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► To cite this version:

P. Bonnand, C. Israel, Maud Boyet, R. Doucelance, Delphine Auclair. Radiogenic and stable Ce isotope measurements by 1 thermal ionisation mass spectrometry. *Journal of Analytical Atomic Spectrometry*, 2019, 34 (3), pp.504-516. 10.1039/c8ja00362a . hal-02110895

HAL Id: hal-02110895

<https://uca.hal.science/hal-02110895>

Submitted on 25 Apr 2019

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1 Radiogenic and stable Ce isotope measurements by
2 thermal ionisation mass spectrometry

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25 **Abstract**

26 Techniques for the separation of Cerium (Ce) from silicate matrices and for the analysis of radiogenic
27 ($\epsilon^{138}\text{Ce}$) and mass dependent ($\delta^{142}\text{Ce}$) Ce isotope variations by Thermal Ionisation Mass Spectrometer
28 (TIMS) are presented in this study. We developed a static acquisition method associated with $10^{13} \Omega$
29 amplifiers that allows (i) the precise determination of the ^{140}Ce peak tailing effect on the lighter Ce
30 isotopes, and (ii) the reduction of the counting time necessary to obtain high precision isotopic
31 composition. The long-term reproducibility obtained for our Ce reference material (Ce-LMV) on the
32 $^{138}\text{Ce}/^{142}\text{Ce}$ ratio is $0.02257053 \pm 0.00000061$ (27 ppm, 2 s.d., $n = 48$). The new Ce-LMV has been
33 calibrated against the commonly used AMES reference material ($0.02257426 \pm 0.00000068$ (30 ppm,
34 2 s.d., $n = 25$). The static cup configuration also allows a more stable determination of the tailing effect
35 from the ^{140}Ce isotope peak onto ^{136}Ce and ^{138}Ce . Finally, the $10^{13} \Omega$ amplifiers permit a better
36 determination of the tailing effect during low voltages measurements. A new method to measure
37 mass dependent Ce isotope variations based on the double spike method has also been developed.
38 Uncertainty propagation calculations demonstrate that the best spike mixture is a ^{136}Ce - ^{138}Ce - ^{140}Ce
39 triple spike. We have calibrated an in-house triple spike used to correct for instrumental mass bias
40 effect and fractionation of Ce isotopes during Ce separation. Numerical simulations demonstrate the
41 effect of potential isobaric interferences from Ba, Nd and La and highlight the need for an efficient
42 chemical separation. Two loading techniques were tested for triple spike measurements (oxide and
43 metal). The best reproducibility for $\delta^{142}\text{Ce}$ is obtained for the metal runs and is about $\pm 0.028 \%$.
44 Although this technique has been developed for silicate matrices, the mass spectrometry method can
45 be applied to other matrices such as carbonates. The newly calibrated Ce reference material is
46 available to the community upon request.

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51 1. Introduction

52

53 The Rare Earth Elements (REE) are a group of 17 elements (Lanthanides (La to Lu) as well as
54 Scandium and Yttrium), widely used in the geosciences community because of their similar behaviour
55 in natural systems. REE can be found as minor or trace elements in most natural environments and
56 are sometimes more concentrated in some minerals (e.g. monazite) or CeO₂ nanoparticles. The main
57 characteristic of the REE group is that their oxidation state in most natural system is REE³⁺ except for
58 Ce and Eu. Europium can form Eu(II) ions in reduced conditions and Ce is more stable in Ce(IV) in
59 oxidised conditions. The differences in chemical behaviour between Ce and Eu compared with the rest
60 of the REE have been extensively used in the literature via the positive and negative anomalies. For
61 example, seawater is characterised by a large negative Ce anomaly due to the insolubility of Ce(IV)
62 relative to other REE(III).¹ In this case, Ce is oxidised to Ce(IV) and is removed from seawater leaving
63 the residue Ce depleted and therefore creating a negative Ce anomaly. Cerium anomalies have also
64 been used in high temperature settings such as zircon crystallisation.²⁻⁵ Indeed, the amplitude of the
65 Ce anomaly in zircon is directly proportional to the redox conditions and can potentially be used as an
66 oxybarometer.^{2,3} Cerium is a lithophile element and behaves incompatibly in magmatic systems,
67 meaning that upon melting and/or crystallisation Ce remains in the melt.

68 Cerium has four stable isotopes, ¹³⁶Ce, ¹³⁸Ce, ¹⁴⁰Ce and ¹⁴²Ce with relative abundance of 0.185 %,
69 0.251 %, 88.45 % and 11.114 %, respectively (Fig. 1)⁶. Cerium isotopes vary in relative abundance by
70 two orders of magnitude, which makes analyses more challenging than, for example, Nd, which only
71 vary by a factor of five. Indeed, ¹³⁸Ce and ¹³⁶Ce are about 400 times less abundant than the main Ce
72 isotope (¹⁴⁰Ce). The small Ce isotopic variations observed in natural systems mean that high precision
73 measurements are required. Furthermore, ¹³⁸Ce is affected by isobaric interferences from ¹³⁸Ba, which
74 is the most abundant Ba isotope, and from ¹³⁸La, which is the least abundant La isotope. There is also
75 an isobaric interference from ¹⁴²Nd onto ¹⁴²Ce. Additionally, ¹³⁶Ce and ¹³⁸Ce are affected during
76 measurement on a TIMS by tailing effect from mass ¹⁴⁰Ce.⁷ The measurement of Ce isotopes at high

77 precision is thus challenging. This requires both a good chemical separation between Ce and the
78 isobaric interference elements (mainly Ba and Nd) and a specific analytical setting.

79 Cerium isotopes have been previously studied for the radiogenic variations of ^{138}Ce .⁸⁻¹⁴ The La-Ce
80 systematic is based on the β -decay of ^{138}La to stable ^{138}Ce . The low abundance of ^{138}La and its long
81 half-life (β -decay; $t^{1/2} = 292.5 \times 10^9$ years, 14) means that the observed variations in $^{138}\text{Ce}/^{142}\text{Ce}$ are
82 small (~ 80 - 120 ppm) compared to variations in the Sm-Nd systematic (~ 600 ppm).¹⁶ Nevertheless, the
83 La-Ce system has been successfully applied as a geochemical tracer together with other isotopic
84 systems (Rb-Sr, Sm-Nd, Lu-Hf, Re-Os and U-Th-Pb) and for the age determination of rocks.¹⁷⁻²¹ It has
85 also been successfully used for terrestrial and lunar basalts, manganese nodules and seawater.²²⁻²⁶
86 The Ce isotopes variations can be reported in different notations.¹² In this study, we choose to report
87 the variations in three notations:

$$88 \quad {}^{138}\text{Ce}/{}^{142}\text{Ce}_{\text{sample}} \quad (1)$$

89 which is the tail, oxide and mass fractionated corrected ratio (see text below for details).

$$90 \quad {}^{138}\text{Ce}/{}^{136}\text{Ce} = \frac{{}^{138}\text{Ce}/{}^{142}\text{Ce}}{{}^{136}\text{Ce}/{}^{142}\text{Ce}_{\text{natural}}} \quad (2)$$

91 where the ratio ${}^{136}\text{Ce}/{}^{142}\text{Ce}_{\text{natural}}$ is fixed to 0.01688.²³

$$92 \quad \epsilon^{138}\text{Ce} = \left(\frac{{}^{138}\text{Ce}/{}^{142}\text{Ce}_{\text{sample}}}{{}^{138}\text{Ce}/{}^{142}\text{Ce}_{\text{LMV}}} - 1 \right) * 10000 \quad (3)$$

93 where ${}^{138}\text{Ce}/{}^{142}\text{Ce}_{\text{LMV}}$ is the ratio obtained for our Ames Ce reference material (Ce-LMV).

94 Mass dependent Ce isotopic variations have also been recently explored.²⁷ Due to the chemical
95 behaviour of Ce described above, it has been suggested that Ce isotopes could be used as a redox
96 proxy.²⁸ Mass dependent Ce isotope measurements have been performed for natural Fe-oxides and
97 absorption experiments.²⁹ The results suggest that Ce isotopes are fractionated during absorption

98 onto Fe-oxyhydroxides and that isotopic fractionation occurring in natural systems could be linked to
99 redox reactions. More recently, CeO₂ nanoparticles have also been analysed in order to characterise
100 their impact on natural systems.³⁰ Several studies have presented analytical techniques to separate
101 and analyse mass dependent Ce isotope variations.^{27,30} In these studies, mass dependent Ce isotope
102 variations have been analysed with Multi-Collector Inductively Coupled Plasma Mass spectrometers
103 (MC-ICPMS) using the external doping technique with either Sm²⁶ or Ba.³⁰ The Ce isotopic composition
104 is reported as the per mil variation from the Ce isotope reference material LMV using the equation:

$$105 \quad \delta^{142}\text{Ce} = \left(\frac{{}^{142}\text{Ce}/{}^{140}\text{Ce}_{\text{sample}}}{{}^{142}\text{Ce}/{}^{140}\text{Ce}_{\text{LMV}}} - 1 \right) * 1000 \quad (4)$$

106 In this study, we propose a new methodology to measure radiogenic variations of Ce isotopes. We
107 developed a new static cup configuration on a Thermal Ionisation Mass Spectrometer (TIMS) that
108 allows the simultaneous measurement of Ce isotopes (and its isobaric interference elements) together
109 with four masses used to define the tailing from ¹⁴⁰Ce onto ¹³⁶Ce and ¹³⁸Ce. In comparison to previous
110 techniques that used a multi-static acquisition method (2 to 6 lines), this new method allows the
111 reduction of the length of high precision measurements. We also present a new triple spike (¹³⁶Ce-
112 ¹³⁸Ce-¹⁴⁰Ce) method to measure mass dependent Ce isotope variations with a better precision than
113 previous analytical methodologies.

114 **2. Analytical techniques**

115 **2.1. Chemical separation**

116 Reference materials and samples were prepared in the clean laboratory in class 100 laminar flow
117 hoods at the Laboratoire Magmas et Volcans (Clermont Ferrand). All acids (HCl, HNO₃ and HF) were
118 distilled in the Savillex® acid still DST-1000. PFA Savillex® beakers were cleaned with concentrated
119 HNO₃ and HCl on the hotplate at 115 °C and then rinsed in ultrapure H₂O. Our high purity Ce metal
120 reference material was bought from AMES Laboratory and will be thereafter called Ce-LMV. M.
121 Willbold provided the second reference material analysed in this study (Ce-AMES; 6). The Ce reference

122 material (Ce-LMV) was dissolved in HCl on the hotplate for 48 hours. Approximately 50 mg of whole
123 rock basalts reference materials (BHVO-2 and BCR-2) were dissolved using concentrated HNO₃-HF-HCl
124 acid mixtures. The fully dissolved sample was evaporated to dryness and then re-dissolved in 2.5 M
125 HCl for chemical separation.

126 The chemical separation method used in this study is modified after Tazoe et al. (2007)³¹, Li et al.
127 (2015)³² and Bellot et al. (2015)²⁰. Only a brief description is given here. The chemical separation
128 developed to separate the Ce fraction to silicate matrices involved three columns. The first step was
129 used to separate the REEs from the main cations of the matrix (Fig. 2). In order to achieve this
130 separation, the samples were loaded in 2.5N HCl onto 1 mL of AG50 X8, 200-400 mesh resin in Bio-
131 Rad 10 ml column. Prior to the chemistry, the resin was cleaned with 10 ml 6M HCl. The REE stuck to
132 the resin while the main cations were eluted from the resin. Ba was then eluted in 2M HNO₃ and the
133 REE were finally eluted in 6M HCl (Fig. 2a). The second column procedure was designed to separate
134 Ce⁴⁺ from the other REE using LnSpec Eichrom resin (50-100 μm) in 2 ml Bio-Rad columns.³¹ The
135 oxidation of Ce from Ce³⁺ to Ce⁴⁺ was achieved with 0.5ml of NaBrO₃ (20mM) in 10M HNO₃. Prior to
136 the chemistry, the resin was cleaned with 5 ml 6M HCl. The samples were loaded onto 0.1 mL LnSpec
137 Eichrom resin in 10M HNO₃ + NaBrO₃ and Ce⁴⁺ stuck to the resin while the remaining REE³⁺ were eluted
138 in the loading solution (Fig. 2b). The Ce fraction was eluted in 6M HCl + H₂O₂. Finally, the samples were
139 then processed through the first step of the chemistry to make sure the Ce fraction was cleaned of
140 any remaining matrix cations.

141 **2.2. Mass spectrometry**

142 Isotopic measurements were performed on a ThermoScientific Thermal Ionisation Mass
143 spectrometer Triton Plus (TIMS) at the Laboratoire Magmas et Volcans. The Ce reference materials
144 were analysed in both oxide and metal forms using the double filament technique. For the oxides
145 analyses, the Ce fraction was loaded in HCl onto outgassed Re filament together with 0.5 μL of 1 M
146 H₃PO₄. For the metal runs, the Ce fraction was loaded in HCl onto outgassed C-doped zone refined Re

147 filaments. Aquadag was added to outgassed Re filament and the filament was then re-degassed. The
148 carbon acted as a reducer and stopped the emission and ionisation of Ce oxides. During a typical Ce
149 metal measurement the CeO/Ce ratio was always lower than 0.002.

150 During the course of this study, several cup configurations have been tested (Table 1). Firstly, the
151 Ce-AMES reference material was analysed using the dynamic method previously proposed to measure
152 Ce isotopes.^{7,20} This cup configuration requires a multi-static acquisition method. The first line is for
153 measuring Ce, Nd, La and Ba masses with $^{139}\text{La}^{16}\text{O}$ in the central cup (Table 1). The tailing is measured
154 on the second line after a -0.5 mass unit (MU) jump. In this configuration, both elemental and tailing
155 signals are measured using $10^{11} \Omega$ resistors. For this study, we have established a new cup
156 configuration where mass and half-mass signals are measured simultaneously. In this case, the
157 acquisition is achieved in a static mode and different resistors can be used for both signals and tailing
158 masses. This technique has two main advantages. First, the tailing effect on mass ^{136}Ce and ^{138}Ce can
159 be estimated more precisely. Second, the static acquisition method reduces the duration of our
160 isotopic measurements by a third.

161 The oxide runs were performed in two main cup settings (Table 1). In the first setting (cup
162 configurations #2 and 3), $^{140}\text{Ce}^{16}\text{O}$ was not measured and the signal was adjusted to have 10 V (0.1 nA)
163 of $^{142}\text{Ce}^{16}\text{O}$. In the second setting (cup configuration #4, 5 and 6), $^{140}\text{Ce}^{16}\text{O}$ was measured in H2. The
164 difference between cup configurations in each setting is the amplifier combination (Table 1). The cup
165 configuration #7 was designed to measure all Ce isotopes and isobaric interferences together with
166 tailing masses. Due to the increased amount of ^{136}Ce and ^{138}Ce after spike addition, the $10^{11} \Omega$ and 10^{13}
167 Ω amplifiers were used for all elemental signals and tailing masses, respectively. The cup configuration
168 #8 was designed to measure Ce and its isobaric interference isotopes in metal form. In this setting, all
169 cups were associated with $10^{11} \Omega$ amplifiers and no tailing masses were monitored. Typical runs on
170 the mass spectrometer consist of 27 blocks of 20 cycles with 8.462 seconds integration time. Each
171 block started with a baseline measurement of 30 seconds. The gain calibrations for the 10^{10} , 10^{11} and

172 $10^{12} \Omega$ resistors were performed daily using the ThermoScientific software built in gain routine (at 3.33
173 V). The gain calibrations for the $10^{13} \Omega$ resistors were performed weekly (when used) with Nd signals
174 following the ThermoScientific procedure.

175 **2.3. The triple spike technique**

176 The use of an isotopically enriched solution (“double spike”) to correct for fractionation of stable
177 isotopes during sample processing and for instrumental mass bias effects has long been recognised as
178 a powerful tool.³³⁻³⁵ This methodology has now been successfully applied to many isotopes systems
179 including Fe, Sr, Zn, Cd and Cr.³⁶⁻³⁹ For Ce, the double spike technique is applicable to both terrestrial
180 and extra-terrestrial samples because the Ce isotope radiogenic and nucleosynthetic variations are
181 small and will not generate a large influence in the spike deconvolution. Moreover, this technique
182 allows the determination of Ce concentration by isotope dilution.

183 In this study, we explore the best spike composition to measure mass dependent Ce isotopic
184 variations. Three spikes are commercially available: ^{136}Ce - ^{140}Ce , ^{138}Ce - ^{140}Ce and ^{142}Ce . The ^{142}Ce spike
185 has already been used for isotope dilution measurement in previous studies. In order to optimise
186 carefully the spike composition, a number of mixtures between commercially available spikes have
187 been investigated (Table 2). This requires: (1) establishing the most appropriate spike composition; (2)
188 solving the double spike equations and (3) adding the appropriate amount of spike to the reference
189 material. The optimisation is described by the uncertainty magnification term, γ :

$$190 \quad \gamma = \sigma_{\text{DS}} / \sigma_{\text{nat}}, \tag{5}$$

191 where σ_{DS} is the uncertainty obtained from the double spike deconvolution procedure and σ_{nat}
192 the uncertainty of the natural unspiked run. Our calculations are similar to those described by Galer
193 (1999)⁴⁰ but we deconvolve the runs using the exponential mass fractionation law. The spike
194 compositions used in the calculations are given in Table 2 and the results of the calculations are
195 presented in Figure 3. Three spike mixtures were investigated: ^{136}Ce - ^{140}Ce - ^{142}Ce , ^{138}Ce - ^{140}Ce - ^{142}Ce and
196 ^{136}Ce - ^{138}Ce - ^{140}Ce . In Figure 3, the lower uncertainty magnification term is obtained for the ^{136}Ce - ^{138}Ce -

197 ^{140}Ce triple spike. The best proportion of ^{136}Ce - ^{140}Ce spike in the triple spike mixture is about 50 %. In
198 order to calculate the optimal spike/sample ratio, the deconvolution program is run using different
199 proportions of spike and sample. We use an ion model based on the one described by Ludwig (1986)⁴¹
200 to calculate the uncertainty on signal intensity of each isotope which is then propagated to calculate
201 the uncertainty on the double spike deconvolution procedure. The uncertainty magnification term is
202 calculated using Monte Carlo simulation in which the uncertainties of the four Ce isotopes signals are
203 used to generate 540 data points for each analysis. These points have a Gaussian distribution around
204 the mean value. The results obtained after the Monte Carlo simulations (540 cycles) are processed
205 through the deconvolution procedure and the uncertainty (σ_{DS}) of the deconvolved data is calculated.
206 For the triple spike ^{136}Ce - ^{138}Ce - ^{140}Ce , the uncertainty magnification term is always less than 4. Figure
207 3b illustrates the optimal spike/sample ratio for the two double spikes (^{136}Ce - ^{140}Ce and ^{138}Ce - ^{140}Ce)
208 and the triple spike (^{136}Ce - ^{138}Ce - ^{140}Ce). It is important to note that the two double spikes can produce
209 low uncertainty magnification terms but the proportion of spike required is high (spike/sample ratio
210 = 0.8). The triple spike however has a more flatten uncertainty model curve, which means that not
211 only the uncertainty magnification term is better for almost all mixtures but also that optimal spiking
212 is facilitated. The best spike/sample ratio for the triple spike is 0.33.

213 An in-house ^{136}Ce - ^{138}Ce - ^{140}Ce triple spike was prepared from ^{136}Ce - ^{140}Ce and ^{138}Ce - ^{140}Ce cerium
214 oxides spikes purchased from IsoFlex[®] and their enrichment factors were 42.5 % and 41.6 %,
215 respectively. Two double-spike solutions were made by dissolving the Ce-oxides in 6M HCl-H₂O₂. The
216 Ce spikes were purchased in oxide form and H₂O₂ helped to reduce Ce and facilitated the dissolution.
217 The triple spike was then prepared by mixing the double spikes in the appropriate proportions. The
218 triple spike was calibrated by TIMS at the Laboratoire Magmas et Volcans using the loading techniques
219 described above. The pure Ce-LMV reference material, the pure triple spike and spike/standard
220 mixtures were analysed. The isotopic composition of the triple spike is then calculated by treating the
221 pure triple spike as an unknown. The composition of the triple spike was derived from 26 separate
222 analyses and is reported in Table 3.

223 3. Data Processing

224 The Ce isotopic composition of the samples and reference materials was determined offline but
225 baseline and gain corrections were performed online with the ThermoScientific software. The
226 deconvolution procedures used for unspiked and spiked runs are described in details in the paragraphs
227 below. The deconvolution procedure for both unspiked and spiked runs can be divided in three main
228 steps: tail correction on mass ^{136}Ce and ^{138}Ce , oxide corrections and mass bias fractionation
229 corrections.

230 3.1. Tail correction

231 The large dynamic range in Ce isotopes, with ^{140}Ce accounting for 88.45% of total Ce, has long
232 been recognised as a problem for obtaining high precision Ce isotope measurements (e.g. 7). Indeed,
233 the small proportion of ^{136}Ce and ^{138}Ce , 0.19 and 0.25% respectively, means that we need to measure
234 high intensity beams (e.g. 80 V (0.8 nA) for $^{140}\text{Ce}^{16}\text{O}$) in order to obtain accurate and precise Ce isotopic
235 compositions. It has been shown that running at high intensities produces a tailing effect on mass
236 ^{136}Ce and ^{138}Ce . Classically, the tailing contribution was calculated with half masses analysis (e.g. 7) in
237 a dynamic sequence (cup configuration #1, Table 1). In this contribution, we developed a simultaneous
238 measurement of the Ce isotopes and of the tailing contribution. Two cups were intercalated between
239 masses 152 and 154 and one cup between 154 and 156 (see Table 1, Fig. 4). This new cup configuration
240 allows the measurement of intensities generated by the large ^{140}Ce beam on mass 156.5 and 154.6.
241 The intercalated cup positions were determined by measuring the distance between the cups on large
242 mass scans using a stable Ce beam. This step is critical in order to perform an accurate tail correction.
243 In order to determine the contribution of the tailing on mass ^{136}Ce and ^{138}Ce , we fitted an exponential
244 equation through the measured masses. The increased integration time (from 4s to 8s) compared to
245 our dynamic measurements means that the tailing contribution can be assessed more precisely.
246 Furthermore, the static run suppresses the need for magnet shift and allows a more stable
247 measurement. The uncertainty induced by small offset in magnet position described in details in Willig

248 and Stracke (2017)¹³ can therefore be avoided. The static cup configuration allows a more stable
 249 determination of the tail effect (0.6 to 0.9 ε unit) compared to previous studies (0.0 to 1.6 ε unit⁴² and
 250 0.15 to 1.8 ε unit¹³). All ¹³⁶Ce and ¹³⁸Ce signals mentioned hereafter in the manuscript are tail corrected
 251 (unless noted otherwise).

252 3.2. Oxide correction and mass bias correction

253 During the measurement of Ce isotopes in oxide form, the measured raw signals are the sums of the
 254 isotopes of interest and an oxide interference following the equation:

$$255 \quad {}^X\text{Ce}^{16}\text{O} = I^{(X+16)} - (X-2)\text{Ce}^{18}\text{O} \quad (6)$$

256 where X can be 138, 140 and 142 and $I^{(X+16)}$ is the measured intensities on the mass X+16 corresponding
 257 to the three oxide masses. With $R = {}^{18}\text{O}/{}^{16}\text{O}$, equation 6 can be easily expressed as:

$$258 \quad {}^X\text{Ce}^{16}\text{O} = I^{(X+16)} - (X-2)\text{Ce}^{16}\text{O} * R \quad (7)$$

259 The oxide correction methodology used in this study follows a similar protocol to that of Willig and
 260 Stracke (2017)¹³ although it is adapted for the triple spike deconvolution procedure.

261 For the unspiked runs, an iterative process was followed whereby the ratio R is assumed to be
 262 0.00213 and signals measured on masses 154, 156 and 158 are corrected for the contribution of
 263 ¹³⁶Ce¹⁸O, ¹³⁸Ce¹⁸O and ¹⁴⁰Ce¹⁸O respectively following equation 7. The ¹³⁸Ce/¹⁴²Ce and ¹⁴⁰Ce/¹⁴²Ce ratios
 264 (when measured) were corrected for mass bias fractionation using the exponential law and the
 265 ¹³⁶Ce/¹⁴²Ce ratio of 0.01688.⁴³⁻⁴⁵ Using the obtained Ce isotopes intensities the fractionation factor (β)
 266 is then determined using the exponential mass fractionation law:

$$267 \quad \beta = \frac{\ln\left(\frac{{}^{136}\text{Ce}/{}^{142}\text{Ce}_{true}}{{}^{136}\text{Ce}/{}^{142}\text{Ce}_{measured}}\right)}{\ln\left(\frac{M^{136}\text{Ce}^{16}\text{O}}{M^{142}\text{Ce}^{16}\text{O}}\right)} \quad (8)$$

268 where $^{136}\text{Ce}/^{142}\text{Ce}_{\text{measured}}$ is the tail and oxide corrected $^{136}\text{Ce}^{16}\text{O}/^{142}\text{Ce}^{16}\text{O}$ measured ratio and
 269 $^{136}\text{Ce}/^{142}\text{Ce}_{\text{true}}$ is fixed to 0.01688. $M^{136}\text{Ce}^{16}\text{O}$ and $M^{142}\text{Ce}^{16}\text{O}$ are the atomic masses of $^{136}\text{Ce}^{16}\text{O}$ and
 270 $^{142}\text{Ce}^{16}\text{O}$, respectively. Using the fractionation factor calculated above, a new R value can be calculated
 271 using the equation:

$$272 \quad R = \frac{\frac{^{136}\text{Ce}^{16}\text{O}}{^{142}\text{Ce}^{18}\text{O}}_{\text{measured}}}{\frac{^{136}\text{Ce}}{^{142}\text{Ce}}_{\text{true}}} * \left(\frac{M^{136}\text{Ce}^{16}\text{O}}{M^{142}\text{Ce}^{18}\text{O}} \right)^{\beta} \quad (9)$$

273 where $^{136}\text{Ce}^{16}\text{O}/^{142}\text{Ce}^{18}\text{O}_{\text{measured}}$ is the measured ratio. The new R value is then used to calculate
 274 new oxide contributions on masses 152, 154 and 156. This iterative deconvolution is conducted until
 275 the R value reaches a plateau which is usually obtained after three iterations. The β value obtained on
 276 the last iterative step is used to calculate the corrected Ce isotopic composition. When $^{140}\text{Ce}^{16}\text{O}$ is not
 277 measured, a fixed value for the $^{140}\text{Ce}/^{142}\text{Ce}$ ratio is used to correct the contribution of $^{140}\text{Ce}^{18}\text{O}$ on
 278 $^{142}\text{Ce}^{16}\text{O}$ signals.

279 For the triple spiked analysis, we follow the same principle except that mass bias fractionation is
 280 solved following the equation 10:

$$281 \quad F^i(P_{sp}^{ref}, f_{nat}, f_{mix}) = P_{sp}^{ref} r_{sp}^i + (1 - P_{sp}^{ref}) r_{nat}^i \left(\frac{M^i}{M_{ref}} \right)^{f_{nat}} - r_{mix}^i \left(\frac{M^i}{M_{ref}} \right)^{f_{mix}} = 0 \quad (10)$$

282 where r_{sp}^i is the isotope ratio of i in the spike, r_{nat}^i and r_{mix}^i are the measured isotope ratios of i in
 283 the sample and mixture, and M_i and M_{ref} are the true masses of the isotope oxides (i+16). The F^i
 284 function is a closure function for the spike sample mixture, which must be equal to zero. The equation
 285 is solved using an iterative Newton-Raphson procedure that recovers the proportion of spike in the
 286 mixture (P_{sp}^{ref}), the fractionation factor for the spike-sample mixture (f_{mix}) and finally the fractionation
 287 factor for the sample (f_{nat}). Using the measured $^{136}\text{Ce}^{16}\text{O}/^{142}\text{Ce}^{18}\text{O}$ ratio and the mixture fractionation
 288 factor (f_{mix}), we calculated a new R value which is then used to correct for oxide interferences. The
 289 deconvolution procedure finishes when R value does not change, within 5 ppm, from one iteration

290 step to the other. We then obtain our final f_{nat} value that is used to calculate the isotopic composition
291 of the original sample. The isotope ratios for the Ce-LMV reference material used for referencing our
292 isotope data (to calculate $\delta^{142}\text{Ce}$) in this study were obtained by TIMS by internal normalisation to
293 $^{136}\text{Ce}/^{142}\text{Ce}$ ratio as described above and was recalculated in the ^{140}Ce space (i.e. ^{140}Ce as a
294 denominator). This yielded $^{136}\text{Ce}/^{140}\text{Ce} = 0.00212$, $^{138}\text{Ce}/^{140}\text{Ce} = 0.0248$ and $^{142}\text{Ce}/^{140}\text{Ce} = 0.12588$.

295 For triple spike runs performed in metal form, the same procedure was used with metal Ce
296 intensities except that no tailing and oxide corrections were performed (see below for details).

297 **4. Results and Discussion**

298 **4.1. Separation of Ce from the samples matrix**

299 High precision measurements of Ce isotopes by TIMS require the separation of Ce from the sample
300 matrix in order to minimise isobaric interferences. Several methods have previously been reported to
301 separate Ce from silicate matrices. The main problem with obtaining high precision Ce isotopes
302 measurement, especially in metal mode (see below), is the complete removal of Ba during the
303 chromatography procedure. The efficacy of our Ce separation technique was tested using synthetic
304 multi-elemental solution and a certified basalt reference material (BHVO-2). Figure 2 shows well-
305 defined and separated elution peaks during the chromatography procedure. Importantly, interfering
306 elements such as Ba and Nd are separated from Ce in the first and second step of the column
307 chemistry, respectively. After the three steps column procedure, the Ba/Ce and Nd/Ce ratios are
308 decreased to 0.002 and 0.001 respectively. The total blank of our Ce separation procedure is about
309 0.5 ng, which is negligible (<0.1%) compared to the amount of Ce processed through the columns
310 (~700 ng).

311 **4.2. Accuracy and reproducibility of radiogenic measurements**

312 Two Ce reference materials were analysed during the course of this study for their radiogenic Ce
313 isotope composition. The results obtained in the different analytical setups are summarised in Table
314 4 and Figure 5. Wilbold (2007)⁷ demonstrated that Ce isotope measurements in metal form were

315 strongly affected by Ba interference most likely coming from the filaments. We therefore decided to
316 measure radiogenic Ce isotope in oxide form only, testing several cup configurations. Using the multi-
317 static cup configuration, the $^{138}\text{Ce}/^{142}\text{Ce}$ obtained for the Ce_{AMES} reference material is $0.0225743 \pm$
318 0.0000005 (2 s.d., $n = 5$). For the static cup configuration without $^{140}\text{Ce}^{16}\text{O}$, the $^{138}\text{Ce}/^{142}\text{Ce}$ obtained
319 for the Ce_{AMES} and Ce_{LMV} reference materials are 0.0225743 ± 0.0000007 (2 s.d., $n = 25$) and $0.0225705 \pm$
320 0.0000006 (2 s.d., $n = 48$) respectively. Finally, for the static cup configuration with $^{140}\text{Ce}^{16}\text{O}$, the
321 $^{138}\text{Ce}/^{142}\text{Ce}$ obtained for the Ce_{AMES} and Ce_{LMV} reference materials are 0.0225746 ± 0.0000001 (2 s.d.,
322 $n = 5$) and 0.0225706 ± 0.0000005 (2 s.d., $n = 7$) respectively. The $^{138}\text{Ce}/^{142}\text{Ce}$ ratios obtained for both
323 Ce reference materials in all cup configurations are always identical within uncertainty (Table 4). There
324 is also a good agreement between our data and the literature values but our reproducibility is better
325 than previously reported.^{6,12,18-20} Contrary to earlier studies, the data presented here have not been
326 normalised to a reference session which tends to improve the external reproducibility. In the cup
327 configurations #4, 5 and 6, the $^{140}\text{Ce}/^{142}\text{Ce}$ ratios were also determined and we obtained for our
328 reference materials $^{140}\text{Ce}/^{142}\text{Ce}_{\text{AMES}} = 7.94416 \pm 0.00023$ (2 s.d., $n = 5$) and $^{140}\text{Ce}/^{142}\text{Ce}_{\text{LMV}} = 7.94397 \pm$
329 0.00018 (2 s.d., $n = 7$). There is about 100 ppm difference between our value and the value reported
330 by Willig and Stracke (2017)¹³. The difference between these values is possibly due to the use of two
331 different mass spectrometers with variable faraday cups ages⁴⁶ and/or due to the different cup
332 configurations (^{140}Ce measured in axial and L1 cups). However, this small difference is negligible for
333 the correction of the contribution of $^{140}\text{Ce}^{18}\text{O}$ onto $^{142}\text{Ce}^{16}\text{O}$ when $^{140}\text{Ce}^{16}\text{O}$ is not measured. Two
334 geological reference materials (BHVO-2 and BCR-2) were also analysed for their Ce radiogenic isotopic
335 compositions. The $^{138}\text{Ce}/^{142}\text{Ce}$ ratios together with the $^{140}\text{Ce}/^{142}\text{Ce}$ ratios are given in Table 1. For
336 BHVO-2, the $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{140}\text{Ce}/^{142}\text{Ce}$ ratios obtained are 0.0225650 ± 0.0000004 (2 s.d., $n = 2$) and
337 7.94389 ± 0.00003 (2 s.e., $n = 1$), respectively. For BCR-2, the $^{138}\text{Ce}/^{142}\text{Ce}$ and $^{140}\text{Ce}/^{142}\text{Ce}$ ratios
338 obtained are 0.0225670 ± 0.0000005 (2 s.d., $n = 5$) and 7.94362 ± 0.00003 (2 s.e., $n=1$), respectively.
339 The $^{138}\text{Ce}/^{142}\text{Ce}$ values presented in this study are in agreement with previous estimates of the
340 $^{138}\text{Ce}/^{142}\text{Ce}$ ratios for these two geological reference materials.^{13,19,20}

341 As described above, several cup configurations were tested during the course of this study. Each
342 of those has advantages and inconveniences and we will now try to compare the results with
343 previously published results and highlight the gain of the new technique. In terms of reproducibility,
344 the $^{138}\text{Ce}/^{142}\text{Ce}$ ratio can be measured, using the static cup configuration, at about 25 ppm, which is
345 comparable to the reproducibility obtained for the same reference material during dynamic
346 measurements. However, the run duration is divided by 1.5 and the amount of Ce required also
347 decreases to 700 ng. The main advantage of the method used in this study is the ability to reduce the
348 counting time by 30% to obtain similar internal reproducibility. If the Ce quantity is the same, the
349 signal intensity can be increased and then the internal precision will be better since the counting
350 statistic is the main factor limiting the internal precision. We also performed Ce isotopic
351 measurements with 250 ng of Ce and we could run CeO at about 2.5V (0.025 nA) of $^{142}\text{Ce}^{16}\text{O}$. The
352 reproducibility obtained is about 45 ppm, which is slightly higher than the optimised conditions but
353 still acceptable for many applications. Compared to literature values, our reproducibility is similar or
354 better than recently published Ce isotopes measurements (Table 1).¹³ The second advantage of the
355 simultaneous measurement of Ce isotopes and the half masses tailing is that it does not require mass
356 shift during the run. Finally, the main inconvenience of using our new cup configuration is the
357 correction for Ba interference on the ^{136}Ce and ^{138}Ce isotopes. The static cup configuration uses the
358 less abundant ^{134}Ba (~2.4 %) whereas the multi-static method used the slightly more abundant ^{137}Ba
359 (~11.2 %). This reduces our ability to measure small amount of Ba by about 4 which could potentially
360 be a problem. However, the chemical separation presented in this study is designed to effectively
361 separate Ba from the Ce fraction to level well below detection limit. Furthermore, due to the high
362 ionization potential of BaO^{47} and the likely presence of Ba phosphate, running in oxide mode reduces
363 the amount of emitted Ba, which means that the proposed method enables high precision Ce isotopes
364 measurements.

365 **4.3. The utility of 10^{13} amplifiers**

366 In previous studies, the faraday cups were always coupled with $10^{11} \Omega$ amplifiers and this
367 configuration allows the definition of the tailing from $^{140}\text{Ce}^{16}\text{O}$ when routine beams of 10 V (0.1 nA) of
368 $^{142}\text{Ce}^{16}\text{O}$ were measured. One of the aims of this study is to develop a new method to measure Ce
369 isotopes at high precision with smaller quantities. To this end, we used $10^{13} \Omega$ resistors on the tailing
370 masses. The signal/noise on the $10^{13} \Omega$ resistors is supposed to be 10 times better than the typical 10^{11}
371 Ω resistors. Thus the new amplifiers allow the measurements of small beams with better precision
372 than typical $10^{11} \Omega$ amplifiers. In Figure 6, the intensities measured for the tailing masse 154.5 with
373 two different resistors are shown. The signal measured (0.35 fA) with $10^{13} \Omega$ resistor is less noisy by a
374 factor of five compared to $10^{11} \Omega$ resistor which is comparable to the predicted improvement of ten.
375 The standard deviation for a stable beam of 0.35 fA improves from 0.35 fA when using $10^{11} \Omega$ amplifier
376 and 4 seconds integration time to 0.25 fA ($10^{11} \Omega$ amplifier and 8s integration time) and 0.05 fA (10^{13}
377 Ω amplifier and 8s integration time). For runs at high intensities (0.1 nA $^{142}\text{Ce}^{16}\text{O}$), the tailing measured
378 with $10^{11} \Omega$ resistors is precisely defined (Fig. 4). As expected, the tailing produced during a low
379 intensity Ce isotope measurements (0.03 nA on $^{142}\text{Ce}^{16}\text{O}$) is much smaller than at high intensity
380 although its relative intensity compared to the measured Ce signals is the same (Fig. 4). Using $10^{13} \Omega$
381 resistors, we could define a good tailing where it was more difficult with typical $10^{11} \Omega$ resistors. This
382 indicates that it is possible to produce high precision Ce isotopes measurements with lower signals
383 than previously suggested and 250ng Ce (~ 0.03 nA of $^{142}\text{Ce}^{16}\text{O}$) is enough to obtain a precise
384 $^{138}\text{Ce}/^{140}\text{Ce}$ ratio. We also performed a few experiments with ^{136}Ce and ^{138}Ce signals with $10^{13} \Omega$
385 resistors using the multi-static cup configuration (#1). The slow response time of these resistors means
386 that after the jump, it was not possible for the signals to go back to the baseline values in a reasonable
387 time. We therefore think that it is currently difficult to use $10^{13} \Omega$ resistors in dynamic measurements.
388 The best cup configurations (#4 and #5, Table 1) for radiogenic Ce isotopic measurements are a
389 combination of 10^{10} , 10^{11} , 10^{12} and $10^{13} \Omega$ resistors. If analysed, the main Ce peak ($^{140}\text{Ce}^{16}\text{O}$) is
390 measured with a 10^{10} or $10^{11} \Omega$ resistor in high and low intensity runs, respectively. The second most
391 abundant Ce mass ($^{142}\text{Ce}^{16}\text{O}$) is always measured with $10^{11} \Omega$ resistor. The low intensities signals on

392 masses $^{136}\text{Ce}^{16}\text{O}$ and $^{138}\text{Ce}^{16}\text{O}$ are measured using 10^{12} Ω resistors. Finally, the tailing masses in cups
393 L4, L2, L1 and H1 are measured with 10^{13} Ω resistors. The best cup configuration used for the triple
394 spike runs is a combination of 10^{11} and 10^{13} Ω resistors. The Ce masses and the tailing are measured
395 with 10^{11} and 10^{13} Ω resistors, respectively.

396 The newly developed cup configuration allowed the determination of the tailing effect on masses
397 ^{136}Ce and ^{138}Ce . The lack of jump and the longer integration time of the static measurement mean that
398 the tailing is more stable. The long-term tailing correction for the data presented in this study is 0.73
399 ± 0.13 ϵ which is slightly better than the reproducibility obtained per session using the multi-static cup
400 configuration #1 (from 0.14 to 0.51).⁴² The tailing effect during analysis at low intensity ($3 \text{ V } ^{142}\text{Ce}^{16}\text{O}$)
401 is similar (0.71 ± 0.15 ϵ unit) in size. This indicates that the newly developed cup configuration allows
402 a more reproducible determination of the tailing effect from $^{140}\text{Ce}^{16}\text{O}$ onto masses $^{136}\text{Ce}^{16}\text{O}$ and
403 $^{138}\text{Ce}^{16}\text{O}$.

404 **4.4. Spike calibrations and mass dependent Ce isotope measurements**

405 The triple spike was calibrated in oxide mode and the results are presented in Table 5 and Figure 7.
406 Three spike mixtures were analysed and the $\delta^{142}\text{Ce}$ values recovered by the triple spike technique are
407 within uncertainty of 0 ‰ as expected but the overall average value is slightly positive with $\delta^{142}\text{Ce}$
408 values ranging from -0.015 to 0.023 ‰. The best reproducibility is obtained by the spike/standard
409 mixture ratio of 0.30 and is $\delta^{142}\text{Ce} = 0.023 \pm 0.052$ ‰ (2 s.d., $n = 13$). However, there is no difference
410 between the three spike-sample mixtures analysed in this study. The internal uncertainty (2 s.e.) of
411 measurements of $\delta^{142}\text{Ce}$ in the standard-spike mixture runs is usually better than 0.015‰. The results
412 were deconvolved with and without tail correction. In this case, the tail correction does not change
413 the deconvolved value suggesting that the increase in intensities due to spike addition is sufficient to
414 make the contribution of tailing on masses 154 and 156 negligible. The large difference between our
415 internal uncertainty and our external reproducibility is difficult to understand. One possibility is that

416 this difference originates from the oxide correction applied to the raw data. Further tests are needed
417 to understand this observation.

418 A standard-spike mixture was also analysed in metal mode. In this case, no tailing correction was
419 performed because of the increase in signal intensities with the spike addition. The main difference
420 with the oxide run is the presence of small amount of Ba. The Ba interference correction is important
421 during analysis in metal form. The cup configuration allows the measurement together with the Ce
422 isotopes of ^{137}Ba that is slightly higher than ^{134}Ba . The Ba signals are difficult to control during TIMS
423 measurements and are unpredictable. Several factors seem to favour Ba emission. Among them are a
424 rapid heating and a high ionisation current. However, when the Ba interference is well controlled, the
425 reproducibility obtained on the standard-spike mixture is $\delta^{142}\text{Ce} = -0.083 \pm 0.028\%$, which is better
426 than the reproducibility obtained in oxide mode and in the methods proposed in the literature.^{22,25}
427 This value is slightly lighter than the expected $\delta^{142}\text{Ce}$ value of 0. The main reason for this discrepancy
428 is probably the fact that the correction procedure is different between metal and oxide analyses.

429 **4.5. Effects of isobaric interferences**

430 In most natural samples, Ce is present as a trace element and Ba and Nd can be present as a minor
431 component (Ba/Ce and Nd/Ce ratios up to 200 and 30, respectively). In some rare cases such as
432 monazite, both Ce and Nd can be present at the percent level. The Ce separation is designed to remove
433 the matrix elements and the main isobaric interference elements but it is nevertheless important to
434 carefully consider the potential effects of isobaric interferences from Ba on ^{136}Ce and ^{138}Ce and Nd on
435 ^{142}Ce . In order to correct for isobaric interferences in both unspiked and spiked runs, two key
436 assumptions are made. Firstly, the instrumental mass bias for Ce, Ba and Nd is assumed to be the same
437 for all elements involved. Secondly, the interfering elements are considered to have natural isotopic
438 compositions because it is not possible to determine simultaneously the Ce, Ba and Nd isotopic
439 compositions. It is well documented that cation exchange chromatography can lead to large isotopic

440 fractionation. The chemical separation is designed to remove the isobaric interference and the small
441 quantities remaining in the Ce fraction is likely to be heavily fractionated.

442 In order to test the sensitivity of our interference corrections in the spike deconvolution
443 procedure, we have performed some simple numerical calculations. A spiked Ce-LMV solution is
444 “contaminated” with variable amounts of Ba, Nd and La, which have their isotopic compositions that
445 differ from the “natural” composition by -3 ‰ to +3 ‰. These mixtures are then fractionated using
446 the exponential mass fractionation law by the typical amount of TIMS Ce measurement. The resulting
447 compositions are then put through our triple spike deconvolution procedure, which calculates the
448 isotopic composition of the Ce-LMV reference material. These calculations are performed in metal
449 form and the results are presented in Figure 8. The deconvolution procedure recovers a $\delta^{142}\text{Ce}$ of 0
450 when the natural compositions are assumed for Ba, Nd and La, as would be expected. However, it is
451 important to note that the recovered $\delta^{142}\text{Ce}$ values deviate from zero when non-natural values are
452 assumed. For example, if the contaminant Ba has an isotopic composition that is fractionated from
453 the natural composition by 1 ‰ and the $^{137}\text{Ba}/^{142}\text{Ce} = 0.006$, then the recovered $\delta^{142}\text{Ce}$ value is +0.1
454 ‰ (Fig. 8). This non-negligible interference correction should be applied with care. The chemical
455 separation allows a good separation between Ce and its isobaric interferences. Typical silicate samples
456 analysed in this study, after column chemistry, have $^{138}\text{Ba}/^{138}\text{Ce}$, $^{143}\text{Nd}/^{142}\text{Ce}$ and $^{139}\text{La}/^{138}\text{Ce}$ ratios of
457 less than 0.004, 0.0001 and 0.002 respectively. The uncertainty introduced by the interference
458 correction would be negligible even in the case of non-natural isotopic composition of the
459 contaminants.

460 5. Conclusions

461 A method has been developed that allows effective separation of small quantities of Ce (~700 ng)
462 from silicate samples using a three-step column chemistry procedure. This chemical separation
463 procedure allows the effective separation of Ce from Nd and Ba, two isobaric interference elements.

464 During the course of this study, several cup configurations were tested in order to measure
465 radiogenic Ce isotopes at high precision. The newly developed static acquisition method allows the
466 simultaneous measurement of the four Ce isotopes and their isobaric interferences (^{134}Ba , ^{139}La and
467 ^{143}Nd) together with intercalated masses for tailing correction. The reproducibility obtained with two
468 Ce reference materials (Ce-LMV and Ce-AMES) is about 27 ppm which is similar to previous TIMS
469 methodologies. The main advantage of our new configuration is the reduced counting time necessary
470 to obtain high precision data. This also indicates that high precision measurements can be performed
471 with smaller amount of Ce (~ 700 ng). The use of the 10^{13} Ω resistors to measure the tailing masses
472 allows the measurements of even smaller Ce quantities (~ 250 ng) with a reproducibility of about 43
473 ppm. The new analytical technique allows a more stable determination of the tailing effect on masses
474 ^{136}Ce and ^{138}Ce .

475 A triple spike method has been developed to measure mass dependent Ce isotopic variations. To
476 this end, uncertainty models were calculated on three commercially available Ce spikes and the best
477 mixture is a triple spike containing ^{136}Ce - ^{138}Ce - ^{140}Ce isotopes. The spike/standard ratio of 0.33
478 produces the best spiking mixture in order to reduce the uncertainty magnification produced by
479 adding spike to the natural samples. Two analytical methods were used to measure stable Ce isotopes
480 on the TIMS and the runs in metal produce the best reproducibility. The main problem with Ce
481 isotopes measurements in metal is the correction for Ba interferences on ^{136}Ce and ^{138}Ce . However,
482 the chemical separation described in this study allows an effective separation of Ba and Ce. We have
483 also performed a number of calculations to characterise the sensitivity of our method to the
484 interferences correction and the fact that we always assume natural compositions for the interfering
485 elements. These calculations show that a small change in the isotopic composition will have a big
486 impact on the recovered $\delta^{142}\text{Ce}$ values. It is therefore fundamental to perfectly isolate Ce from the
487 matrix and the isobaric interference elements in order to produce accurate and precise mass
488 dependent stable Ce isotope measurements.

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617 **Conflicts of interest**

618 There are no conflicts to declare.

619 **Acknowledgments**

620 We would like to thank Matthias Willbold for providing his Ce reference material (Ce-AMES). PB
621 would like to thank Alex Halliday for giving him the spikes. The reference material Ce-LMV is
622 available upon request. We would like to thank Hauke Vollstaedt and Claudie Black for helpful
623 discussions. We would like to thank Ryan Ickert for his thorough review that has improved the
624 quality of this manuscript. This project has received funding from the European Research Council
625 (ERC) under the European Union's Horizon 2020 research and innovation programme (Grant
626 Agreement No 682778 - ISOREE). This is Laboratory of Excellence ClerVolc contribution number XXX.
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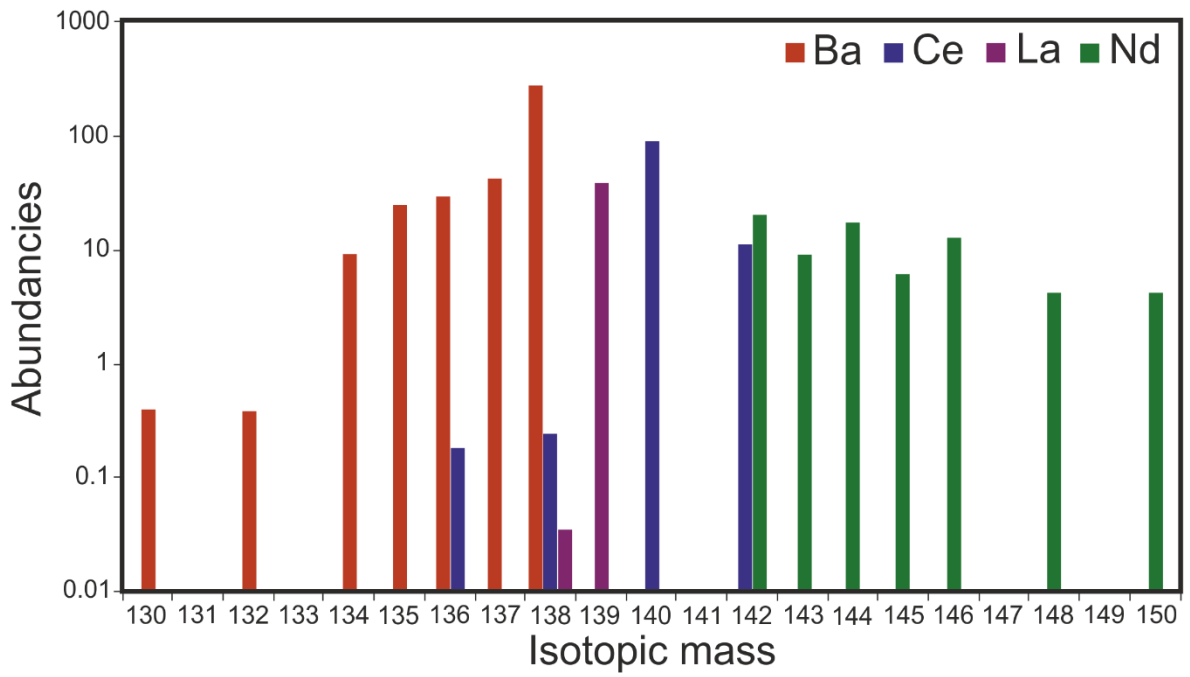
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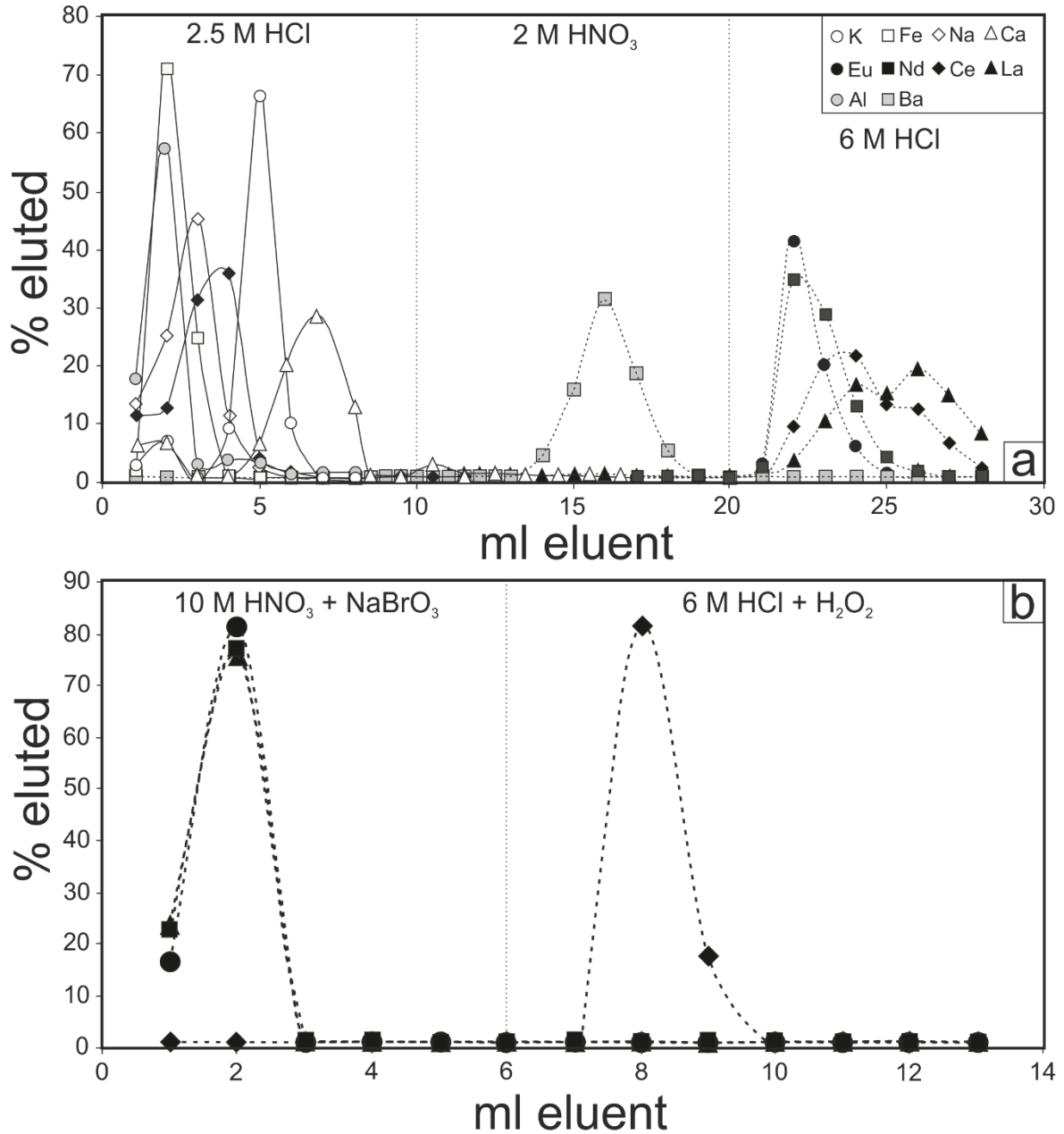
633 Figures:



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635 Figure 1: Ce, Nd, La and Ba isotopes abundances normalised to the primitive mantle elemental
636 abundances.⁴⁸ Note the logarithmic scale.

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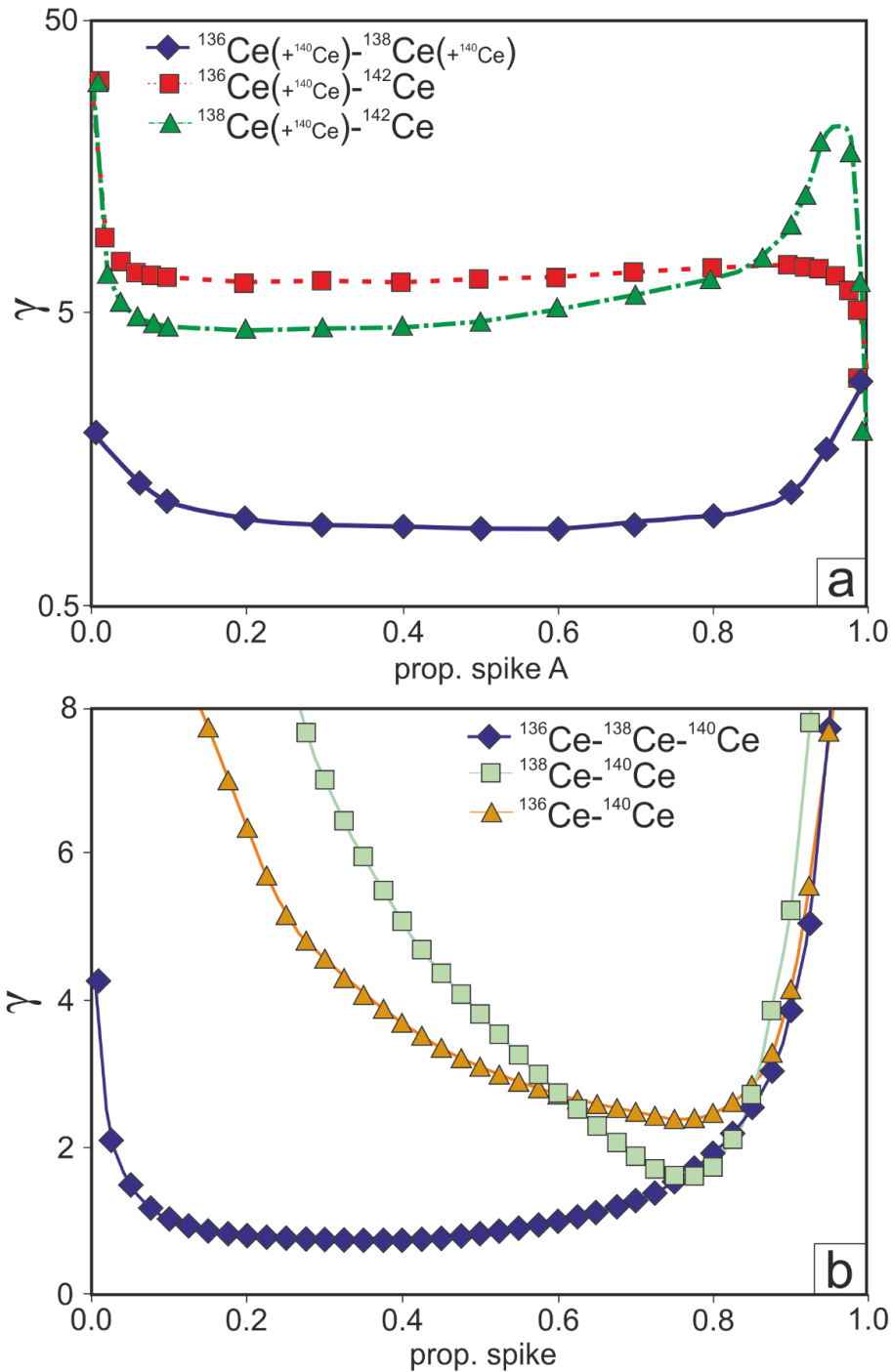
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659 Figure 2: Elution curves for the first (a) and second (b) steps of the purification protocol used in this
 660 study. The first step was performed using AG50 X8, 200-400 mesh in 10 ml Bio-Rad columns. The
 661 second step was performed using using LnSpec Eichrom resin (50-100 μ m) in 2 ml Bio-Rad columns.

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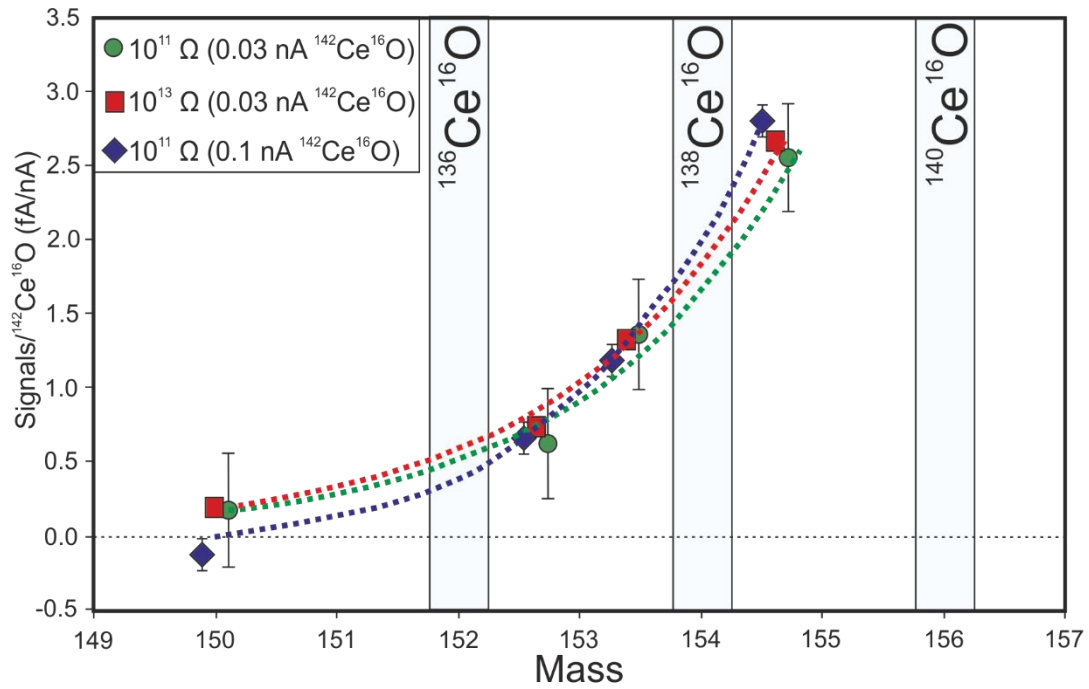
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666 Figure 3: (a) Uncertainty magnification term (γ) for the deconvolved $^{142}\text{Ce}/^{140}\text{Ce}$ ratio as a function of
 667 the proportion of spike A in the spike mixtures. The spike A is the first spike in the legend (for
 668 example spike A is ^{136}Ce in the spike mixture $^{136}\text{Ce}-^{142}\text{Ce}$). (b) Uncertainty magnification term (γ) for
 669 three spikes (commercially available ^{136}Ce and ^{138}Ce spikes and a 50-50% mixing on these two same
 670 spikes) versus the proportion of spike in the standard spike mixtures (see text for details). A lower
 671 gamma (γ) value indicate a better spike mixture (a) or a better proportion of spike (b).

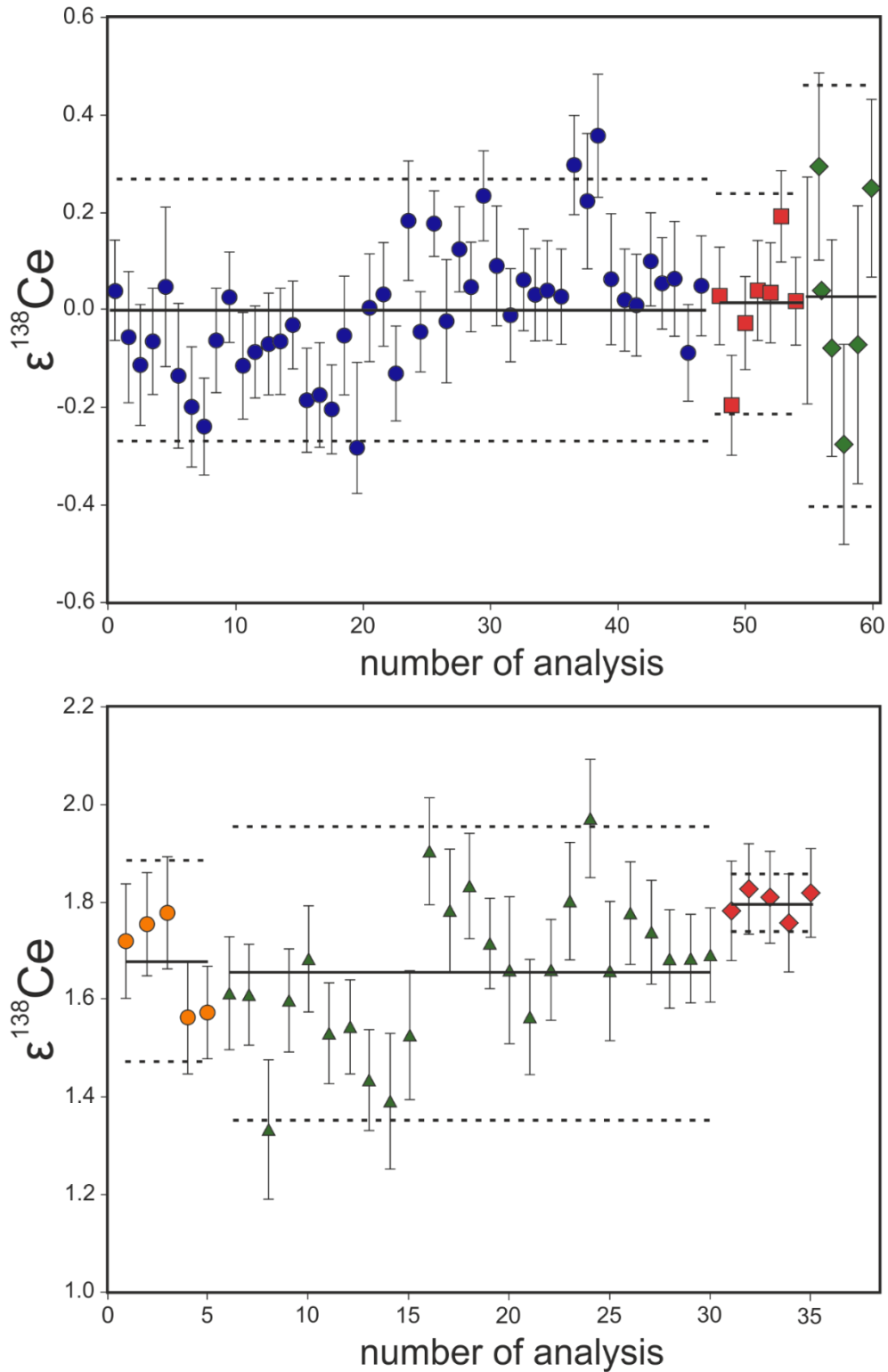


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673 Figure 4: Tailing measured in three analytical settings: green is the tailing with high intensities using
 674 $10^{11} \Omega$ resistor, blue is the tailing measured at low intensities using $10^{11} \Omega$ resistors and red is the
 675 tailing measured at low intensities using $10^{13} \Omega$ resistors (See text for details). The measured
 676 intensities (fA) on the tailing masses were divided by the intensities measured on $^{142}\text{Ce}^{16}\text{O}$ for each
 677 runs (~ 0.03 nA for green and red and ~ 0.1 nA for blue). All tailing masses were measured on the same
 678 masses but for a better visibility of the tailing on the figure, the green and blue points are artificially
 679 moved by $+0.1$ and -0.1 mass unit respectively.

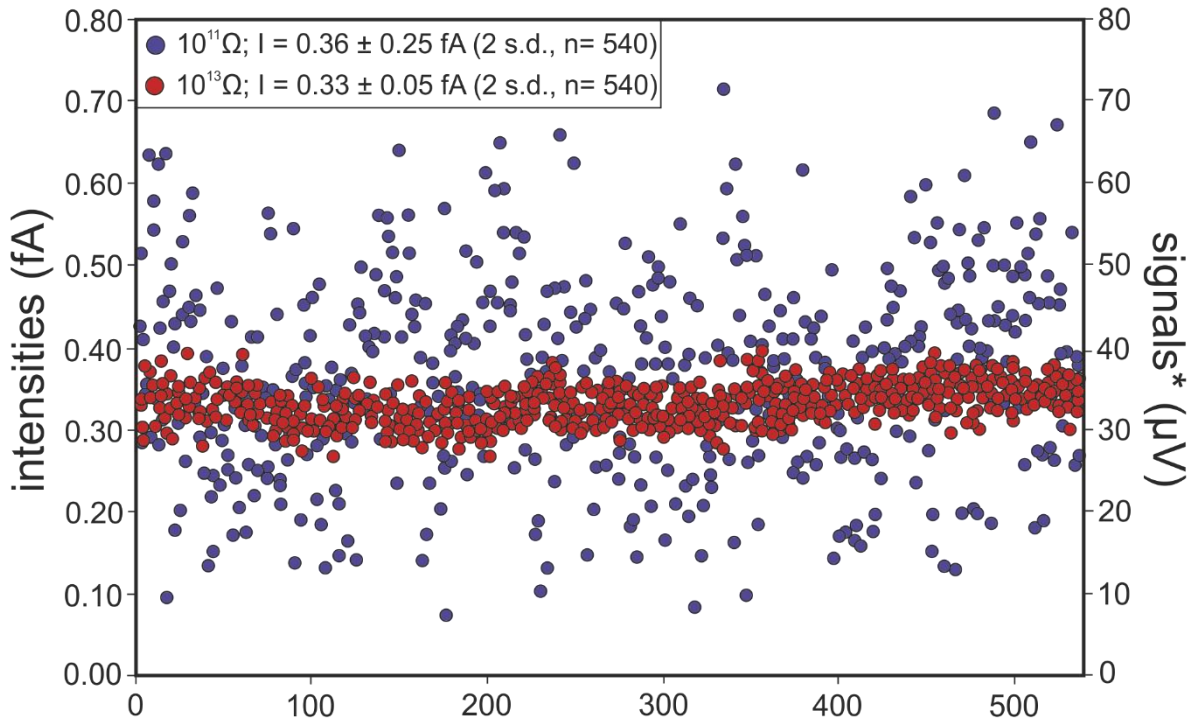
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683 Figure 5: Long-term reproducibility of $\epsilon^{138}\text{Ce}$ for the LMV-Ce (a) and AMES-Ce (b) reference
 684 materials. (a) The blue circles, red squares and green diamonds data were obtained with cup
 685 configurations #3, #4 and #5. The green diamonds were run at lower intensities. (b) The orange
 686 circles, green triangles and red diamonds data were obtained with cup configurations #1, #2 and #4.
 687 The solid and dashed lines are the mean and 2 s.d. values for each configuration used in this study.



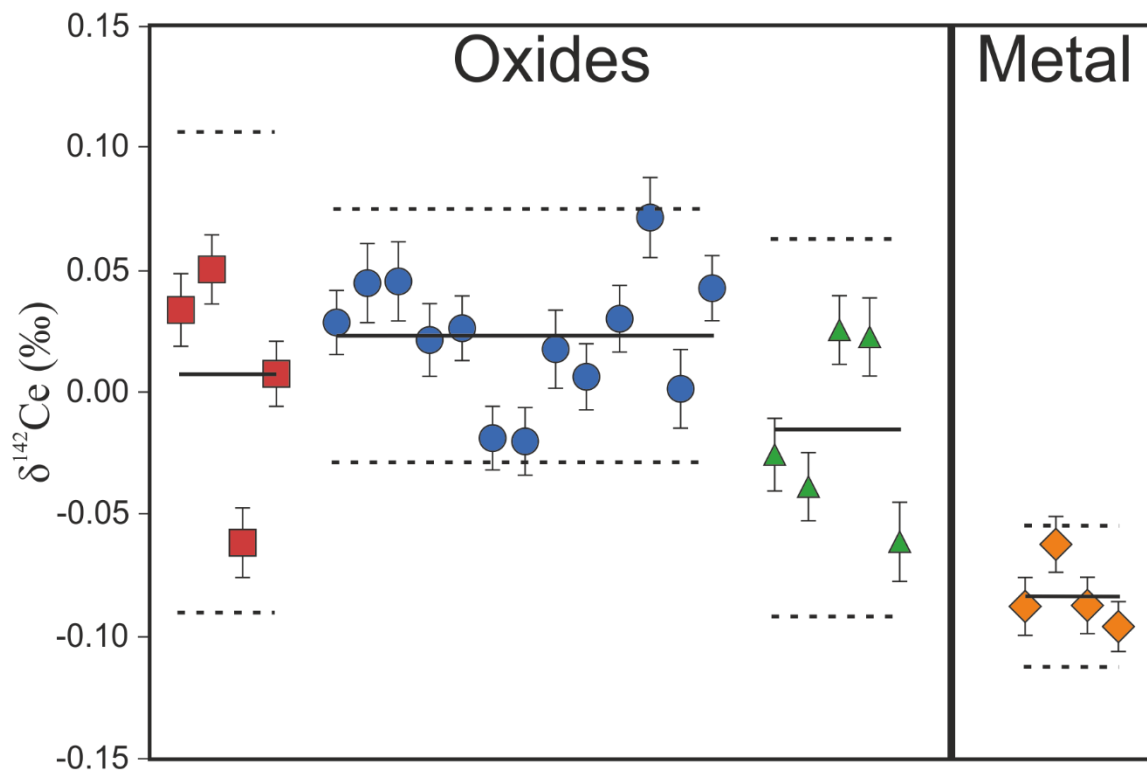
688

689 Figure 6: Typical signals measured at the tailing mass 154.5 with $10^{11} \Omega$ (blue) and $10^{13} \Omega$ (red)
 690 amplifiers during two measurements performed with 0.1 nA on $^{142}\text{Ce}^{16}\text{O}$. The signals expressed in
 691 voltages have been calculated relative to 10^{11} amplifiers.

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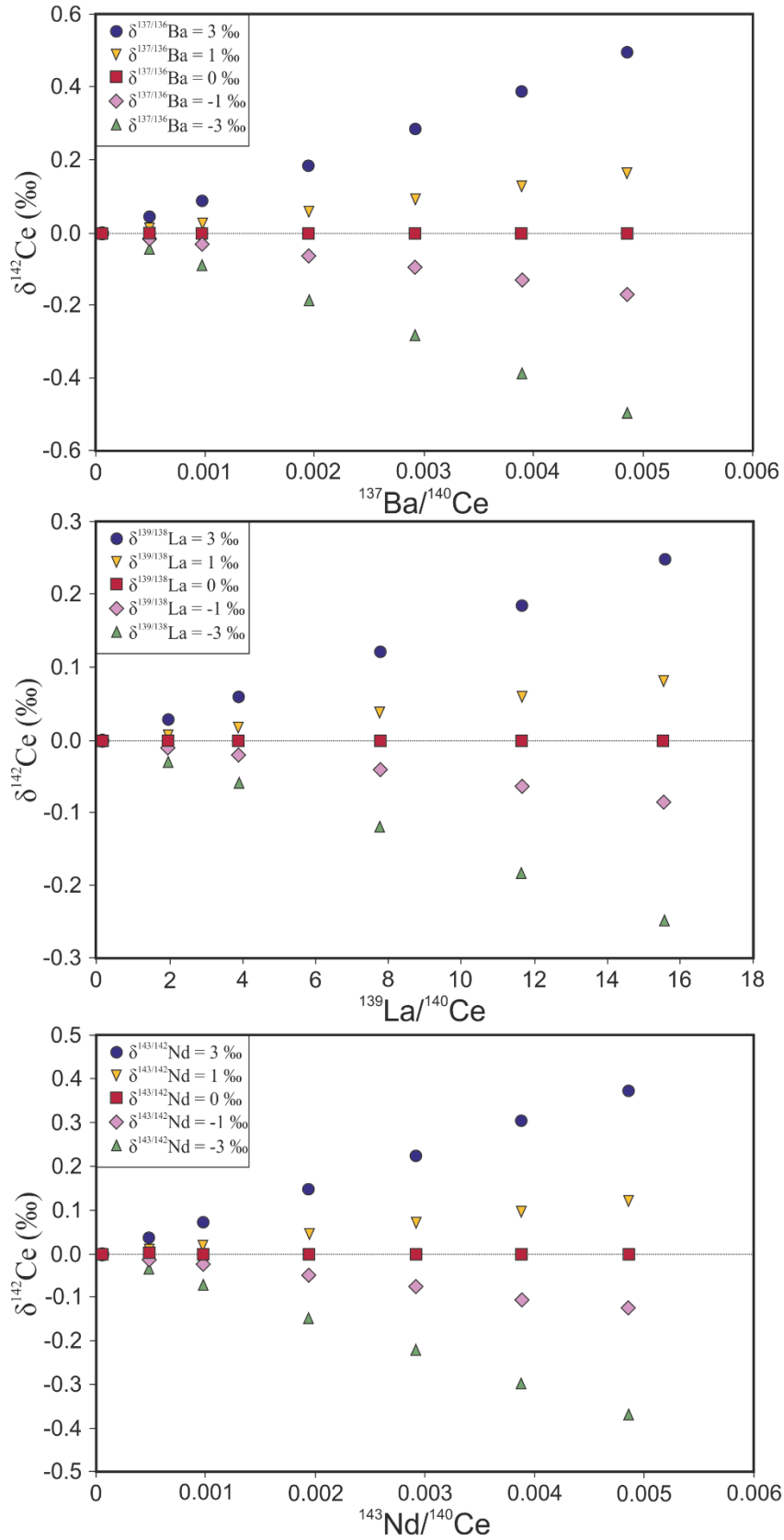
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696 Figure 7: Mass dependent Ce isotopic compositions ($\delta^{142}\text{Ce}$) for the Ce-LMV reference material. The
 697 squares, circles and triangles data points are three standard-spike mixtures run in oxides mode. The
 698 orange diamonds are one standard-spike mixture run in metal mode (see text for details). The error
 699 bars are internal uncertainties for each run. The solid and dashed lines are the mean and 2 s.d.
 700 values for the four standard-spike mixtures, respectively.

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703 Figure 8: Effects of “non-natural” isobaric interferences from (a) Barium, (b) Lanthanum and (c)
 704 Neodymium on $\delta^{142}\text{Ce}$ as a function of the element/ ^{140}Ce ratio. The changing isotopic compositions for the interfering elements are shown by the different symbols.
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706 Tables

707 Table 1: Cup configurations used on the Thermo-Scientific Triton plus TIMS at the Laboratoire Magmas et Volcans during the course of this study. The main
 708 isotope masses are in bold; the interference masses are in italic. $^{134}\text{Ba}^{16}\text{O}$ is also ^{150}Sm and ^{150}Nd . $^{142}\text{Ce}^{18}\text{O}$ is also $^{143}\text{Nd}^{16}\text{O}$.

run type	config #	lines	Collectors									integration time (s)
			L4	L3	L2	L1	C	H1	H2	H3	H4	
unspiked	1	1	<i>$^{134}\text{Ba}^{16}\text{O}$</i>	$^{136}\text{Ce}^{16}\text{O}$	$^{136}\text{Ce}^{17}\text{O}$	$^{138}\text{Ce}^{16}\text{O}$	<i>$^{139}\text{La}^{16}\text{O}$</i>	$^{142}\text{Ce}^{16}\text{O}$	$^{142}\text{Ce}^{17}\text{O}$	<i>$^{142}\text{Ce}^{18}\text{O}$</i>	8.39	
		2	150	152	153	154	155	158	159	160	4.19	
		ampli (Ω)	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}		
unspiked	2	1	<i>$^{134}\text{Ba}^{16}\text{O}$</i>	$^{136}\text{Ce}^{16}\text{O}$	152.6	153.4	$^{138}\text{Ce}^{16}\text{O}$	154.6	$^{140}\text{Ce}^{17}\text{O}$	$^{142}\text{Ce}^{16}\text{O}$	<i>$^{142}\text{Ce}^{18}\text{O}$</i>	8.39
		ampli (Ω)	10^{11}	10^{12}	10^{11}	10^{11}	10^{12}	10^{11}	10^{11}	10^{11}	10^{11}	
unspiked	3	1	<i>$^{134}\text{Ba}^{16}\text{O}$</i>	$^{136}\text{Ce}^{16}\text{O}$	152.6	153.4	$^{138}\text{Ce}^{16}\text{O}$	154.6	$^{140}\text{Ce}^{17}\text{O}$	$^{142}\text{Ce}^{16}\text{O}$	<i>$^{142}\text{Ce}^{18}\text{O}$</i>	8.39
		ampli (Ω)	10^{13}	10^{12}	10^{13}	10^{13}	10^{12}	10^{13}	10^{11}	10^{11}	10^{11}	
unspiked	4	1	<i>$^{134}\text{Ba}^{16}\text{O}$</i>	$^{136}\text{Ce}^{16}\text{O}$	152.6	153.4	$^{138}\text{Ce}^{16}\text{O}$	154.6	$^{140}\text{Ce}^{16}\text{O}$	$^{142}\text{Ce}^{16}\text{O}$	<i>$^{142}\text{Ce}^{18}\text{O}$</i>	8.39
		ampli (Ω)	10^{13}	10^{12}	10^{13}	10^{13}	10^{12}	10^{13}	10^{10}	10^{11}	10^{11}	
unspiked	5	1	<i>$^{134}\text{Ba}^{16}\text{O}$</i>	$^{136}\text{Ce}^{16}\text{O}$	152.6	153.4	$^{138}\text{Ce}^{16}\text{O}$	154.6	$^{140}\text{Ce}^{16}\text{O}$	$^{142}\text{Ce}^{16}\text{O}$	<i>$^{142}\text{Ce}^{18}\text{O}$</i>	8.39
		ampli (Ω)	10^{13}	10^{12}	10^{13}	10^{13}	10^{12}	10^{13}	10^{11}	10^{11}	10^{11}	
unspiked	6	1	<i>$^{134}\text{Ba}^{16}\text{O}$</i>	$^{136}\text{Ce}^{16}\text{O}$	152.6	153.4	$^{138}\text{Ce}^{16}\text{O}$	154.6	$^{140}\text{Ce}^{16}\text{O}$	$^{142}\text{Ce}^{16}\text{O}$	<i>$^{142}\text{Ce}^{18}\text{O}$</i>	8.39
		ampli (Ω)	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{12}	
spiked	7	1	<i>$^{134}\text{Ba}^{16}\text{O}$</i>	$^{136}\text{Ce}^{16}\text{O}$	152.6	153.4	$^{138}\text{Ce}^{16}\text{O}$	154.6	$^{140}\text{Ce}^{16}\text{O}$	$^{142}\text{Ce}^{16}\text{O}$	<i>$^{142}\text{Ce}^{18}\text{O}$</i>	8.39
		ampli (Ω)	10^{13}	10^{11}	10^{13}	10^{13}	10^{11}	10^{13}	10^{11}	10^{11}	10^{12}	
spiked	8	1		<i>^{134}Ba</i>	^{136}Ce	<i>^{137}Ba</i>	^{138}Ce	<i>^{139}La</i>	^{140}Ce	^{142}Ce	<i>^{143}Nd</i>	8.39
		ampli (Ω)	10^{13}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	10^{11}	

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717 Table 2: spikes isotopic compositions used in the theoretical calculations presented in Figure 3. See
 718 text for details.

spike	¹³⁶ Ce	¹³⁸ Ce	¹⁴² Ce
¹³⁶ Ce/ ¹⁴⁰ Ce	0.001	0.809	0.021
¹³⁸ Ce/ ¹⁴⁰ Ce	0.745	0.015	0.021
¹⁴² Ce/ ¹⁴⁰ Ce	0.046	0.080	20.234

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725 Table 3: Ce isotopic composition of the triple spike calibrated in this study.

	¹³⁶ Ce/ ¹⁴⁰ Ce	2 s.d.	¹³⁸ Ce/ ¹⁴⁰ Ce	2 s.d.	¹⁴² Ce/ ¹⁴⁰ Ce	2 s.d.
LMV-Ce (n = 48)	0.00212484	0.00000008	0.0028412	0.0000001	0.125879	0.000005
Triple spike (n =21)	0.38706	0.00003	0.39570	0.00003	0.062070	0.000005

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738 Table 4: Results for the radiogenic Ce isotopic composition of two solution reference materials (Ce-LMV and Ce-AMES) and two rock reference materials
 739 together with data from the literature. *the uncertainties are 2 standard errors.

sample name	config #	$^{142}\text{Ce}/^{16}\text{O}$ (V)	$^{138}\text{Ce}/^{142}\text{Ce}$	2 s.d.	$^{138}\text{Ce}/^{136}\text{Ce}$	2 s.d.	$\epsilon^{138}\text{Ce}_{\text{LMV}}$	2 s.d.	$^{140}\text{Ce}/^{142}\text{Ce}$	2 s.d.	n	ref
LMV Ce	3	9.9	0.02257053	0.00000061	1.337116	0.000036	0.00	0.27	N/A	N/A	48	This study
LMV Ce	4	9.6	0.02257056	0.00000051	1.337118	0.000030	0.01	0.23	7.94397	0.00014	7	This study
LMV Ce	5	2.4	0.02257059	0.00000098	1.337120	0.000058	0.03	0.43	7.94417	0.00025	6	This study
LMV-Ce	6	2.77	0.02257062	0.00000097	1.337122	0.000057	0.04	0.43	7.94403	0.00018	10	This study
AMES-Ce	1	10.1	0.02257431	0.00000046	1.337341	0.000027	1.68	0.20	N/A	N/A	5	This study
AMES-Ce	2	9.55	0.02257426	0.00000068	1.337338	0.000040	1.66	0.30	N/A	N/A	25	This study
AMES-Ce	4	10	0.02257458	0.00000013	1.337357	0.000008	1.80	0.06	7.94416	0.00023	5	This study
AMES-Ce			0.02257497	0.00000050	1.337380	0.000030	1.97	0.22	N/A	N/A	35	Willbold 2007
AMES-Ce			0.02257468	0.00000100	1.337363	0.000059	1.84	0.44	N/A	N/A	53	Doucelance et al. 2014
AMES-Ce			0.02257320	0.00000180	1.337275	0.000107	1.18	0.80	N/A	N/A	89	Bellot et al. 2015
AMES-Ce			0.02257474	0.00000048	1.337366	0.000028	1.87	0.21	7.94333	0.00031	9	Willig and Stracke 2017
BCR-2	3	10.7	0.02256689	0.00000055	1.336901	0.000033	-1.61	0.24	N/A	N/A	5	This study
BCR-2*	4	11.2	0.02256696	0.00000020	1.336905	0.000012	-1.58	0.09	7.943620	0.000025	1	This study
BCR-2			0.02256678	0.00000066	1.336894	0.000039	-1.66	0.29	N/A	N/A	3	Doucelance et al. 2014
BCR-2			0.02256620	0.00000070	1.336860	0.000041	-1.92	0.31	N/A	N/A	4	Bellot et al. 2015
BCR-2			0.02256719	0.00000063	1.336919	0.000037	-1.48	0.28	N/A	N/A	20	Willig and Stracke 2017
BHVO-2	3	8.7	0.02256489	0.00000047	1.336782	0.000028	-2.50	0.21	N/A	N/A	2	This study
BHVO-2*	4	10	0.02256499	0.00000024	1.336788	0.000014	-2.45	0.11	7.943886	0.000032	1	This study
BHVO-2			0.02256550	0.00000154	1.336819	0.000091	-2.23	0.68	N/A	N/A	8	Doucelance et al. 2014
BHVO-2			0.02256460	0.00000170	1.336765	0.000101	-2.63	0.75	N/A	N/A	6	Bellot et al. 2015
BHVO-2			0.02256482	0.00000059	1.336778	0.000035	-2.53	0.26	N/A	N/A	24	Willig and Stracke 2017

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743 Table 5: Results for triple spike runs performed using the Ce-LMV reference material.

sample name	run type	cup config.	spike/std	$\delta^{142}\text{Ce}$	2 s.d.	n
LMV-Ce	oxide	5	0.20	0.008	0.099	4
LMV-Ce	oxide	5	0.33	0.023	0.052	13
LMV-Ce	oxide	5	0.50	-0.015	0.077	5
LMV-Ce	metal	6	0.33	-0.083	0.028	4

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