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La–Ce isotope measurements by multicollector-ICPMS†

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The ^{138}La–^{138}Ce decay system (half-life 1.02 × 10^{11} years) is a potentially highly useful tool to unravel information about the timing of geological processes and about the interaction of geological reservoirs on earth, complementing information from the more popular ^{147}Sm–^{143}Nd and ^{176}Lu–^{176}Hf isotope systems. Previously published analytical protocols were limited to TIMS. Here we present for the first time an analytical protocol that employs MC-ICPMS, with an improved precision and sensitivity. To perform sufficiently accurate La–Ce measurements, an efficient ion-chromatographic procedure is required to separate Ce from the other rare earth elements (REE) and Ba quantitatively. This study presents an improved ion-chromatographic procedure that separates La and Ce from rock samples using a three-step column separation. After REE separation by cation exchange, Ce is separated employing an Ln Spec column and selective oxidation. In the last step, a cation clean-up chemistry is performed to remove all remaining interferences. Our MC-ICPMS measurement protocol includes all stable Ce isotopes (^{136}Ce, ^{138}Ce, ^{140}Ce and ^{142}Ce), by employing a 10^{10} ohm amplifier for the most abundant isotope ^{140}Ce. An external reproducibility of ±0.25ε-units (2 r.s.d) has been routinely achieved for ^{138}Ce measurements for as little as 150–600 ng Ce, depending on the sample–skimmer cone combinations being used. Because the traditionally used JMC-304 Ce reference material is not commercially available anymore, a new reference material was prepared from AMES laboratory Ce metal (Cologne-AMES). In order to compare the new material with the previously reported isotopic composition of AMES material prepared at Mainz (Mainz-AMES), Cologne-AMES and JMC-304 were measured relative to each other in the same analytical session, demonstrating isotope heterogeneity between the two AMES and different JMC-304 batches used in the literature. To enable sufficiently precise age correction of radiogenic ^{138}Ce and to perform isochron dating, a protocol was developed where La and Ce concentrations are determined by isotope dilution (ID), using an isotope tracer enriched in ^{138}La and ^{142}Ce. The new protocols were applied to determine the variations of Ce isotope compositions and La–Ce concentrations of certified geochemical reference materials (CRMs): BCR-2, BCR-1, BHVO-2, JR-1, JA-2, JB-3, JG-1, JR-1, JB-1b, AGV-1 and one in-house La Palma standard.

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1 Introduction

The nuclide ^{138}La (relative abundance 0.089%) decays by branched decay to both ^{138}Ce (0.25%) and ^{138}Ba (71.66%) with a long half-life (1.02 × 10^{11} years[1]) by β$^-$ decay and electron capture (EC), respectively (Fig. 1).

Due to a different behavior of La and Ce during geological processes, the ^{138}La–^{138}Ce isotope system can provide viable

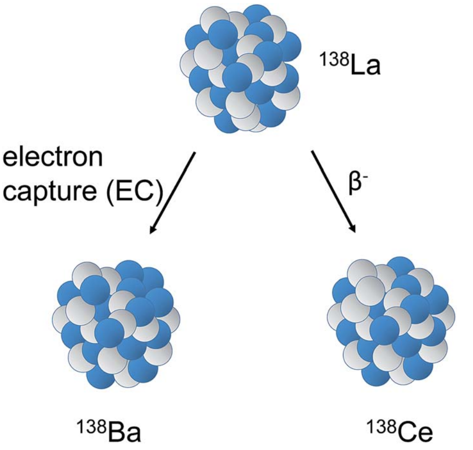

Fig. 1 Sketch illustrating decay of ^{138}La to stable ^{138}Ba (electron capture (EC), 65.5%) and ^{138}Ce (β$^-$ decay, 34.4%, $t_{1/2}$ = 1.02 × 10^{11} years).

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geological information, especially when coupled with other radiogenic isotope systems like ^{147}Sm–^{143}Nd and ^{176}Lu–^{176}Hf. So far, previously published analytical protocols for the ^{138}La–^{138}Ce decay system focused on thermal ionisation mass spectrometry (TIMS).[2–5]

Pioneering studies on the ^{138}La–^{138}Ce geochronometer in the 1980's focused on age determinations.[4] Since this first geochemical application, the ^{138}La–^{138}Ce isotope system has also been used as a geochemical tracer.[6–16] In the past, Ce isotope measurements have shown to be very challenging because of the isobaric interference from ^{138}Ba (relative abundance 71.7%) on ^{138}Ce (0.251%) and of ^{142}Nd (27.2%) on ^{142}Ce (11.114%). A further challenge is the simultaneous measurement of all Ce isotopes due to the extremely high abundance of ^{140}Ce (88.450%) relative to the much smaller ^{136}Ce (0.185%) and radiogenic ^{138}Ce (0.251%).[17]

Interfering elements such as Ba and Nd can be separated from Ce by cation-exchange chromatography. The first routine protocol for Ce separation was introduced by Tanaka and Masuda using α-hydroxy-isobutyric acid (α-HIBA) and a AG50W-X8 resin columns.[4] Similar procedures based on this separation scheme have been further developed for rock samples.[6,18–21] The separation of Ce from other REE using an oxidative extraction technique was first proposed by Rehkämper *et al.*[22] Tazoe *et al.*[23] proposed the separation of Ce using oxidative extraction technique with chelating resin (Ln Spec). Ohno and Hirata[24] used a combination of a TRU Spec resin column and a Ln Spec column to separate Ce.

Previous isotope measurements of Ce in geological material have been performed using TIMS or MC-ICP-MS.[2–5,24] In all of these studies, only the isotopes ^{136}Ce, ^{138}Ce and ^{142}Ce were measured, with two exceptions where ^{140}Ce was also measured.[9,10] In most previous studies, ^{138}Ce abundances were reported as ^{138}Ce/^{142}Ce.[3,5,14,25,26] As reference material, JMC-304 Ce has been predominantly used as a synthetic standard, and BCR-1 as a natural geological standard.[19,20,27,28] In few studies, no measurements of reference materials were explicitly reported, making direct comparisons of reported Ce isotope values for geological samples difficult.[10,11,29] In more recent studies, AMES Ce metal prepared at MPI Mainz was introduced (below referred to as Mainz AMES) and proposed as a reference standard material, as the original stock of JMC-304 is not commercially available anymore.[2,3,21] A direct comparison of Ce isotope data from different studies is therefore not straightforward and there is an urgent need for a validated and widely available reference material.

Precise and accurate concentration measurements of La and Ce are required for age correction of measured Ce isotope values and for isochron dating. However, sufficiently precise measurements by employing isotope dilution have rarely been performed.[6,15,19,27] The goal of this work is the development of an analytical protocol for sufficiently precise and accurate Ce isotope and La–Ce concentration measurements for geological samples using MC-ICPMS. Two new synthetic reference standards (Cologne-AMES and JMC-304 batch number: 15952) were prepared and calibrated against the Mainz-AMES standard used in previous studies. Additionally, for concentration measurements, a ^{138}La–^{142}Ce spike was prepared and calibrated. The new protocol has been validated by performing combined Ce isotope and La–Ce concentration measurements by isotope dilution on a variety of geological reference materials.

2 Analytical protocols

Reagents and sample digestion procedures

For comparison with previous studies, a new JMC-304 solution was prepared from an own batch of JMC 304 Ce-oxide (batch number: 15952). In 2007, Willbold prepared a new reference material from Ce-AMES metal (Mainz-AMES).[2] In addition to this reference material, a new solution was also prepared from Ce-AMES metal during the course of this study (below referred to as Cologne-AMES), expecting that both synthetic Ce-AMES standards are isotopically indistinguishable. These 3 different standards (Mainz-AMES, Cologne-AMES and Cologne-JMC-304) were all used as reference solutions for Ce-IC and Ce-ID measurements in our study and were also calibrated relative to each other in terms of their Ce isotope composition. Additionally, a diluted La-Alfa Aesar™ standard solution and a La solution prepared from AMES metal were used as reference materials for La-ID measurements.

Concentrated HF (24 M), HCl (12 M) and HNO_3 (14 M) were single-distilled to minimize acid blanks which were monitored before each batch of samples. Reagent grade H_2O_2 (30%) and $KBrO_3$ (purity $\geq$ 99.8%) were used. The total Ce chemistry blanks for isotope measurements ranged from 286 pg to 567 pg and can be neglected. Depending on the Ce concentrations, 70–240 mg of sample were used for measurements. The reference materials BHVO-2, BCR-2, JG-1, BCR-1, JB-3 and BIR-1 provided by USGS and GSJ and an in house standard (La Palma basalt LP-1) were analyzed during the course of this study. These samples were digested in a 1 : 1 mixture of HF (24 N) and HNO_3 (14 N) at 120 °C in Savillex® beakers on a hotplate. The standards AGV-1, JR-1, JB-1b and JA-2 also provided by USGS and GSJ were digested in a 1 : 1 mixture of HF (24 N) and HNO_3 (14 N) at 180 °C in Parr® bombs to ensure complete dissolution of refractory minerals. After both digestion steps, 1 mL of $HClO_4$ was added to prevent precipitation of La/Ce-bearing fluorides. Following this step, the samples were dried down, re-dissolved once in 2 mL HNO_3 (14 N), and evaporated to dryness on the hotplate again. Complete dissolution was ensured by dissolving in 6 N HCl solution overnight. After digestion, each sample solution was split into two aliquots. One aliquot, typically *ca.* 90% of the aliquot, was used for Ce isotope measurements (IC cut) while the remaining 10% aliquot (ID cut) was spiked with a mixed La–Ce isotope tracer prepared during the course of this study (see below). The spiked ID cut was put on the hotplate for at least 12 hours to ensure full sample–spike equilibrium. Both cuts were dried down and each was taken up in 1 mL 1 N HCl/(0.1 N HF) prior to ion exchange chemistry.

Chemical separation procedures for cerium isotope measurements (Ce-IC) and La–Ce concentration measurements (La–Ce-ID)

The ion chromatographic procedure for Ce separation consists of three steps (Table 1). In the first step (modified from Patchett

Table 1 Column dimensions and three-stage column separation procedures for our La–Ce protocols: (1) separation of REE from matrix elements; (2) separation of Ce from all other REE or La using redox conditioning; (3) clean- up chemistry for La and Ce cuts

1	BIORAD AG-50W-X8 (Resin volume: 5 mL)	
Step	Resin volumes (rv)	Acid
Precondition	2 rv	1 N HCl/(0.1 N HF)
Load sample	0.2 rv	1 N HCl/(0.1 N HF)
Rinse matrix	2.8 rv	1 N HCl/(0.1 N HF)
Sr	10 rv	2.5 N HCl
Ba	4 rv	3 N HNO_3
REE	7 rv	6 N HCl
Cleaning	10 rv	6 N HCl
	10 rv	3 N HNO_3

2	LN-SPEC® (Resin volume: 0.5 mL)	
Step	Resin volumes (rv)	Acid
Cleaning	12 rv	10 N HNO_3
Precondition	12 rv	10 N HNO_3/20 mM $KBrO_3$
Eluting REE^{3+}	16 rv	10 N HNO_3/20 mM $KBrO_3$
Washout	4 rv	10 N HNO_3
Washout	4 rv	Milli Q
Eluting Ce^{3+}	10 rv	6 N HCl/1% H_2O_2

3	BIORAD AG-50W-X8 (Resin volume: 2 mL)			BIORAD AG-50W-X8 (Resin volume: 2 mL resin)	
Step	Resin volumes (rv)	Acid	Step	Resin volumes (rv)	Acid
Precondition	5 rv	3 N HNO_3	Precondition	5 rv	3 N HNO_3
Load sample	0.25 rv	3 N HNO_3	Load sample	0.25 rv	3 N HNO_3
Eluting Ba, K	3.25 rv	3 N HNO_3	Eluting Ba,K	3.25 rv	3 N HNO_3
Washout	3 rv	6 N HCl	Eluting Ce	7.5 rv	6 N HCl
Eluting La	7.5 rv	6 N HCl	Cleaning	10 rv	6 N HCl
Cleaning	10 rv	6 N HCl		10 rv	3 N HNO_3
	10 rv	3 N HNO_3			

and Tatsumoto[30]), the REE fraction was separated from the bulk matrix using 5 mL cation resin (height = 23.5 cm, internal diameter = 8 mm, BIORAD® AG-50W-X8, 200–400 mesh, hydrogen form). The column was preconditioned in 2 resin volumes (rv) 1 N HCl (optional 1 N HCl/0.1 N HF). The centrifuged sample was loaded in 1 mL 1 N HCl/(0.1 N HF). After loading, the matrix was eluted with 2.8 rv 1 N HCl/(0.1 N HF). Strontium and Ba were eluted with 10 rv 2.5 N HCl and 4 rv 3 N HNO_3, respectively. Finally, the REEs were eluted with 7 rv 6 N HCl (Fig. 2).

The second step is based on protocols in Tazoe *et al.*[23] and Hirahara *et al.*[31] The extracted REE fraction was dissolved in 10 N HNO_3/20 mM $KBrO_3$ and loaded onto a 0.5 mL Ln Spec® resin column (height = 8.5 cm, internal diameter = 5 mm). In this step, Ce^{3+} is oxidized to Ce^{4+}, while all other REE remain in trivalent state. For cleaning, the column was rinsed two times with 4 rv 10 N HNO_3 and conditioned three times with 4 rv 10 N HNO_3/20 mM $KBrO_3$. Trivalent REE were subsequently eluted with 16 rv 10 N HNO_3/20 mM $KBrO_3$ and Ce was eluted as Ce^{3+} after reduction with 6 N HCl/1% H_2O_2 (Fig. 3). The yields of Ce were generally very high, with more than 95%. The collected Ce fraction was dried down and re-dissolved two times in 250 μL 14 N HNO_3 with 10 μL H_2O_2 and subsequently taken up in 0.5 mL 3 N HNO_3 for clean-up chemistry.

In the third step, a clean-up of the Ce was performed to remove remaining Ba and K. This separation step is based on the last 2 steps of the first stage chemistry employing cation resin. The dissolved Ce cut was loaded onto a 2 mL AG50-X8

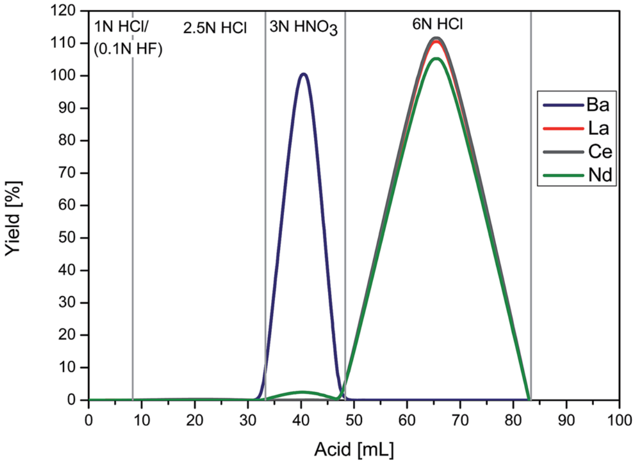

Fig. 2 Elution scheme illustrating separation of the REEs from the matrix using cation resin in stage 1.

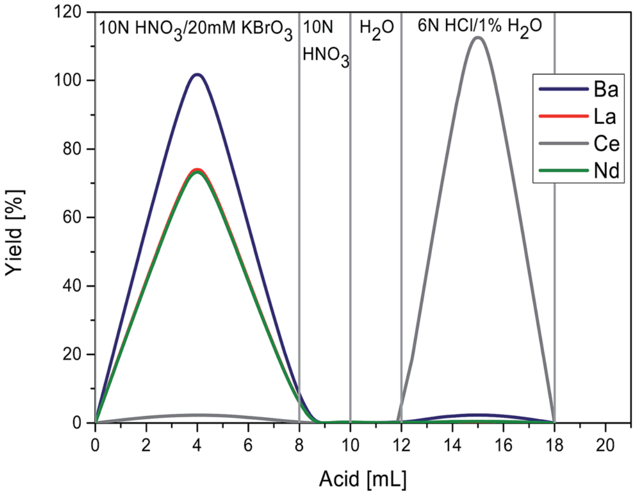

Fig. 3 Elution scheme illustrating separation of Ce from REEs using Ln Spec (stage 2).

column (height = 17 cm, internal diameter = 7 mm) and Ba and K were eluted with 3 rv 3 N HNO_3. Ce was stripped with 7.5 rv mL 6 N HCl. The yield of this 3 step column calibration was better than 80%.

In contrast to hitherto published ion-chromatographic procedures, the technique presented here is rapid, because the resin volumes could be reduced and pH-dependent α-HIBA is not used anymore.[3] In addition, this technique could be used for samples sizes up to 250 mg (ref. 31) and an efficient clean-up chemistry was developed to remove all remaining impurities. Otherwise, no accurate measurement by MC-ICPMS is possible.

For La- and Ce-ID measurements, the same ion exchange procedure as described above was used, except for collecting the complete REE^{3+} fraction in the 2nd column stage and a small modification in the clean-up chemistry. During the clean-up chemistry, the first 3 rv 6 N HCl in the stripping step were discarded and only the following 7.5 rv 6 N HCl were collected because only then all of the La is eluted from the column.

Preparation of a mixed La–Ce isotope tracer

In order to accurately calibrate the mixed La–Ce tracer solution, gravimetric dilution was performed by using a Mettler Toledo analytical balance to prepare one mixed standard solution from concentrated stock solutions of each element, using 99.996% pure La and 99.996% pure Ce metal ingots provided by AMES laboratory as starting material. The metals were first dissolved in 14 N HNO_3 and then ultimately diluted to a 1.4 N HNO_3 solution. The element concentrations of the La–Ce normal are known to within 0.1% including all propagated errors (characterization was performed using MC-ICPMS). A mixed isotope tracer was prepared using two individual concentrated solutions of isotopically enriched ^{138}La and ^{142}Ce, respectively. To prepare these concentrated solutions, *ca.* 0.87 mg of $^{138}La_2O_3$ powder (^{138}La enrichment 7%, Oak Ridge National Laboratory, USA) and *ca.* 47 mg of $^{142}CeO_2$ powder (^{142}Ce enrichment 95.1%, Campro Scientific, Germany) were each dissolved in 14 N HNO_3. Prior to mixing, the purity of both tracer solutions was verified by MC-ICPMS through the measurement of potentially interfering isobars. The ^{138}La isotope trace solution was checked for the masses 136, 137, 140, 142 and 144 and the ^{142}Ce isotope trace solution was checked for the masses 137, 139 and 144.

The isotope tracer was calibrated using variable mixtures of tracer and normal solutions. For the separation of La and Ce fractions from these mixtures, two different separation procedures were used. In the first calibration run, a 2.5 mL Ln Spec column (height = 25 cm, internal diameter = 3.2 mm) was preconditioned in 7.5 rv 0.15 N HCl. The spike/normal mixtures were loaded onto a 2.5 mL Ln Spec column in 0.5 mL 0.15 N HCl, and La was eluted in 7.5 rv 0.15 N HCl. Cerium was eluted with 17.5 rv 6 N HCl (Table 2 and Fig. 4). This method was also tested for the Ce separation of rock samples but for two reasons the method is not used anymore. First, a substantial fraction of Pr was collected together with Ce. Saji *et al.*[32] have pointed out that the molecular interference of ^{141}PrH affects the mass ^{142}Nd during MC-ICPMS measurements. Secondly, the yield of this method varies between different sample matrices, possibly due to non-reproducible redox conditions on the column (Ce^{3+}/Ce^{4+}).

The second calibration run was performed employing steps 2–3 of the standard procedure described above (Table 1).

In order to determine the isotope compositions and the concentrations of each element in the mixed La–Ce tracer, 9

Table 2 Miniaturized separation procedure for La and Ce used for spike calibrations

	Ln SPEC	
	(Resin volume: 2.5 mL)	
Step	Resin volumes	Acid
Precondition	7.5 rv	0.15 N HCl
Load sample	0.2 rv	0.15 N HCl
La	7.5 rv	0.15 N HCl
REE	17.5 rv	6 N HCl
Cleaning	20 rv	6 N HCl

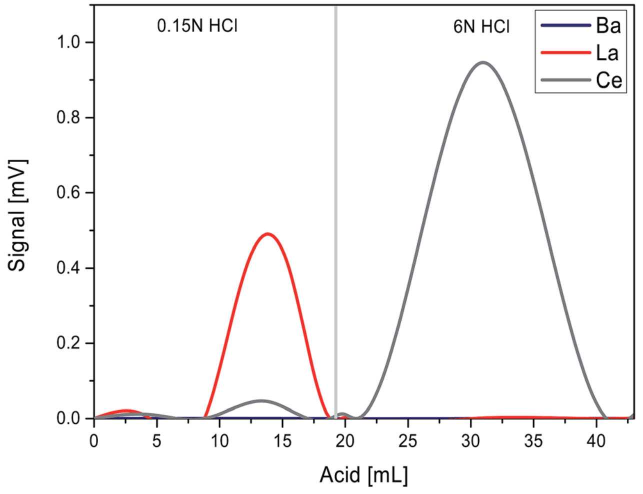

Fig. 4 Elution scheme illustrating separation of La and Ce from REEs using a long Ln Spec column (see also Table 2).

different mixtures of the spike and diluted AMES metal solution (La–Ce normal I) were prepared and analyzed after chemical separation. The mass fraction of Ce and La in the mixed spike La–Ce mix I are 922.6 ± 0.2 ng g^{-1} Ce (2 r.s.d) and 126.1 ± 1.1 ng g^{-1} La (2 r.s.d), respectively. The La/Ce ratio was calculated as 0.1370 ± 0.00004 (2 r.s.d, corresponding to ±0.22%), where errors denote the external reproducibility obtained by the different mixtures. Details and abundances of minor isotopes in the mixed isotope tracer are given in Table 3.

La–Ce measurements by MC-ICP-MS

Ce-IC measurements. All isotope ratio measurements were performed on a Thermo Finnigan™ Neptune MC-ICP-MS at joint Cologne-Bonn isotope facility. The mass spectrometer was equipped with a Cetac ARIDUS II™ desolvation system to improve the elemental sensitivity. The PFA nebulisers operated at uptake rates of *ca.* 100 μL min^{-1}, using 0.14 N HNO_3 as measurement solution. If not mentioned otherwise, standard Ni sample cones and H-type skimmer cones were used. All measurements were performed in low resolution mode (R = 300). Typical operating conditions are given in ESI Table 1.† A 10^{10} ohm amplifier was used for mass ^{140}Ce and two 10^{12} ohm amplifiers were used for ^{134}Xe and ^{137}Ba, monitoring interferences of ^{136}Xe and ^{138}Ba. The detailed Faraday cup configuration and interferences are shown in Faraday cup configuration for Ce isotope measurements using the Neptune MC-ICP-MS at Cologne/Bonn (Table 4).

Each analysis consisted of 60 cycles (2 blocks of 30 cycles with 8.389 s integration time), resulting in *ca.* 10 minutes of data collection. All Ce isotopes (136, 138, 140 and 142) were measured in static mode. During the different measurement sessions, the ^{140}Ce ion beam intensity was kept at 250–280 V for both standards and samples. Measured Ce isotope ratios were normalized to both ^{136}Ce/^{140}Ce 0.002124072 (ref. 18 and 33) and ^{136}Ce/^{142}Ce of 0.01688 (ref. 33) to correct for mass bias using the exponential law. The accuracy of measured Ce isotopes ratios is affected by the isobars ^{136}Xe, ^{136}Ba, ^{138}Ba, ^{138}La, and ^{142}Nd. To correct the ^{142}Ce signal, the measured signal on mass 144 was monitored, using a ^{142}Nd/^{144}Nd ratio of 1.141870 (ref. 34) that was artificially fractionated using the measured ^{136}Ce/^{140}Ce mass bias and then subtracted from the ^{142}Ce signal. Likewise, the ^{138}Ce signal was corrected for ^{138}Ba and ^{138}La using the measured masses 137 and 139 and artificially fractionated Ba and La isotope abundances ratios of ^{138}Ba/^{137}Ba = 6.383458 (ref. 17) and ^{138}La/^{139}La = 0.000902414.[33] The ^{136}Ce signal was corrected using the measured masses ^{134}Xa and ^{137}Ba and artificially fractionated Xe and Ba isotope abundance ratios of ^{136}Xe/^{134}Xe = 0.848750 (ref. 17) and ^{136}Ba/^{137}Ba = 0.699163105,[17] respectively.

The external reproducibility achieved for ^{138}Ce measurements, as determined by multiple analyses of JMC-304, was significantly better, once ^{136}Ce/^{140}Ce was used for mass bias correction (±25 ppm) rather than ^{136}Ce/^{142}Ce (±40 ppm, all 2 r.s.d). Samples were measured using the standard-sample bracketing approach with our in house JMC-304 solution as standard. In recent studies, Mainz-AMES has been used as reference standard but the amounts of Mainz-AMES available were insufficient to perform larger amounts of measurements.[2,3,21] Therefore, the Mainz-AMES and Cologne-AMES standards were measured relative to our in house JMC-304 solution *ca.* 3 times before and after the standard-sample bracketing sequence. The daily mean value of the JMC-304 standard were used to calculate ε^{138}Ce (eqn (1))

Table 3 Details of the La–Ce mixed isotope tracer

Isotope	^{138}La [μmol g^{-1}] [2 r.s.d]	^{142}Ce [μmol g^{-1}] [2 r.s.d]	^{138}La/^{139}La [2 s.e.]	^{136}Ce/^{142}Ce [2 s.e.]	^{138}Ce/^{142}Ce [2 s.e.]	^{140}Ce/^{142}Ce [2 s.e.]
	7.128×10^{-5} ± 0.16%	6.183×10^{-3} ± 0.12%	0.08507 ± 0.12%	0.0000600 ± 0.92%	0.000100 ± 1.42%	0.05200 ± 0.01%

Table 4 Faraday cup configuration for Ce isotope measurements using the Neptune MC-ICP-MS at Cologne/Bonn. Isobaric interferences from Ba, La and Nd are shown as well. All measurements were performed in low resolution mode (R = 300)

Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Measured isotopes	^{134}Xe	^{135}Ba	^{136}Ce	^{137}Ba	^{138}Ce	^{139}La	^{140}Ce	^{142}Ce	^{144}Nd
Amplifier	10^{12}	10^{11}	10^{11}	10^{12}	10^{11}	10^{11}	10^{10}	10^{11}	10^{11}
Interferences			^{136}Xe, ^{136}Ba		^{138}Ba, ^{138}La			^{142}Nd	

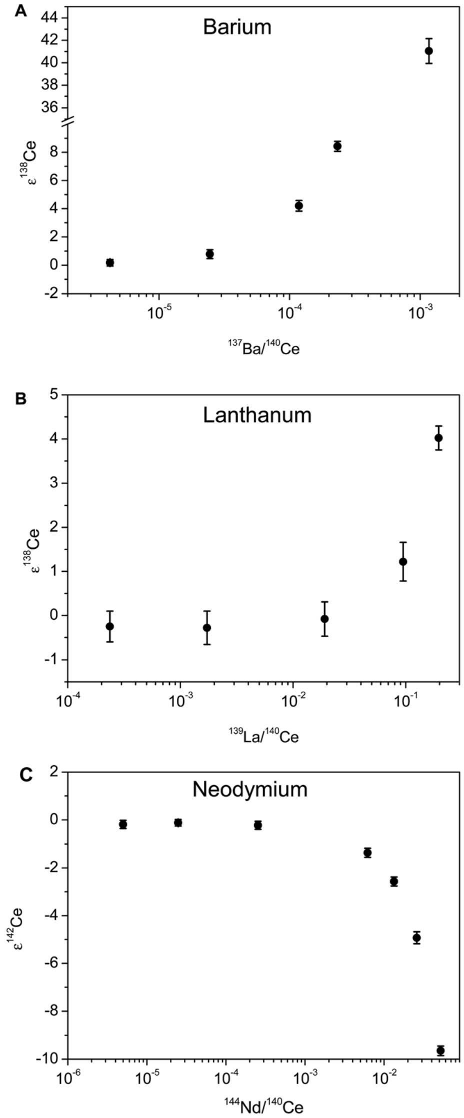

Fig. 5 Measured ε^{138}Ce values and ε^{142}Ce value plotted against measured ratios of (A) ^{137}Ba/^{140}Ce (B) ^{139}La/^{140}Ce (C) ^{144}Nd/^{140}Ce.

$$\varepsilon^{138}\mathrm{Ce}_{\mathrm{JMC\ 304}} = [(^{138}\mathrm{Ce}/^{136}\mathrm{Ce})_{\mathrm{sample}}/(^{138}\mathrm{Ce}/^{136}\mathrm{Ce})_{\mathrm{JMC\ 304}} - 1] \times 10^{4} \qquad (1)$$

Details for re-calculating ε^{138}Ce from $\varepsilon^{138}\mathrm{Ce}_{\mathrm{JMC\ 304}}$ relative to Cologne-AMES, Mainz-AMES and CHUR can be found below.

The effects of interfering Ba, La and Nd on the accuracy of measured Ce isotope ratios measurements were evaluated using a *ca.* 600 ppb JMC-304 Ce standard solution doped with each interfering element at different concentrations (ESI Table 2† and Fig. 5). The accuracy of measured ε^{138}Ce values is compromised at ^{137}Ba/^{140}Ce higher than *ca.* 4×10^{-6}, ^{139}La/^{140}Ce higher than 2×10^{-2}, and the accuracy of measured ε^{142}Ce values is affected at ^{144}Nd/^{140}Ce higher than 2.5×10^{-4}.

Given the typical abundance sensitivity of MC-ICPMS instruments (during the course of measurements *ca.* 2 ppm), a tailing correction may be required for isotopes on the low mass side of ^{140}Ce with a relative abundance by a factor of *ca.* 100 higher than those of ^{138}Ce and ^{136}Ce. In contrast to TIMS measurements, where the instrumental back end vacuum may vary during the course of a single measurement, vacuum conditions during MC-ICPMS measurements are more stable, as the system is operated in steady state.[3] Consequently, tail measurements were only made at the beginning and at the end of each analytical session using the JMC 304 standard with the cup configuration shown in Table 5. The integration time was 8.389 seconds with a total number of 30 integrations. Although both tail measurements typically are consistent within the uncertainty, sample standard bracketing was always applied in order to monitor putative short term variations in instrumental vacuum condition. The tail correction was made offline after the measurement using an algorithm fit (eqn (2)) through the individual half mass data points to obtain the best-fit parameters $a(1)$, $a(2)$, and $a(3)$.[2,35]

$$I(m) = a(1)\exp\left(\frac{m - 134.5}{a(3)}\right) + a(4) \qquad (2)$$

Typical values were $a(1) = 1 \times 10^{-15}$ to 1×10^{-10}, $a(3) = 0.3$–0.2 and $a(4) = 1 \times 10^{-5}$ to 1×10^{-6}. The tailing ratio ^{138}Ce/^{140}Ce was then calculated by dividing $I(m)$ by the ^{140}Ce intensity. Throughout the course of our measurements peak tailing varied between 1×10^{-7} and 1×10^{-8}, which is regarded as negligible, as it only would cause shifts in the measured ^{138}Ce abundances between 0.001 ε-units and 0.0001 ε-units.

La/Ce-isotope dilution (ID) measurements. For geochronology the measurement of parent/daughter ratios at high precision and accuracy is necessary. Due to the rapid measurement protocol (5 minutes) MC-ICPMS is used for isotope dilution measurements. All isotope dilution measurements were performed on a Thermo Finnigan™ Neptune MC-ICP-MS at Cologne/Bonn, but using a different sample introduction system than for the IC measurements (Scott-type glass spray chamber and 50 μL PFA nebulizer) in order to avoid memory effects. The Faraday cup configuration for Ce-ID measurements was the same as used for Ce-IC measurements (Table 4) except for the 10^{10} ohm amplifier on mass 140 that was replaced by a 10^{11} ohm amplifier. The detailed Faraday cup configuration for La is shown in Table 6. Isotope dilution measurements of La and Ce were performed by measuring ^{138}La/^{139}La and ^{142}Ce/^{140}Ce. Both ratios were mass

Table 5 Faraday cup configuration for ^{140}Ce tail measurements on half masses using the MC-ICP-MS at Cologne/Bonn. Measured values are used together with the corresponding ^{140}Ce intensity to calculate the abundance sensitivity

Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Measured mass		135.5		137.5	138.5	139.5	140.5	142.5	144.5
Amplifier		10^{11}		10^{12}	10^{11}	10^{11}	10^{10}	10^{11}	10^{11}

Table 6 Faraday cup configuration for La isotope dilution measurements using the MC-ICP-MS at Cologne-Bonn

Cup	L4	L3	L2	L1	C	H1	H2	H3	H4
Isotope	^{136}Ce	^{137}Ba	^{138}La(Ce)	^{139}La	^{140}Ce	^{142}Ce	^{144}Nd	^{146}Nd	^{147}Sm
Amplifier	10^{12}	10^{11}	10^{11}	10^{12}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}
Interference	^{136}Xe, ^{136}Ba		^{138}Ce(La), ^{138}Ba			^{142}Nd			

bias corrected employing doped Ba(Ce) and Nd(La) and using the exponential law for mass bias correction. For external normalization a ^{137}Ba/^{135}Ba value of 1.70383 (ref. 17) for Ce and a ^{142}Nd/^{144}Nd value of 1.14187 (ref. 34) for La were used, respectively.

3 Cerium isotope compositions of synthetic reference materials and rock standards

Synthetic reference materials (JMC-304, cologne and Mainz-AMES batches)

In this study, three different Ce reference materials were used to evaluate analytical precision, reproducibility and accuracy of the Ce measurements by MC-ICPMS. The three solutions are (i) Johnson Matthey reference material JMC-304 (batch 15952), (ii) AMES metal solution distributed by M. Willbold (Mainz-AMES) and (iii) AMES metal solution prepared at Cologne (Cologne-AMES). As already described above, two highly concentrated (1000 ppm) stock solutions of Ce have been prepared by dissolving 1 g high-purity CeO_2 powder (JMC-304 (batch 15952)) and 1 g of AMES Laboratory Ce metal (Cologne-AMES) in 14 N HNO_3. Splits of these solutions were diluted in 0.1 N HNO_3 to running solutions with typical concentrations of 450 ppb.

Results of repeated measurements in one analytical session are shown as example in Fig. 6. The mean values for ε^{138}Ce relative to JMC-304 for this session are −0.03 ± 0.12 (2 r.s.d) for JMC-304, +0.73 ± 0.11 for Cologne-AMES and +2.44 ± 0.14 for AMES. Fig. 6 shows also clearly discernable ε^{138}Ce compositions of the three standards, indicating that Cologne-AMES and Mainz-AMES are isotopically heterogeneous.

Results of long term measurements for the standards Cologne-AMES and Mainz-AMES are shown in ESI Table 3† and Fig. 7. The means for ε^{138}Ce relative to the JMC-304 are +0.83 ± 0.10 for Cologne-AMES and +2.61 ± 0.09 for Mainz-AMES, respectively. The results are in a good agreement with the results of the single analytical session illustrated in Fig. 6.

The hitherto published ^{138}Ce isotope values for the JMC-304 standard display a large scatter even after adjusting for the different mass fractionation procedures being applied.[3] A probable source of these differences is the use of different JMC-304 batches that appear to be isotopically heterogeneous. Therefore, any direct data comparison with older studies is difficult because the individual JMC-304 batches used in the different studies have not always been specified. Comparison of data obtained using two different JMC-304 batches relative to Mainz-AMES (this study and Bellot *et al.*[3]) confirm that the two JMC-304 batches used are compositionally different. Whereas

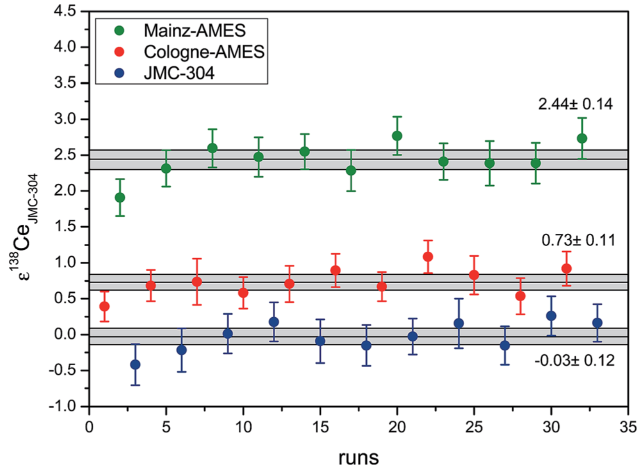

Fig. 6 Comparison of ^{138}Ce compositions of (i) JMC 304 reference material, (ii) Cologne-AMES and (iii) Mainz-AMES for a single analytical session (March 2015). All values are given relative to JMC-304. The ε^{138}Ce value is calculated as ^{138}Ce/^{136}Ce, normalized to ^{136}Ce/^{140}Ce using a ^{136}Ce/^{140}Ce of 0.002124072 (ref. 18 and 33) and the exponential law. The weighted means of ε^{138}Ce are −0.03 ± 0.12 for JMC-304, +0.73 ± 0.11 for Cologne-AMES and +2.44 ± 0.14 for Mainz-AMES (all 2 r.s.d).

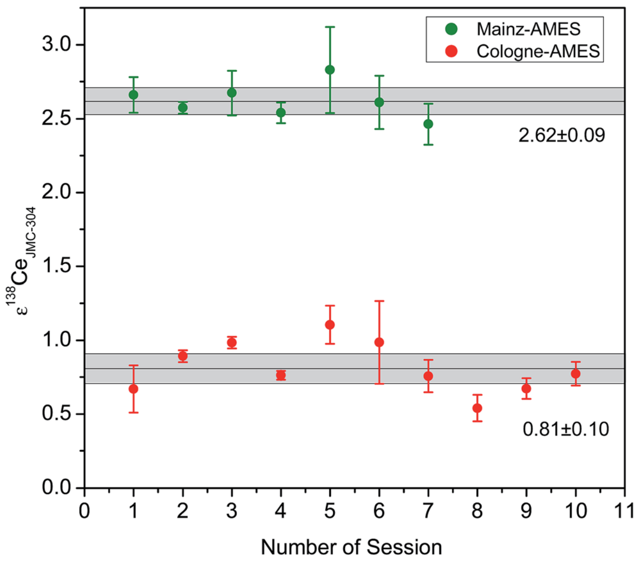

Fig. 7 Long term comparison of the ^{138}Ce compositions of Cologne-AMES and Mainz-AMES. All values are given relative to JMC-304, measured during 10 analytical sessions. The weighted means are ε^{138}Ce +0.81 ± 0.10 for Cologne-AMES and +2.62 ± 0.09 for Mainz-AMES (all 2 r.s.d).

the ε^{138}Ce value for the JMC-304 batch relative to Mainz-AMES in Bellot *et al.*[3] is given as −1.15 ± 0.38 (2 r.s.d), the ε^{138}Ce value for the JMC-304 batch used in this study relative to Mainz-AMES is −2.46 ± 0.28 (2 r.s.d). Both values are outside analytical uncertainty, confirming that the two JMC-304 batches are clearly isotopically distinguishable.

ESI Table 4† and Fig. 8 shows the results of absolute ^{138}Ce/^{136}Ce ratio measurements for the Mainz-AMES standard that has previously been characterized.[2] As mentioned above, the tailing effects in this study were negligible and no offline tailing correction was applied. A ratio of ^{136}Ce/^{140}Ce of 0.002124072 (ref. 18 and 33) was initially used in our study to correct the mass bias (blue dots in Fig. 8), because the external reproducibility is significantly better. To compare our measured ^{138}Ce/^{136}Ce ratios with those obtained in recent TIMS studies (Willbold,[2] Doucelance *et al.*[21] and Bellot *et al.*[3]), the measured ^{138}Ce/^{136}Ce ratios were also normalized to ^{136}Ce/^{142}Ce of 0.01688 (ref. 33) and these data are additionally shown in ESI Table 4† and Fig. 8 (red dots). Importantly, Doucelance *et al.*[21] and Bellot *et al.*[3] both used this ^{136}Ce/^{142}Ce ratio for normalization.

The average absolute ^{138}Ce/^{136}Ce normalized to ^{136}Ce/^{142}Ce were 1.33738 ± 0.00001 in Willbold,[2] 1.33736 ± 0.00001 in Doucelance *et al.*[21] 1.33725 ± 0.00005 in Bellot *et al.*[3] and 1.33745 ± 0.00004 in this study (10 individual sessions). The absolute ^{138}Ce/^{136}Ce normalized to ^{136}Ce/^{140}Ce obtained in this study was 1.33748 ± 0.00003. Both values agree within error, but a tentative systematic difference of +0.52ε-units for ^{138}Ce/^{136}Ce normalized to ^{136}Ce/^{142}Ce compare to Willbold[2] and the larger scatter in our study can be explained through non-ideal mass bias correction and cup efficiency. Importantly, the external reproducibility of our analytical protocol within an individual session is significantly better (±0.25 ε-units), because run parameters are not changed and measured sample values are always referenced to the standards measured in the individual session.

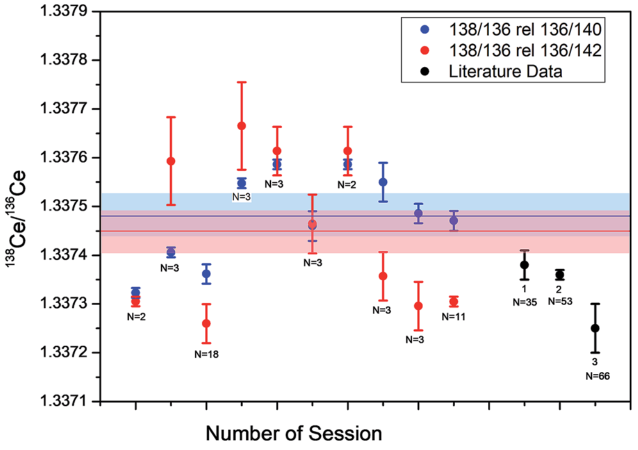

Fig. 8 Absolute ^{138}Ce/^{136}Ce composition (error bars 2 r.s.d.) obtained for the Mainz AMES standard for 10 different analytical sessions (red/blue dots). The black dots are literature data: (1) Willbold,[2] (2) Doucelance *et al.*,[21] (3) Bellot *et al.*[3]

Recalculation relative to the chondritic uniform reservoir (CHUR) value

By direct measurements of meteorite samples, Makishima *et al.*[18] and Makishima and Masuda[27] defined the average chondritic uniform reservoir (CHUR) value by an ^{138}Ce/^{142}Ce value of 0.0225652 ± 0.0000024 which is in a good agreement with the ^{138}Ce/^{142}Ce value of 0.0225654 ± 0.0000007 obtained for two chondrites:[3] both studies used the same ^{136}Ce/^{138}Ce value (^{136}Ce/^{138}Ce = 0.01688 (ref. 33)) for mass bias correction. In this study, no meteorites were measured but the same reference standards (Mainz-AMES, JMC-304) were used. A comparison with CHUR values reported in older studies is not straightforward, as the JMC-304 batches used in the different studies do not appear to be homogenous, as pointed out above. If the ε^{138}Ce of JMC-304 from Makashima and Nakamura[18] is recalculated relative to their own CHUR value, an ε^{138}Ce$_{\mathrm{CHUR}}$ of +1.46 is obtained for JMC-304. In contrast, the reported ε^{138}Ce$_{\mathrm{CHUR}}$ for JMC-304 relative to CHUR in the study of Bellot *et al.*[3] is +2.30. This indicates that the different JMC-304 batches used in these two studies are not identical. If the JMC-304 measurements relative to Mainz-AMES in the Bellot *et al.*[3] study (ε^{138}Ce$_{\mathrm{AMES}}$ = −0.93) and in our study (ε^{138}Ce$_{\mathrm{AMES}}$ = −2.61) are now considered, there appears to be clear evidence that different JMC-304 batches have been utilized in all three studies. In summary, our results indicate that JMC-304 is not a suitable standard to accurately cross-reference CHUR values reported from older studies. In our study, the ε^{138}Ce value reported for Mainz-AMES relative to CHUR of +3.24 ± 0.23 from the study of Bellot *et al.*[3] was used for calculating the standard data reported in this study relative to CHUR because two unambiguously identical splits of the same reference standard were used in both studies.

Cerium isotope composition and La–Ce concentration measurements for geological reference materials

Both accuracy and precision of our new MC-ICPMS protocol were further tested by La–Ce measurements of replicate digestions of the geological reference material BCR-2. Five fractions of this basaltic reference standard were digested following the procedure described above. The measured mean ε^{138}Ce value obtained using a standard Ni sample cone and a H-type skimmer cone (H) is 0.11 ± 0.14 (2 r.s.d) relative to CHUR. Furthermore, the same solutions were measured with an X-Skimmer cone in combination with a standard Ni sample cone (X) to improve sensitivity. The sensitivity for Ce was improved by a factor of *ca.* 2.4 using the X-skimmer cone, and a mean ε^{138}Ce value of 0.28 ± 0.33 (2 r.s.d) relative to CHUR was obtained which is indistinguishable within uncertainty. The mean values obtained for the element concentrations of BCR-2 were 24.97 ± 0.22 (2 r.s.d) for La [ppm] and 53.21 ± 0.54 for Ce [ppm], the La/Ce ratio is 0.4693 ± 0.0008. The data are reported in ESI Fig. 1 and Table 7.†

The ε^{138}Ce values obtained for different cone combinations are in a good agreement. As a result, Ce isotope composition studies can also be performed by using a standard Ni sample cone and an X-type skimmer cone, where the amount of sample being required can be decreased by a factor of *ca.* 2.4. The study of Raczek *et al.*[36] showed, that the two rock standards BCR-1 and BCR-2 have indistinguishable Nd isotope compositions. Therefore, it can be assumed that the Ce isotope compositions are also identical (*cf.* Bellot *et al.*[3]). Independent of the cone combination our ε^{138}Ce(CHUR) results are in a good agreement with the result of BCR-1.[8] But the ε^{138}Ce(CHUR) value obtained for BCR-2 of this study overlaps barely with a recent TIMS study.[3] Notably, Bellot *et al.*[3] assume an analytical bias as cause for the discrepancy of their BCR-2 data and the BCR-1 data of Tanaka *et al.*[8] The La–Ce isotope dilution data obtained BCR-2 are in a good agreement with the studies of Raczek *et al.*[36] and Baker *et al.*[37] that also employed isotope dilution. In addition to multiple analyses of the BCR-2 reference material, further La–Ce analyses were performed for 9 reference rock samples (BCR-1, BHVO-2, JR-1, JA-2, JB-3, JG-1, JB-1b, AGV-1, JR-1) and one La Palma basalt (LP-1, in-house standard). The results are reported in Table 7 and Fig. 9.

The external reproducibility of our new analytical protocol was tested by multiple processing of BCR-2 (Table 7 and Fig. 9). The uncertainty for BCR-2 using a standard Ni sample cone and an H-type skimmer cone is ±0.14ε, which is significantly smaller than in previous studies (±0.31ε to ±1.1ε).[3,8] The

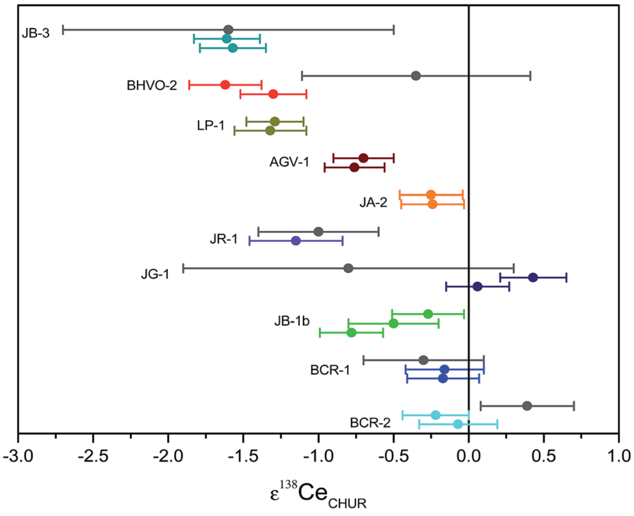

Fig. 9 Measured Ce isotope ratios for rock reference samples given in ε-units relative CHUR. Reported uncertainties correspond to 2 r.s.d. Grey dots are literature data from Tanaka[8] (JR-1, JG-1, JB-3 and BCR-1) and Bellot *et al.*[3] (BHVO-2 and BCR-2).

Table 7 Cerium isotope compositions and La–Ce elemental concentrations obtained for geological reference materials and different types of skimmer cones (X/H) for BCR-2. Ce isotope data are given relative to the average JMC-304 ratio measured during one analytical session and relative to CHUR[3]

Sample	Type of cone	ε^{138}Ce (JMC304)	2 r.s.d [ppm]	ε^{138}Ce (CHUR)	2 r.s.d [ppm]	ε^{138}Ce (CHUR)/ literature data	Ce [ppm]	La [ppm]	La/Ce	^{138}La/^{136}Ce	^{138}La/^{142}Ce	La/Ce literature data
1 BCR-2	H	−0.78	0.30	−0.15	0.30		53.04	24.90	0.4695	0.2280	0.003852	
	X	−0.44	0.36	0.19	0.36							
2 BCR-2	H	−0.46	0.34	0.17	0.34		52.83	24.81	0.4695	0.2280	0.003853	
	X	−0.51	0.29	0.12	0.29							
3 BCR-2	H	−0.37	0.23	0.26	0.23		53.36	25.05	0.4694	0.2280	0.003852	
4 BCR-2	H	−0.59	0.25	0.04	0.25		53.27	25.01	0.4696	0.2281	0.003853	
	X	−0.80	0.39	0.17	0.39							
5 BCR-2	H	−0.88	0.22	0.25	0.22		53.53	25.08	0.4685	0.2276	0.003845	
	X	−1.28	0.25	0.63	0.25							
Mean ± 2 r.s.e	**H**	**−0.61**	**0.14**	**0.11**	**0.14**		**53.21**	**24.97**	**0.4693**	**0.2279**	**0.003851**	
	X	**−0.76**	**0.33**	**0.28**	**0.33**							
JR-1 batch 1		−1.78	0.31	−1.15	0.31	−1.0 ± 0.4 (ref. 8)	58.91	36.47	0.6192	0.3014	0.005092	
JB-1b batch 1	H	−1.41	0.21	−0.78	0.21		68.83	39.59	0.5752	0.2800	0.004730	
JB-1b batch 2	H	−1.13	0.30	−0.50	0.30		69.15	39.73	0.5746	0.2797	0.004750	
JB-1b batch 3	H	−0.90	0.24	−0.27	0.24		68.88	39.83	0.5783	0.2815	0.004756	
AGV-1 batch 1	H	−1.39	0.20	−0.76	0.20		58.81	36.25	0.6164	0.3000	0.005069	0.5651 (ref. 36)
AGV-1 batch 2	H	−1.33	0.20	−0.70	0.20		58.95	37.28	0.6325	0.3078	0.005200	
LP-1 batch 1	H	−1.95	0.24	−1.32	0.24		170.40	85.33	0.5008	0.2438	0.004118	
LP-1 batch 2	H	−1.92	0.19	−1.29	0.19		170.12	85.03	0.4998	0.2433	0.004110	
BHVO-2 batch 1	H	−1.93	0.22	−1.30	0.22	−0.35 ± 0.76 (ref. 3)	37.84	15.35	0.4056	0.1974	0.003335	0.4053 (ref. 36)
BHVO-2 batch 2	H	−2.25	0.24	−1.62	0.24		37.91	15.35	0.4050	0.1971	0.003330	
BCR-2 batch 1	H	−0.70	0.26	−0.07	0.26	0.39 ± 0.31 (ref. 3)	53.36	25.27	0.4735	0.2305	0.003894	0.4707 (ref. 36)
BCR-2 batch 2	H	−0.85	0.22	−0.22	0.22		53.35	25.17	0.4714	0.2296	0.003879	0.4712 (ref. 37)
JG-1 batch 1	H	−0.57	0.21	+0.06	0.21	−0.8 ± 1.1 (ref. 8)	54.49	26.32	0.4831	0.2351	0.003973	
JG-1 batch 2	H	−0.20	0.22	+0.43	0.22		39.44	18.56	0.4705	0.2290	0.003870	
JA-2 batch 1	H	−0.87	0.21	−0.24	0.21		33.63	16.11	0.4791	0.2332	0.003939	
JA-2 batch 2	H	−0.88	0.21	−0.25	0.21		33.75	16.14	0.4782	0.2327	0.003932	
BCR-1 batch 1	H	−0.80	0.24	−0.17	0.24	−0.3 ± 0.4 (ref. 8)	53.79	25.36	0.4714	0.2294	0.003877	0.4709 (ref. 36)
BCR-1 batch 2	H	−0.79	0.26	−0.16	0.26		54.01	25.49	0.4720	0.2298	0.003882	0.4716 (ref. 37)
JB-3 batch 1	H	−2.20	0.22	−1.57	0.22	−1.6 ± 1.1 (ref. 8)	21.27	8.42	0.3958	0.1927	0.003255	
JB-3 batch 2	H	−2.24	0.22	−1.61	0.22		21.32	8.44	0.3957	0.1926	0.003254	

external reproducibility was also assessed for other reference materials by double processing of each sample. The mean ε^{138}Ce value for all BCR-2 sample using a standard Ni sample cone and an H-type skimmer cone is 0.04 ± 0.14 (2 r.s.d) which overlaps only slightly within error with the value reported in a recent TIMS study. As discussed in the previous section, it is possible that an analytical bias cause the discrepancy of 0.5ε-units.[3] The study of Raczek *et al.*[36] showed, that the two rock standards BCR-1 and BCR-2 have the same Nd isotope composition. Therefore, it was previously assumed (Bellot *et al.*[3]) that the Ce isotope compositions are also identical which is confirmed by our results (Table 7 and Fig. 9). The data obtained for BCR-1 in our study are also in a good agreement with literature data for BCR-1, if normalized relative to CHUR.[8] The analytical bias mentioned above might also be an explanation for the difference of the BHVO-2 data between our study and the study of Bellot *et al.*[3]

The Ce isotope composition and the La–Ce concentration data obtained in this study are in an excellent agreement between two duplicates for the samples BCR-1, BCR-2, BHVO-2, JB-3, JA-2, LP-1, JB-1b, JR-1 and AGV-1. The granite sample JG-1 shows good agreement with respect to measured Ce isotope compositions,[8] but also shows deviations in measured La–Ce concentration data which could be an indication of sample heterogeneity.

By the advent of special interface cone designs like wide-angle skimmer cones (X-cones) or "Jet"-sample cones with wider aperture, the sensitivity of MC-ICPMS instruments could be increased by up to an order of magnitude of 4–6.5 for Nd measurements.[38] To assess the potential of MC-ICPMS for high sensitivity measurements, the effects of four different Ni-cone combinations were investigated: standard sample cone with H-type skimmer cone (H), standard sample cone with X-type skimmer cone (X), "Jet" sample cone with H-type skimmer cone (J), and "Jet" sample cone with X-type skimmer cone (J/X). By using "Jet" sample cone and H-type skimmer cone, the signal sensitivity for a given concentration of Ce could be improved by a factor of 2.4. The same factor can be achieved by using X-type skimmer cone and standard Ni sample cone. By using a combination of X-type skimmer cone and "Jet" sample cone, the signal sensitivity for Ce could be improved by a factor of *ca.* 4. The Ce isotope results for the different cone combinations are shown in ESI Table 5† and Fig. 10. In general, the Ce isotope data are in a good agreement, independent of the cone combination used, and no increase of the standard error of the mean is observed at a given intensity. This observation indicates that our ion exchange protocol produced sufficiently clean Ce-cuts to avoid matrix effects, in particular during use of "Jet" sample cone.[39,40]

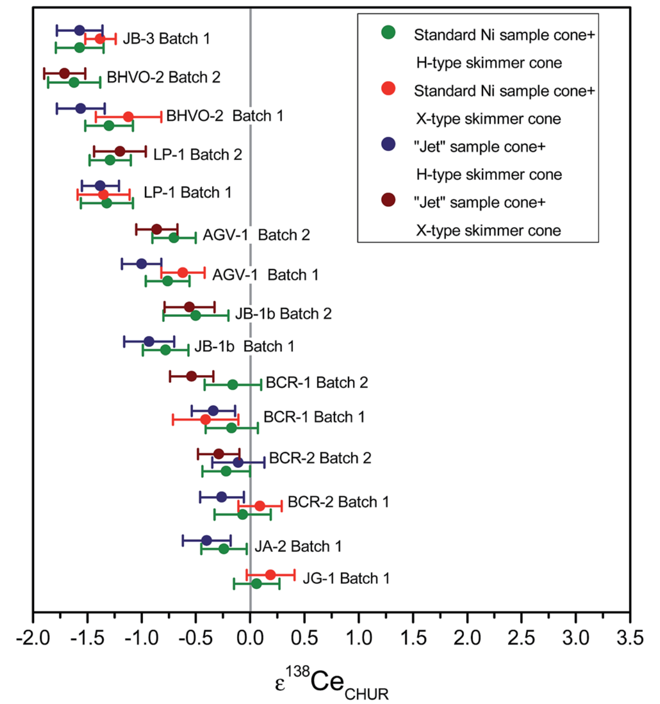

Fig. 10 Measured Ce isotope ratios for rock reference samples using different interface cone combinations. ^{138}Ce/^{136}Ce ratios are expressed in ε-units relative to CHUR. Reported uncertainties correspond to 2 s.e.

4 Conclusions

Our study presents the first complete MC-ICPMS protocol for separation of La–Ce from rock matrices and measurements of Ce isotope compositions as well as La–Ce concentrations by isotope dilution. The protocol enables static measurements of all Ce isotopes (^{136}Ce, ^{138}Ce, ^{140}Ce and ^{142}Ce), also including the large abundance isotope ^{140}Ce that is measured with a 10^{10} ohm amplifier. The external reproducibility achieved for ^{138}Ce measurements was significantly better, once ^{136}Ce/^{140}Ce was used for mass bias correction (±0.25), rather than ^{136}Ce/^{142}Ce (±0.40, all 2 r.s.d.). Two synthetic reference solutions (Cologne-AMES and JMC-304 batch 15952) were prepared and were measured relative to each other and relative to the Mainz-AMES reference material in 10 analytical sessions. The weighted means relative to JMC-304 of ε^{138}Ce are 0.0 ± 0.12 (all 2 r.s.e) for JMC-304, 0.83 ± 0.11 for Cologne-AMES and 2.61 ± 0.09 for Mainz-AMES, with better external reproducibilities than have been previously reported.[2] The average ^{138}Ce/^{136}Ce value measured in this study is 1.33745 ± 4 (2 r.s.e, $N = 51$) for Mainz-AMES; the deviation of +0.52ε-units from the value published by Willbold[2] can be explained through non-ideal mass bias correction and possibly by cup efficiency.

A comparison with other TIMS studies demonstrates isotopic heterogeneity between different JMC-304 batches and shows that there are at least 3 different batches being analysed in different laboratories.[3,8] There is also a clearly resolvable isotopic heterogeneity between the Cologne-AMES batch prepared during the course of this study and the Mainz-AMES batch. This underlines that there is an urgent need for a consensus on reference materials being used for Ce isotope measurements.

For La–Ce concentration measurements by isotope dilution, a mixed ^{138}La/^{142}Ce isotope tracer was prepared and calibrated against a solution prepared from high-purity AMES metal. The external reproducibility achieved for replicate digestions of the

BCR-2 basaltic reference material was ±1.02 (2 r.s.d., %) for La and ±0.90 (2 r.s.d., %) for Ce concentration measurements and ±0.19 (2 r.s.d., %) for La/Ce ratios.

Measurements of Ce isotope compositions and La–Ce concentrations were performed on 10 geological reference material (JG-1, JA-2, BCR-2, BCR-1, JB-1b, AGV-1, BHVO-2, JR-1 and JB-3) and one in house La Palma basalt standard (LP-1). Replicate digestion of 5 BCR-2 splits has shown the high accuracy and precision of the presented analytical method (±0.38, 2 r.s.d). A repetitive measurement of different rock samples using variable interface/cone combinations involving "Jet"-sample cones and X-skimmer cones showed a good agreement of the results within analytical resolution. The signal sensitivity of cerium could be improved by a factor of 2.4 by using the X-skimmer cones and by a factor of 4 by using X-skimmer cones and "Jet"-sample cones.

In summary, the new analytical protocol for MC-ICPMS measurements presented here opens new avenues for applying the La–Ce geochronometer to a variety of terrestrial rock samples and meteorites. The results will open new avenues to investigate geodynamic processes on earth and to better understand processes active during the formation of the earth and the solar system.

Conflicts of interest

There are no conflicts of interest.

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