

Rb, Sr, Sm and Nd elemental concentrations and Sr and Nd isotopic ratios of 13 Chinese rock reference materials using isotope dilution TIMS and MC-ICP-MS

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ABSTRACT

The suitability of 13 Chinese silicate rock certified reference materials for Sr and Nd isotope analyses was investigated. To indicate their homogeneity and to provide information values, we report Sr and Nd isotopic data and Rb, Sr, Sm and Nd concentrations for reference materials GBW07 103–105, 109–113 and 121–125 spanning a broad compositional range. Test portions were spiked with tracers enriched in ⁸⁷Rb–⁸⁴Sr and ¹⁴⁹Sm–^{145,146,150}Nd and digested using HF, HNO₃, and HClO₄ acid-dissolution procedures. Chemical purification involved cation-exchange and HEHEHP or Ln resins. Analyses involved different instruments at four laboratories, including thermal ionisation mass spectrometry (TIMS) and multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS). This study provides a comprehensive report of the Rb–Sr and Sm–Nd isotopic compositions of the reference materials, and the results indicate that the materials are comparable to those of well-characterised and widely utilized reference materials from the US Geological Survey and the Geological Survey of Japan. This is the first report of the Sr and Nd isotopic composition of standards GBW07111, GBW07112, GBW07121, GBW07122, GBW07123, GBW07124 and GBW07125. Our results are useful for quality control and assurance between laboratories and provide a robust reference-rock dataset for future studies involving classical Sr and Nd isotopic geochemistry.

1. Introduction

Quality assurance, quality control, and metrological traceability during the chemical analysis of geological samples require the characterization of reference materials [1–3]. Rapid developments in multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) have enabled precise isotopic ratio measurements for elements such as Li, B, Ca, Mg, Fe, Cu, Sr, Nd, Hf and Pb, resulting in widespread application of radiogenic isotope systems in geochemistry, cosmochemistry and environmental sciences [4–6]. Similarly, recent improvements in thermal-ionisation mass spectrometry (TIMS) have led to more precise analyses [7–15]. Mass-bias corrections in MC-ICP-MS are strongly

dependent on sample purity [16–22]. The plasma source produces more complex interferences than the TIMS source and is susceptible to matrix effects, as has long been recognised from single-collector ICP-MS studies [21]. Furthermore, the intrinsic instability of the plasma source means that most MC-ICP-MS analyses are run in static mode [17,18].

Quality-control protocols for the monitoring of accuracy and precision generally demand well-characterised, homogenous rock reference materials [1]. Furthermore, matrix effects can significantly affect accuracy, contrary to initial perceptions. Therefore, it is critical for a broad compositional range of isotopic reference materials to be available so that appropriate matrix-matched reference materials can be selected for the analysis of suites of unknown samples [3,23–25]. the US Geological

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Survey (USGS) and the Geological Survey of Japan (GSJ) rock reference materials with widespread distribution have been widely utilized for quality monitor in geochemistry communities.

Rock reference materials are essential for quality-control purposes in isotope-based research to ensure accurate analyses, testing the precision of measurement procedures, and inter-laboratory comparisons. The most useful and widely distributed reference materials have certified values for major elements, trace elements, and various isotopic systems [1,26–28]. For the most commonly utilized rock reference materials, many publications have reported major- and trace-element and isotope analyses involving reference materials of the USGS, such as the BCR-2, BHVO-2 and AGV-2, and the GSJ, such as JA-2, JB-2 and JG-2 [3,5,7–9,11,12].

In contrast, Chinese rock reference materials have been well characterised for only major- and trace-element compositions since their domestic distribution began in 1985 [29–35], and there is often little information concerning their isotopic compositions [3,25,27,36–42]. Considering their wide distribution and easy accessibility, the demand for such isotopic reference materials is understandable [41]. The Chinese reference materials will likely become a viable choice as supplies of USGS and GSJ standards near exhaustion after many years of usage or consumption.

There are currently no systematic Sr or Nd isotope databases for Chinese rock reference materials. Richardson et al. [36] first reported $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the basalt reference material GSR-3. Then, Li et al. [24] reported $^{143}\text{Nd}/^{144}\text{Nd}$ data for GSR-7, GSR-8 and GSR-11. The Sr and Nd isotopic compositions of GSR-3 were further reported by Fourny et al. [3]; Bao et al. [40] reported such data for GSR-1 and GSR-3, Yang et al. [41] for GSR-2 and GSR-7, and Guo et al. [42] for GSR-1, GSR-2 and GSR-3; and Liu et al. [43] reported Sr isotopic data for GSR-11. Recently Yang et al. [44] reported comprehensive Lu–Hf isotopic data for 13 Chinese rock reference materials. Sr and Nd isotopic data for GSR-3 have been reported by five particular laboratories, but not by others.

To expand the database for Chinese reference materials and to promote their application in geochemical analyses, we undertook systematic determinations of Rb, Sr, Sm and Nd concentrations and Sr and Nd isotopic compositions for 13 reference materials spanning a broad compositional range. The aims of the study were to provide comprehensive sets of high-precision Rb, Sr, Sm and Nd compositional and Sr and Nd isotopic data, to determine the isotopic homogeneity of the materials, and to provide information values. Our results indicate that the materials are comparable to the well-characterised and widely utilized USGS and GSJ reference materials, and that their Rb–Sr and Sm–Nd isotopic data should be useful in bulk geochemical analyses.

2. Sample descriptions

Chinese rock reference materials GBW07 103–105, 109–113 and 121–125, also known as GSR 1–3, 7–11 and 14–18 were obtained from the National Research Center for Certified Reference Materials (NRC–CRM), Beijing, China (<http://igeo.cags.ac.cn/>). Sample information of these rock reference materials and their major-element compositions in detail have been described elsewhere [41].

Volcanic: (1) GSR-2 is hornblende-phyric andesite with partial secondary carbonatization, obtained in the vicinity of the Meishan iron mine, Nanjing. (2) GSR-3 is an olivine basalt (primarily plagioclase, olivine, magnetite and augite) collected at Zhangjiakou, Hebei province. (3) GSR-8 is a trachyte from Late Jurassic subvolcanic 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. (4) 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 grayish-purple rock are feldspar, quartz, apatite, epidote,

magnetite, with a small amount of chlorite, sericite, and calcite. (5) GSR-16 is a diabase collected from an unknown location.

Plutonic: (1) GSR-1 is gray medium-grained biotite granite, collected at Chengzhou, Hunan province. There is tungsten, tin, and molybdenum mineralization in the contact zone between the granite and carbonate rocks. (2) GSR-7 is an early intrusive black aegirine nepheline syenite collected at Saima, Liaoning province. The Saima alkaline complex consists of grayish-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. (3) GSR-9 was collected from about 2.5 km northwest of Zhoukoudian Town, Fangshan County, Beijing. The dense, gray massive rocks belong to the Upper Jurassic Xishantou Formation and are semi-automorphic granular or porphyritic. The main rock-forming minerals are plagioclase, potassium feldspar, quartz, amphibole and biotite, with a small amount of magnetite, apatite, titanite etc. (4) GSR-10 was collected from the top of the ore-bearing strata at the bottom of the fault in the Lanjia volcanic deposit in the Panzhuhua rock mass, Dukou, Sichuan Province. The black-gray, dense, massive rock comprises iron-bearing gabbro in a coarse-grained 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. (5) GSR-14 is a granitic gneiss sample collected from the Archaean block in Fuping County, Hebei Province. The concentrations of most trace elements are low in this sample. (6) GSR-15 is an amphibolite sample collected from the Archaean block in Benxi City, Liaoning Province. Its protolith is a tholeiite and it is characterized by low rare earth element (REE) contents. (7) GSR-18 is pegmatite from an unknown location.

Ultramafic: (1) GSR-17 is a kimberlite from an unknown location, although it may be from the Ordovician Mengyin kimberlite in the North China Craton.

These 13 rock materials vary in chemical composition from felsic to mafic, which makes them well suitable for quality control of sample preparation and interlaboratory calibration. An aliquot (about ~5 g) of each rock powder was transferred into a small sample tube by using a piece of weighing paper and randomly deliver to different labs for interlaboratory comparison. USGS rock powders AGV-2 (andesite), BCR-2 (basalt), DNC-1 (dolerite) and GSP-2 (granite) and NRC CRMs GBW04411 (K-feldspar) and GBW04419 (basalt) were also used for quality-control purposes.

3. Analytical procedures

Analyses involved mainly TIMS using the following four instruments: MAT 262, Triton, Triton Plus (Thermo Fisher Scientific, Germany) and Isoprobe T (GV Instruments, England). Four institutes were involved in the study: the Institute of Geology, Chinese Academy of Geological Sciences (IG–CAGS), Beijing, China; Tianjin Center, China Geological Survey (TJC–CGS), Tianjin; Beijing Research Institute of Uranium Geology, China National Nuclear Corporation (BRIUG–CNNC), Beijing; and the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG–CAS), Beijing. Meanwhile, the Sm, Nd concentrations and Sr, Nd isotopic compositions of some aliquots were determined by MC–ICP–MS (Neptune Plus, Thermo Fisher Scientific, Germany) at the IGG–CAS.

All sample digestion and purification procedures were undertaken in Class 100 fume hoods in a Class 1000 clean laboratory. Elemental mass-fraction and isotope analyses were undertaken in Class 10,000 laboratories. Concentrated hydrochloric, nitric and hydrofluoric acids (Beijing Institute of Chemical Reagents) were twice purified using the Savillex™ DST-1000 apparatus sub-boiling distillation system. HClO_4 (Acros Organics, Geel, Belgium) were directly used. Procedures for sample dissolution, purification and MS analysis have been described elsewhere [5,6,10–14,43,45–50] and relative information for comparison is

summarised in Table 1. Brief descriptions for each laboratory measurement procedures follow.

3.1. IG-CAGS laboratory

3.1.1. Sample digestion

Rock powder was weighed into a Savillex PFA vials and concentrated HNO_3 , HF, HClO_4 were added to dissolve the sample at 100°C – 120°C over 10 day. After cooling, the solution was gently evaporated to dryness. HCl ($10\text{ mL } 6\text{ mol L}^{-1}$) was then added to the residue and evaporated to dryness. This step was repeated and the residue dissolved in $10\text{ mL } 4\text{ mol L}^{-1}\text{ HCl}$ at 100°C overnight. The sample solution was split into two aliquots, one chips ($\sim 15\%$) spiked with mixed ^{87}Rb – ^{84}Sr and ^{149}Sm – ^{146}Nd tracers for the determination of Rb, Sr, Sm and Nd concentrations using isotope dilution (ID) method, and the other ($\sim 85\%$) was analysed for Sr and Nd isotope composition (IC) without spike addition. The capsule was resealed and placed on a hot plate overnight at $\sim 100^\circ\text{C}$ in preparation for purification.

3.1.2. Sample purification

The sample solution was loaded onto a column packed with cation-exchange resin. The resin was washed with $4\text{ mol L}^{-1}\text{ HCl}$ to remove matrix elements. Rb and Sr fractions were eluted with a further 5 and 10 mL of $4\text{ mol L}^{-1}\text{ HCl}$, respectively. Finally, the rare-earth element (REE) fraction was eluted with $20\text{ mL } 4\text{ mol L}^{-1}\text{ HCl}$. The Rb, Sr and REE fractions were measured for the mixing ratios, using a MAT 262 TIMS for the Rb, Sr, Sm and Nd concentrations by ID method.

For Sr and Nd IC, the collected Sr fraction of high Rb/Sr samples (i.e., for GSR-1, GSR-8, GSR-11 and GSR-18) was further purified on a second cation-exchange column prior to TIMS analysis. The REE fraction was loaded onto an HEHEHP resin. The column was pre-cleaned using $2\text{ mL } 0.2\text{ mol L}^{-1}\text{ HCl}$ and 2.5 mL ultra pure water (Milli-Q, Millipore), and the REE fraction was evaporated to dryness and redissolved in $0.2\text{ mL } 0.2\text{ mol L}^{-1}\text{ HCl}$ before loading. After rinsing four times with $0.1\text{ mL } 0.2\text{ mol L}^{-1}\text{ HCl}$, most Ba, La, Ce and Pr were eluted with nine 0.2 mL aliquots of $0.2\text{ mol L}^{-1}\text{ HCl}$. Nd was eluted with 10 times of $0.2\text{ mol L}^{-1}\text{ HCl}$ for TIMS analysis [12–14,47].

3.1.3. Mass spectrometry

A MAT 262 was used for Rb, Sr, Sm and Nd isotope analyses. NIST SRM 987 Sr and GSB 04-3258-2015 Nd [51] were also analysed during the TIMS runs. The average $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the SRM 987 and GSB 04-3258-2015 reference solutions over all analytical sessions were 0.710250 ± 0.000010 and 0.512438 ± 0.000012 (2sd; $n = 12$), respectively. All Sr and Nd isotopic ratios were internally corrected

for mass fractionation based on $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively, with the exponential law. For Rb and Sm isotope analyses, measurement runs comprised 3–5 blocks of data acquisition with 10 cycles per block. Isotopic fractionation of $^{149}\text{Sm}/^{147}\text{Sm}$ was corrected off-line using $^{152}\text{Sm}/^{147}\text{Sm} = 0.56081$ as a reference value.

BCR-2, GBW04411 and GBW04419 were analysed during the above procedure (Table 2). Mean ratios for $^{87}\text{Sr}/^{86}\text{Sr}$ were 0.705005 ± 0.000032 (2sd; $n = 6$) for BCR-2 and 0.760123 ± 0.000022 (2sd; $n = 13$) for GBW04411; for $^{143}\text{Nd}/^{144}\text{Nd}$, they were 0.512633 ± 0.000017 (2sd; $n = 7$) for BCR-2 and 0.512734 ± 0.000029 (2sd; $n = 11$) for GBW04419, consistent with reference values [8,46,47,52,53].

3.2. TJC-CGS laboratory

3.2.1. Sample digestion

Rock powder was weighed into Savillex Teflon PFA vials and dissolved in a mixture of HF, HNO_3 , HClO_4 at 150°C for one week. The sample solution was then evaporated to dryness. The residue was re-dissolved in $6\text{ mol L}^{-1}\text{ HCl}$ and dried again. This step was repeated and after final drying, the residues were dissolved in $5\text{ mL } 2.5\text{ mol L}^{-1}\text{ HCl}$ at 100°C overnight. The sample solution was spiked with mixed ^{87}Rb – ^{84}Sr and ^{149}Sm – ^{146}Nd tracer for Rb, Sr, Sm and Nd concentrations, and the unspiked sample was conducted for Sr and Nd IC analysis. The capsule was resealed and placed on a hot plate overnight at $\sim 100^\circ\text{C}$ in preparation for purification.

3.2.2. Chemistry purification

The purification of Rb, Sr and REEs from the sample matrix was undertaken with a cation-exchange column. The resin was first washed with $2\text{ mL } 2.5\text{ mol L}^{-1}\text{ HCl}$, followed by $2.5\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$ to remove matrix elements. Rb was eluted with $1.5\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$ before the resin was rinsed with $3.5\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$ to remove residual Rb. The Sr fraction was then eluted with $3\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$, and the REE fraction with $10\text{ mL } 6\text{ mol L}^{-1}\text{ HCl}$. Some high-Rb samples as above-mentioned were treated a second time using cation exchange to eliminate ^{87}Rb interference with ^{87}Sr [43].

The isolation of Nd and Sm involved an HEHEHP resin. The column was pre-cleaned using $5\text{ mL } 6\text{ mol L}^{-1}\text{ HCl}$, $10\text{ mL } 3\text{ mol L}^{-1}\text{ HCl}$ and 2.5 mL ultra pure water (Milli-Q, Millipore). The REE fraction was evaporated gently to dryness, then dissolved in $0.2\text{ mL } 0.1\text{ mol L}^{-1}\text{ HCl}$. Using $0.4\text{ mL } 0.1\text{ mol L}^{-1}\text{ HCl}$, most of the Ba, La, Ce and Pr were eluted with $3\text{ mL } 0.2\text{ mol L}^{-1}\text{ HCl}$. Nd was then eluted with $1.5\text{ mL } 0.2\text{ mol L}^{-1}\text{ HCl}$, and the Sm fraction with $1.5\text{ mL } 0.4\text{ mol L}^{-1}\text{ HCl}$ [43].

Table 1

Information summary for Rb-Sr and Sm-Nd isotopic analyses in four laboratories.

Laboratories	n	Weight	Spiker	Resin for Rb, Sr, REE	Resin for Sm/Nd	Mass Fractions	Isotope Ratio	$^{87}\text{Sr}/^{86}\text{Sr}$ (MS)	$^{143}\text{Nd}/^{144}\text{Nd}$ (MS)
IG-CAGS	2	$\sim 150\text{ mg}$	^{87}Rb – ^{84}Sr , ^{149}Sm – ^{146}Nd	Bio-Rad AG50W-X8 (2.5 mL, 200–400 mesh)	HEHEHP	ID	IC	MAT 262 MAT 262	MAT 262 MAT 262
TJC-CGS	1	$\sim 100\text{ mg}$	^{87}Rb – ^{84}Sr , ^{149}Sm – ^{146}Nd	Bio-Rad AG50W-X12 (2 mL, 200–400 mesh)		ID		Triton	Triton
	1	$\sim 100\text{ mg}$			HEHEHP		IC	Triton	Triton
BRIUG-CNNC	2	$\sim 120\text{ mg}$	^{87}Rb – ^{84}Sr , ^{149}Sm – ^{145}Nd	Bio-Rad AG50W-X8 (2.5 mL, 200–400 mesh)	HEHEHP	ID	ID	Isoprobe-T	Isoprobe-T
IGG-CAS	2	$\sim 120\text{ mg}$	^{87}Rb – ^{84}Sr , ^{149}Sm – ^{150}Nd	Bio-Rad AG50W-X12 (2.5 mL, 200–400 mesh)	Eichrom Ln (2 mL, 100–150 μm)	ID	ID	Triton Plus	Neptune Plus
	2–3	$\sim 100\text{ mg}$		Eichrom Sr-specific (0.2 mL, 100–150 μm)			IC	Neptune Plus	Neptune Plus

The n means the duplicate analyses of rock powder. IG-CAGS: Institute of Geology, Chinese Academy of Geological Sciences, Beijing; TJC-CGS: Tianjin Center, China Geological Survey, Tianjin; BRIUG-CNNC: Beijing Research Institute of Uranium Geology, China National Nuclear Corporation; IGG-CAS: Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. N is the number of digestion. ID and IC mean isotope dilution and isotope composition, respectively. HEHEHP is from Beijing Research Institute of Chemical Engineering and Metallurgy and the particle size is 75–100 μm .

Table 2

Rb, Sr, Sm, Nd concentrations and Sr-Nd isotopic results for USGS and Chinese reference materials in four laboratories.

Sample	Rb [$\pm 2\text{sd}$] ($\mu\text{g g}^{-1}$)	Sr [$\pm 2\text{sd}$] ($\mu\text{g g}^{-1}$)	$^{87}\text{Rb}/^{86}\text{Sr}$ [$\pm 2\text{sd}$]	$^{87}\text{Sr}/^{86}\text{Sr}$ [$\pm 2\text{sd}$]	n	Sm [$\pm 2\text{sd}$] ($\mu\text{g g}^{-1}$)	Nd [$\pm 2\text{sd}$] ($\mu\text{g g}^{-1}$)	$^{147}\text{Sm}/^{144}\text{Nd}$ [$\pm 2\text{sd}$]	$^{143}\text{Nd}/^{144}\text{Nd}$ [$\pm 2\text{sd}$]	n	Remarks	Reference
BCR-2	47.6[2.9]	340[19]	0.405 [0.002]	0.705005 [32]	6	6.571 [0.064]	29.09 [0.53]	0.1366 [0.0024]	0.512633[17]	7	IG-CAGS	This work
Basalt	47.0[0.5]	340[7]	0.399 [0.008]	0.705020 [20]	10	6.516 [0.083]	28.52 [0.30]	0.1381 [0.0011]	0.512643[20]	10	TJC-CGS	This work
	47.1	340	0.401	0.704993 [12]	1	6.560	28.66	0.1384	0.512650[09]	1	IGG-CAS	This work
				0.705013 [10]	13				0.512637[12]	11		[3]
DNC-1	3.68	148	0.0715	0.705839 [12]	1	1.688	5.693	0.1792	0.512457[18]	1	IGG-CAS	This work
Dolerite	3.1	144		0.705821 [20]	15	1.43	4.9		0.512473[22]	12		[3]
GSP-2				0.765157 [07]	2				0.511375[12]	2	TJC-CGS	This work
Granodiorite				0.765144 [75]	8				0.511374[03]	5		[3]
AGV-2	64.7[0.6]	653[4]	0.286 [0.001]	0.703978 [32]	3	5.449 [0.116]	30.11 [0.69]	0.1094 [0.0009]	0.512796[12]	3	IGG-CAS	This work
Andesite				0.703981 [09]	10				0.512791[13]	8		[3]
GBW04411	258 [22]	159[4]	4.37[0.34]	0.760123 [122]	13						IG-CAGS	This work
K-feldspar	250 [16]	159[1]	4.87[0.29]	0.760063 [95]	4						BRIUG- CNNC	This work
	249 [3]	159[2]	4.59[0.15]	0.759990 [250]	9							[46]
				0.760008 [23]	1						IG-CAGS	[47]
GBW04419						3.134 [0.247]	10.16 [0.66]	0.1865 [0.0076]	0.512734[29]	11	IG-CAGS	This work
Basalt						3.055 [0.234]	10.01 [0.82]	0.1845 [0.0018]	0.512722[27]	4	BRIUG- CNNC	This work
						3.032 [0.072]	10.10 [0.26]	0.1815 [0.0016]	0.512725[15]	7		[53]

The [$\pm 2\text{sd}$] is the 2 standard deviation and on the average $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the duplicate analyses (n) reported as times 10^6 . IG-CAGS: Institute of Geology, Chinese Academy of Geological Sciences, Beijing; TJC-CGS: Tianjin Center, China Geological Survey, Tianjin; BRIUG-CNNC: Beijing Research Institute of Uranium Geology, China National Nuclear Corporation; IGG-CAS: Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing.

3.2.3. Mass spectrometry

The Rb, Sr, Sm and Nd isotope analyses employed a Triton TIMS. The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively, using the exponential law. The NIST SRM 987 Sr and GSJ JNdi-1 Nd standards were used to TIMS measurement. The mean $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were 0.710251 ± 0.000016 and 0.512114 ± 0.000012 (2sd; n = 12), respectively, consistent with previously reported values [12,13,43]. For the Rb and Sm isotope analyses, the Rb sample was first dissolved in 20 μL 2.5 mol L^{-1} HCl, and 5 % of the sample was loaded onto the Re filament. Isotopic fractionation of $^{149}\text{Sm}/^{147}\text{Sm}$ was corrected using a $^{152}\text{Sm}/^{147}\text{Sm}$ ratio of 0.56081 as an off-line reference value [10,11].

USGS GSP-2 and BCR-2 powder rock reference materials were analysed using the same analytical procedures (Table 2), yielding respective ratios as follows: $^{87}\text{Sr}/^{86}\text{Sr} = 0.765157 \pm 0.000007$ (2sd; n = 2) and 0.705020 ± 0.000020 (2sd; n = 10); $^{143}\text{Nd}/^{144}\text{Nd} = 0.511375 \pm 0.000012$ (2sd; n = 2) and 0.512643 ± 0.000020 (2sd; n = 10), consistent with previous values [8,43].

3.3. BRIUG–CNNC laboratory

3.3.1. Sample digestion

Rock powder was weighed into Savillex PFA beakers and spiked with ^{87}Rb – ^{84}Sr and ^{149}Sm – ^{145}Nd isotopic tracer solution. Samples were then dissolved in concentrated HF + HNO_3 at 150 $^\circ\text{C}$. After cooling, the

solution was evaporated to dryness before 2 mL concentrated HNO_3 was added, and the solution was again heated to dryness. 6 mol L^{-1} HCl was then added to the residue and evaporated to dryness. This was repeated, and after the samples were again dry the residues were dissolved in 5 mL 4 mol L^{-1} HCl at 100 $^\circ\text{C}$ overnight.

3.3.2. Sample purification

The sample solution was loaded onto a cation-exchange resin. The resin was washed using 17 mL 2 mol L^{-1} HCl to remove most matrix elements. The Rb and Sr fractions were then eluted with 5 mL 2 mol L^{-1} HCl and 10 mL 3 mol L^{-1} HCl, respectively. Finally, the REE fraction was eluted with 15 mL 6 mol L^{-1} HCl.

The separation of Nd and Sm employed an HEHEHP resin pre-cleaned using 5 mL 3 mol L^{-1} HCl, 10 mL 0.3 mol L^{-1} HCl and 2.5 mL Milli-Q H_2O . The REE eluate from the cation-exchange step was evaporated to dryness, redissolved in 0.3 mL 0.05 mol L^{-1} HCl and loaded onto the HEHEHP resin. After rinsing using 0.4 mL 0.1 mol L^{-1} HCl, most of the Ba, La, Ce and Pr was eluted with 3.0 mL 0.2 mol L^{-1} HCl. The Nd fraction was then eluted with 4.5 mL 0.15 mol L^{-1} HCl, and the Sm fraction was eluted with 6 mL 0.3 mol L^{-1} HCl [48].

3.3.3. Mass spectrometry

Rb, Sr, Sm and Nd isotope analyses involved an Isoprobe-T TIMS [10, 11, 48]. Data reduction was performed off-line using a self-written Excel visual basic macro program for interference corrections, spike

subtraction and mass-fractionation correction. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were corrected for mass fractionation against ratios of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively. Measured values for NIST SRM 987 and JNdi-1 standards were $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245 \pm 0.000016$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512113 \pm 0.000010$ (2sd; $n = 12$), consistent with published values [10,11]. Measured $^{149}\text{Sm}/^{147}\text{Sm}$ ratios were corrected for mass fractionation against a $^{152}\text{Sm}/^{147}\text{Sm}$ ratio of 0.56081 [10]. The Rb analyses were undertaken as for Sm.

GBW04411 and GBW04419 standards were analysed for Sr and Nd isotopic compositions to monitor the accuracy of analytical procedures (Table 2). Measured ratios were $^{87}\text{Sr}/^{86}\text{Sr} = 0.760063 \pm 0.000095$ for GBW04411 and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512722 \pm 0.000027$ (2sd; $n = 4$) for GBW04419, consistent with reference values [47,52,53].

3.4. IGG-CAS laboratory

3.4.1. Sample digestion

Sample powder was weighed into Savillex PFA vials, mixed with ^{87}Rb - ^{84}Sr and ^{149}Sm - ^{150}Nd tracer solution and gently evaporated to dryness. Residues were dissolved in $\text{HF} + \text{HNO}_3 + \text{HClO}_4$ at 100°C - 120°C over one week. After cooling, the solution was gently evaporated to dryness, and then to HClO_4 fumes. The residue was re-dissolved twice in $1.5\text{ mL } 6\text{ mol L}^{-1}\text{ HCl}$ and re-evaporated. After the final drying, the residue was dissolved in $1.5\text{ mL } 2.5\text{ mol L}^{-1}\text{ HCl}$ at 100°C in preparation for purification.

3.4.2. Sample purification

The sample solution was loaded onto a quartz column packed with cation-exchange resin preconditioned using $2\text{ mL } 2.5\text{ mol L}^{-1}\text{ HCl}$. The resin was then washed using a further $2\text{ mL } 2.5\text{ mol L}^{-1}\text{ HCl}$ and $2.5\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$ to remove unwanted matrix elements. Rb was eluted with $1.5\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$. To minimise the isobaric interference of ^{87}Rb on ^{87}Sr , the resin was rinsed using $4\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$ to remove residual Rb. Finally, the Sr fraction was eluted with $3\text{ mL } 5\text{ mol L}^{-1}\text{ HCl}$ and gently evaporated to dryness. The REE fraction was eluted with $6\text{ mL } 6\text{ mol L}^{-1}\text{ HCl}$.

Residue from the Sr eluate was dissolved in $1\text{ mL } 3.0\text{ mol L}^{-1}\text{ HNO}_3$, and this solution was loaded onto a Bio-Rad polypropylene column freshly packed with Sr-specific resin. The resin was rinsed using $20\text{ mL } 3\text{ mol L}^{-1}\text{ HNO}_3$, and Sr was eluted with a 3 mL of $0.05\text{ mol L}^{-1}\text{ HNO}_3$. The first mL was discarded, and the next 5 mL was collected for TIMS or MC-ICP-MS analysis. This further Sr purification is particularly necessary for high-Rb/Sr samples such as granite, rhyolite, amphibolite and pegmatite due to the isobaric interference of ^{87}Rb on ^{87}Sr .

The REE fraction was gently evaporated and redissolved in $0.5\text{ mL } 0.25\text{ mol L}^{-1}\text{ HCl}$ and loaded onto an Ln spec resin. La, Ce and Pr were eluted with $6\text{ mL } 0.25\text{ mol L}^{-1}\text{ HCl}$ before Nd was eluted with a further $6\text{ mL } 0.25\text{ mol L}^{-1}\text{ HCl}$. Finally, the Sm fraction was eluted with $10\text{ mL } 0.4\text{ mol L}^{-1}\text{ HCl}$.

3.4.3. Mass spectrometry

The Rb and Sr isotopic ratios were determined using a Triton Plus. The corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were then normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ by applying the exponential law. The mean measured $^{87}\text{Sr}/^{86}\text{Sr}$ value of NIST SRM 987 reference solution, over all analytical sessions, was 0.710250 ± 0.000016 (2sd; $n = 16$), consistent with previously published data. For Rb isotope analyses, the Rb sample was dissolved in $20\text{ }\mu\text{L } 2.5\text{ mol L}^{-1}\text{ HCl}$, and 5 % was loaded onto the Ta filament.

The Sm and Nd isotope analyses involved a Neptune Plus. The raw data were exported and reduced off-line to correct for instrumental mass bias and tracer contributions. Nd concentrations were calculated from the corrected $^{150}\text{Nd}/^{144}\text{Nd}$ ratio, using the ID equation. Data reduction employed a self-written Excel VBA (Visual Basic for Applications) macro program, with which interference corrections and spike subtractions were made, followed by a mass-fractionation correction based on the

exponential law ($^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$). These calculations were performed cycle by cycle. For mass-fractionation correction, Sm was normalised to $^{147}\text{Sm}/^{149}\text{Sm} = 1.0868$ using the exponential law. The mean measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of JNdi-1, over all analytical sessions, was 0.512115 ± 0.000012 (2sd; $n = 16$).

USGS BCR-2, AGV-2 and DNC-1 were analysed for quality-control purposes using the same procedure (Table 2). The Sr and Nd isotopic ratios of BCR-2, DNC-1 and AGV-2 were $^{87}\text{Sr}/^{86}\text{Sr} = 0.704993 \pm 0.000012$ (2sd), 0.705839 ± 0.000012 (2sd) and 0.703978 ± 0.000032 (2sd; $n = 3$); $^{143}\text{Nd}/^{144}\text{Nd} = 0.512650 \pm 0.000009$ (2sd), 0.512457 ± 0.000018 (2sd) and 0.512796 ± 0.000012 (2sd; $n = 3$), respectively, consistent with reported reference values [3,5–7,12,13].

4. Results and discussion

Tables 2–4.

For comparison between laboratories, all data for geological samples are reported relative to the NIST SRM 987 and JNdi-1 reference values of $^{87}\text{Sr}/^{86}\text{Sr} = 0.710248$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$, respectively. For the USGS and NRC-CRM certified reference materials [3,8,46,47,53], there were no significant discrepancies in $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ ratios within or between laboratories (Table 2), indicating that the materials provide data of high quality for use in Sr and Nd isotope analyses.

The Rb, Sr, Sm and Nd concentrations and Sr and Nd isotopic data for the 13 Chinese rock reference materials analysed in the four laboratories are summarised in Table 3. There were negligible differences between Nd isotopic ratios obtained with or without spikes, and individual measurement repeatability (2sd) for spiked and unspiked aliquots were comparable. High $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ internal precision was achieved in every run (e.g., ± 0.000010 to ± 0.000018 for GSR-18). Any reasonable differences in Sr isotopic compositions are likely due to high Rb/Sr ratios, as in GSR-1, GSR-8, GSR-11 and GSR-18. Published isotopic ratios are provided in Table 4 for comparison, and comparisons between our data and data from previous studies are illustrated in Figs. 1–4.

4.1. Volcanic reference materials GSR-2, GSR-3, GSR-8, GSR-11 and GSR-16

Our measured mean Rb and Sr concentrations of GSR-2 andesite are respectively $40.4 \pm 5.8\text{ }\mu\text{g g}^{-1}$ (2sd; $n = 6$) and $840 \pm 43\text{ }\mu\text{g g}^{-1}$ (2sd; $n = 7$) (Table 3), with a corresponding mean $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 0.135 ± 0.010 (2sd; $n = 4$) (see Fig. 1). All Sr isotopic compositions (spiked and non-spiked) agree well with a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.704923 ± 0.000037 (2sd; $n = 8$), consistent with the previously published value of 0.704929 ± 0.000012 (2sd) [42] and 0.704914 ± 0.000015 (2sd) [44]. Similarly, the GSR-2 sample yielded mean Sm and Nd concentrations of 3.27 ± 0.17 and $17.91 \pm 0.83\text{ }\mu\text{g g}^{-1}$ (2sd; $n = 7$), respectively (Table 3), with a corresponding mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1101 ± 0.0016 , consistent with the published value of 0.1099 [49]. All measured Nd isotopic compositions (spiked and non-spiked) are identical to each other, with a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512393 ± 0.000032 (2sd; $n = 8$), consistent with published values of 0.512377 ± 0.000014 (2sd, $n = 17$) [42], 0.512395 ± 0.000008 (2sd, $n = 1$) [49] and 0.512382 ± 0.000010 (2sd, $n = 1$) (Table 4) [44].

For GSR-3 basalt, the five laboratories had previously reported $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios (Table 4). Richardson et al. firstly presented a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.704080 ± 0.000020 (2sd; $n = 2$) [39]. The Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia (UBC), Canada, has undertaken systematic analyses of Sr–Nd–Hf–Pb isotopic compositions using MC-ICP-MS and TIMS, with reported $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.704076 ± 0.000018 (2sd; $n = 5$) and 0.512901 ± 0.000011 (2sd; $n = 11$), respectively [3]. Bao et al. [40] reported mean $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.704089 ± 0.000025 (2sd; $n = 5$) and 0.512899 ± 0.000009 (2sd; $n = 6$), respectively, and Yang et al. [49] recorded

Table 3
Individual Rb, Sr, Sm, Nd concentrations and Sr-Nd isotopic ratios of Chinese rock reference materials.

Sample [Aliquot no]	No	Rb [$\mu\text{g g}^{-1}$]	Sr [$\mu\text{g g}^{-1}$]	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr} (\pm 2\text{se})$	$^{87}\text{Sr}/^{86}\text{Sr}^a (\pm 2\text{se})$	Sm [$\mu\text{g g}^{-1}$]	Nd [$\mu\text{g g}^{-1}$]	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd} (\pm 2\text{se})$	$^{143}\text{Nd}/^{144}\text{Nd}^a (\pm 2\text{se})$
GBW07103	a1	513	114	13.1	0.738371(13)		9.77	43.93			
(GSR-1)	a2	510	110	13.4	0.738378(15)		9.67	43.02	0.1358	0.512250(08)	
Granite	b1	471	109				9.54	44.06	0.1309	0.512224(04)	
[490,288]	c1	505	110				9.65	44.70			
	c2	505	110			0.738408(16)	9.56	44.20	0.1307	0.512220(10)	0.512249(06)
	d1	471	108	12.6	0.738383(12)	0.738363(12)	9.56	44.46	0.1300	0.512242(07)	0.512245(07)
	d2				0.738336(08)	0.738409(17)	9.71	45.85	0.1281	0.512234(06)	0.512226(05)
Mean [$\pm 2\text{sd}$]		496[39]	111[05]	13.0[0.8]	0.738378[51]		9.64[0.17]	44.32[1.72]	0.1311[57]	0.512236[24]	
GBW07104	a1	40.8	854	0.138	0.704913(10)		3.29	17.94			
(GSR-2)	a2	40.7	839	0.140	0.704948(16)		3.29	18.09	0.1099	0.512401(07)	
Andesite	b1	36.8	818	0.130	0.704886(07)		3.23	17.94	0.1090	0.512375(10)	
[14,054]	c1	41.6	831				3.22	17.60			
	c2	44.8	882			0.704940(15)	3.44	18.70	0.1112	0.512367(06)	0.512409(05)
	d1	37.4	828	0.131	0.704925(10)	0.704926(14)	3.22	17.63	0.1103	0.512387(10)	0.512407(05)
	d2		830		0.704923(14)	0.704919(20)	3.19	17.47	0.1104	0.512391(12)	0.512410(08)
Mean [$\pm 2\text{sd}$]		40.4[5.8]	840[43]	0.135[0.010]	0.704923[37]		3.27[0.17]	17.91[0.83]	0.1101[16]	0.512393[32]	
GBW07105	a1	41.1	1212	0.0981	0.704120(13)		10.13	50.21	0.1220	0.512932(08)	
(GSR-3)	a2	40.6	1217	0.0966	0.704093(14)		10.24	49.24			
Basalt	b1	37.5	1182	0.0919	0.704047(08)		10.40	52.33	0.1201	0.512898(07)	
[630,270]	c1	41.5	1167				9.94	49.50			
	c2	41.3	1169			0.704066(13)	10.10	51.10			0.512902(08)
	d1	38.4	1151	0.0964	0.704107(11)	0.704075(14)	10.01	50.03	0.1209	0.512906(09)	0.512879(10)
	d2	38.2	1162	0.0951	0.704056(15)	0.704092(17)	10.25	50.96	0.1215	0.512914(05)	0.512899(18)
Mean [$\pm 2\text{sd}$]		39.8[3.4]	1180[51]	0.0956[0.0047]	0.704082[51]		10.15[0.31]	50.48[2.13]	0.1211[17]	0.512904[32]	
GBW07109	a1	138	1283	0.312	0.709587(12)		9.16	63.90	0.0867	0.511873(10)	
(GSR-7)	a2	141	1301	0.313	0.709564(12)		9.21	64.17			
Syenite	b1				0.709499(08)		9.15	65.82	0.0840	0.511824(06)	
	c1	145	1256				9.26	65.60			
	c2	145	1256			0.709519(13)	9.28	65.60	0.0855	0.511821(08)	
	d1	130	1231	0.306	0.709543(13)	0.709556(20)	9.20	66.13	0.0841	0.511834(06)	0.511831(08)
	d2	134	1214			0.709545(14)	9.07	65.02	0.0843	0.511840(06)	0.511853(14)
Mean [$\pm 2\text{sd}$]		139[12]	1257[64]	0.313[0.011]	0.709545[58]		9.19[0.14]	65.18[1.70]	0.0849[23]	0.511840[36]	
GBW07110	a1	194	341	1.65	0.710295(16)		8.20	45.89			
(GSR-8)	a2	196	345	1.64	0.710303(15)		8.26	46.50	0.1074	0.512201(10)	
Trachyte	b1	186	344	1.56	0.710244(08)		8.20	47.21	0.1050	0.512207(09)	
	c1	199	337				8.34	47.40	0.1064	0.512196(07)	
	c2	191	339			0.710289(11)	8.22	46.70	0.1064		0.512184(10)
	d1	186	332	1.62	0.710321(14)	0.710292(19)	8.20	47.19	0.1050	0.512189(07)	0.512168(06)
	d2	182	334	1.58	0.710296(16)	0.710287(12)	8.30	47.76	0.1050	0.512180(08)	0.512188(08)
Mean [$\pm 2\text{sd}$]		190[12]	339[10]	1.61[0.07]	0.710291[44]		8.25[0.11]	46.95[1.26]	0.1058[22]	0.512189[25]	
GBW07111	a1	76.2	1310	0.168	0.705686(14)		7.69	47.91			
(GSR-9)	a2	76.3	1325				7.70	47.74			
Granodiorite	b1	70.6	1279	0.160	0.705668(09)		7.59	48.56	0.0945	0.511824(06)	
	c1	76.9	1259				7.51	47.20	0.0962	0.511804(15)	
	c2	78.4	1286			0.705673(14)	7.60	47.70			
	d1	72.2	1296	0.161	0.705707(10)	0.705711(16)	7.63	48.80	0.0945	0.511839(07)	0.511826(07)
	d2	71.8	1258	0.165	0.705716(11)	0.705690(23)	7.52	47.64	0.0954	0.511846(08)	0.511838(08)
Mean [$\pm 2\text{sd}$]		75[6]	1288[50]	0.164[0.008]	0.705693[38]		7.61[0.15]	47.94[1.11]	0.0951[16]	0.511833[33]	

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Table 3 (continued)

Sample [Aliquot no]	No	Rb [$\mu\text{g g}^{-1}$]	Sr [$\mu\text{g g}^{-1}$]	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\text{se}$)	$^{87}\text{Sr}/^{86}\text{Sr}^a$ ($\pm 2\text{se}$)	Sm [$\mu\text{g g}^{-1}$]	Nd [$\mu\text{g g}^{-1}$]	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2\text{se}$)	$^{143}\text{Nd}/^{144}\text{Nd}^a$ ($\pm 2\text{se}$)
GBW07112 (GSR-10)	a1	1.92	730	0.00760	0.704390(12)		1.37	3.95	0.2100	0.512804(05)	
	a2	2.04	749	0.00790	0.704428(12)		1.39	4.47	0.1875	0.512806(08)	
Gabbro	b1	1.72	636				1.23	4.04	0.1836	0.512790(06)	
	c1	1.94	625				1.23	3.99	0.1864	0.512752(08)	
	c2	1.99	635			0.704374(18)	1.24	4.01	0.1870	0.512770(08)	0.512765(16)
	d1	1.81	641	0.00820	0.704429(17)	0.704437(20)	1.24	4.04	0.1854	0.512763(17)	0.512785(17)
	d2	1.85	659	0.00810	0.704386(11)	0.704398(18)	1.26	4.11			0.512789(18)
Mean [$\pm 2\text{sd}$]		1.89[0.22]	667[101]	0.00795[0.00053]	0.704406[50]		1.28[0.14]	4.09[0.35]	0.1900[198]	0.512780[38]	
GBW07113 (GSR-11)	a1	226	41.8				12.00	64.69			
	a2	223	41.3				11.83	63.94			
Rhyolite	b1	211	39.4	15.5	0.733955(09)		11.73	65.15	0.1089	0.512406(05)	
	c1	219	41.0	15.4	0.734050(14)		11.30	61.90	0.1104	0.512407(09)	
	c2	239	43.1	16.0	0.734058(19)		11.30	61.90	0.1104	0.512370(09)	
	d1	215	40.8	15.3	0.733973(12)	0.733969(17)	11.99	66.72	0.1086	0.512402(35)	0.512415(08)
	d2	215	40.9			0.733976(18)	11.97	66.80	0.1083	0.512415(12)	0.512406(06)
	d3	211	40.2			0.733963(18)	11.88	65.89	0.1090	0.512424(10)	0.512409(06)
Mean [$\pm 2\text{sd}$]		220[19]	41.0[2.2]	15.5[0.6]	0.733987[85]		11.84[0.48]	65.12[3.25]	0.1092[16]	0.512406[30]	
GBW07121 (GSR-14)	a1	61.6	785	0.227	0.709409(15)		3.33	19.95	0.1007	0.511084(06)	
	a2	61.1	777	0.228	0.709492(16)		3.21	19.35	0.1002	0.511111(08)	
Granitic gneiss [110,014]	b1	55.0	722	0.220	0.709405(12)		3.34	21.07			
	c1	61.3	745				3.22	19.50			
	c2	61.5	734			0.709478(12)	3.23	19.70			0.511073(10)
	d1	57.3	728	0.228	0.709460(19)	0.709476(15)	3.13	18.72	0.1011	0.511094(12)	0.511057(08)
	d2	57.1	726	0.228	0.709448(18)	0.709451(11)	3.12	19.03	0.0992	0.511075(13)	0.511084(10)
Mean [$\pm 2\text{sd}$]		59.3[5.5]	745[51]	0.226[0.007]	0.709452[63]		3.23[0.17]	19.62[1.52]	0.1003 [17]	0.511083 [34]	
GBW07122 (GSR-15)	a1	27.2	145	0.541	0.719439(13)		2.12	6.15	0.2088	0.512914(10)	
	a2	27.8	150	0.535	0.719478(14)		2.20	6.38	0.2089	0.512893(09)	
Amphibolite [0332]	b1	25.9	138	0.542	0.719387(10)		2.20	6.57			
	c1	28.5	144				2.15	6.33			
	c2	28.5	144			0.719426(20)	2.16	6.38	0.2047	0.512875(05)	0.512878(09)
	d1	26.4	142	0.540	0.719471(11)	0.719452(17)	2.28	6.74	0.2046	0.512894(18)	0.512860(11)
	d2	26.4	141	0.543	0.719438(15)	0.719455(11)	2.30	6.81	0.2044	0.512898(22)	0.512890(13)
Mean [$\pm 2\text{sd}$]		27.3[2.3]	144[8]	0.540[0.006]	0.719443[57]		2.20[0.13]	6.48[0.47]	0.2063[47]	0.512888[33]	
GBW07123 (GSR-16)	a1	48.2	539	0.259	0.711680(14)		9.29	44.96	0.1249	0.512034(14)	
	a2	47.8	535	0.259	0.711707(15)		9.22	43.61	0.1278	0.512007(08)	
Diabase	b1	43.8	478	0.265	0.711641(04)		9.00	44.86	0.1212	0.511998(05)	
	c1	48.6	501				8.82	43.00	0.1240	0.512010(10)	
	c2	47.5	492			0.711687(18)	8.84	43.60	0.1226	0.511973(09)	0.512007(09)
	d1	45.0	509	0.256	0.711658(11)	0.711689(17)	9.38	46.12	0.1230	0.512018(06)	0.512017(09)
	d2	45.1	511	0.256	0.711653(13)	0.711697(18)	9.28	45.73	0.1227	0.512017(06)	0.511994(09)
Mean [$\pm 2\text{sd}$]		46.6[3.8]	509[44]	0.259[0.008]	0.711676[47]		9.12[0.46]	44.56[2.35]	0.1237[43]	0.512008[33]	

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Table 3 (continued)

Sample [Aliquot no]	No	Rb [$\mu\text{g g}^{-1}$]	Sr [$\mu\text{g g}^{-1}$]	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\text{se}$)	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\text{se}$)	Sm [$\mu\text{g g}^{-1}$]	Nd [$\mu\text{g g}^{-1}$]	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2\text{se}$)	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2\text{se}$)
GBW07124 (GSR-17) Kimberlite	a1	27.1	304	0.258	0.713541(13)	0.713541(13)	6.35	44.62	0.0860	0.512123(06)	0.512123(06)
	a2	27.7	300	0.268	0.713584(12)	0.713584(12)	6.52	45.67	0.0863	0.512119(07)	0.512119(07)
	b1						6.07	43.87	0.0837	0.512083(04)	0.512083(04)
	c1	27.8	282				6.28	44.30	0.0857	0.512088(07)	0.512088(07)
	c2	28.1	288			0.713554(16)	6.28	44.30	0.0857	0.512088(07)	0.512088(07)
	d1	25.6	282	0.263	0.713553(10)	0.713554(16)	6.18	44.34	0.0842	0.512109(08)	0.512099(06)
	d2	25.8	283	0.265	0.713573(10)	0.713576(13)	6.18	44.38	0.0842	0.512104(07)	0.512086(09)
Mean [$\pm 2\text{sd}$]		27.0[2.1]	290[20]	0.264[0.008]	0.713561[32]		6.25[0.29]	44.45[1.18]	0.0850[20]	0.512097[33]	
GBW07125 (GSR-18) Pegmatite	a1	168	48.1				0.257	1.82	0.0854	0.511656(14)	
	a2	168	47.7	10.2	0.740853(15)		0.262	1.70	0.0934	0.511642(09)	
	b1	159	44.8							0.511673(10)	
	c1	163	45.0	10.5	0.740843(16)		0.234	1.43			
	c2	167	47.4				0.232	1.44			
	d1	159	45.5	10.2	0.740795(17)		0.240	1.52	0.0955	0.511620(08)	
	d2	159	45.6	10.1	0.740801(13)	0.740851(23)	0.233	1.46	0.0964	0.511623(10)	
Mean [$\pm 2\text{sd}$]		163[9]	46.3[2.8]	10.3[0.3]	0.740829[57]		0.243[0.027]	1.56[0.32]	0.0927[100]	0.511643[44]	

^a Means unspiked, other spiked. The [$\pm 2\text{sd}$] is the 2 standard deviation and on the average. $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the replicate analyses reported as times 10^6 . The [$\pm 2\text{sd}$] is the 2 standard deviation and on the average. $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the replicate analyses reported as times 10^4 . a means analysis in Institute of Geology, Chinese Academy of Geological Sciences (IG-CAGS), Beijing; b means analysis in Tianjin Center, China Geological Survey (TJ-CGS), Tianjin; c means analysis in Beijing Research Institute of Uranium Geology, China National Nuclear Corporation (BRIUG-CNNC); d means analysis in Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG-CAS), Beijing.

mean $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.1224 ± 0.0067 and 0.512909 ± 0.000010 (2sd; $n = 2$), respectively. More recently, Guo et al. [42] presented mean $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios of 0.704093 ± 0.000010 (2sd; $n = 52$) and 0.512885 ± 0.000018 (2sd; $n = 17$), respectively. Our mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for eight aliquots was 0.704082 ± 0.000051 (2sd; $n = 8$), consistent with earlier data. The GSR-3 sample yielded mean Sm and Nd concentrations of 10.15 ± 0.31 and $50.48 \pm 2.13 \mu\text{g g}^{-1}$ (2sd; $n = 7$), respectively (Table 4). The corresponding mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is 0.1211 ± 0.0017 (2sd; $n = 4$), and all Nd isotopic compositions (spiked and non-spiked) agree well with a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512904 ± 0.000032 (2sd; $n = 7$), consistent with previously determined values [3,27,39,40,42,49]. Results for GSR-3 basalt from this and previous studies indicate its homogeneity in Sr and Nd isotopic compositions.

Our mean Rb and Sr concentrations of GSR-8 trachyte are 190 ± 12 and $339 \pm 10 \mu\text{g g}^{-1}$ (2sd; $n = 7$), respectively, with a corresponding mean $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 1.61 ± 0.07 (2sd; $n = 5$). All Sr isotopic compositions (spiked and non-spiked) are equal with a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710291 ± 0.000044 (2sd; $n = 8$). The GSR-8 sample yielded mean Sm and Nd concentrations of 8.25 ± 0.11 and $46.95 \pm 1.26 \mu\text{g g}^{-1}$ (2sd; $n = 7$), respectively (Table 4). The corresponding mean $^{147}\text{Sm}/^{144}\text{Nd}$ is 0.1058 ± 0.0022 (2sd; $n = 5$), and all Nd isotopic compositions (spiked and non-spiked) are identical, with a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512189 ± 0.000025 (2sd; $n = 10$), consistent with the previously published value of 0.512176 ± 0.000010 (2sd; $n = 4$) [24].

For GSR-11 rhyolite, the mean Rb and Sr concentrations are 220 ± 19 and $41.0 \pm 2.2 \mu\text{g g}^{-1}$ (2sd; $n = 8$), respectively, with corresponding mean $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 15.5 ± 0.6 (2sd; $n = 5$) and 0.733987 ± 0.000085 (2sd; $n = 8$), the latter of which is consistent with the previously published value of 0.734135 ± 0.000023 (2sd; $n = 4$) [43]. The GSR-11 sample yielded mean Sm and Nd concentrations of 11.84 ± 0.48 and $65.12 \pm 3.25 \mu\text{g g}^{-1}$ (2sd; $n = 8$), respectively, with corresponding mean $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of 0.1092 ± 0.0016 (2sd; $n = 6$) and 0.512406 ± 0.00030 (2sd; $n = 9$), respectively, the latter of which is consistent with the previously published value of 0.512397 ± 0.000036 (2sd; $n = 4$) [43].

The Rb content of GSR-16 diabase ranges from 43.8 to $48.6 \mu\text{g g}^{-1}$, with Sr concentrations of 478 – $539 \mu\text{g g}^{-1}$ and a mean $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 0.259 ± 0.008 (2sd; $n = 5$). All Sr isotopic compositions (spiked and non-spiked) are identical, with a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.711676 ± 0.000047 (2sd; $n = 8$). The sample yielded mean Sm and Nd concentrations of 9.12 ± 0.46 and $44.56 \pm 2.35 \mu\text{g g}^{-1}$ (2sd; $n = 7$), respectively (Table 4). The corresponding mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio is 0.1237 ± 0.0043 (2sd; $n = 7$), and all Nd isotopic compositions (spiked and non-spiked) are identical, with a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512008 ± 0.000033 (2sd; $n = 10$). To our knowledge, the Sr–Nd isotopic compositions presented here are the first reported for GSR-16 (Table 4).

4.2. Plutonic reference materials GSR-1, GSR-7, GSR-9, GSR-10, GSR-14, GSR-15 and GSR-18

The mean Rb and Sr concentrations of GSR-1 granite are 496 ± 39 and $111 \pm 5 \mu\text{g g}^{-1}$ (2sd; $n = 6$), respectively (Table 4), with a mean $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 13.0 ± 0.8 (2sd; $n = 3$). All Sr isotopic compositions (spiked and non-spiked) are in agreement within reason error range, with a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.738378 ± 0.000051 (2sd; $n = 7$). This sample yielded mean Sm and Nd concentrations of 9.64 ± 0.17 and $44.32 \pm 1.72 \mu\text{g g}^{-1}$ (2sd; $n = 7$), respectively (Table 4), with a corresponding mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1311 ± 0.0057 . All Nd isotopic compositions (spiked and non-spiked) are consistent with a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512236 ± 0.000024 (2sd; $n = 8$). These Sr–Nd isotopic data are consistent with recently determined values of $^{87}\text{Sr}/^{86}\text{Sr} = 0.738329 \pm 0.000060$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512223 \pm 0.000011$ (2sd; $n = 6$) [40,42].

For GSR-7 syenite, the Rb and Sr concentrations are 130 – 145 and 1214 – $1301 \mu\text{g g}^{-1}$, respectively, with a mean $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of $0.313 \pm$

Table 4

Comparison of Rb, Sr, Sm, Nd concentrations and Sr-Nd isotopic ratios of Chinese rock reference materials.

Sample	Rb ($\pm 2\text{sd}$) [$\mu\text{g g}^{-1}$]	Sr ($\pm 2\text{sd}$) [$\mu\text{g g}^{-1}$]	$^{87}\text{Rb}/^{86}\text{Sr}$ ($\pm 2\text{sd}$)	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2\text{sd}$)	n	Sm ($\pm 2\text{sd}$) [$\mu\text{g g}^{-1}$]	Nd ($\pm 2\text{sd}$) [$\mu\text{g g}^{-1}$]	$^{147}\text{Sm}/^{144}\text{Nd}$ ($\pm 2\text{sd}$)	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2\text{sd}$)	n	References
GBW07103	496(39)	111(5)	13.0(0.8)	0.738378(51)	7	9.64(0.17)	44.32 (1.72)	0.1311(0.0057)	0.512236(24)	8	This work
(GSR-1)				0.738296(19)	30				0.512210(12)	17	[42]
				0.738329(60)	6				0.512223(11)	6	[40]
				0.738262(35)	1				0.512199(06)	1	[37,38]
	466(17)*	106(6)*		0.738262		9.7(0.8)*	47(4)*		0.512199		GeoReM
GBW07104	40.4(5.8)	840(43)	0.135(0.010)	0.704923(37)	8	3.27(0.17)	17.91 (0.83)	0.1101(0.0016)	0.512393(32)	8	This work
(GSR-2)				0.704929(12)	45				0.512377(14)	17	[42]
						3.20	17.60	0.1099	0.512395(08)	1	[49]
				0.704914(15)	1				0.512382(10)	1	[44]
	38(3)*	790(35)*		0.704914		3.4(0.2)*	19(2)*		0.512382		GeoReM
GBW07105	39.8(3.4)	1180(51)	0.0956 (0.0047)	0.704082(51)	8	10.15 (0.31)	50.48 (2.13)	0.1211(0.0017)	0.512904(32)	7	This work
(GSR-3)				0.704093(10)	52				0.512885(18)	17	[42]
						10.1(0.54)	49.77 (0.09)	0.1224(0.0067)	0.512909(10)	2	[49]
				0.704090(16)	3				0.512900(12)	3	[27]
				0.704089(25)	5				0.512899(09)	5	[40]
	39(2.6)	1121(2.5)		0.704076(18)	5	10.5(1.9)	54.0(2.2)		0.512901(11)	5	[3]
				0.704080(20)	2					2	[39]
	37(4)*	1100(64)*		0.704090		10.2(0.5)*	54(4)*		0.512902		GeoReM
GBW07109	139(12)	1257(64)	0.313(0.011)	0.709545(58)	7	9.19(0.14)	65.18 (1.70)	0.0849(0.0023)	0.511840(36)	7	This work
(GSR-7)				0.709544(16)	1				0.511832(10)	1	[44]
									0.511820(10)	4	[24]
	130(5)*	1160(58)*		0.709544		9.7(0.7)*	65.1(4.1)*		0.511832		GeoReM
GBW07110	190(12)	339(10)	1.61(0.07)	0.710291(44)	8	8.25(0.11)	46.95 (1.26)	0.1058(0.0022)	0.512189(25)	8	This work
(GSR-8)									0.512176(10)	4	[24]
	183(7)*	318(8)*				8.63(0.23)*	47.2(2.5)*				
GBW07111	75(6)	1288(50)	0.164(0.008)	0.705693(38)	7	7.61(0.15)	47.94 (1.11)	0.0951(0.0016)	0.511833(33)	6	This work
(GSR-9)											
	70.1(3.9)*	1198(47)*				7.74(0.28)*	48.1(2.6)*				
GBW07112	1.89(0.22)	667(101)	0.00795 (0.00053)	0.704406(50)	7	1.28(0.14)	4.09(0.35)	0.1900(0.0198)	0.512780(38)	9	This work
(GSR-10)											
	4.79*	612(35)*				1.22(0.06)*	4.10(0.46)*				
GBW07113	220(19)	41.0(2.2)	15.5(0.6)	0.733987(85)	7	11.84 (0.48)	65.12 (3.25)	0.1092(0.0016)	0.512406(30)	9	This work
(GSR-11)				0.734135(23)	4						
									0.512397(36)	4	[43] [24]
	213(6)*	43.0(2.2)*				11.7(0.3)*	64.5(4.8)*				
GBW07121	59.3(5.5)	745(51)	0.226(0.007)	0.709452(63)	8	3.23(0.17)	19.62 (1.52)	0.1003(0.0017)	0.511083(34)	7	This work
(GSR-14)											
	57(5)*	690(20)*				3.3(0.3)*	21(4)*				
GBW07122	27.3(2.3)	144(8)	0.540(0.006)	0.719443(57)	8	2.20(0.13)	6.48(0.47)	0.2063(0.0047)	0.512888(33)	8	This work
(GSR-15)											
	29(5)*	142(9)*				2.13(0.2)*	6.5(1.4)*				
GBW07123	46.6(3.8)	509(44)	0.259(0.008)	0.711676(47)	8	9.12(0.46)	44.56 (2.35)	0.1237(0.0043)	0.512008(33)	10	This work
(GSR-16)											
	47.4(3.7)*	470(15)*				8.6(0.8)*	42.8(1.5)*				
GBW07124	27.0(2.1)	290(20)	0.264(0.008)	0.713561(32)	7	6.25(0.29)	44.45 (1.18)	0.0850(0.0020)	0.512097(33)	10	This work
(GSR-17)											
	28.4(4.2)*	262(12)*				6.5(0.4)*	49.0(4.2)*				
GBW07125	163(9)	46.3(2.8)	10.3(0.3)	0.740829(57)	5	0.243 (0.027)	1.56(0.32)	0.0927(0.0100)	0.511643(44)	5	This work
(GSR-18)											
	155(8)*	45.5(2.4)*				0.24*	1.5(0.2)*				

The ($\pm 2\text{sd}$) is the 2 standard deviation and on the average $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of the replicate analyses reported as times 10^6 . * means recommended value from Refs. [50,52].

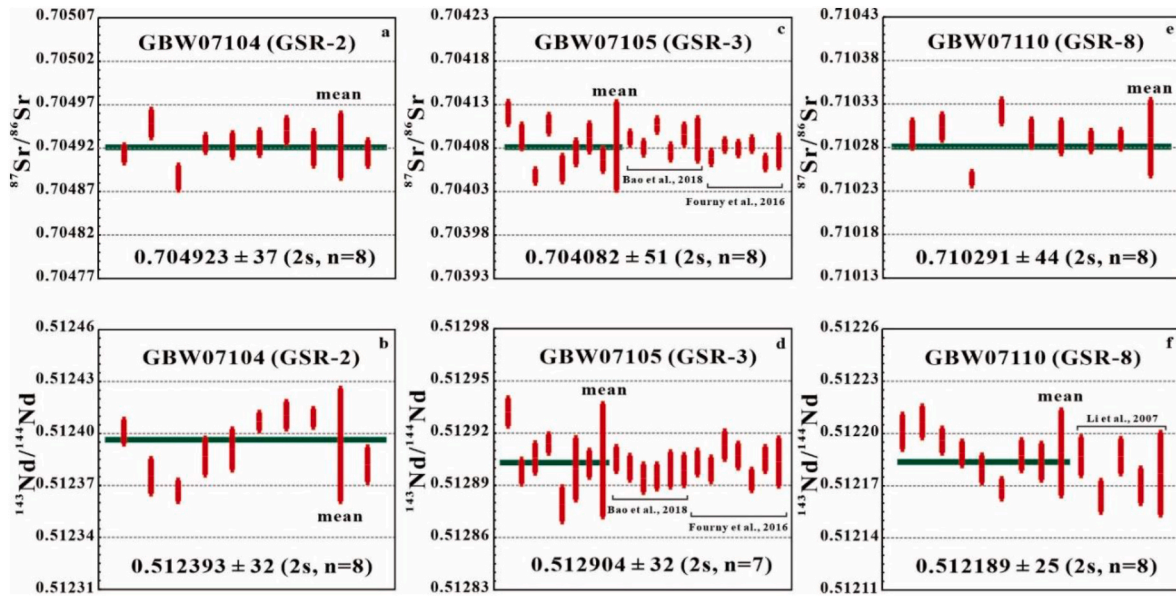


Fig. 1. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio values of GSR-2, GSR-3 and GSR-8 obtained in this work and previously published data (Yang et al. [44] presented $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of GSR-7; Bao et al. [39] and Fourny et al. [3] presented $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of GSR-3; Li et al. [24] presented $^{143}\text{Nd}/^{144}\text{Nd}$ of GSR-8). The range bar of each measured value is given in 2sd.

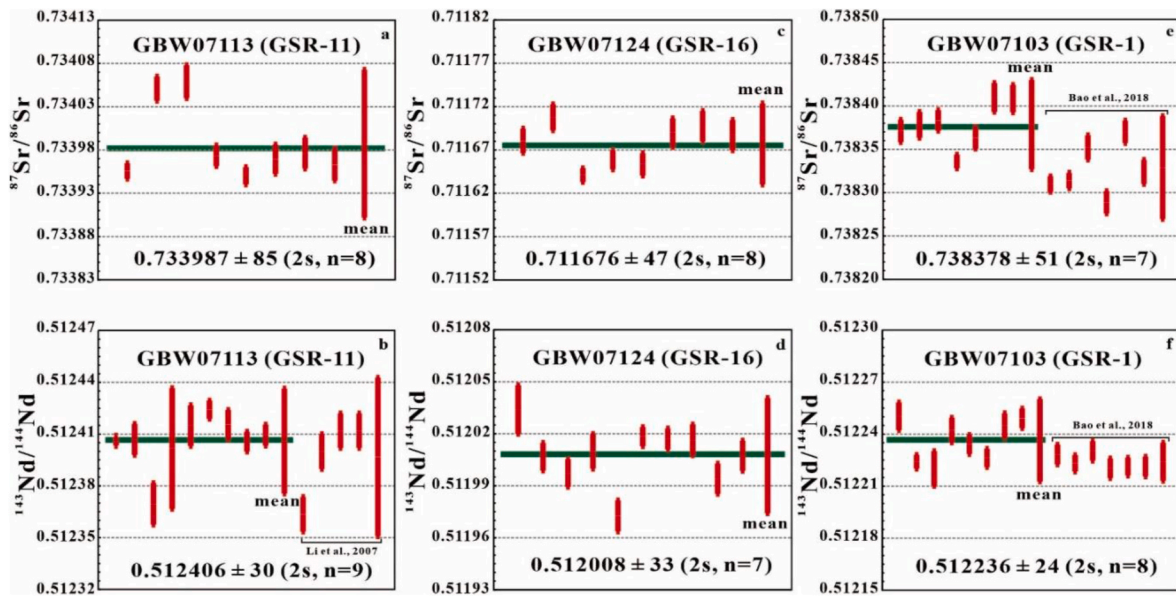


Fig. 2. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio values of GSR-11, GSR-16 and GSR-1 obtained in this study and previously reported data (Li et al. [24] presented $^{143}\text{Nd}/^{144}\text{Nd}$ of GSR-11 using MAT 262 TIMS; Bao et al. [40] presented $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of GSR-1 using Nu MC-ICP-MS). The range bar of each measured value is given in 2sd.

0.011 (2sd; n = 3). All Sr isotopic compositions are identical each other with a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.709545 ± 0.000058 (2sd; n = 7). The sample yielded mean Sm and Nd concentrations of 9.19 ± 0.14 and $65.18 \pm 1.70 \mu\text{g g}^{-1}$ (2sd; n = 7), respectively (Table 4), and a corresponding mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.0849 ± 0.0023 (2sd; n = 5). All Nd isotopic compositions (spiked and non-spiked) are in good agreement with a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511840 ± 0.000036 (2sd; n = 7) (Fig. 5). These Sr–Nd isotopic data are consistent with recently determined values of $^{87}\text{Sr}/^{86}\text{Sr} = 0.709544 \pm 0.000016$ (2sd) and $^{143}\text{Nd}/^{144}\text{Nd} = 0.511832 \pm 0.000010$ (2sd) [44].

Here, the first reported mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for GSR-9, GSR-10, GSR-14, GSR-15 and GSR-18 were 0.705693 ± 0.000038 (2sd; n = 7), 0.704406 ± 0.000050 (2sd; n = 7), 0.709452 ± 0.000063 (2sd; n = 8), 0.719443 ± 0.000057 (2sd; n = 8) and 0.740829 ± 0.000057 (2sd; n =

5), respectively. The corresponding $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were 0.511833 ± 0.000033 (2sd; n = 7), 0.512780 ± 0.000038 (2sd; n = 9), 0.511083 ± 0.000034 (2sd; n = 7), 0.512888 ± 0.000033 (2sd; n = 8) and 0.511643 ± 0.000044 (2sd; n = 5), respectively.

4.3. Ultramafic reference material GSR-17

Kimberlitic GSR-17 yielded mean Rb and Sr concentrations of 27.0 ± 2.1 and $290 \pm 20 \mu\text{g g}^{-1}$ (2sd; n = 6), respectively, with a corresponding mean $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 0.264 ± 0.008 (2sd; n = 4). All Sr isotopic compositions (spiked and non-spiked) are identical each other, with a mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.713561 ± 0.000032 (2sd; n = 7). Mean Sm and Nd concentrations are 6.25 ± 0.29 and $44.45 \pm 1.18 \mu\text{g g}^{-1}$ (2sd; n = 7), respectively (Table 4), with a corresponding mean

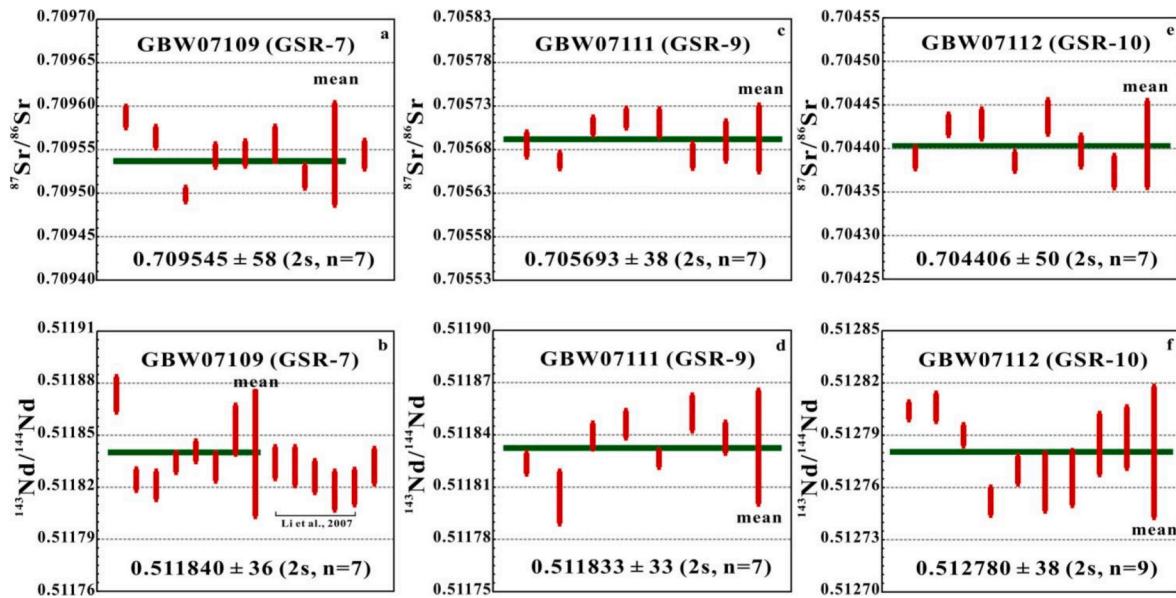


Fig. 3. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio values of GSR-7, GSR-9 and GSR-10 obtained in this study and previously published data (Li et al. [24] presented $^{143}\text{Nd}/^{144}\text{Nd}$ of GSR-7 by MAT 262 TIMS; Yang et al. [44] presented $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ of GSR-7 by Neptune MC-ICP-MS). The range bar of each measured value is given in 2sd.

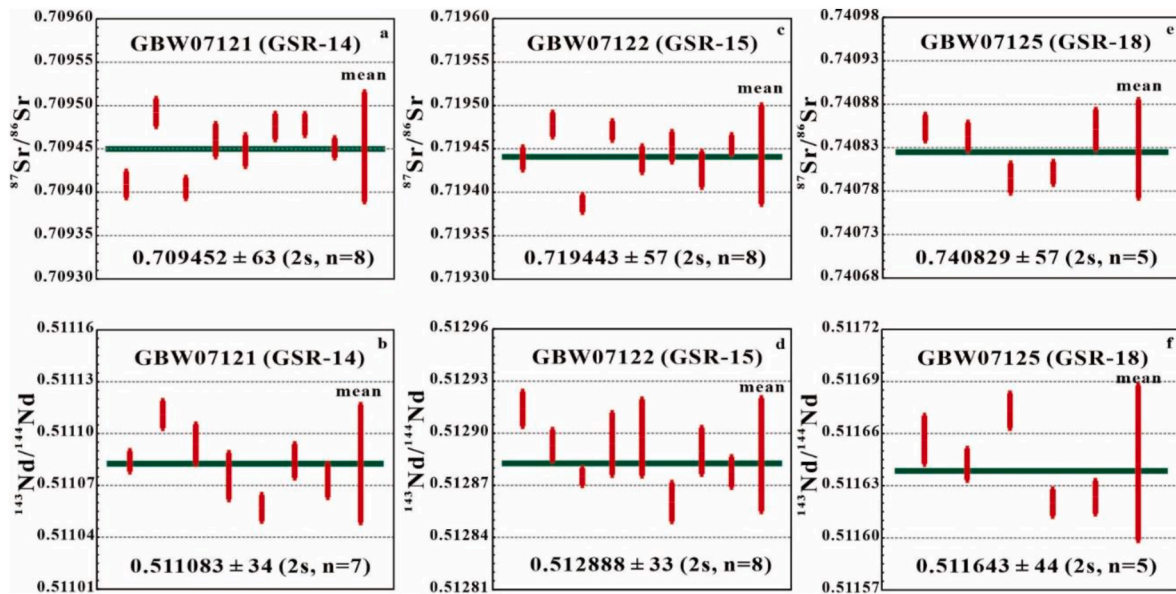


Fig. 4. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio values of GSR-14, GSR-15 and GSR-18 obtained in this study. The range bar of each measured value is given in 2sd.

$^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.0850 ± 0.0020 . All Nd isotopic compositions (spiked and non-spiked) are almost equal, with a mean $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.512097 ± 0.000033 (2sd; $n = 10$). To our knowledge, the Sr–Nd isotopic compositions presented here are the first reported for kimberlitic GSR-17 (Table 4).

4.4. Inter-laboratory comparison

Recommended compositions of the 13 Chinese rock reference materials as given in the Handbook of Elemental Abundance for Applied Geochemistry [50,52] are included in Table 4 for comparison, but no data are available for Rb, Sr, Sm and Nd concentrations determined by ID method apart from those obtained in this study.

As summarised in Table 3, although duplicate data from the same laboratory are consistent (RSD = ~1%), there are differences between

laboratories. Different Sm–Nd mixed-spike solutions (^{149}Sm – 145 , 146 , ^{150}Nd) are used among the laboratories; therefore, $^{147}\text{Sm}/^{144}\text{Nd}$ ratios are more comparable than Sm or Nd concentrations for indicating the homogeneity of the reference materials. The RSD of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for most samples is generally <2% (Table 3), indicating the homogeneity of Sm–Nd isotopic composition. Nevertheless, there are outliers for GSR-1 (a2, d1), GSR-7 (a1), GSR-10 (a1) and GSR-18 (a1), likely because of handling errors during sample weighing or digestion and powder heterogeneity. The RSD of $^{147}\text{Sm}/^{144}\text{Nd}$ ratios for GSR-18 is higher than those of the other 12 samples because GSR-18 has the lowest Sm and Nd concentrations of the studied samples.

Although a mixed ^{87}Rb – ^{84}Sr spike solution was used in the four laboratories, the RSD of $^{87}\text{Rb}/^{86}\text{Sr}$ ratios is generally higher than that for $^{147}\text{Sm}/^{144}\text{Nd}$ (Table 3) ratios, especially for high-Rb/Sr samples (GSR-1, GSR-8, GSR-10 and GSR-18). The Rb/Sr RSD values of most samples is

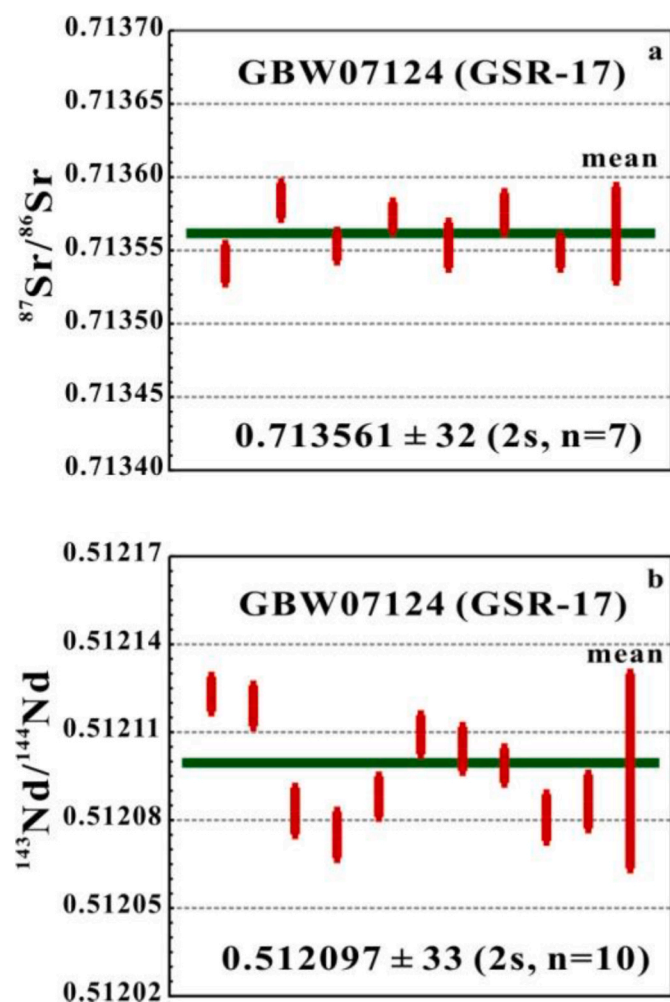


Fig. 5. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratio values of GSR-17 obtained in this study. The range bar of each measured value is given in 2sd.

usually <4%, but there are outliers for GSR-2 (b1) and GSR-10 (a1, c1, c2). As Rb has only two isotopes (^{85}Rb and ^{87}Rb), it is impossible to determine Rb mass fractionation during TIMS analysis [5,10–13], and matrix elements remaining in the Rb fraction after cation exchange may affect TIMS Rb analyses. Furthermore, under- or over-spiking for the wide range of $^{87}\text{Rb}/^{86}\text{Sr}$ ratios in the samples (0.01–16) is not avoidable. For high-Rb/Sr samples, there is likely inhomogeneity, as in GSR-1, NBS607 and GSP-2, and variable ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios would be expected [8,40].

4.5. Comparison between USGG, GSJ, and Chinese rock reference materials

Compared to widely distributed and utilized USGS or GSJ geological materials, although Chinese rock reference materials have been developed and gradually dispensed since the late 1980s [29,30], the main focus is on characterization of major and trace elements [31–35] and there is often little information concerning their isotopic compositions. Recently with development of MC-ICP-MS, radiogenic and stable isotopes have also begun to pay more attention to Chinese rock samples [2, 3,40,41,44]. The homogeneity of rock reference materials is of concern. As shown in Table 4, the most accumulated result of GSR-3 from multiple laboratories indicate that its Sr-Nd isotopes have good homogeneity [3,27,39,40,42,49]. The analytical results of GSR-1, 2, 7, 8, and 11 indicate that Sr or Nd isotopes also show this potential or trend. With the accumulation of analytical data, Chinese reference materials will likely

become a viable choice as supplies of USGS and GSJ reference materials in the near future.

5. Conclusions

This is the first comprehensive study of Rb, Sr, Sm and Nd concentrations and Sr and Nd isotopic compositions of 13 readily available Chinese geochemical reference materials, undertaken to assess their homogeneity and to provide first benchmark values. Most data generated are consistent with the limited number of previously published values, and our results indicate that these materials are suitable for use in Rb–Sr and Sm–Nd isotope analyses. The Sr and Nd isotopic compositions of GBW07111, GBW07112, GBW07121, GBW07122, GBW07123, GBW07124 and GBW07125 are first reported here. Our results indicate that the 13 materials are suitable and applicable for use as primary reference materials for a range of unknown sample compositions and can be used to provide analytical quality control. Being widely available, they may in time become as well utilized as USGS and GSJ reference materials. The comprehensive Rb–Sr and Sm–Nd isotopic data provided here may be useful elsewhere in bulk geochemical analyses.

CRediT authorship contribution statement

Yue-Heng Yang: Conceptualization, Funding acquisition, Validation, Writing – original draft, Writing – review & editing. **Suo-Han Tang:** Methodology, Validation. **Wen-Gang Liu:** Methodology, Validation. **Yan Yan:** Methodology, Validation. **Lie-Wen Xie:** Investigation, Supervision. **Chao Huang:** Data curation, Validation. **Shi-Tou Wu:** Methodology, Writing – review & editing. **Hao Wang:** Writing – review & editing. **Jin-Hui Yang:** Supervision, Writing – review & editing. **Fu-Yuan Wu:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] K.P. Jochum, J. Enzweiler, Reference materials in geochemical and environmental research, in: second ed., in: H.D. Holland, K.K. Turekian (Eds.), *Treatise on Geochemistry*, vol. 15, Elsevier, Oxford, 2014, pp. 43–70.
- [2] F.Z. Teng, Q.Z. Yin, C.V. Ullmann, R. Chakrabarti, P.A.E. Pogge von Strandmann, W. Yang, W.Y. Li, S. Ke, F. Sedaghatpour, J. Wimpenny, A. Meixner, R.L. Romer, U. Wiechert, S.B. Jacobsen, Interlaboratory comparison of magnesium isotopic compositions of 12 felsic to ultramafic igneous rock standards analyzed by MC-ICPMS, *G-cubed* 16 (2015) 3197–3209.
- [3] A. Fourny, D. Weis, J.S. Scoates, Comprehensive Pb–Sr–Nd–Hf isotopic, trace element, and mineralogical characterization of mafic to ultramafic rock reference materials, *G-cubed* 17 (2016) 739–773.

- [4] Q. Ma, M. Yang, H. Zhao, N.J. Evans, Z.Y. Chu, L.W. Xie, C. Huang, Z.D. Zhao, Y. H. Yang, Accurate and precise determination of Lu and Hf contents and Hf isotopic composition at the subnanogram level in geological samples using MC-ICP-MS, *J. Anal. At. Spectrom.* 34 (2019) 1256–1262.
- [5] Y.H. Yang, H.F. Zhang, Z.Y. Chu, L.W. Xie, F.Y. Wu, Combined chemical separation of Lu, Hf, Rb, Sr, Sm and Nd from a single rock digest and precise and accurate isotope determinations of Lu-Hf, Rb-Sr and Sm-Nd isotope systems using multi-collector ICP-MS and TIMS, *Int. J. Mass Spectrom.* 290 (2010) 120–126.
- [6] Y.H. Yang, Z.Y. Chu, F.Y. Wu, L.W. Xie, J.H. Yang, Precise and accurate determination of Sm, Nd concentrations and Nd isotopic compositions in geological samples by MC-ICP-MS, *J. Anal. At. Spectrom.* 26 (6) (2011) 1237–1244.
- [7] D. Weis, B. Kieffer, C. Maerschalk, W. Pretorius, J. Barling, High-precision Pb-Sr-Nd-Hf isotopic characterization of USGS BHVO-1 and BHVO-2 reference materials, *G-cubed* 6 (2005) Q02002.
- [8] D. Weis, B. Kieffer, C. Maerschalk, J. Barling, J. De Jong, G. Williams, D. Hanano, W. Pretorius, N. Mattielli, J.S. Scoates, A. Goolaeys, R. Friedman, J.B. Mahoney, High-precision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS, *G-cubed* 7 (2006) Q08006.
- [9] D. Weis, B. Kieffer, D. Hanano, I.N. Silva, J. Barling, W. Pretorius, C. Maerschalk, N. Mattielli, Hf isotopic compositions of U.S. Geological Survey reference materials, *G-cubed* 8 (2007) Q06006.
- [10] Z.Y. Chu, F.K. Chen, Y.H. Yang, J.H. Guo, Precise determination of Sm, Nd concentrations and Nd isotopic compositions at the nanogram level in geological samples by thermal ionization mass spectrometry, *J. Anal. At. Spectrom.* 24 (2009) 1534–1544.
- [11] Z.Y. Chu, J.H. Guo, Y.H. Yang, L. Qi, C.F. Li, Precise determination of Sm and Nd concentrations and Nd isotopic compositions in highly depleted ultramafic reference materials, *Geostand. Geoanal. Res.* 38 (2014) 61–72.
- [12] C.F. Li, J.H. Guo, Y.H. Yang, Z.Y. Chu, X.C. Wang, Single-step separation scheme and high-precision isotopic ratios analysis of Sr–Nd–Hf in silicate materials, *J. Anal. At. Spectrom.* 29 (2014) 1467–1476.
- [13] C.F. Li, X.C. Wang, J.H. Guo, Z.Y. Chu, L.J. Feng, Rapid separation scheme of Sr, Nd, Pb, and Hf from a single rock digest using a tandem chromatography column prior to isotope ratio measurements by mass spectrometry, *J. Anal. At. Spectrom.* 31 (2016) 1150–1159.
- [14] C.F. Li, H.Q. Wu, Z.Y. Chu, X.C. Wang, Y.L. Li, Precise determination of radiogenic Sr and Nd isotopic ratios and Rb, Sr, Sm, Nd elemental concentrations in four coal ash and coal fly ash reference, *Microchem. J.* 146 (2019) 906–913.
- [15] Y.L. Li, C.F. Li, J.H. Guo, Re-evaluation and optimisation of dissolution methods for strontium isotope stratigraphy based on chemical leaching of carbonate certificated reference materials, *Microchem. J.* 154 (2020) 104607.
- [16] F. Albarède, P. Telouk, J. Blichert-Toft, M. Boyet, A. Agranier, B.K. Nelson, Precise and accurate isotopic measurements using multiple-collector MC-ICP-MS, *Geochim. Cosmochim. Acta* 68 (2004) 2725–2744.
- [17] J. Barling, D. Weis, Influence of non-spectral matrix effects on the accuracy of Pb isotope ratio measurement by MC-ICP-MS: implications for the external normalization method of instrumental mass bias correction, *J. Anal. At. Spectrom.* 23 (2008) 1017–1025.
- [18] J. Barling, D. Weis, An isotopic perspective on mass bias and matrix effects in multi-collector inductively-coupled-plasma mass spectrometry, *J. Anal. At. Spectrom.* 27 (2012) 653–662.
- [19] A.J. Pietruszka, A.D. Reznik, Identification of a matrix effect in the MC-ICP-MS due to sample purification using ion exchange resin: an isotopic case study of molybdenum, *Int. J. Mass Spectrom.* 270 (2008) 23–30.
- [20] I.G. Nobre Silva, D. Weis, J. Barling, J.S. Scoates, Leaching systematics and matrix elimination for the determination of high-precision Pb isotope compositions of ocean island basalts, *G-cubed* 10 (2009) Q08012.
- [21] J. Lin, Y.S. Liu, Y.H. Yang, Z.C. Hu, Calibration and correction of LA-ICP-MS and LA-MC-ICP-MS analyses for element contents and isotopic ratios, *Sol. Earth Sci.* 1 (2016) 5–27.
- [22] E. Frères, D. Weis, K. Newman, M. Amini, K. Gordon, Oxide formation and instrumental mass bias in MC-ICP-MS: an isotopic case study of Neodymium, *Geostand. Geoanal. Res.* 45 (2021) 501–523.
- [23] I. Raczek, K.P. Jochum, A.W. Hofmann, Neodymium and strontium isotope data for USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, GSP-1, GSP-2 and eight MPI-DING reference glasses, *Geostand. Newsl.* 27 (2003) 173–179.
- [24] X.H. Li, Y. Liu, Y.H. Yang, F.K. Chen, X.L. Tu, C.S. Qi, Rapid separation of Lu-Hf and Sm-Nd from a single rock dissolution and precise measurement of Hf-Nd isotopic ratios for natural rock standards, *Acta Petrol. Sin.* 23 (2007) 221–226 (in Chinese with English abstract).
- [25] T. Cheng, O. Nebel, P. Sossi, F.K. Chen, Assessment of hafnium and iron isotope compositions of Chinese national igneous rock standard materials GSR-1 (granite), GSR-2 (andesite), and GSR-3 (basalt), *Int. J. Mass Spectrom.* 386 (2015) 61–66.
- [26] S.T. Wu, G. Worner, K.P. Jochum, B. Stoll, K. Simon, A. Kronz, The preparation and preliminary characterization of three synthetic andesite reference glass materials (ARM-1, ARM-2, ARM-3) for in situ microanalysis, *Geostand. Geoanal. Res.* 43 (2019) 567–584.
- [27] S.T. Wu, Y.H. Yang, K.P. Jochum, R.L. Romer, J. Glodny, I.P. Savov, S. Agostini, J. C.M. De Hoog, S.T.M. Peters, A. Kronz, C. Zhang, Z.A. Bao, X.J. Wang, Y.L. Li, G. Q. Tang, L.J. Feng, H.M. Yu, Z.X. Li, Z. Le, J. Lin, Y. Zeng, C.X. Xu, Y.P. Wang, Z. Cui, L. Deng, J. Xiao, Y.H. Liu, D.X. Xue, Z. Di, L.H. Jia, H. Wang, L. Xu, C. Huang, L.W. Xie, A. Pack, G. Worner, M.Y. He, C.F. Li, H.L. Yuan, F. Huang, Q. L. Li, J.H. Yang, X.H. Li, F.Y. Wu, Isotopic compositions (Li-Bi-Si-O-Mg-Sr-Nd-Hf-Pb) and $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios of three synthetic andesite glass reference materials (ARM-1, ARM-2, ARM-3), *Geostand. Geoanal. Res.* 45 (2021) 719–745.
- [28] S.T. Wu, A. Audétat, K.P. Jochum, H. Wang, J.Y. Chen, B. Stoll, C. Zhang, Z.A. Bao, S.Y. Zhang, C.F. Li, X.F. Wang, C.X. Xu, L. Xu, C. Huang, L.W. Xie, Y.H. Yang, J. H. Yang, Three natural andesitic to rhyolitic glasses (OJY-1, OH-1, OA-1) as reference materials for in situ microanalysis, *Geostand. Geoanal. Res.* 46 (2022) 673–700.
- [29] X.J. Xie, M.C. Yan, L.Z. Li, H.J. Shen, Useable values for Chinese standard reference samples of stream sediments, soils and rocks: GSD 9-12, GSS 1-8 and GSR 1-6, *Geostand. Newsl.* 9 (1985) 277–280.
- [30] X.J. Xie, M.C. Yan, C.S. Wang, Geochemical standard reference samples GSD 9-12, GSS 1-8, GSR 1-6, *Geostand. Newsl.* 13 (1989) 83–179.
- [31] Y.J. Zhang, X.B. Li, L.S. Song, Multi-elemental neutron activation analysis of Chinese Geochemical reference samples, *Geostand. Newsl.* 10 (1986) 61–71.
- [32] Y.Q. Tang, K.E. Jarvis, J.G. Williams, Determination of trace elements in eleven Chinese geological reference materials by ICP-MS, *Geostand. Newsl.* 16 (1992) 61–70.
- [33] N.W. Bower, C.M. Lewis, J.M. Galbraith, G. Luedemann, Elemental concentrations of Chinese rock standards GSR 1-6: a comparison with the certificate values, *Geostand. Newsl.* 17 (1993) 117–121.
- [34] L. Qi, D.C. Grégoire, Determination of trace elements in twenty six Chinese geochemistry reference materials by inductively coupled plasma-mass spectrometry, *Geostand. Newsl.* 24 (2000) 51–63.
- [35] C.S. Wang, T.X. Gu, Q.H. Chi, W.D. Yan, M.C. Yan, New series of rock and sediment geochemical reference materials, *Geostand. Newsl.* 25 (2001) 145–152.
- [36] J.M. Richardson, P.C. Lightfoot, H. de Souza, Current laboratories programs and their quality assurance underpinnings, *Geostand. Newsl.* 20 (1996) 141–156.
- [37] F.Q. Dai, Z.F. Zhao, Y.F. Zheng, Partial melting of the orogenic lower crust: geochemical insights from post-collisional alkaline volcanics in the Dabie orogen, *Chem. Geol.* 454 (2017) 25–43.
- [38] F.Q. Dai, Z.F. Zhao, Y.F. Zheng, G.C. Sun, The geochemical nature of mantle sources for two types of Cretaceous basaltic rocks from Luxi and Jiaodong in east-central China, *Lithos* 344 (2019) 409–424.
- [39] J.M. Richardson, P.C. Lightfoot, H. de Souza, Current laboratories programs and their quality assurance underpinnings, *Geostand. Newsl.* 20 (1996) 141–156.
- [40] Z.A. Bao, C.L. Zong, L.R. Fang, H.L. Yuan, K.Y. Chen, M.N. Dai, Determination of Hf–Sr–Nd isotopic ratios by MC-ICP-MS using rapid acid digestion after flux-free fusion in geological materials, *Acta Geochim.* 37 (2018) 244–256.
- [41] M. Yang, Y.H. Yang, N.J. Evans, L.W. Xie, C. Huang, S.T. Wu, J.H. Yang, F.Y. Wu, Precise and accurate determination of Lu and Hf contents and Hf isotopic compositions in Chinese rock reference materials by MC-ICP-MS, *Geostand. Geoanal. Res.* 44 (2020) 543–565.
- [42] K. Guo, J.M. Yu, D. Fan, Z.F. Hu, Y.L. Liu, X. Zhang, Y. Precise determination of Sr and Nd isotopic compositions of Chinese Standard Reference samples GSR-1, GSR-2, GSR-3 and GBW07315 by TIMS, *Geosystems and Geoenvironment* 2 (2023) 100210.
- [43] W.G. Liu, S. Wei, J. Zhang, C. Ao, F.T. Liu, B. Cai, H.Y. Zhou, J.L. Yang, C.F. Li, An improved separation scheme for Sr through fluoride coprecipitation combined with a cation exchange resin for geological samples with high Rb/Sr ratios for high-precision determination of Sr isotope ratios, *J. Anal. At. Spectrom.* 35 (2020) 953–960.
- [44] Y.H. Yang, M. Yang, K.P. Jochum, S.T. Wu, H. Zhao, L.W. Xie, C. Huang, X.C. Zhan, J.H. Yang, F.Y. Wu, High-precision Sr–Nd–Hf–Pb isotopic composition of Chinese geological standard glasses CGSG-1, CGSG-2, CGSG-4 and CGSG-5 reference materials by MC-ICP-MS and TIMS, *Geostand. Geoanal. Res.* 44 (2020) 567–579.
- [45] Y.H. Yang, F.Y. Wu, Z.C. Liu, Z.Y. Chu, L.W. Xie, J.H. Yang, Evaluation of Sr chemical purification technique for natural geological samples using common cation-exchange and Sr-specific extraction chromatographic resin prior to MC-ICP-MS or TIMS measurement, *J. Anal. At. Spectrom.* 27 (2012) 516–522.
- [46] Z.C. Zhang, G.H. Wang, An investigation on the mineral standard reference material for Rb-Sr dating, *Acta Metrol. Sin.* 11 (3) (1990) 173–178 (In Chinese with English abstract).
- [47] S.H. Tang, X.K. Zhu, J. Li, J.H. Wang, B. Yan, Separation and isotopic measurement of Sr in rock samples using selective specific resins, *Chin. J. Anal. Chem.* 38 (2010) 999–1002 (In Chinese with English abstract).
- [48] Y.A. Liu, J.Y. Cui, X.M. Wang, L.Y. Pei, S.T. Tang, Factors of influence on accurate determination of Sm–Nd isotopic ratios, *Uranium Geol.* 31 (2015) 606–610 (in Chinese with English abstract).
- [49] M. Yang, Y.H. Yang, S.L. Kamo, R.L. Romer, N.M.W. Roberts, H. Wang, L.W. Xie, C. Huang, J.H. Yang, F.Y. Wu, Natural allanite reference materials for in situ U–Th–Pb and Sm–Nd isotopic analysis by LA-(MC)-ICP-MS, *Geostand. Geoanal. Res.* 46 (2022) 169–203.
- [50] Q.H. Chi, M.C. Yan, Handbook of Elemental Abundance for Applied Geochemistry, Geological Publishing House, Beijing, China, 2007 (In Chinese with English abstract).
- [51] J. Li, S.H. Tang, X.K. Zhu, C.X. Pan, Production and certification of the reference material GSB 04-3258-2015 as a $^{142}\text{Nd}/^{144}\text{Nd}$ isotope ratio reference, *Geostand. Geoanal. Res.* 41 (2017) 255–262.
- [52] Y.M. Wang, T.X. Gu, X.H. Wang, Y.S. Gao, K.P. Jochum, W.E.G. Müller, Practical Handbook of Reference Materials for Geoanalysis, second ed., Geological Publishing House, Beijing, 2013 (In Chinese with English abstract).
- [53] Z.Q. Zhang, X.J. Ye, S.H. Tang, J.H. Wang, X. Huang, J. Pang, Y.X. Lin, Z.C. Li, Y. X. Wang, J.D. Yang, J.Y. Li, G.C. Zhang, P. Zhang, Reference material for Sm–Nd dating, *Dixueyanjiu* 28 (1995) 153–167 (In Chinese with English abstract).