

## Electronic Supplementary Information

# Three Natural Zircon Reference Materials for *In Situ* Hf Isotope Analysis Covering a Wide Range of $^{176}\text{Yb}/^{177}\text{Hf}$ Ratios

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## ANOVA calculation processes.

Homogeneity evaluation of the Hf isotopic composition in the three potential zircon RMs was assessed using a one-way analysis of variance (ANOVA).<sup>1-3</sup>

The experimental F ratio, defined as the ratio of the among-unit variance ( $S^2_{among}$ ) to the within-unit variance ( $S^2_{within}$ ), was calculated as:

$$F = \frac{S^2_{among}}{S^2_{within}}$$

Here,  $S^2_{among}$  is the among-unit variance, calculated as the among-unit sum of squares ( $SS_{among}$ ) divided by the among-unit degrees of freedom ( $v_{among}$ ), and  $S^2_{within}$  is the within-unit variance, calculated as the within-unit sum of squares ( $SS_{within}$ ) divided by the within-unit degrees of freedom ( $v_{within}$ ):

$$S^2_{among} = \frac{SS_{among}}{v_{among}}$$

$$S^2_{within} = \frac{SS_{within}}{v_{within}}$$

The degrees of freedom are given by:

$$v_{among} = m - 1$$

$$v_{within} = N - m$$

where  $m$  is the number of units (fragments) analysed, and  $N$  is the total number of measurements.

## References:

1. J. S. Kane, P. J. Potts, M. Wiedenbeck, J. Carignan and S. Wilson, *Geostandards Newsletter*, 2003, **27**, 227-244.
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**Table S1**Zircon RMs with relatively high  $^{176}\text{Yb}/^{177}\text{Yb}$  ratios reported in the literature.

Name	$^{176}\text{Hf}/^{177}\text{Hf}$ (mean $\pm$ 2s)		$^{176}\text{Yb}/^{177}\text{Hf}$ (mean $\pm$ 2s)	Description or references
	Solution MC-ICP-MS	LA-MC-ICP-MS	LA-MC-ICP-MS	
R33	0.282764 $\pm$ 0.000014	0.282749 $\pm$ 0.000046	0.07 $\pm$ 0.06	(Black et al., 2004; Fisher et al., 2014) <sup>4,5</sup>
LV-11	0.282837 $\pm$ 0.000028	—	0.166 $\pm$ 0.011	(Heinonen et al., 2010) <sup>6</sup>
FCT	0.282538 $\pm$ 0.000039	—	0.034 $\pm$ 0.015*	(Schmitz and Bowring, 2001); Wotzlaw et al., 2013) <sup>7,8</sup>
FC-1/AS3	0.282184 $\pm$ 0.000016	0.282680 $\pm$ 0.000042	0.032 $\pm$ 0.038*	(Takehara et al., 2018; Woodhead and Hergt, 2005) <sup>9,10</sup>
TEMORA	0.282685 $\pm$ 0.000011	0.282680 $\pm$ 0.000031	0.032 $\pm$ 0.015	(Black et al., 2003; Wu et al., 2006) <sup>11,12</sup>
Grey Hill	0.282805 $\pm$ 0.000010	0.282812 $\pm$ 0.000057	0.18 $\pm$ 0.08	Significant radiogenic $^{176}\text{Hf}$ ingrowth from $^{176}\text{Lu}$ decay (de Sampaio et al., 2025) <sup>13</sup>

\* Since some literature sources did not report  $^{176}\text{Yb}/^{177}\text{Hf}$  ratios, these values were calculated from elemental content data using the equation:  $^{176}\text{Yb}/^{177}\text{Hf} = (\text{Yb}/\text{Hf}) \times (12.76/18.60)$

—not reported

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**Table S2.**

Instrument setup and measurement parameters for *in situ* elemental analysis by LA-ICP-MS.

<b>Laser ablation system</b>	NWR213, ESL
Laser type	Nd:YAG
Wavelength	213 nm
Pulse width	4 ns
Carrier gas	550 mL min <sup>-1</sup>
Spot size	44 μm
Pulse frequency	4 Hz
Energy density	3 J cm <sup>-2</sup>
<b>ICP-MS</b>	PlasmaQuant MS, Analytik Jena
RF power	1300 W
Plasma gas flow rate	9.0 L min <sup>-1</sup>
Auxiliary gas flow rate	1.65 L min <sup>-1</sup>
Makeup gas flow rate	0.86 L min <sup>-1</sup>
Sampling depth	5.0 mm
Sampler	1.1 mm Ni
Skimmer	0.5 mm Ni
Oxide formation (CeO <sup>+</sup> /Ce <sup>+</sup> )	0.5%
Dwell time per isotope	7 ms
Detector mode	Auto
Monitored isotopes	<sup>7</sup> Li, <sup>23</sup> Na, <sup>25</sup> Mg, <sup>27</sup> Al, <sup>39</sup> K, <sup>42</sup> Ca, <sup>45</sup> Sc, <sup>47</sup> Ti, <sup>51</sup> V, <sup>52</sup> Cr, <sup>55</sup> Mn, <sup>57</sup> Fe, <sup>59</sup> Co, <sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>71</sup> Ga, <sup>85</sup> Rb, <sup>88</sup> Sr, <sup>89</sup> Y, <sup>91</sup> Zr, <sup>93</sup> Nb, <sup>97</sup> Mo, <sup>133</sup> Cs, <sup>109</sup> Ba, <sup>139</sup> La, <sup>140</sup> Ce, <sup>141</sup> Pr, <sup>146</sup> Nd, <sup>147</sup> Sm, <sup>153</sup> Eu, <sup>158</sup> Gd, <sup>159</sup> Tb, <sup>163</sup> Dy, <sup>165</sup> Ho, <sup>166</sup> Er, <sup>169</sup> Tm, <sup>172</sup> Yb, <sup>175</sup> Lu, <sup>178</sup> Hf, <sup>181</sup> Ta, <sup>205</sup> Tl, <sup>208</sup> Pb, <sup>232</sup> Th, <sup>238</sup> U

**Table S3**

Trace element mass fractions (n=45) of the three potential zircon RMs (ML-2, US-2, and MADA) characterised for *in situ* Hf isotope analysis.

	ML-2			US-2			MADA		
	mean	s	RSD(%)	mean	s	RSD(%)	mean	s	RSD(%)
Sc	271	8.80	3	244	5.37	2	253	18.6	7
Ti	1405	64.7	5	1251	45.8	4	1275	42.7	3
Y	348	430	123	1411	620	44	2972	800	27
Nb	7.38	10.8	146	32.3	25.2	78	14.3	10.6	74
Ag	3.99	0.22	6	2.97	0.28	9	3.16	0.19	6
Cd	768	54.9	7	574	48.4	8	629	57.8	9
Ba	0.65	0.24	37	0.6	0.27	48	31.6	34.6	109
La	0.09	0.05	63	0.16	0.12	79	53	55.2	105
Ce	3.06	5.95	194	0.29	0.26	91	104	106	102
Pr	0.13	0.21	167	0.05	0.04	88	7.73	8.72	113
Nd	1.76	2.90	165	1.05	0.77	73	30.4	33.2	109
Sm	2.30	4.18	182	3.61	3.12	87	13.2	11.4	86
Eu	1.53	2.83	185	0.49	0.46	94	2.39	2.27	95
Gd	9.84	17.0	173	20.9	21.2	101	38.5	15.6	41
Tb	3.16	4.95	157	13.1	11.5	87	15.6	4.93	32
Dy	37.5	53.2	142	195	132	68	219	61.8	28
Ho	13.1	16.6	127	74.4	35.9	48	91.7	24.1	26
Er	62.5	71.8	115	446	160	36	519	125	24
Tm	13.2	14.1	107	135	49.8	37	126	27.6	22
Yb	120	124	104	1564	653	42	1230	245	20
Lu	22.8	22.4	98	304	143	47	237	38.8	16
Hf	6416	971	15	30414	6620	22	10719	495	5
Ta	5.74	13.3	232	19.4	8.98	46	4.10	0.78	19
Pb	6.57	11.6	177	6.15	5.36	87	55.5	25.0	45
Th	87.1	159	182	53.3	48.0	90	992	496	50
U	187	253	136	4.98	2.19	44	8180	2279	28

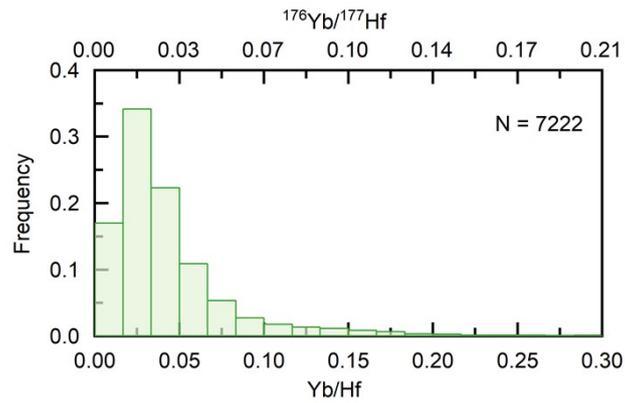
**Table S4**

ANOVA results for the homogeneity assessment of *in situ*  $^{176}\text{Hf}/^{177}\text{Hf}$  in the three potential zircon RMs measured by LA-MC-ICP-MS.

	$\bar{x}^*$	$SS_{\text{among}}$	$SS_{\text{within}}$	F	p	$F_{\text{critical}}(8, 36; 0.05)$
ML-2	0.252458	$1.3 \times 10^{-9}$	$3.5 \times 10^{-8}$	0.1679	0.9939	2.2085
US-2	0.282199	$1.6 \times 10^{-9}$	$2.0 \times 10^{-8}$	0.3515	0.9391	2.2085
MADA	0.282492	$1.4 \times 10^{-9}$	$6.3 \times 10^{-8}$	0.1010	0.9990	2.2085

m=9, N=45;  $\nu_{\text{among}}=8$ ,  $\nu_{\text{within}}=36$

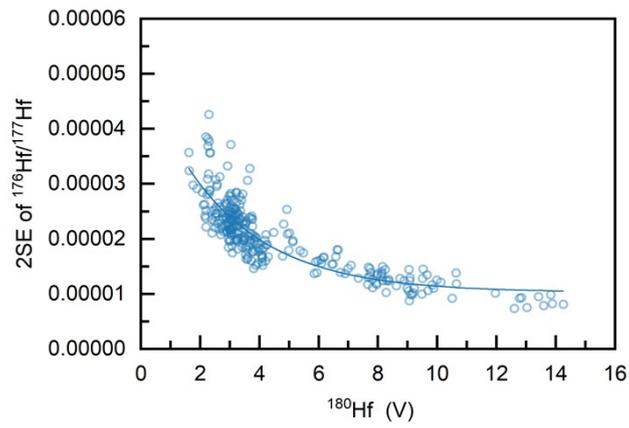
\* the mean value of all measurements across the nine fragments in this systematic session



**Fig. S1** Compilation of Yb/Hf ratios for published natural zircons. The  $^{176}\text{Yb}/^{177}\text{Hf}$  ratio was calculated using the equation:  $^{176}\text{Yb}/^{177}\text{Hf} = (\text{Yb}/\text{Hf}) \times (12.76/18.60)$ . Data are from Martin (2024) via the compilation database (<https://doi.org/10.5880/digis.e.2024.003>).<sup>14</sup>

Reference:

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**Fig. S2** Correlation between repeatability precision (2SE) of the measured  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios and the average  $^{180}\text{Hf}$  signal intensities obtained by LA-MC-ICP-MS. Data were collected from zircon samples including PLE, Mud Tank, Tanz, ML-2, US-2, and MADA.