf and one-stage Lu purification) in little time (10–20 min per analysis).

Appendix

Scheme for multidynamic measurement of $^{176}\text{Hf}/^{177}\text{Hf}$

The exponential fractionation law (Russell et al. 1978) is the only law that results in a consistent fractionation factor for all ratios. We have used a notation where, for example, M_{178} is the atomic mass of ^{178}Hf . The cups are assigned according to Table 7. We assume that, during one cycle of three consecutively measured sequences, the efficiency of cup X is a constant α_x . The corrected and reference ratios are noted with subscript d and r, respectively. We get, from sequence 2

$$\left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_r = \frac{\alpha_{Ax}}{\alpha_{H1}} \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_2 \left(\frac{M_{178}}{M_{177}}\right)^f \quad (1)$$

where f is the mass fractionation factor and, from sequence 3

$$\left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_r = \frac{\alpha_{L1}}{\alpha_{Ax}} \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_3 \left(\frac{M_{178}}{M_{177}}\right)^f \quad (2)$$

$$\left(\frac{^{179}\text{Hf}}{^{177}\text{Hf}}\right)_r = \frac{\alpha_{L1}}{\alpha_{H1}} \left(\frac{^{179}\text{Hf}}{^{177}\text{Hf}}\right)_3 \left(\frac{M_{179}}{M_{177}}\right)^f \quad (3)$$

Multiplying Eqs. (1) and (2) gives

$$\left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_r^2 = \frac{\alpha_{L1}}{\alpha_{H1}} \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_2 \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_3 \left(\frac{M_{178}}{M_{177}}\right)^{2f} \quad (4)$$

Subtracting the logarithms of Eqs. (3) and (4), the efficiency ratios cancel and we get

$$f = \frac{2 \ln \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_r - \ln \left(\frac{^{179}\text{Hf}}{^{177}\text{Hf}}\right)_r - \ln \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_2 - \ln \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_3 + \ln \left(\frac{^{179}\text{Hf}}{^{177}\text{Hf}}\right)_3}{2 \ln \left(\frac{M_{178}}{M_{177}}\right) - \ln \left(\frac{M_{179}}{M_{177}}\right)}$$

or

$$f = \frac{\ln \left[\frac{\left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_r \left(\frac{^{178}\text{Hf}}{^{179}\text{Hf}}\right)_r}{\left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_2 \left(\frac{^{178}\text{Hf}}{^{179}\text{Hf}}\right)_3} \right]}{\ln \left[\frac{\left(\frac{M_{178}}{M_{177}}\right)}{\left(\frac{M_{179}}{M_{177}}\right)} \right]} \quad (5)$$

Taking the geometric average of the two expressions (5) for the two couples of sequences 1–2 and 2–3 conserves the full advantage of the measurement, and we finally obtain

$$f = \frac{\ln \left[\frac{\left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_r \left(\frac{^{178}\text{Hf}}{^{179}\text{Hf}}\right)_r}{\sqrt{\left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_1 \left(\frac{^{178}\text{Hf}}{^{177}\text{Hf}}\right)_2 \left(\frac{^{178}\text{Hf}}{^{179}\text{Hf}}\right)_2 \left(\frac{^{178}\text{Hf}}{^{179}\text{Hf}}\right)_3}} \right]}{\ln \left[\frac{\left(\frac{M_{178}}{M_{177}}\right)}{\left(\frac{M_{179}}{M_{177}}\right)} \right]}$$

The mass fractionation coefficient f can now be calculated from the reference ratios $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{178}\text{Hf}/^{179}\text{Hf}$. The cup efficiency

Table 7 Analysis data structure of multiple dynamic peak switching routine for fractionation corrected $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic measurement

Faraday cup position	Low 1	Axial	High 1
Nominal amu collected			
Sequence 1	175	176	177
Sequence 2	176	177	178
Sequence 3	177	178	179

ratios can be retrieved from Eqs. (1) and (2), and from sequences 1 and 2 we get the expressions

$$\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_d = \frac{\alpha_{\text{Hf1}}}{\alpha_{\text{Ax}}} \left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_1 \left(\frac{M_{176}}{M_{177}}\right)^f$$

$$\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_d = \frac{\alpha_{\text{Ax}}}{\alpha_{\text{L1}}} \left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_2 \left(\frac{M_{176}}{M_{177}}\right)^f$$

For better statistics, these two expressions are combined as

$$\left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_d = \sqrt{\frac{\alpha_{\text{Hf1}}}{\alpha_{\text{L1}}} \left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_1 \left(\frac{^{176}\text{Hf}}{^{177}\text{Hf}}\right)_2} \times \left(\frac{M_{176}}{M_{177}}\right)^f$$

The $^{180}\text{Hf}/^{177}\text{Hf}$ ratio is dynamically corrected through a similar procedure.

Acknowledgements We would like to thank Béatrice Luais for sharing the burden of getting started with a new type of instrument. Andrew Walder, Ian Bowen, Andrew Entwistle, and Steve Bloomfield from VG Elemental patiently spent endless hours breaking in the mass spectrometer. Vincent Salters was a patient, inspiring, and helpful advisor for Hf chemistry. As soon as Philippe Télouk joined our group, he ingeniously improved the performance of the Plasma 54. Long discussions with Jon Patchett encouraged us to keep confident in the value of the present work. Al Hofmann made sure to provide us with enough pure Gd metal solution to create a new anomaly in the regional REE patterns. Liliane Savoyant and Simone Pourtalès responded quickly to numerous impatient requests for quadrupole ICP-MS data. The trust of the Curator of the Geological Museum of Copenhagen, Asger Ken Pedersen, in a technique yet to be established gave us the opportunity to work on precious samples at an early stage in the project. Likewise, Minik Rosing kindly provided rare samples from Isua. Constructive reviews by Vincent Salters, Jeff Vervoort, and an anonymous reviewer helped improve this manuscript. The European Union supported this research through grant ERB4001GT931301 to JBT and FA. This work was also supported by the CNRS DBT program “Terre Profonde”. We further wish to thank the Institut des Sciences de l’Univers, the Ministère de l’Education Nationale, and Région Rhône-Alpes for funding the Plasma 54.

References

- Albarède F (1995) Introduction to geochemical modeling. Cambridge University Press, Cambridge
- Barovich KM, Beard BL, Cappel JB, Johnson CM, Kyser TK, Morgan BE (1995) A chemical method for hafnium separation from high-Ti whole-rock and zircon samples. *Chem Geol* 121: 303–308
- Beard BL, Johnson CM (1993) Hf isotope composition of late Cenozoic basaltic rocks from northwestern Colorado, USA: new constraints on mantle enrichment processes. *Earth Planet Sci Lett* 119: 495–509
- Bennett VC, Nutman AP, McCulloch MT (1993) Nd isotopic evidence for transient, highly depleted mantle reservoirs in the early history of the Earth. *Earth Planet Sci Lett* 119: 299–317
- Blichert-Toft J, Albarède F (1994) Short-lived chemical heterogeneities in the Archean mantle with implications for mantle convection. *Science* 263: 1593–1596
- 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* (in press)
- Cassidy RM (1988) Determination of rare-earth elements in rocks by liquid chromatography. *Chem Geol* 67: 185–195
- Cerrai E, Testa C (1963) Separations of rare earths by means of small columns of KEL-F supporting di(2-ethylmethyl) orthophosphoric acid. *J Inorg Nucl Chem* 25: 1045–1050
- Chase CG, Patchett PJ (1988) Stored mafic/ultramafic crust and early Archean mantle depletion. *Earth Planet Sci Lett* 91: 66–72
- Chauvel C, Albarède F, Walder AJ, Keller D (1993) Application of plasma source mass spectrometry to high precision-high sensitivity measurement of Hf isotope composition in basaltic samples. *EOS Trans Am Geophys Union* 74: 339
- Corfu F, Noble SR (1992) Genesis of the southern Abitibi greenstone belt, Superior Province, Canada: evidence from zircon Hf isotope analyses using a single filament technique. *Geochim Cosmochim Acta* 56: 2081–2097
- De Bièvre P, Gallet M, Holden NE, Barnes IL (1984) Isotopic abundances and atomic weights of the elements. *J Phys Chem Ref Data* 13: 809–891
- Eugster O, Tera F, Burnett DS, Wasserburg GJ (1970) Isotopic composition of gadolinium and neutron-capture effects in some meteorites. *J Geophys Res* 75: 2753–2768
- Galer SJG, Goldstein SL (1991) Early mantle differentiation and its thermal consequences. *Geochim Cosmochim Acta* 55: 227–239
- Gast PW, Hubbard NJ, Wiesmann H (1970) Chemical composition and petrogenesis of basalts from Tranquillity Base. *Proc 2nd Lunar Sci Conf, Geochim Cosmochim Acta Suppl* 1: 1143–1163
- Goldstein SL, Galer SJG (1992) On the trail of early mantle differentiation: $^{142}\text{Nd}/^{144}\text{Nd}$ ratios of early Archean rocks. *EOS Trans Am Geophys Union* 73: 323
- Goldstein SL, Galer SJG (1993) Early mantle differentiation and the Nd paradox. *EOS Trans Am Geophys Union* 74: 655–656
- Govindaraju K, Mevelle G (1987) Fully automated dissolution and separation methods for inductively coupled plasma atomic emission spectrometry rock analysis. Application to the determination of rare earth elements. *J Anal At Spectrom* 2: 615–621
- Gruau G, Cornichet J, Le Coz-Bouhnik M (1988) Improved determination of Lu/Hf ratio by chemical separation of Lu from Yb. *Chem Geol* 72: 353–356
- Gruau G, Chauvel C, Arndt NT, Cornichet J (1990) Aluminium depletion in komatiites and garnet fractionation in the early Archean mantle: hafnium isotopic constraints. *Geochim Cosmochim Acta* 54: 3095–3101
- Halliday AN, Lee D-C, Christensen JN, Walder AJ, Freedman PA, Jones CE, Hall CM, Yi W, Teagle D (1995) Recent developments in inductively coupled plasma magnetic sector multiple collector mass spectrometry. *Int J Mass Spectrom Ion Proc (Nier Vol)* 146/147: 21–33
- Harper CL, Jacobsen SB (1992) Evidence from coupled ^{147}Sm - ^{143}Nd and ^{146}Sm - ^{142}Nd systematics for very early (4.5-Gyr) differentiation of the Earth’s mantle. *Nature* 360: 728–732
- Hart SR, Brooks C (1977) The geochemistry and evolution of early Precambrian mantle. *Contrib Mineral Petrol* 61: 109–128
- Hirata T (in press) Lead isotopic analysis using multiple collector-inductively coupled plasma mass spectrometry coupled with modified external correction method for mass discrimination effect. *The Analyst*
- Johnson CM, Beard BL (1993) Evidence from hafnium isotopes for ancient sub-oceanic mantle beneath the Rio Grande rift. *Nature* 362: 441–444
- Lee D-C, Halliday AN (1995) Precise determination of the isotopic compositions and atomic weights of molybdenum, tellurium, tin and tungsten using ICP magnetic sector multiple collector mass spectrometry. *Int J Mass Spectrom Ion Proc (Nier Vol)* 146/147: 35–46
- McCulloch MT, Rosman KJR, De Laeter JR (1977) The isotopic and elemental abundance of ytterbium in meteorites and terrestrial samples. *Geochim Cosmochim Acta* 41: 1703–1707
- McCulloch MT, Bennett VC (1993) Evolution of the early earth: constraints from ^{143}Nd - ^{142}Nd isotopic systematics. *Lithos* 30: 237–255
- Patchett PJ (1983a) Hafnium isotope results from mid-ocean ridges and Kerguelen. *Lithos* 16: 47–51
- Patchett PJ (1983b) Importance of the Lu-Hf isotopic system in studies of planetary chronology and chemical evolution. *Geochim Cosmochim Acta* 47: 81–91
- Patchett PJ, Tatsumoto M (1980a) Hafnium isotope variations in oceanic basalts. *Geophys Res Lett* 7: 1077–1080

- Patchett PJ, Tatsumoto M (1980b) A routine high-precision method for Lu-Hf isotope geochemistry and chronology. *Contrib Mineral Petrol* 75: 263–267
- Patchett PJ, Tatsumoto M (1980c) Lu-Hf total-rock isochron for the eucrite meteorites. *Nature* 288: 571–574
- Patchett PJ, Tatsumoto M (1981) Lu/Hf in chondrites and definition of a chondritic hafnium growth curve (abstract). *Lunar Science Abstr XII*: 822–824
- Patchett PJ, Kouvo O, Hedge CE, Tatsumoto M (1981) Evolution of continental crust and mantle heterogeneity: evidence from Hf isotopes. *Contrib Mineral Petrol* 78: 279–297
- Pettingill HS, Patchett PJ (1981) Lu-Hf total-rock age for the Amitsoq gneisses, West Greenland. *Earth Planet Sci Lett* 55: 150–156
- Richard P, Shimizu N, Allègre CJ (1976) $^{143}\text{Nd}/^{144}\text{Nd}$, a natural tracer: an application to oceanic basalts. *Earth Planet Sci Lett* 31: 269–278
- Russell WA, Papanastassiou DA, Tombrello TA (1978) Ca isotope fractionation on the Earth and other solar system materials. *Geochim Cosmochim Acta* 42: 1075–1090
- Salters VJM (1994) $^{176}\text{Hf}/^{177}\text{Hf}$ determination in small samples by a high-temperature SIMS technique. *Anal Chem* 66: 4186–4189
- Salters VJM (1996) The generation of mid-ocean ridge basalts from the Hf and Nd isotope perspective. *Earth Planet Sci Lett* 141: 109–123
- Salters VJM, Hart SR (1991) The mantle sources of ocean ridges, islands and arcs: the Hf-isotope connection. *Earth Planet Sci Lett* 104: 364–380
- Salters VJM, Zindler A (1995) Extreme $^{176}\text{Hf}/^{177}\text{Hf}$ in the sub-oceanic mantle. *Earth Planet Sci Lett* 129: 13–30
- Sguigna AP, Larabee AJ, Waddington JC (1982) The half-life of ^{176}Lu by a γ - γ coincidence measurement. *Can J Phys* 60: 361–364
- Shirey SB, Hanson GN (1986) Mantle heterogeneity and crustal recycling in Archean granite-greenstone belts: evidence from Nd isotopes and trace elements in the Rainy Lake area, Superior Province, Ontario, Canada. *Geochim Cosmochim Acta* 50: 2631–2651
- Smith HL, Hoffman DC (1956) Ion-exchange separations of the lanthanides and actinides by elution with ammonium alpha-hydroxy-isobutyrate. *J Inorg Nucl Chem* 3: 243–247
- Smith PE, Tatsumoto M, Farquhar RM (1987) Zircon Lu-Hf systematics and the evolution of the Archean crust in the southern Superior Province, Canada. *Contrib Mineral Petrol* 97: 93–104
- Stevenson RK, Patchett PJ (1990) Implications for the evolution of continental crust from Hf isotope systematics of Archean detrital zircons. *Geochim Cosmochim Acta* 54: 1683–1697
- Stille P, Unruh DM, Tatsumoto M (1983) Pb, Sr, Nd and Hf isotopic evidence of multiple sources for Oahu, Hawaii basalts. *Nature* 304: 25–29
- Stille P, Unruh DM, Tatsumoto M (1986) Pb, Sr, Nd and Hf isotopic constraints on the origin of Hawaiian basalts and evidence for a unique mantle source. *Geochim Cosmochim Acta* 50: 2303–2319
- Tatsumoto M, Unruh DM, Patchett PJ (1981) U-Pb and Lu-Hf systematics of Antarctic meteorites. *Proc 6th Symposium on Antarctic Meteorites*. Natl Inst Polar Res, Tokyo, pp 237–249
- Taylor PDP, De Bièvre P, Walder AJ, Entwistle A (1995) Validation of the analytical linearity and mass discrimination correction model exhibited by a multiple collector inductively coupled plasma mass spectrometer by means of a set of synthetic uranium isotope mixtures. *J Anal At Spectrom* 10: 395–398
- Vervoort JD, Patchett PJ (1996) Behavior of hafnium and neodymium isotopes in the crust: constraints from Precambrian crustally derived granites. *Geochim Cosmochim Acta* 60: 3717–3733
- Vervoort JD, Patchett PJ, Gehrels GE, Nutman AP (1996) Constraints on early earth differentiation from hafnium and neodymium isotopes. *Nature* 379: 624–627
- Walder AJ, Freedman PA (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 AJ, Platzner I, Freedman PA (1993) Isotope ratio measurement of lead, neodymium and neodymium-samarium mixtures, hafnium and hafnium-lutetium mixtures with a double focusing multiple collector inductively coupled plasma mass spectrometer. *J Anal At Spectrom* 8: 19–23
- White WM, Patchett J (1984) Hf-Nd-Sr isotopes and incompatible element abundances in island arcs: implications for magma origins and crust-mantle evolution. *Earth Planet Sci Lett* 67: 167–185