




# Precise and Accurate Determination of Lu and Hf Contents, and Hf Isotopic Compositions in Chinese Rock Reference Materials by MC-ICP-MS

Ming Yang (1, 2, 3) , Yue-Heng Yang (1, 2, 3)\* , Noreen J. Evans (4), Lie-Wen Xie (1, 2, 3),  
Chao Huang (1, 2, 3), Shi-Tou Wu (1, 2, 3) , Jin-Hui Yang (1, 2, 3) and Fu Yuan Wu (1, 2, 3)

(1) State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, 100029, China

(2) University of Chinese Academy of Sciences, Beijing, 100049, China

(3) Innovation Academy of Earth Science, Chinese Academy of Sciences, Beijing, 100029, China

(4) School of Earth and Planetary Science, John de Laeter Centre, Curtin University, WA, Australia

\* Corresponding author. e-mail: yangyueheng@mail.iggcas.ac.cn

In this contribution, we report Hf isotopic data and Lu and Hf mass fractions for thirteen Chinese rock reference materials (GBW07 103–105, 109–113 and 121–125, that is GSR 1–3, 7–11 and 14–18, respectively) that span a broad compositional range. Powdered samples were spiked with a  $^{176}\text{Lu}$ - $^{180}\text{Hf}$  enriched tracer and completely digested using conventional HF, HNO<sub>3</sub> and HClO<sub>4</sub> acid dissolution protocols. Fluoride salts were dissolved during a final H<sub>3</sub>BO<sub>3</sub> digestion, and chemical purification was performed using a single Ln resin. All measurements were carried out on a MC-ICP-MS. This work provides the first comprehensive report of the Lu-Hf isotopic composition of Chinese geochemical rock reference materials, and results indicate that they are of comparable quality to the well-characterised and widely used USGS and GSJ rock reference materials.

Keywords: Lu-Hf isotope, Chinese rock reference material, MC-ICP-MS.

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Rapid developments in multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) have enabled precise Lu-Hf isotope ratio measurement, resulting in widespread application of the  $^{176}\text{Lu}$ - $^{176}\text{Hf}$  radiogenic isotope system in geochemistry, cosmochemistry and environmental sciences since 1990s (Blichert-Toft *et al.* 1997). Therefore, routine analysis of Lu and Hf content and Hf isotopic composition in geological samples by MC-ICP-MS has been facilitated (Blichert-Toft 2001, Münker *et al.* 2001, Bizzarro *et al.* 2003, Yang *et al.* 2010, 2011, Fourny *et al.* 2016). Nevertheless, mass bias corrections in MC-ICP-MS are strongly dependent on the cleanliness of the sample (Albarède and Beard 2004, Albarède *et al.* 2004, Lin *et al.* 2016). The plasma source produces more complex interferences than the thermal ionisation mass spectrometry (TIMS) source and is also susceptible to matrix effects, as has long been known from single collector ICP-MS studies. Furthermore, the intrinsic instability of the plasma source means that most MC-ICP-MS analyses are run in static mode

(Weis *et al.* 2007). Therefore, it is critical to have a broad compositional range of isotopic reference materials available so that appropriate matrix-matched rock reference materials can be selected for analysis with suites of unknown samples (Raczek *et al.* 2003, Li *et al.* 2005, Weis *et al.* 2005, 2006, 2007, Li *et al.* 2015, Jweda *et al.* 2016, Bao *et al.* 2018).

The most useful and widely distributed rock reference materials have certified values for major elements, trace elements, and various isotopic systems (Jochum *et al.* 2005, Jochum and Enzweiler 2014). There are abundant publications including major, trace and isotopic values (e.g., Li, B, Ca, Mg, Sr, Nd, Hf and Pb) for the most commonly used United States Geological Survey (USGS) rock reference materials (BCR-2, BHVO-2, AGV-2, GSP-2, etc.) (Raczek *et al.* 2003, Weis *et al.* 2005, 2006, 2007, Li *et al.* 2007, Li *et al.* 2014, 2016, Fourny *et al.* 2016, Jweda *et al.* 2016, Bao *et al.* 2018) and Japanese Geological Survey (GSJ)

reference materials (JA-1, JA-2, JA-3; JB-1, JB-2, JB-3; JG-1, JG-2, JG-3; etc.) (Hanyu *et al.* 2005, Li *et al.* 2007, Lu *et al.* 2007, Li *et al.* 2014, 2016). In contrast, Chinese rock reference materials are only well-characterised for major and trace element composition (Xie *et al.* 1985, 1989, Zhang *et al.* 1986, Tang *et al.* 1992, Bower *et al.* 1993, Qi and Grégoire 2000, Qi *et al.* 2005, Fourny *et al.* 2016) with rare Hf isotopic data reported to date. Li *et al.* (2005, 2007) firstly presented  $^{176}\text{Hf}/^{177}\text{Hf}$  data for six GSR rock reference materials (i.e., GSR-3, GSR-7, GSR-8, GSR-10, GSR-11 and GSR-17, respectively). The Hf isotopic composition of basalt GSR-3 further was reported by Yang *et al.* (2011). Recently, Cheng *et al.* (2015) reported new Lu-Hf elemental and isotopic measurements for GSR-1, GSR-2 and GSR-3 reference materials using ID-MC-ICP-MS. Bao *et al.* (2018) presented new Hf isotopic measurement for GSR-1 and GSR-3. Only five laboratories have reported Hf isotope data for GSR-3 (Li *et al.* 2005, 2007, Yang *et al.* 2011, Cheng *et al.* 2015, Fourny *et al.* 2016, Bao *et al.* 2018).

To expand this database and enhance the applicability of Chinese rock reference materials, we undertook systematic analysis of the Lu and Hf mass fractions and Hf isotopic composition in thirteen Chinese geochemical rock reference materials spanning a broad compositional range [GBW07 103–105, 109–113 and 121–125 (i.e., GSR 1–3, 7–11 and 14–18)]. The aim of this work is to present a comprehensive set of high-precision Lu and Hf mass fraction, and Hf isotopic composition data for Chinese rock reference materials, in order to demonstrate isotopic homogeneity and present reference values to the broader analytical geochemistry community.

## Experimental procedure

All chemical separations and mass spectrometry were undertaken at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. The chemical procedures were performed in a class 100 laminar flow hood in a class 10000 clean room environment. Chemical separation was undertaken by conventional ion-exchange techniques. The detailed procedure is discussed elsewhere (Yang *et al.* 2010, Ma *et al.* 2019), and only a brief introduction is given here.

## Sample description

The thirteen Chinese rock reference materials [GBW07 103–105, 109–113 and 121–125, respectively; (i.e., GSR 1–3, 7–11 and 14–18, respectively)] are from the National Research Center for Certified Reference Materials (NRC CRM), and the major oxide mass fractions ( $\text{g } 100 \text{ g}^{-1}$ )

of Chinese rock reference materials are summarised in Table 1.

**Volcanic rocks:** (a) GSR-2 is a hornblende-phyric andesite with partial secondary alteration to carbonate minerals, obtained in the vicinity of the Meishan iron mine, Nanjing. (b) GSR-3 is an olivine basalt (primarily plagioclase, olivine, magnetite and augite) collected at Zhangjiakou, Hebei province. (c) GSR-8 is a trachyte from Late Jurassic sub-volcanic rocks, collected at Fanchang, Anhui province. The matrix is microcrystalline and rough, and main rock-forming minerals are plagioclase, potassium feldspar, biotite and a small amount of quartz and apatite. (d) GSR-11 is from the rhyolite porphyry of the Jiuliping Formation of the Upper Jurassic Moshishan Group. It was collected from the south of Banba Village, 8 km south of Shangyu County, Zhejiang Province. The main rock-forming minerals in this massive greyish-purple rock are feldspar, quartz, apatite, epidote and magnetite, with a small amount of chlorite, sericite and calcite. (e) GSR-16 is a diabase collected from Lulong, Hebei Province (Table 1).

**Plutonic rocks:** (a) GSR-1 is grey medium-grained biotite granite, collected from Chengzhou, Hunan province. There is tungsten, tin and molybdenum mineralisation in the contact zone between the granite and carbonate rocks. (b) GSR-7 is an early intrusive black aegirine nepheline syenite collected at Saima, Liaoning province. The Saima alkaline complex consists of greyish-brown, massive nepheline syenites. Microscopically, GSR-7 has a semi-automorphic structure and the main rock-forming minerals are syenite, perthite, nepheline, calcium nepheline, aegirine and a small amount of sodalite, biotite and apatite. (c) GSR-9 was collected from about 2.5 km northwest of Zhoukoudian Town, Fangshan County, Beijing. The dense, grey massive rocks belong to the Upper Jurassic Xishantou Formation and are semi-automorphic granular or porphyritic in texture. The main rock-forming minerals are plagioclase, potassium feldspar, quartz, amphibole and biotite, with a small amount of magnetite, apatite, titanite, etc. (d) GSR-10 was collected from the top of the ore-bearing strata in the footwall of a fault in the Lanjia volcanic deposit in the Panzhihua rock mass, Dukou, Sichuan Province. The black-grey, dense, massive rock comprises iron-bearing gabbro in a coarse- to medium-grained flow-layered iron-bearing gabbro. The rock intruded into the dolomitic limestone of Dengying Formation of Sinian and the primary flow structure and magmatic differentiation of the rock mass is obvious. The main rock-forming minerals are plagioclase, augite, titanium and iron oxide and a small amount of olivine. (e) GSR-14 is a granitic gneiss collected from the Archaean block in Fuping County, Hebei Province. The mass fractions of most trace elements are low in this

**Table 1.**  
Major oxide mass fractions (g 100 g<sup>-1</sup>) of Chinese rock reference materials investigated in this study

RM	Rock type	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3(T)</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
GBW07103 (GSR-1)	Granite	72.83	0.287	13.40	2.14	0.060	0.42	1.55	3.13	5.01	0.093
GBW07104 (GSR-2)	Andesite	60.62	0.515	16.17	4.90	0.083	1.72	5.20	3.86	1.89	0.236
GBW07105 (GSR-3)	Basalt	44.64	2.369	13.83	13.40	0.169	7.77	8.81	3.38	2.32	0.946
GBW07109 (GSR-7)	Syenite	54.48	0.48	17.72	6.04	0.12	0.65	1.39	7.16	7.48	0.018
GBW07110 (GSR-8)	Trachyte	63.06	0.80	16.1	4.51	0.089	0.84	2.47	3.06	5.17	0.36
GBW07111 (GSR-9)	Granodiorite	59.68	0.77	16.56	2.64	0.094	2.81	4.72	4.05	3.50	0.34
GBW07112 (GSR-10)	Gabbro	35.69	7.69	14.14	9.90	0.193	5.25	9.86	2.11	0.15	0.028
GBW07113 (GSR-11)	Rhyolite	72.78	0.30	12.96	1.14	0.14	0.16	0.59	2.57	5.43	0.045
GBW07121 (GSR-14)	Granitic gneiss	66.3	0.297	16.3	3.12	0.056	1.63	2.66	5.3	2.60	0.131
GBW07122 (GSR-15)	Amphibolite	49.6	0.922	13.8	14.8	0.207	7.2	9.6	2.07	0.48	0.086
GBW07123 (GSR-16)	Diabase	49.88	2.94	13.21	13.40	0.207	5.08	7.83	3.17	1.49	0.55
GBW07124 (GSR-17)	Kimberlite	35.88	0.71	3.73	6.53	0.116	17.56	12.64	0.1	0.49	0.30
GBW07125 (GSR-18)	Pegmatite	76.40	0.61	13.19	0.24	0.013	0.13	0.1	1.60	6.22	0.18

Data from Wang *et al.* (2013, pp. 111–113).

sample. (f) GSR-15 is an amphibolite collected from the Archaean block in Benxi City, Liaoning Province. Its protolith is a tholeiite, and it is characterised by low rare earth element (REE) contents. (g) GSR-18 is pegmatite from Fengning, Hebei Province (Table 1).

**Ultramafic rocks:** (a) GSR-17 is a kimberlite from the Ordovician Fuxian kimberlite, Liaoning Province (Table 1).

## Reagents and materials

Ultrapure water (18.2 MΩ cm resistivity at 25 °C) from Millipore (Elix-Millipore, USA) was used for all sample chemical preparation. Pre-packed extraction chromatography material (Ln Spec, 100–150 μm particle size, 2 ml) was purchased from Eichrom Industries (Darien, IL, USA).

Concentrated hydrochloric, nitric and hydrofluoric acids (BV-III grade, from Beijing Institute of Chemical Reagents) were twice purified using the Savillex™ DST-1000 apparatus sub-boiling distillation system (Minnetonka, MN, USA). 70% *m/m* HClO<sub>4</sub> (Acros Organics, Geel, Belgium), high purity H<sub>3</sub>BO<sub>3</sub> (Acros Organics) and 30% *m/m* H<sub>2</sub>O<sub>2</sub> (Extra-pure grade, from Beijing Institute of Chemical Reagents, Beijing, China) were directly used without additional purification. H<sub>3</sub>BO<sub>3</sub> (3% H<sub>3</sub>BO<sub>3</sub> in 3 mol l<sup>-1</sup> HCl) was prepared as

follows: 12 g high purity H<sub>3</sub>BO<sub>3</sub> was weighed into a clean PTFE beaker and dissolved with 300 ml water. Then, 100 ml of PTFE-distilled 12 mol l<sup>-1</sup> HCl was added to the solution.

Standard solutions of 1000 μg ml<sup>-1</sup> Lu (Stock No. 35765) and 10000 ng μl<sup>-1</sup> Hf (Stock No. 14374) purchased from Alfa Aesar (Johnson Matthey Company) (plasma standard solution, Specpure) were used to gravimetrically prepare standard solutions, diluted with 2% HNO<sub>3</sub> + trace HF for mass spectrometric measurements. As in-house standard solutions, 50 ng ml<sup>-1</sup> of Lu and 200 ng ml<sup>-1</sup> of Hf solution were prepared and used during the actual measurement. Additionally, 100 ng ml<sup>-1</sup> of JMC 475 Hf from P.J. Patchett was used for quality control of instrumental performance. For Lu and Hf tracers from Oak Ridge National Laboratory, USA, the solutions were calibrated by reverse isotope dilution against gravimetric standards (Yang *et al.* 2010). Besides the thirteen Chinese rock reference materials, USGS rock reference materials of BCR-2, AGV-2 and BIR-1a were used to evaluate and monitor the whole chemical procedure.

## Sample digestion

About 100–150 mg of powder and <sup>176</sup>Lu-<sup>180</sup>Hf spike were weighed (both to 0.1 mg precision) into 7 ml Savillex

PFA vials (basalt including GSR-3, BCR-2, BIR-1a and AGV-2) or 10 ml high-pressure PTFE-lined stainless steel bomb (other samples). The samples were dissolved on a hot plate at 100–120 °C for one week using an acid mix of 2 ml 22 mol l<sup>-1</sup> HF, 1 ml 14 mol l<sup>-1</sup> HNO<sub>3</sub> and 0.2 ml 70% *m/v* HClO<sub>4</sub>. After cooling, the capsule was opened, gently heated to dryness and evaporated to fuming HClO<sub>4</sub>. Then, 3 ml of 6 mol l<sup>-1</sup> HCl was added to the residue and dried, and this procedure was repeated. After the samples were dried again, the residues were completely dissolved in 3–5 ml 3 mol l<sup>-1</sup> HCl + 3% *m/v* H<sub>3</sub>BO<sub>3</sub> mixtures at 100 °C on a hot plate overnight. The amount of the latter solution was in proportion to the sample mass. When gently heated to dryness on a hot plate at ~ 100 °C and cooled, the residue was re-dissolved in 5 ml of 3 mol l<sup>-1</sup> HCl + 3% *m/v* H<sub>3</sub>BO<sub>3</sub>. The capsule was resealed and placed on a hot plate at ~ 100 °C overnight in preparation for chemical purification.

### Chromatographic separation

The sample solution was centrifuged and then loaded onto pre-conditioned 2 ml Ln Spec resin for separation of Lu and Hf from the sample matrix. First, matrix elements were eluted with 3 mol l<sup>-1</sup> HCl, and light REE was washed with 4 mol l<sup>-1</sup> HCl sequentially. The Lu (+Yb) fraction was eluted with 4 mol l<sup>-1</sup> HCl, evaporated to dryness and then diluted to 1 ml with 2% HNO<sub>3</sub> prior to mass spectrometry measurements. In order to minimise the isobaric interference of <sup>176</sup>Lu and <sup>176</sup>Yb on <sup>176</sup>Hf, the column was rinsed with ~ 40 ml of 6 mol l<sup>-1</sup> HCl to effectively remove Lu and Yb residues before collecting the Hf (+Zr) fraction. Titanium was separated from Hf using a 4 mol l<sup>-1</sup> HCl + 0.5% H<sub>2</sub>O<sub>2</sub> mixture. Finally, Hf-Zr fractions were eluted with 5 ml 2 mol l<sup>-1</sup> HF, collected in a 7 ml PFA beaker and gently evaporated to dryness. This fraction was taken up in 2 mol l<sup>-1</sup> HF, diluted to 1 ml with 2% HNO<sub>3</sub> and was then ready for Hf isotopic analysis. The recovery yields of Lu and Hf were greater than 50% and 90%, respectively.

### Mass spectrometry

A Thermo Fisher Scientific Neptune MC-ICP-MS (Bremen, Germany), housed at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS) and equipped with nine Faraday cups, was used for all isotope ratio measurements. All detectors used normal pre-amplifiers with a 10<sup>11</sup> Ω resistor. The plug-in quartz torch with quartz injector was fitted with a platinum guard electrode. Instrument optimisation was performed following standard procedures outlined in the manufacturer's manual. In brief, the instrument was tuned to achieve the highest sensitivity while

**Table 2.**  
Typical operating parameters for Lu and Hf isotopic measurement using the Neptune MC-ICP-MS

Parameter	Setting
RF forward power	1320 W
Cooling gas	16 l min <sup>-1</sup>
Auxiliary gas	0.8 l min <sup>-1</sup>
Sample gas	~ 1.00 l min <sup>-1</sup> (optimised daily)
Extraction	-2000 V
Focus	-650 V
Detection system	Nine Faraday collectors
Acceleration voltage	10 kV
Interface cones	Standard cone
Nebuliser type	Micromist PFA nebuliser
Sample uptake rate	50 µl min <sup>-1</sup>
Uptake mode	Free aspiration
Instrument resolution	~ 400 (low)
Typical sensitivity on <sup>180</sup> Hf	~ 20 V/µg ml <sup>-1</sup> (10 <sup>-11</sup> Ω resistors)
Sampling mode	9 blocks of 7 cycles for Hf 1 block of 45 cycles for Lu
Integration time	4 s for Hf and 4 s for Lu
Baseline/background determination	ca. 1 min on peak in 2% HNO <sub>3</sub>

maintaining low oxides, flat-topped square peaks and stable signals.

Details of instrument operating conditions, data acquisition and Faraday cup configuration are summarised in Tables 2 and 3. The sample solution was introduced with a standard introduction system (SIS) using a self-aspirating 50 µl min<sup>-1</sup> PFA nebuliser. Carrier gas Ar flow rates were finely tuned daily to get maximum intensity using 200 ng ml<sup>-1</sup> Alfa Hf 14374 standard solution, while 2% HNO<sub>3</sub> + 0.1% HF was used as carrier and washing solution. The 100 ng ml<sup>-1</sup> Hf or JMC475 was measured every ten samples to check instrument stability. In general, the signal intensity of <sup>176</sup>Yb and <sup>176</sup>Lu is less than 5 × 10<sup>-5</sup> V after the chemical purification described above, resulting in a variability of about 1 × 10<sup>-5</sup> on the <sup>176</sup>Hf/<sup>177</sup>Hf ratios, which is almost equal to the typical measurement repeatability. In addition, signals corresponding to masses 181 and 183 were also measured to monitor any isobaric interference from <sup>180</sup>Ta and <sup>180</sup>W on <sup>180</sup>Hf, considering that enriched <sup>180</sup>Hf tracer was used in this study. However, the levels of W and Ta were found to be very low in every case. The signal intensities of <sup>181</sup>Ta and <sup>183</sup>W were usually less than 1 × 10<sup>-3</sup> V after chemical separation (Table 3). The mass bias behaviour of Lu was assumed to follow that of Yb for the interference correction of <sup>176</sup>Yb on <sup>176</sup>Lu using the exponential law (Yang *et al.* 2010). The Hf isotopic data were reduced offline in order to correct for instrumental mass bias and tracer contribution with normalisation to <sup>179</sup>Hf/<sup>177</sup>Hf = 0.7325 using the exponential law (Patchett

**Table 3.**  
**Faraday cup configurations for Lu and Hf isotopic measurement by Neptune MC-ICP-MS**

Element	L4	L3	L2	L1	C	H1	H2	H3	H4
Lu	<sup>168</sup> [Er + Yb]	<sup>170</sup> [Er + Yb]	<sup>171</sup> Yb	<sup>172</sup> Yb	<sup>173</sup> Yb	<sup>174</sup> [Yb + Hf]	<sup>175</sup> Lu	<sup>176</sup> [Lu + Yb + Hf]	<sup>178</sup> Hf
Hf	<sup>173</sup> Yb	<sup>175</sup> Lu	<sup>176</sup> [Hf + Yb + Lu]	<sup>177</sup> Hf	<sup>178</sup> Hf	<sup>179</sup> Hf	<sup>180</sup> [Hf + Ta + W]	<sup>181</sup> Ta	<sup>183</sup> W

and Tatsumoto 1980). Usually, it takes *ca.* 7 min to complete one Hf isotopic measurement, while one Lu content measurement took about 5 min in this work. All data for geological samples are reported relative to the JMC 475 reference value of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$  (Vervoort and Blichert-Toft 1999).

During the period of data acquisition, USGS BCR-2, BIR-1a and AGV-2 powder rock reference materials were analysed using the analytical procedure described above. Measurement results for  $^{176}\text{Hf}/^{177}\text{Hf}$  in BCR-2, BIR-1a and AGV-2 were  $0.282877 \pm 0.000003$  ( $2s$ ,  $n = 3$ ),  $0.283260 \pm 0.000010$  ( $2s$ ,  $n = 3$ ) and  $0.282966 \pm 0.000004$  ( $2s$ ,  $n = 3$ ), respectively, comparable to the  $^{176}\text{Hf}/^{177}\text{Hf}$  values  $0.282865 \pm 0.000013$  for BCR-2,  $0.283273 \pm 0.000014$  for BIR-1a and  $0.282973 \pm 0.000010$  for AGV-2, respectively, agree well with other reported values (e.g., Bizzarro *et al.* 2003, Jochum *et al.* 2005, Li *et al.* 2005, Weis *et al.* 2005, 2006, 2007, Yang *et al.* 2010, Fourny *et al.* 2016, Jweda *et al.* 2016, Bao *et al.* 2018).

## Results and discussion

Lu and Hf mass fractions, and Hf isotope data (duplicate or triplicate analyses) for the thirteen Chinese rock reference materials are summarised in Table 4. There was insignificant difference between the Hf isotope ratios obtained with or without the Hf spike, and individual within-run precision ( $2s$ ) on spiked and unspiked aliquots was comparable. Good  $^{176}\text{Hf}/^{177}\text{Hf}$  instrumental repeatability was achieved in every run (for example,  $\pm 0.000004$  to  $\pm 0.000014$  for GBW07125 (GSR-18), a pegmatite with  $0.864 \mu\text{g g}^{-1}$  Hf). This demonstrates that the purity of Hf fractions was adequate for MC-ICP-MS measurements. Comparative isotopic ratios from the literature were reported only when the number of duplicates was greater than one, and are given in Table 5 (Li *et al.* 2005, 2007, Yang *et al.* 2011, Cheng *et al.* 2015, Fourny *et al.* 2016, Bao *et al.* 2018).

### Volcanic reference materials (GSR-2, GSR-3, GSR-8, GSR-11 and GSR-16)

As shown in Table 4, the mean value of Lu and Hf mass fractions for GSR-2 andesite is  $0.104 \pm 0.001 \mu\text{g g}^{-1}$  ( $2s$ ,

$n = 3$ ) and  $2.501 \pm 0.087 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 3$ ), respectively, in this work. The corresponding mean  $^{176}\text{Lu}/^{177}\text{Hf}$  is  $0.00590 \pm 0.00014 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 3$ ), and all Hf isotope compositions (spiked and non-spiked) are identical within analytical precision with a calculated mean of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282642 \pm 0.000020$  ( $2s$ ,  $n = 4$ ). This value is in excellent agreement with  $0.282641 \pm 0.000010$  ( $2s$ ,  $n = 10$ ), obtained using a Neptune Plus MC-ICP-MS as reported by Cheng *et al.* (2015).

There are several Hf isotopic data previously reported for GSR-3 basalt in five different studies (Table 3). Li *et al.* (2005) presented a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282983 \pm 0.000007$  ( $2s$ ,  $n = 4$ ) with three aliquots measured on a Neptune MC-ICP-MS and one aliquot on a Micromass Isoprobe MC-ICP-MS. Yang *et al.* (2011) reported three replicates with a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282985 \pm 0.000014$  ( $2s$ ,  $n = 3$ ). Recently, Cheng *et al.* (2015) reported Lu and Hf mass fractions and Hf isotopic compositions by ID-MC-ICP-MS and obtained a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282985 \pm 0.000010$  ( $2s$ ,  $n = 10$ ) (spiked and non-spiked). More recently, the Pacific Centre for Isotopic and Geochemical Research (PCIGR) at the University of British Columbia (UBC) has undertaken a systematic analysis of Sr-Nd-Hf-Pb isotopic compositions of GSR-3 by Nu Instruments MC-ICP-MS and/or TIMS and Triton TIMS, and reported  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282985 \pm 0.000009$  ( $2s$ ,  $n = 5$ ) (Fourny *et al.* 2016). Furthermore, Bao *et al.* (2018) presented a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282976 \pm 0.000008$  ( $2s$ ,  $n = 5$ ) by Nu Plasma II MC-ICP-MS and Aridus II desolvation nebuliser system. In this work, our obtained  $^{176}\text{Hf}/^{177}\text{Hf}$  value for four aliquots was  $0.282991 \pm 0.000009$  ( $2s$ ,  $n = 4$ ), which agrees with previous data within reported precision (Li *et al.* 2005, Yang *et al.* 2011, Cheng *et al.* 2015, Fourny *et al.* 2016, Bao *et al.* 2018).

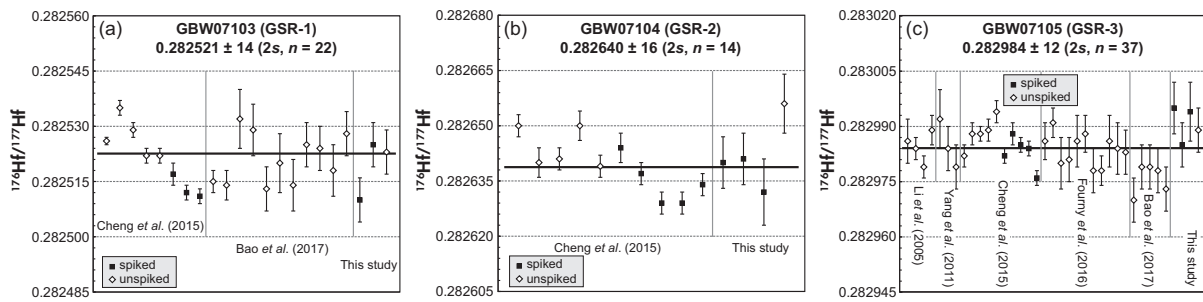
The mean value of Lu and Hf mass fractions of GSR-8 trachyte is  $0.483 \pm 0.005 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 3$ ) and  $8.239 \pm 0.147 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 3$ ), respectively, in this work. The corresponding mean  $^{176}\text{Lu}/^{177}\text{Hf}$  is  $0.00834 \pm 0.00024$  ( $2s$ ,  $n = 3$ ), and all Hf isotope compositions (spiked and non-spiked) resulted in a calculated mean of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282495 \pm 0.000010$  ( $2s$ ,  $n = 4$ ). This is in excellent agreement with  $0.282499 \pm 0.000021$  ( $2s$ ,

**Table 4.**  
Lutetium and Hf mass fractions, and Hf isotope ratios of Chinese rock reference materials obtained in this study

Sample nameRock type [Aliquot No.]	Lu [ $\mu\text{g g}^{-1}$ ]	Hf [ $\mu\text{g g}^{-1}$ ]	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$ ( $\pm 2s$ )	$^{176}\text{Hf}/^{177}\text{Hf}$ <sup>a</sup> ( $\pm 2s$ )
GBW07103 (GSR-1) Granite [490288]	1.177	5.639	0.02966	0.282510 (09)	0.282523 (10)
	1.199	5.528	0.03081	0.282525 (10)	
	Mean $\pm 2s$	1.188 [0.030]	5.583 [0.157]	0.03024 [0.00162]	
GBW07104 (GSR-2) Andesite [14054]	0.104	2.489	0.00592	0.282640 (07)	0.282656 (08)
	0.103	2.465	0.00596	0.282641 (07)	
	Mean $\pm 2s$	0.104 [0.001]	2.501 [0.087]	0.00590 [0.00014]	
GBW07105 (GSR-3) Basalt [630270]	0.157	6.179	0.00361	0.282995 (07)	0.282989 (06)
	0.154	6.160	0.00355	0.282985 (06)	
	Mean $\pm 2s$	0.155 [0.004]	6.171 [0.021]	0.00357 [0.00008]	
GBW07109 (GSR-7) Syenite	0.448	36.63	0.00174	0.282321 (04)	0.282312 (08)
	0.442	36.65	0.00171	0.282320 (06)	
	Mean $\pm 2s$	0.446 [0.007]	36.62 [0.06]	0.00173 [0.00003]	
GBW07110 (GSR-8) Trachyte	0.482	8.283	0.00827	0.282498 (06)	0.282494 (06)
	0.486	8.154	0.00847	0.282488 (07)	
	Mean $\pm 2s$	0.483 [0.005]	8.239 [0.147]	0.00834 [0.00024]	
GBW07111 (GSR-9) Granodiorite	0.229	5.185	0.00627	0.282138 (07)	0.282132 (06)
	0.233	5.730	0.00578	0.282137 (09)	
	Mean $\pm 2s$	0.232 [0.006]	5.651 [0.865]	0.00586 [0.00075]	
GBW07112 (GSR-10) Gabbro	0.0462	0.780	0.00842	0.282870 (10)	0.282883 (09)
	0.0469	0.793	0.00840	0.282892 (11)	
	Mean $\pm 2s$	0.0481 [0.0055]	0.790 [0.019]	0.00865 [0.00082]	
GBW07113 (GSR-11) Rhyolite	0.694	10.87	0.00907	0.282714 (06)	0.282694 (07)
	0.649	11.45	0.00806	0.282697 (05)	
	Mean $\pm 2s$	0.668 [0.046]	11.11 [0.61]	0.00855 [0.00102]	
GBW07121 (GSR-14) Granitic gneiss [110014]	0.105	2.843	0.00524	0.281513 (06)	0.281499 (06)
	0.105	3.282	0.00456	0.281485 (08)	
	Mean $\pm 2s$	0.105 [0.002]	3.040 [0.446]	0.00491 [0.00068]	
GBW07122 (GSR-15) Amphibolite [0332]	0.370	1.523	0.0345	0.283006 (08)	0.283008 (08)
	0.374	1.515	0.0351	0.283017 (09)	
	Mean $\pm 2s$	0.372 [0.004]	1.583 [0.224]	0.0335 [0.0045]	
GBW07123 (GSR-16) Diabase	0.329	7.716	0.00606	0.282191 (06)	0.282186 (09)
	0.325	7.595	0.00607	0.282195 (07)	
	Mean $\pm 2s$	0.327 [0.005]	7.669 [0.129]	0.00605 [0.00006]	
GBW07124 (GSR-17) Kimberlite	0.156	4.411	0.00502	0.282276 (10)	0.282264 (10)
	0.159	4.528	0.00498	0.282269 (10)	
	Mean $\pm 2s$	0.156 [0.006]	4.388 [0.307]	0.00505 [0.00017]	
GBW07125 (GSR-18) Pegmatite	0.0336	0.852	0.00561	0.282173 (10)	0.282166 (14)
	0.0406	0.870	0.00662	0.282168 (13)	
	Mean $\pm 2s$	0.0359 [0.0081]	0.864 [0.021]	0.00590 [0.00126]	

The ( $\pm 2s$ ) instrumental repeatability value of the  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio in the individual sample analysis, reported as  $\times 10^6$ .

<sup>a</sup> Mean without spike, others mean with spike. The ( $\pm 2s$ ) is the 2 standard deviation on the mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of the replicate analyses [intermediate precision], also reported as  $\times 10^6$ .



**Figure 1.** The measured  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of GSR-1, GSR-2 and GSR-3 for all available data [data from this work and Li *et al.* (2005, 2007), Yang *et al.* (2011), Cheng *et al.* (2015), Fourny *et al.* (2016), Bao *et al.* (2018)].  $\pm 2s$  is the 2 standard deviation of the mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of the replicate analyses (intermediate precision) reported as times  $10^6$ .

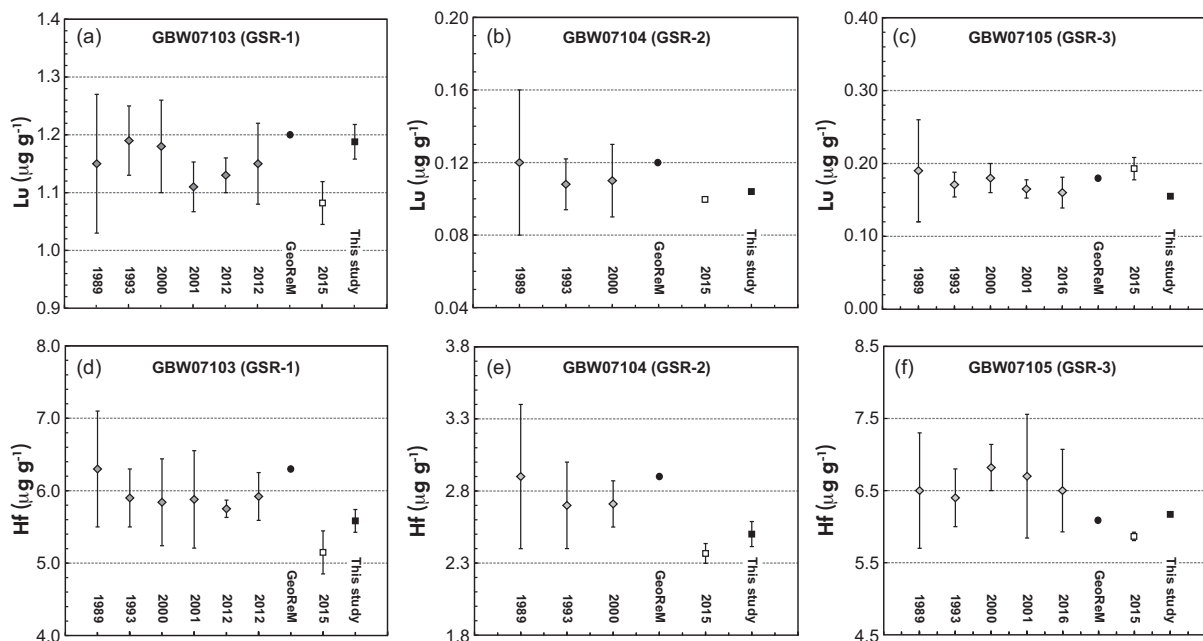
$n = 4$ ), reported by Li *et al.* (2007). For GSR-11 rhyolite, Li *et al.* (2007) presented a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282699 \pm 0.000014$  ( $2s$ ,  $n = 4$ ). In this work, the  $^{176}\text{Hf}/^{177}\text{Hf}$  value for four aliquots was  $0.282701 \pm 0.000018$  ( $2s$ ,  $n = 4$ ), which agrees with previous data within respective intermediate precision (Table 4).

The Lu mass fraction of GSR-16 diabase ranged from 0.325 to 0.329  $\mu\text{g g}^{-1}$ , and Hf mass fraction results range from 7.595 to 7.716  $\mu\text{g g}^{-1}$ . The mean  $^{176}\text{Lu}/^{177}\text{Hf}$  value was  $0.00605 \pm 0.006$  ( $2s$ ,  $n = 3$ ), and all Hf isotope compositions (spiked and non-spiked) were identical within

analytical reproducibility with a calculated mean of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282189 \pm 0.000009$  ( $2s$ ,  $n = 4$ ). To our knowledge, the Hf isotopic compositions presented in this study are the first reported for GSR-16 (Table 4).

#### Plutonic reference materials (GSR-1, GSR-7, GSR-9, GSR-10, GSR-14, GSR-15 and GSR-18)

As shown in Table 4, the mean value of Lu and Hf mass fractions for GSR-1 granite is  $1.188 \pm 0.030 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 2$ ) and  $5.583 \pm 0.157 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 2$ ), respectively. The mean  $^{176}\text{Lu}/^{177}\text{Hf}$  is  $0.03024 \pm 0.00162$  ( $2s$ ,  $n = 2$ ),



**Figure 2.** Comparison of Lu and Hf mass fractions of GSR-1, GSR-2 and GSR-3 obtained in this study with published values for Chinese rock reference materials.

**Table 5.**
**Comparison of Lu and Hf contents, and Hf isotope ratios obtained in this study with published values for Chinese rock reference materials**

Sample name	Lu [ $\pm 2s$ ] [ $\mu\text{g g}^{-1}$ ]	<i>n</i>	Hf [ $\pm 2s$ ] [ $\mu\text{g g}^{-1}$ ]	<i>n</i>	$^{176}\text{Lu}/^{177}\text{Hf}$ [ $\pm 2s$ ]	$^{176}\text{Hf}/^{177}\text{Hf}$ [ $\pm 2s$ ]	<i>n</i>	References
GBW07103 (GSR-1)	1.15 [0.12]		6.3 [0.8]					Xie <i>et al.</i> (1989)
	1.19 [0.06]		5.9 [0.4]					Bower <i>et al.</i> (1993)
	1.18 [0.08]	6	5.84 [0.60]	6				Qi and Grégoire (2000)
	1.11 [0.04]	4	5.88 [0.67]	4				Yu <i>et al.</i> (2001)
	1.13 [0.03]	5	5.75 [0.12]	4				Cotta and Enzweiler (2012)
	1.15 [0.07]	3	5.92 [0.33]	3				Zhang <i>et al.</i> (2012)
	1.15		6.3					Wang <i>et al.</i> (2013)
	1.082 [0.037]	3	5.148 [0.297]	3	0.02987 [0.00256]	0.282522 [17]	8	Cheng <i>et al.</i> (2015)
1.188 [0.030]	2	5.583 [0.157]	2	0.03024 [0.00162]	0.282519 [17]	3	This study	
					0.282521 [18]	5	Bao <i>et al.</i> (2018)	
					0.282522 [10]	6	Bao <i>et al.</i> (2018)	
GBW07104 (GSR-2)	0.12 [0.04]		2.9 [0.5]					Xie <i>et al.</i> (1989)
	0.108 [0.014]		2.7 [0.3]					Bower <i>et al.</i> (1993)
	0.11 [0.02]	4	2.71 [0.16]	4				Qi and Grégoire (2000)
	0.12		2.9					Wang <i>et al.</i> (2013)
	0.0997 [0.0014]	5	2.3664 [0.0686]	5	0.00599 [0.00014]	0.282639 [15]	10	Cheng <i>et al.</i> (2015)
0.104 [0.001]	3	2.501 [0.087]	3	0.00590 [0.00014]	0.282642 [20]	4	This study	
GBW07105 (GSR-3)	0.19 [0.07]		6.5 [0.8]					Xie <i>et al.</i> (1989)
	0.171 [0.017]		6.4 [0.4]					Bower <i>et al.</i> (1993)
	0.18 [0.02]	4	6.82 [0.32]	4				Qi and Grégoire (2000)
	0.165 [0.021]	3	6.7 [0.6]	3				Dulski (2001)
	0.18		6.1					Wang <i>et al.</i> (2013)
	0.1929 [0.0153]	5	5.865 [0.058]	5	0.00467 [0.00036]	0.282983 [07]	4	Li <i>et al.</i> (2005)
	0.16 [0.013]	5	6.5 [0.9]	5	0.00350	0.282985 [14]	3	Yang <i>et al.</i> (2011)
	0.155 [0.004]	3	6.171 [0.021]	3	0.00357 [0.00008]	0.282985 [10]	10	Cheng <i>et al.</i> (2015)
GBW07109 (GSR-7)	0.43		34					Fourny <i>et al.</i> (2016)
	0.446 [0.007]	3	36.62 [0.06]	3	0.00173 [0.00003]	0.282976 [08]	5	Bao <i>et al.</i> (2018)
						0.282991 [09]	4	This study
						0.282309 [06]	4	Wang <i>et al.</i> (2013)
						0.282316 [10]	4	Li <i>et al.</i> (2007)
								This study



**Table 5 (continued).**
**Comparison of Lu and Hf contents, and Hf isotope ratios obtained in this study with published values for Chinese rock reference materials**

Sample name	Lu [ $\pm 2s$ ] [ $\mu\text{g g}^{-1}$ ]	<i>n</i>	Hf [ $\pm 2s$ ] [ $\mu\text{g g}^{-1}$ ]	<i>n</i>	$^{176}\text{Lu}/^{177}\text{Hf}$ [ $\pm 2s$ ]	$^{176}\text{Hf}/^{177}\text{Hf}$ [ $\pm 2s$ ]	<i>n</i>	References
GBW07110 (GSR-8)	0.53		8.09					Wang <i>et al.</i> (2013)
	0.483 [0.005]	3	8.239 [0.147]	3	0.00834 [0.00024]	0.282499 [21] 0.282495 [10]	4 4	Li <i>et al.</i> (2007) This study
GBW07111 (GSR-9)	0.25		5.13					Wang <i>et al.</i> (2013)
	0.232 [0.006]	3	5.651 [0.865]	3	0.00586 [0.00075]	0.282133 [12]	4	This study
GBW07112 (GSR-10)	0.06		0.65					Wang <i>et al.</i> (2013)
	0.0481 [0.0055]	3	0.790 [0.019]	3	0.00865 [0.00082]	0.282905 [18] 0.282881 [18]	3 4	Li <i>et al.</i> (2005) This study
GBW07113 (GSR-11)	0.67		10.8			0.282699 [14]	4	Li <i>et al.</i> (2007)
	0.668 [0.046]	3	11.11 [0.61]	3	0.00855 [0.00102]	0.282701 [18]	4	Wang <i>et al.</i> (2013) This study
GBW07121 (GSR-14)	0.11 [0.02]	8	3.3 [1.0]	6				Wang <i>et al.</i> (2001)
	0.11 0.105 [0.002]	3	3.3 3.040 [0.446]	3	0.00491 [0.00068]	0.281500 [23]	4	Wang <i>et al.</i> (2013) This study
GBW07122 (GSR-15)	0.38 [0.1]		1.5 [0.4]	5				Wang <i>et al.</i> (2001)
	0.38 0.372 [0.0004]	3	1.5 1.583 [0.224]	3	0.0335 [0.0045]	0.283014 [14]	3	Wang <i>et al.</i> (2013) This study
GBW07123 (GSR-16)	0.34		9.2					Wang <i>et al.</i> (2013)
	0.327 [0.005]	3	7.669 [0.129]	3	0.00605 [0.00006]	0.282189 [09]	4	This study
GBW07124 (GSR-17)	0.16		4.9			0.282257 [02]	3	Li <i>et al.</i> (2005)
	0.156 [0.006]	3	4.388 [0.307]	3	0.00505 [0.00017]	0.282267 [13]	4	Wang <i>et al.</i> (2013) This study
GBW07125 (GSR-18)	0.03		0.8					Wang <i>et al.</i> (2013)
	0.0359 [0.0081]	3	0.864 [0.021]	3	0.00590 [0.00126]	0.282170 [07]	4	This study

[ $\pm 2s$ ] is the 2 standard deviation value of the mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of the replicate analyses [intermediate precision] reported as  $\times 10^6$ .

and all Hf isotope compositions (spiked and non-spiked) are identical within measurement repeatability with a calculated mean of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282519 \pm 0.000017$  ( $2s$ ,  $n = 3$ ). This value is in excellent agreement with the previously determined value ( $0.282521 \pm 0.000017$  ( $2s$ ,  $n = 10$ ); Cheng *et al.* 2015). Furthermore, Bao *et al.* (2018) presented a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282521 \pm 0.000018$  ( $2s$ ,  $n = 5$ ) and  $0.282520 \pm 0.000010$  ( $2s$ ,

$n = 6$ ) using two different digestion procedures and a Nu Plasma II MC-ICP-MS and Aridus II desolvation nebuliser system. For GSR-7 syenite, Lu mass fractions are tightly constrained ( $0.442$ – $0.449 \mu\text{g g}^{-1}$ ), and Hf mass fractions range from  $36.59$  to  $36.65 \mu\text{g g}^{-1}$ . The mean  $^{176}\text{Lu}/^{177}\text{Hf}$  is  $0.00173 \pm 0.00003$  ( $2s$ ,  $n = 3$ ), and all Hf isotope compositions are identical within intermediate measurement precision with a calculated mean of  $^{176}\text{Hf}/^{177}\text{Hf} =$

$0.283216 \pm 0.000010$  ( $2s$ ,  $n = 4$ ). This value is identical to that reported by Li *et al.* (2007) [ $0.282309 \pm 0.000006$  ( $2s$ ,  $n = 4$ )].

Similarly, all Hf isotope compositions for GSR-9 granodiorite yielded a mean of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282133 \pm 0.000012$  ( $2s$ ,  $n = 4$ ). This is the first reported Hf isotopic composition for GSR-9. Hf isotopic compositions are reported for four different GSR-10 gabbro aliquots, with all the measured data yielding a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of  $0.282881 \pm 0.000018$  ( $2s$ ,  $n = 4$ ), consistent with  $0.282905 \pm 0.000018$  ( $2s$ ,  $n = 4$ ) reported data by Li *et al.* (2005). This work presents the first  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios for GSR-14, GSR-15 and GSR-18 ( $0.281500 \pm 0.000023$  ( $2s$ ,  $n = 4$ ),  $0.283014 \pm 0.000014$  ( $2s$ ,  $n = 4$ ) and  $0.282170 \pm 0.000007$  ( $2s$ ,  $n = 4$ ), respectively) (Table 4).

### Ultramafic reference material (GSR-17)

Kimberlitic sample GSR-17 yielded Lu mass fractions ranging from  $0.153$  to  $0.159 \mu\text{g g}^{-1}$ , and Hf mass fractions ranging from  $4.224$  to  $4.528 \mu\text{g g}^{-1}$  (mean Lu and Hf;  $0.156 \pm 0.006 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 3$ ) and  $4.388 \pm 0.307 \mu\text{g g}^{-1}$  ( $2s$ ,  $n = 3$ ); Table 4). The corresponding mean  $^{176}\text{Lu}/^{177}\text{Hf}$  is  $0.00505 \pm 0.00017$  ( $2s$ ,  $n = 3$ ), and all Hf isotope compositions (spiked and non-spiked) are identical within intermediate measurement precision with a calculated mean of  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282267 \pm 0.000013$  ( $2s$ ,  $n = 4$ ). This value is identical to that reported by Li *et al.* (2005) ( $0.282257 \pm 0.000002$ ;  $2s$ ,  $n = 3$ ) and also close to duplicate analyses presented by Yang *et al.* (2009) for sample MY15, from the Ordovician Mengyin kimberlite in the North China Craton [ $0.282294 \pm 0.000008$  ( $2s$ ) and  $0.282294 \pm 0.000007$  ( $2s$ )].

### Comparison with previously published values and suitability as reference material

In Figure 1, we illustrated the  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of GSR-1, GSR-2 and GSR-3 based on all available data. Cheng *et al.* (2015) observed a large variation in  $^{176}\text{Hf}/^{177}\text{Hf}$  ( $0.282310$  and  $0.282510$ ) for GSR-1 and proposed sample inhomogeneity, but this finding was not supported by later work (Bao *et al.* 2018). If all the individual analyses are included, the  $^{176}\text{Hf}/^{177}\text{Hf}$  value of GSR-1 is  $0.282521 \pm 0.000014$  ( $2s$ ,  $n = 22$ ) (Figure 1a) except for two spurious data points. The Hf isotopic data for GSR-2 andesite from two laboratories are relatively reproducible and yields consistent  $^{176}\text{Hf}/^{177}\text{Hf}$  isotopic data. If all the individual analyses are included, the obtained  $^{176}\text{Hf}/^{177}\text{Hf}$  value of GSR-2 andesite is  $0.282640 \pm 0.000016$  ( $2s$ ,  $n = 14$ ) (Figure 1b). Combining all reported literature values

and those from this work, GSR-3 basalt (Figure 1c) yields a mean  $^{176}\text{Hf}/^{177}\text{Hf}$  value of  $0.282984 \pm 0.000012$  ( $2s$ ,  $n = 37$ ). This  $^{176}\text{Hf}/^{177}\text{Hf}$  reproducibility of GSR-3 suggests it could be as useful as the USGS basalt BCR-2 or BHVO-2 reference material (Foumy *et al.* 2016, Jweda *et al.* 2016).

Similarly, as shown in Figure 2 and Table 5, we compared the Lu and Hf content of GSR-1, GSR-2 and GSR-3 based on all available data by XRF, INNA, ICP-MS or ID-MC-ICP-MS (Xie *et al.* 1989, Bower *et al.* 1993, Qi and Grégoire 2000, Dulski 2001, Yu *et al.* 2001, Cotta and Enzweiler 2012, Zhang *et al.* 2012, Cheng *et al.* 2015, Foumy *et al.* 2016). The Hf content by isotope dilution method is slightly lower than that of ICP-MS. The Hf content values show a trend of decreasing with time because of new generation instrumentation, while for the Lu content, there is no obvious phenomenon, which may be due to the unclear isobaric interferences during ICP-MS measurement (e.g., light REE oxide interference on heavy REE). Meanwhile, as for the Lu/Hf ratios, our obtained  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios for GSR-1 and GSR-2 are inconsistent with those of Cheng *et al.* (2015), although there is a slightly larger difference for GSR-3 in this study and in Cheng *et al.* (2015) (Table 5). Compared with so many data accumulation of USGS and GSJ rock reference materials (e.g., BCR-2, BHVO-2, AGV-2, JA-2 and JB-2) (Schudel *et al.* 2015), although GSR rock reference materials have been issued and distributed for nearly 30 years (Xie *et al.* 1989), there are not many relevant data reports, which is also a principal reason for this work. In summary, we believe that isotope dilution method is still more reliable and recommended technique.

### Conclusions

In this contribution, we provide the first comprehensive study of Lu and Hf content and Hf isotopic data for thirteen readily available Chinese geochemical reference materials. Most of the data generated agree with the limited number of previously published values, and our results indicate that these rock reference materials are suitable for Lu-Hf isotopic analysis. Moreover, the Hf isotopic composition of GSR-9, GSR-14, GSR-15, GSR-16 and GSR-18 are only reported in this work. Our results indicate that these materials are suited to serve as primary reference materials for a range of unknown sample compositions and can be used to provide analytical quality control for inter-laboratory comparison. Widely available, they may become as broadly utilised as the well-characterised USGS and GSJ rock reference materials in the geochemical community.

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