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Determination of Zirconium isotopic composition of the new isotopic standard NRC ZIRC-1 using MC-ICP-MS

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Abstract

High precision analytical methods for ‘non-traditional’ stable isotopes rely upon standards for normalizing isotopic ratios, correcting instrumental mass fractionation, and comparing data between different laboratories. Zirconium isotope measurements are a new and rapidly expanding field, displaying potential for tracing the history of magmatic differentiation, as well as the formation and evolution of crustal reservoirs. However, previous studies have reported Zr isotopic data relative to different Zr standards, with IPGP-Zr standard being most commonly used. This situation hinders direct inter-laboratory comparison thereby enlarging uncertainties when converting the data. Here the Zr isotopic composition of a new, commercially available isotopic standard ZIRC-1 is systematically calibrated relative to IPGP-Zr through a collaborative approach between two different laboratories using sample-standard bracketing and the double spike method. Moreover, the Zr isotopic composition of the certified reference materials BHVO-2 and AGV-2, alongside the widely studied Allende chondrite, are reported to ensure the robustness of our data and allow for future inter-laboratory data comparison. Consistent results are obtained from the two laboratories and the average $\delta^{94}\text{Zr}_{\text{IPGP-Zr}}$ (the permil deviation of the $^{94}\text{Zr}/^{90}\text{Zr}$ of the sample from the IPGP-Zr standard) of ZIRC-1 is -0.220 ± 0.006 ‰ (2SD, n=7). The $\delta^{91}\text{Zr}_{\text{IPGP-Zr}}$, $\delta^{92}\text{Zr}_{\text{IPGP-Zr}}$, $\delta^{94}\text{Zr}_{\text{IPGP-Zr}}$ and $\delta^{96}\text{Zr}_{\text{IPGP-Zr}}$ values of ZIRC-1 follow a mass-dependent relationship. The $\delta^{94}\text{Zr}_{\text{IPGP-Zr}}$ and $\delta^{94}\text{Zr}_{\text{ZIRC-1}}$ values of the CV3 carbonaceous chondrite Allende are -0.041 ± 0.021 ‰ and 0.179 ± 0.022 ‰ (2SD, n=7), respectively, and lower than those of bulk Earth, which has $\delta^{94}\text{Zr}_{\text{IPGP-Zr}}$ and $\delta^{94}\text{Zr}_{\text{ZIRC-1}}$ values of 0.041 ± 0.041 ‰ and 0.261 ± 0.041 ‰ respectively, according to the reference of Tian et al. (2021)¹. The BHVO-2 and AGV-2 aliquots analyzed along with ZIRC-1 show agreement with literature data, demonstrating that the data from this study is accurate. The renormalized delta values of all other Zr isotopic standards are listed in Table 1, allowing for further inter-laboratory comparison.

1. Introduction

The development of multi-collector inductively coupled plasma mass

38 spectrometry (MC-ICP-MS) has permitted the routine acquisition of high precision
39 natural isotopic variations of ‘non-traditional’ elements, such as Fe, Mg, Zn, K, Ca, Ti,
40 or Si ². The choice of a common normalization standard is of great importance for
41 inter-laboratory data comparison ^{2,3}.

42 Zirconium is the second element in Group IV B of the periodic table, with the
43 atomic number of 40. It is a refractory, incompatible (the partition coefficient between
44 rock-forming minerals and melt being smaller than 1⁴), insoluble and lithophile
45 element, and it is classified as a High Field Strength Element (HFSE). Zirconium is a
46 main constituent of zircon (ZrSiO₄) and baddeleyite (ZrO₂), which are common
47 minerals in many terrestrial rocks and have also been documented in some meteorites.
48 Zirconium has five naturally occurring stable isotopes: ⁹⁰Zr (51.45%), ⁹¹Zr (11.22%),
49 ⁹²Zr (17.15%), ⁹⁴Zr (17.38%), and ⁹⁶Zr (2.80%). The isotopic variations of Zr can be
50 used to study the formation of the solar system and Earth’s Moon ⁵⁻⁷, trace magmatic
51 differentiation or the magmatic cooling history of igneous rocks ⁸⁻¹¹, or to trace the
52 biokinetic activities in human bodies ¹².

53 More recently, Zr isotope analysis has attracted much interest, owing to its
54 petro-genetic importance and the development of high precision analytical method on
55 MC-ICP-MS, using sample decomposition or direct solid sampling analysis ^{1, 9-11, 13-18}.
56 The typical reproducibility for the isotopic ratios is 7-10 ppm (part per mil) per u.
57 Several investigations have revealed large Zr isotope fractionation (> 0.5‰ for the
58 ⁹⁴Zr/⁹⁰Zr ratio) in magmatic systems and discussed the origin of the isotopic
59 fractionation ^{9-11, 13}. For example, the Zr isotope compositions of highly evolved lavas
60 (>65% SiO₂) from Hekla (Iceland) show a strong positive correlation with SiO₂ and
61 negative correlation with Zr contents, which is interpreted as reflecting the saturation
62 and segregation of isotopically light zircons from the residual melt ¹⁴. Some studies
63 showed that felsic rock standards have heavier Zr isotopic compositions than mafic
64 reference materials, and the Zr isotope composition of the upper continental crust is
65 heavier than that of the mantle ^{1, 14-16, 19}. Zirconium isotopes can provide a new
66 approach to study magmatic differentiation, crustal evolution, or other high
67 temperature processes. This newly emerged field requires additional work to explore
68 isotopic fractionation mechanisms. To improve the accuracy and precision of isotopic
69 data, inter-laboratory data comparison is indispensable. Thus, a certified, isotopically
70 homogenous and widely available standard is necessary.

71 Zirconium isotope data are reported in the standard delta notation, that is, the per
72 mil deviations of ⁹ⁱZr/⁹⁰Zr ratios (*i* = 1,2,4,6) relative to a standard, among which
73 δ⁹⁴Zr (‰) is typically reported in the literature. However, various standards have been
74 used, including IPGP-Zr, NIST SRM 3169, NIST (RM8299, denoted as NIST here, to
75 keep consistency with earlier work), Alfa Aesar (#63-061671G), and the GJ-1 zircon ^{5,}
76 ^{8, 11, 13-15, 17, 19, 20}.

77 Recently, the absolute isotopic ratios of a new commercialized isotopic Zr
78 standard solution, NRC ZIRC-1, have been investigated in detail ²¹, and based on its
79 absolute isotopic composition it was suggested that it has a δ⁹⁴Zr_{IPGP-Zr} value of ~

80 -0.19%. However, if the NRC ZIRC-1 standard is to be widely used as a standard in Zr
81 isotopic analysis, and since the IPGP-Zr has been the most widely used standard, it is
82 important to precisely determine the isotopic composition of ZIRC-1 against IPGP-Zr.
83 This will allow future renormalization of the data between these two standards. A
84 careful systematic investigation of the isotopic offset between the NRC ZIRC-1 and
85 IPGP-Zr were performed in the present study, conducted in two different laboratories
86 (Institut de Physique du Globe de Paris, IPGP, and GLOBE Institute, University of
87 Copenhagen), using double spike and sample-standard bracketing methods.
88 Furthermore, the Zr isotopic composition of the most intensively studied and widely
89 available primitive meteorite Allende, is reported for the first time in this study. The
90 delta values of other existing Zr standards relative to NRC ZIRC-1 are also
91 summarized here to facilitate future inter-laboratory data comparison.

92 93 **2. Materials (reagents, standards, samples/RMs)**

94 Selectipur® grade concentrated nitric, hydrochloric and hydrofluoric acids
95 purchased from BASF France were purified by sub-boiling distillation using
96 Savillex™ Teflon stills before use. Ultrapure water (resistivity $\geq 18.2 \text{ M}\Omega \text{ cm}$) was
97 obtained using a Merk™ Millipore Milli-Q® (MQ) purification system. Bio-Rad
98 AG1-X8 (200–400 mesh) resin and Eichrom N, N, N', N'-tetra-n-octyldiglycolamide
99 (DGA, 50–100 μm particle size) resin were used for chromatographic separation of Zr
100 from the sample matrix.

101 Pure Zr standard solutions used in the measurements include NRC ZIRC-1 and
102 IPGP-Zr. The NRC ZIRC-1, stored in 2% (w/w) HNO_3 and 0.1% (w/w) HF at 1000 mg
103 L^{-1} [Zr], was obtained through dilution (10 fold) of a Zr standard solution at 10,018 mg
104 L^{-1} in 5% (w/w) HNO_3 and 0.5% (w/w) HF, originated from Sigma Aldrich - Oakville,
105 ON, Canada. Its absolute isotopic composition has been determined using a regression
106 model which relies upon log-linear drifts in the analyte and calibrant elements²¹. Five
107 aliquots of the NRC ZIRC-1 solution, including one un-spiked and four double spiked
108 aliquots were measured in this study. The un-spiked aliquot serves to evaluate
109 whether its Zr isotopic ratios follow a mass-dependent relationship. The IPGP-Zr
110 standard (PlasmaCal™ 1000 mg L^{-1} ICP standard; Lot: 5131203028, 2015) is
111 commonly used for δ -notation normalization in the Earth Science community.

112 Samples analyzed in this study include a CV3 carbonaceous chondrite - Allende,
113 widely available from different institutes, including the Smithsonian Institution
114 collection (U.S.) and the Natural History Museum collection (U.K.), and the basaltic
115 and andesitic reference materials BHVO-2 and AGV-2 from the United States
116 Geological Survey (USGS). The analysis of BHVO-2 (in both laboratories) and
117 AGV-2 (only at IPGP) together with NRC ZIRC-1 were conducted for data quality
118 control and inter-laboratory comparison purposes.

119 120 **3. Procedures**

121

122 3.1 Sample preparation and spiking

123 At IPGP, two sample preparation methods were used: 1) in Teflon bombs (for two
124 respective replicates of BHVO-2 and AGV-2) and 2) in Parr bombs (for Allende). The
125 steps were described in elsewhere¹⁴, but with slight modifications in this study. First, a
126 5:1 ratio of HF (27 mol/L) : HNO₃ (16 mol/L) was used. Second, the heating
127 temperature of the Parr bombs were raised from 150 °C to 185 °C. After heating for 4~5
128 days, the mixed acid solution was dried down. Then elimination of insoluble fluorides
129 was achieved by using 6 mol/L HCl, and heating the solutions at 140 °C for about 12
130 hours. Following the dryness of 6 mol/L HCl, aqua regia was added to dissolve the
131 residual oxides and fluorides.

132 The ⁹¹Zr-⁹⁶Zr double spike was carried out either with the addition of HF and
133 HNO₃ (for one BHVO-2 and one AGV-2), or during the treatment with 6M HCl (for the
134 remaining samples), at an optimal double spike: sample ratio of 43:57. An aliquot of the
135 stock solution of ZIRC-1 was also spiked following the same proportions.

136 At GLOBE Institute, a 10-μg dried aliquot of the NRC ZIRC-1 standard (received
137 from IPGP) was re-dissolved in 1 mL of 0.5 mol/L HNO₃ + 0.01 mol/L HF by refluxing
138 on a hotplate overnight at 100 °C. A single 3-μg Zr aliquot of the IPGP-Zr standard and
139 three 200-ng Zr aliquots of the NRC ZIRC-1 solution were spiked individually with the
140 ⁹¹Zr-⁹⁶Zr double-spike, aiming for a spike proportion of 43%. The spiked aliquots were
141 fluxed on the hotplate overnight at 100 °C to achieve sample-spike equilibration.

142 To assess the performance of the MC-ICP-MS, a purified Zr aliquot of BHVO-2
143 was analyzed in the same sequence as NRC ZIRC-1. Thus, the spiked BHVO-2 (lot#
144 2791) was digested in a Parr pressure bomb, in a 2:1 mixture of HF (23 mol/L) and
145 HNO₃ (14 mol/L) in an oven for 1 day at 150 °C followed by five days at 210 °C. After
146 evaporation to dryness, fluorides were dissolved by fluxing with concentrated
147 hydrochloric acid (12 mol/L) on the hotplate at 120 °C for a minimum of two days.
148 After fluoride dissolution, the BHVO-2 was evaporated to dryness and re-dissolved and
149 stored in 10 mL of 6 mol/L HCl.

150 3.2 Zirconium separation

151 3.2.1 Procedure at the IPGP laboratory

152 At IPGP, the separation of Zr involved a two-step chromatography procedure. The
153 procedure details are described elsewhere^{14, 15}. In summary, the matrix elements were
154 eluted in 4 mol/L HF and then Zr was collected in 6 mol/L HCl + 0.01 mol/L HF, using
155 the the first AG1-X8 (200–400 mesh) column. Since insoluble fluorides were formed in
156 4 mol/L HF before sample loading, the sample aliquots were heated for at least 3 hours,
157 sonicated for 1 hour, centrifuged and the supernatant decanted into another clean
158 Teflon beaker. The remaining sample residue was treated with the same procedure
159 twice more. All supernatant cuts were combined before loading onto the column. After
160 the first column, the purification of Zr from the remaining matrices (eg. Ca, Fe, Ti and
161 Mo) was achieved by purification on a DGA column. 12 mol/L HNO₃ and 3 mol/L
162 HNO₃ were used to wash the column, and 3 mol/L HNO₃ + 0.2 mol/L HF was added
163 onto the column for the Zr elution.

164 It is noted that between the AG1-X8 and DGA column, the samples were treated
165 with 12 mol/L HNO₃ and evaporated to dryness to remove any HCl as it would
166 compromise the next step on the DGA resin. Additionally, to bring the dried samples
167 into the solution for Zr isotope determination using MC-ICP-MS, 200 µL of 16 mol/L
168 HNO₃ was added and the mixture was heated at 120 °C for 2 h, to eliminate any
169 organic residues eluted from the resin during chemical separation processes.

170 3.2.2 Procedure at the GLOBE Institute

171 At GLOBE Institute, the aliquot of BHVO-2 was processed through a four-step
172 chromatographic purification scheme. The first two steps followed the protocols
173 outlined by Connelly et al.²², and the third and fourth step follows the Zr-Hf separation
174 in Bouvier et al.²³ and Bizzarro et al.²⁴, and the Zr-Mo separation followed that of
175 Tompkins et al.¹⁷, respectively.

176 In the first step, Zr and other HFSE were separated from matrix (including Ca, Fe,
177 Mg) and rare-earth elements (REEs) using a 300-µL column and AG50W-X8 cation
178 exchange resin (Eichrom Technologies, 100-200 mesh). The Zr-double-spiked
179 BHVO-2 aliquot was loaded on the column in 0.5 mol/L HCl, and the HFSE were
180 eluted by the addition of 0.5 mol/L HCl + 0.15 mol/L HF. In the second step, Zr and Hf
181 were separated from matrix elements (Ti, Al and remaining Ca, Fe and Mg) using
182 180-µL columns filled with DGA-Normal resin (Eichrom Technologies, 50-100 mesh).
183 The HFSE cut from step one, in 3.5 mol/L HNO₃ + 0.06 mol/L, was loaded on the
184 column H₃BO₃, followed by elution of matrix elements in 3.5 mol/L HNO₃ and, finally,
185 elution of Zr and Hf in 1 mol/L HNO₃ + 0.35 mol/L HF. In the third step, Zr was further
186 separated from Hf and remaining Ti and REEs using a 120-µL column and TEVA resin
187 (Eichrom Technologies, 100-150 mesh). The Zr-Hf cut from the second chemistry step,
188 in 10.5 mol/L HCl + 0.001 mol/L H₃BO₃, was loaded on the column, followed by
189 elution of Ti, REEs and Hf in 10.5 mol/L and 9.5 mol/L HCl. Zirconium was eluted in 6
190 mol/L HCl. The last step served to remove Mo, employing a 55-µL column and
191 AG1-X8 anion exchange resin (Eichrom Technologies, 100-200 mesh). The Zr cut, in 6
192 mol/L HCl + 0.06 mol/L HF, was loaded on the column, and Zr was eluted with an
193 additional aliquot of 300 µL of the same acid. Finally, the Zr cut was evaporated to
194 dryness and fluxed with 0.5 mL of 14 mol/L HNO₃ at 120 °C on the hotplate for at least
195 12 hours to revoke organics introduced through the chromatographic procedure.

196 3.3 Analysis using MC-ICP-MS

197 Zirconium isotope measurements were performed using two Thermo Scientific
198 Neptune Plus MC-ICP-MS systems, one located at the Institut de Physique du Globe de
199 Paris (IPGP), France, and the other at GLOBE Institute, University of Copenhagen.

200 At IPGP, the solutions, taken up in 0.5 mol/L HNO₃ + 0.1 mol/L HF were
201 introduced in the ICP via an APEX HF desolvating nebulizer (Elemental Scientific Inc.,
202 USA), adapted directly onto a sapphire torch injector, with an uptake rate of 50 µL/min,
203 while part of the Allende aliquots were measured using a Savillex™ PFA cyclonic
204 spray chamber as described by Tian et al.¹⁵. H Skimmer and Nickel Jet Sample cones
205 were used. Measurements were performed at low mass resolution mode. Under static

206 configuration, $^{90}\text{Zr}^+$, $^{91}\text{Zr}^+$, $^{92}\text{Zr}^+$, $^{94}\text{Zr}^+$, $^{95}\text{Mo}^+$ and $^{96}\text{Zr}^+$ were collected simultaneously
207 to Faraday cups fitted with $10^{11} \Omega$ pre-gain amplifiers, except $^{95}\text{Mo}^+$ which was
208 collected in a cup coupled to a $10^{12} \Omega$ amplifier, in order to improve the accuracy for
209 monitoring the low signal intensity for this isotope. The $^{95}\text{Mo}^+$ intensities were used to
210 monitor and correct the isobaric interferences from $^{94}\text{Mo}^+$ and $^{96}\text{Mo}^+$ on $^{94}\text{Zr}^+$ and $^{96}\text{Zr}^+$.
211 Amplifier gains were calibrated weekly. The bracketing standard IPGP-Zr was
212 analyzed every two unknown measurements. Between each two analyses, washes were
213 performed by a rinse with 1 mol/L HNO_3 + 0.1 mol/L HF for 5min, followed by a rinse
214 in a 0.5 mol/L HNO_3 + 0.1 mol/L HF solution. These latter washes also served as the
215 on-peak-zero (OPZ) measurement, which were recorded using an 110 s uptake and 40 s
216 on-peak analyses. Well characterized reference materials (BHVO-2 and AGV-2) were
217 bracketed every four analyses to monitor the performance of the instrument. The spike
218 proportions in the spike-spike mixture for all spiked aliquots, including the IPGP-Zr
219 standard, varied between 42 and 46%, which is close to the optimal value 43% and
220 within the range 38-58% suggested by Inglis et al.¹⁴.

221 At the GLOBE institute in Copenhagen, the pure Zr fractions, dissolved in 0.5
222 mol/L HNO_3 + 0.01 mol/L HF, were introduced into the plasma source via a same
223 configuration as at IPGP. Jet skimmer and X sample nickel cones were used.
224 Measurements were also performed at low mass resolution mode. The $^{90}\text{Zr}^+$, $^{91}\text{Zr}^+$,
225 $^{92}\text{Zr}^+$, $^{94}\text{Zr}^+$, $^{95}\text{Mo}^+$, $^{96}\text{Zr}^+$, $^{98}\text{Mo}^+$ and $^{99}\text{Ru}^+$ masses were collected simultaneously in
226 Faraday cups fitted with $10^{11} \Omega$ pre-gain amplifiers, except $^{95}\text{Mo}^+$, $^{98}\text{Mo}^+$ and $^{99}\text{Ru}^+$, for
227 which $10^{13} \Omega$ amplifiers were used. For the session with Zr double-spike, the intensity
228 of $^{95}\text{Mo}^+$ was used to correct the isobaric interferences from $^{94,96}\text{Mo}^+$ on $^{94}\text{Zr}^+$ and $^{96}\text{Zr}^+$.
229 In all cases, the abundance of Ru was negligible and, thus, it was not necessary to
230 correct for the isobaric interference of $^{96}\text{Ru}^+$ on $^{96}\text{Zr}^+$. For the session without Zr
231 double-spike, the intensities of $^{95}\text{Mo}^+$ and $^{99}\text{Ru}^+$ were used to monitor and correct the
232 isobaric interferences from $^{92,94,96}\text{Mo}^+$ and $^{96}\text{Ru}^+$ on $^{92}\text{Zr}^+$, $^{94}\text{Zr}^+$ and $^{96}\text{Zr}^+$. Gains were
233 also performed weekly. In the session with spiked samples, each analysis comprised a
234 total of 630 s of baseline measurements (75 scans integrated over 8.39 s, obtained on
235 peak) and 420 s of data acquisition (50 scans integrated over 8.39 s). In the session with
236 the un-spiked ZIRC-1 aliquot, each analysis comprised a total of 1,680 s (100 scans
237 integrated over 16.8 s). Sample analyses were interspaced by analyses of the IPGP-Zr
238 standard and each sample was systematically analyzed 5 times for the spiked aliquots
239 and 10 times for the un-spiked aliquot. The spike/sample proportions for all spiked
240 aliquots, including the IPGP-Zr standard, varied between 43 and 45%.

241 **3.4 Data reduction for double spike method**

242 Double spike data reduction was achieved using the *IsoSpike* software, which can
243 perform several thousands of double spike inversions per second. Double spike
244 equations (1) and (2) are involved in a binary mixing between the double spike and the
245 sample and combination of mass discrimination from instrumental and natural isotopic
246 fractionation.

247
$$(1) R_{sample}^i = R_{std}^i \left(\frac{M_i}{M} \right)^\alpha$$

$$(2)r^i = \left[\lambda R_{spike}^i + (1 - \lambda) R_{std}^i \left(\frac{M_i}{M} \right)^\alpha \right] \left(\frac{M_i}{M} \right)^\beta$$

249

250 Where i and M_i denote the interest isotopes and corresponding absolute mass; M is
 251 the mass of the denominator isotope, r^i describes the measured isotope ratio of the
 252 spike-sample mixture; R_{sample}^i , R_{std}^i , and R_{spike}^i represent the isotopic ratios of the
 253 sample, standard, and double spike; λ is the mass proportion of the denominator isotope
 254 from double spike in the spike-sample mixture; α and β refer to the natural and
 255 instrumental mass fractionation factors. The r^i , R_{std}^i , and R_{spike}^i are the inputs for data
 256 inversion to get the solutions for the three unknowns λ , α and β . Thus, three isotopic
 257 ratios are required for solving three equations. $^{91}\text{Zr}/^{90}\text{Zr}$, $^{94}\text{Zr}/^{90}\text{Zr}$ and $^{96}\text{Zr}/^{90}\text{Zr}$ were
 258 used for Zr isotopic data calculation. Before starting the calculation of raw ratios,
 259 superposition of signals from $^{94}\text{Mo}^+$ and $^{96}\text{Mo}^+$ on $^{94}\text{Zr}^+$ and $^{96}\text{Zr}^+$ were subtracted as
 260 follows:

$$\text{corr}^{9j}\text{Mo} = ^{95}\text{Mo} * \text{nat}^{9j/95}\text{Mo} * (M_{9j\text{Mo}} / M_{95\text{Mo}})^\beta$$

262 Where $j = 4$ or 6 ; $\text{corr}^{9j}\text{Mo}$ means the intensities of $^{94}\text{Mo}^+$ and $^{96}\text{Mo}^+$ calculated
 263 based on the measured ^{95}Mo intensities, which are to be subtracted from $^{94}\text{Zr}^+$ and $^{96}\text{Zr}^+$;
 264 $\text{nat}^{9j/95}\text{Mo}$ means natural ratios of $^{9j}\text{Mo}/^{95}\text{Mo}^{25}$; $M_{9j\text{Mo}} / M_{95\text{Mo}}$ denotes the mass of Mo
 265 isotopes; β refers to the mass fractionation factor. This procedure was repeated such
 266 that the mass bias (and, thus, corrected ratios) converged on a constant value.

267 However, the majority of chondrites were reported to display ^{96}Zr isotopic
 268 anomaly relative to the terrestrial mass-dependent fractionation line, denoted as $\varepsilon^{96}\text{Zr}$
 269 (in 10^4 units)⁶, including Allende. Therefore, an adapted $^{96}\text{Zr}/^{90}\text{Zr}$ ratio for the standard
 270 has to be used when processing data for Allende chondrite, according to equation (3):

$$(3)R_{std-adapted}^i = R_{std}^i (1 + \varepsilon^i)$$

272 where ε^i means i isotope anomaly. In this study i is 96 and ε^i equals to 1.21 ± 0.19 ,
 273 according to Akram et al.⁶.

274

275 4. Results and Discussion

276 The Zr isotopic compositions of the new isotopic standard ZIRC-1, reference
 277 materials BHVO-2, AGV-2, and Allende obtained in this study using MC-ICP-MS,
 278 expressed as δ -values relative to IPGP-Zr and ZIRC-1, and δ -values of existing Zr
 279 standards GJ-1, SRM 3169, NIST relative to ZIRC-1, converted from those reported
 280 relative to IPGP-Zr, are presented in Table 1 and Fig. 1.

281 4.1 Determination of the Zr isotopic composition of ZIRC-1

282 The Zr isotopic composition of ZIRC-1 was determined following (i)
 283 sample-standard bracketing (SSB) and (ii) double spike methods.

284 4.1.1 Standard-sample bracketing method

285 In order to investigate mass dependency of the new standard solution, an aliquot of

286 un-spiked NRC ZIRC-1 was analyzed at the GLOBE Institute *versus* the IPGP-Zr using
 287 standard sample bracketing (SSB) method. $\delta^{91}\text{Zr}_{\text{IPGP-Zr}}$, $\delta^{92}\text{Zr}_{\text{IPGP-Zr}}$, $\delta^{94}\text{Zr}_{\text{IPGP-Zr}}$, and
 288 $\delta^{96}\text{Zr}_{\text{IPGP-Zr}}$ were determined as $-0.057 \pm 0.009\%$, $-0.110 \pm 0.015\%$, $-0.220 \pm 0.031\%$,
 289 $-0.319 \pm 0.048\%$ (2SD, n = 10) respectively, following mass dependent relationships:

$$\frac{\delta^{9i}\text{Zr}}{\delta^{9j}\text{Zr}} \approx \frac{\ln\alpha_{9i/90}^{\text{sam-std}}}{\ln\alpha_{9j/90}^{\text{sam-std}}} = \frac{\left(\frac{1}{M} - \frac{1}{M_i}\right)}{\left(\frac{1}{M} - \frac{1}{M_j}\right)}$$

290 where i and j = 1, 2, 4, 6; M, M_i and M_j are mass of isotope ^{90}Zr , ^{9i}Zr and ^{9j}Zr ;
 291 $\alpha_{9i/90}^{\text{sam-std}}$ and $\alpha_{9j/90}^{\text{sam-std}}$ are isotopic fractionation factors between the sample and
 292 standard. As such, ZIRC-1 meets the prerequisite to be a certified candidate isotopic
 293 reference standard as it is fully mass-dependently fractionated compared to IPGP-Zr.

294 4.1.2 Double spike method

295 For the purpose of systematically evaluating the isotopic composition of ZIRC-1,
 296 one aliquot of spiked ZIRC-1 was analyzed at IPGP separately and independently three
 297 times, and three aliquots of ZIRC-1 were spiked and measured separately at the
 298 GLOBE Institute. The results are summarized in Table 2. Combined average values of
 299 $\delta^{94}\text{Zr}_{\text{IPGP-Zr}}$ obtained by the two laboratories were identical: $-0.219 \pm 0.016\%$ (2SD,
 300 n=12) and $-0.219 \pm 0.023\%$ (2SD, n=15), and they were in agreement with the value
 301 obtained through the SSB method. The overall average is $-0.220 \pm 0.006\%$ (2SD, n = 7).
 302 Within each laboratory, consistent results were also yielded between different sessions
 303 or replicates, as shown in Table 2.

304 We first calibrated the isotopic offset between ZIRC-1 and the conventional
 305 standard IPGP-Zr. Prior to this work, only the absolute Zr isotopic composition of
 306 ZIRC-1 has been characterized. By doing the following calculation:

$$307 \delta^{94}\text{Zr}_{\text{ZIRC-1-IPGP-Zr}} = \delta^{94}\text{Zr}_{\text{SRM-3169-IPGP-Zr}} - \delta^{94}\text{Zr}_{\text{SRM-3169-ZIRC-1}}$$

308 a value of $\delta^{94}\text{Zr}_{\text{ZIRC-1-IPGP-Zr}}$ was suggested to be -0.19% by He et al. (2021)²¹,
 309 through a least-squares adjustment meta-analysis of over 80 reported results that
 310 include more than 40 reference materials. The difference between -0.19% and -0.220%
 311 is within the uncertainty of Zr isotopic measurements with current-day MC-ICP-MS
 312 (7-10 ppm per amu), indicating the accuracy of the obtained results. More importantly,
 313 the excellent agreement of $\delta^{94}\text{Zr}_{\text{IPGP-Zr}}$ results between the un-spiked and spiked
 314 sessions in the two laboratories demonstrate the reliability and reproducibility of the
 315 proposed value.

316 4.2 Zr isotopic composition of terrestrial reference materials and Allende 317 chondrite

318 To further evaluate the reliability of data obtained in the present study, we also
 319 measured BHVO-2, AGV-2 and Allende in the course of the current study - with
 320 Allende being analyzed over a period of two years.

321 As can be seen, whether at IPGP or at the GLOBE Institute, the Zr isotopic results
 322 of all the reference materials analyzed in this study are in good agreement with the

323 literature data from Inglis et al.¹⁴ and Tian et al.¹⁵, and within the accepted uncertainty.

324 The Zr isotopic composition of Allende is reported for the first time, with
325 consistent values obtained over a two-year period. Allende ($\delta^{94/90}\text{Zr}_{\text{IPGP-Zr}} = -0.041 \pm$
326 0.021%) is isotopically lighter than Earth ($\delta^{94/90}\text{Zr}_{\text{IPGP-Zr}} = 0.041 \pm 0.041\%$)¹. Further
327 work is required to investigate the origin of this difference, but, Allende could be used
328 as a reference material in the future to evaluate the quality of the data.

329 Overall, the results of these reference materials and Allende prove the accuracy
330 and long-term reproducibility of the data reported in this study.

331 4.3 Cross-calibration

332 Data for pure Zr solutions IPGP-Zr, NIST SRM 3169, NIST, Alfa Aesar
333 (#63-061671G), and zircon standard GJ-1 have been reported. Except Alfa Aesar,
334 which was used as a bracketing standard for the study of Zr isotope anomalies, the other
335 standards were characterized for mass-dependent stable Zr isotopic composition^{13, 15, 19}.
336 As shown in Table 1, to convert the delta data from IPGP-Zr to ZIRC-1, the calculation
337 $\delta^{94}\text{Zr}_{\text{ZIRC-1}} = \delta^{94}\text{Zr}_{\text{IPGP-Zr}} - (-0.220 \pm 0.006)$ can be used, and vice versa.

338

339 5. Conclusion

340 To improve inter-laboratory data comparisons for Zr isotopic studies in the future,
341 we first characterized the high precision mass-dependent stable Zr isotopic
342 composition of the new standard solution NRC ZIRC-1 relative to the IPGP-Zr
343 standard, using SSB and double spike method on MC-ICP-MS in two different
344 laboratories.

345 Identical results were obtained from both laboratories. The NRC ZIRC-1 is
346 isotopically lighter than IPGP-Zr by $0.220 \pm 0.006\%$ ($\delta^{94}\text{Zr}$) and its isotopic
347 fractionation is mass dependent. This result agrees with the recommended value from a
348 least-squares adjustment meta-analysis based on literature data. Allende is isotopically
349 lighter relative to Earth by $0.082 \pm 0.046\%$ (2SD).

350

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365 solution.

366

367 **Table**

Table 1. Zirconium isotopic compositions of existing standards and samples analyzed in this study

standards	$\delta^{94}\text{Zr}$ (‰) _{IPGP-Zr}	2SD	$\delta^{94}\text{Zr}$ (‰) _{ZIRC-1}	2SD ^a	n ^b
NRC ZIRC-1	-0.220	0.006	0		7
IPGP-Zr	0		0.220	0.006	7
GJ-1 ^c	-0.008	0.022	0.212	0.023	3
SRM3169 ^c	0.026	0.028	0.246	0.029	16
NIST ^c	0.033	0.042	0.253	0.042	18
Samples					
BHVO-2 (IPGP)	0.068	0.026	0.288	0.027	3
Replicate	0.069	0.011	0.289	0.013	8
BHVO-2 (Copenhagen)	0.060	0.039	0.280	0.039	5
ref. value ^c	0.044	0.037	0.264	0.038	45
AGV-2 (IPGP)	0.032	0.037	0.252	0.038	10
Replicate (IPGP)	0.050	0.029	0.270	0.030	3
ref. value ^d	0.044	0.050	0.264	0.050	4
Allende-1	-0.022	0.065	0.198	0.065	6
Allende-2	-0.040	0.048	0.180	0.048	4
Allende-3	-0.054	0.048	0.166	0.048	4
Allende-4	-0.039	0.014	0.181	0.015	4
Allende-5	-0.049	0.039	0.171	0.039	4
Allende-6	-0.049	0.069	0.171	0.069	3
Allende-7	-0.037	0.020	0.184	0.021	4
Average	-0.041	0.021	0.179	0.022	7

368 ^a The 2SD of $\delta^{94}\text{Zr}$ (‰)_{ZIRC-1} of Zr standards and samples are obtained via error
369 propagation from the 2SD of $\delta^{94}\text{Zr}$ (‰)_{IPGP-Zr} of NRC ZIRC-1 and $\delta^{94}\text{Zr}$ (‰)_{IPGP-Zr} of
370 themselves.

371 ^b n = number of measurements

372 ^c The literature data are from Tian et al. (2020a)¹⁵.

373 ^d The literature value is from Inglis et al. (2018)¹⁴.

374

Table 2 Zr isotopic compositions of NRC ZIRC-1 from two laboratories

Spiked session			
IPGP	$\delta^{94}\text{Zr}$ (‰) _{IPGP-Zr}	2SD	n ^a
NRC ZIRC-1 ^b	-0.216	0.018	6
NRC ZIRC-1 ^b	-0.220	0.013	3
NRC ZIRC-1 ^b	-0.223	0.015	3
Average	-0.220	0.007	3
GLOBE Institute	$\delta^{94}\text{Zr}$ (‰) _{IPGP-Zr}	2SD	n

NRC ZIRC-1 1# ^c	-0.217	0.025	5
NRC ZIRC-1 2# ^c	-0.224	0.022	5
NRC ZIRC-1 3# ^c	-0.217	0.025	5
Average	-0.219	0.008	3
Un-spiked session			
GLOBE Institute	delta values	2SD	n
$\delta^{91}\text{Zr}$ (‰) _{IPGP-Zr}	-0.057	0.009	10
$\delta^{92}\text{Zr}$ (‰) _{IPGP-Zr}	-0.110	0.015	10
$\delta^{94}\text{Zr}$ (‰) _{IPGP-Zr}	-0.220	0.031	10
$\delta^{96}\text{Zr}$ (‰) _{IPGP-Zr}	-0.319	0.048	10
average of all $\delta^{94}\text{Zr}$ (‰) _{IPGP-Zr}	-0.220	0.006	7

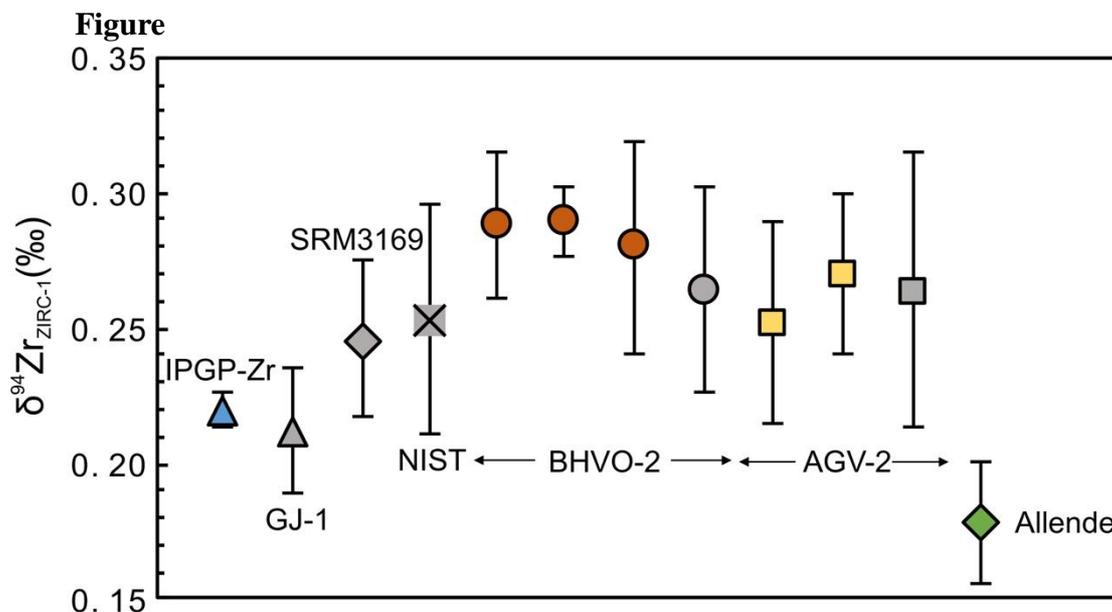
375 ^a n = number of measurements

376 ^b One aliquot of NRC ZIRC-1 solution was analyzed three times at IPGP.

377 ^c Three aliquots of NRC ZIRC-1 solution were analyzed once at the Globe Institute.

378

379



380

Zr standards and Samples

381 **Figure 1.** Zirconium delta values relative to NRC ZIRC-1 of the existing Zr standards
 382 and the samples analyzed in this study. Colorful symbols represent the data obtained in
 383 this study, while symbols filled with grey denote the data converted from the literature:
 384 Inglis et al. (2018)¹⁴ and Tian et al. (2020a)¹⁵.

385

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