

High-Precision Sr-Nd-Hf-Pb Isotopic Composition of Chinese Geological Standard Glass Reference Materials CGSG-1, CGSG-2, CGSG-4 and CGSG-5 by MC-ICP-MS and TIMS

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To assess the homogeneity of and provide the first Sr-Nd-Hf-Pb isotopic reference values for the Chinese Geological Standard Glasses CGSG-1, CGSG-2, CGSG-4 and CGSG-5, we measured these isotopes in several measurement sessions over the course of nearly 3 years. The results were obtained by high-precision MC-ICP-MS and TIMS. Our investigation indicates that these CGSG glass reference materials are homogenous with regard to Sr-Nd-Hf-Pb isotopic distribution and are therefore suitable geochemical materials for Sr-Nd-Hf-Pb isotope measurements. Clear differences in Sr-Nd-Hf-Pb isotopic composition were observed between the glasses and the original powdered rock reference materials (CGSG-2 and GSR-7, and especially CGSG-5 and GSR-2) because of flux addition during preparation of the glasses. The new Sr-Nd-Hf-Pb isotope data provided here might be useful to the geochemical community for *in situ* and bulk analysis.

Keywords: Sr-Nd-Hf-Pb isotope composition, Chinese Geological Standard Glasses, MC-ICP-MS, TIMS, Glass Reference Materials.

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Glass reference materials play an important role in microanalysis, using techniques such as EPMA, LA-(MC)-ICP-MS and SIMS (Jochum and Enzweiler 2014). They are usually used as known or unknown samples for calibration, method development, quality control and interlaboratory comparison (Jochum *et al.* 2000, 2005a, 2006, Klemme *et al.* 2008, Bao *et al.*, 2011). For example, the National Institute for Standards and Technology (NIST) series standard reference material (SRM) glasses (e.g., NIST SRM 610, 612 and 614; Woodhead and Hergt 2000, 2001, Jochum *et al.* 2005b, 2005c, Liu *et al.* 2008, 2010, Jochum *et al.* 2009, 2011, Nebel *et al.* 2009, Liu *et al.* 2013), the various United States Geological Survey (USGS) glass materials (i.e., BCR-2G, BHVO-2G, BIR-1G, TB-1G, NKT-1G, GSA-1G, GSC-1G, GSD-1G and GSE-1G; Gao *et al.* 2002, Elburg *et al.* 2005, Guillong *et al.* 2005, Matthews *et al.* 2011, Tong

et al. 2015) and MPI-DING (i.e., KL2-G, ML3B-G, StHs6/80-G, GOR128-G, GOR132-G, BM90/21-G, T1-G and ATHO-G; Jochum *et al.* 2000, 2005a, 2006, 2014, Raczek *et al.* 2003, Matthews *et al.* 2011) are widely used as microanalytical reference materials (Wu *et al.* 2019). The widespread distribution and use of glass reference materials, not only because of their major and trace element, but also their isotopic characterisations, make them significant reference materials for microanalysis (Pearce *et al.* 1997, Rocholl *et al.* 1997, Rocholl 1998). Because of the wide distribution of NIST, USGS and MPI-DING series glasses, there are various publications focused on their isotopic composition (e.g., for H, Li, B, O, Ca, Mg, Sr, Nd, Hf, Pb, Th and U; Jochum *et al.* 2000, 2005a, 2006, 2009, 2011, Woodhead and Hergt 2000, 2001, Guillong *et al.* 2005, Weis *et al.* 2005, 2006, 2007, Liu *et al.* 2008, 2010, 2013, Nebel *et al.*

2009, Matthews *et al.* 2011, Yuan *et al.* 2013, Chu *et al.* 2014, 2015, Cheng *et al.* 2015, Tong *et al.* 2015, Li *et al.* 2016, Ma *et al.* 2019).

However, the major element compositions of the NIST glasses are very different from those of any geological matrix. To provide reference glasses of natural composition, the USGS as well as the MPI-DING prepared large amounts of homogeneous glasses, the latter a series of eight glasses covering the spectrum from ultramafic to highly siliceous compositions (Jochum and Enzweiler 2014). Subsequently, the USGS basaltic glasses BCR-2G, BHVO-2G and BIR-1G have been extensively analysed by numerous laboratories. Nevertheless, due to the growing use of microanalytical applications, the demand for suitable reference glasses with natural compositions has increased considerably in the past few years (Hu *et al.* 2011). This is especially valid for geological samples with non-basaltic compositions. For this reason, Hu *et al.* (2011) prepared and provided the first analytical data for Chinese Geological Standard Glasses (i.e., CGSG-1, CGSG-2, CGSG-4 and CGSG-5) using a variety of analytical techniques (wet chemistry, XRF, EPMA, ICP-AES, ICP-MS and LA-ICP-MS) performed in nine laboratories and calculated preliminary reference and information values for fifty-five elements. However, there are only a few reports concerning isotope data for the CGSG series. Recently, Deton *et al.* (2013) reported U-Th elemental and isotopic data for CGSG reference glasses by ID-TIMS and MC-ICP-MS, and Chen *et al.* (2014) presented Pb isotopic data for CGSG reference glasses by fs-LA-MC-ICP-MS. More recently, Wu *et al.* (2016) investigated elemental fractionation and the homogeneity of CGSG reference glasses, in order to promote further quality assessment and application.

Bearing in mind these considerations, the aim of this work is, first, to test the homogeneity of the Sr-Nd-Hf-Pb isotopes and, second, to present a comprehensive set of high-precision Sr, Nd, Hf and Pb isotope data for CGSG-1, CGSG-2, CGSG-4 and CGSG-5 obtained by MC-ICP-MS and TIMS, the results of which might be useful for *in situ* and bulk analysis of silicate materials.

Experimental

Chemical digestion and purification were carried out in Class 100 fume hoods located in a Class 1000 clean laboratory, with mass fraction and isotopic measurements carried out in Class 10000 laboratories, at the State Key Laboratory of Lithospheric Evolution (SKLLE), Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing. Analytical techniques for sample dissolution, Sr-Nd-Hf-Pb chemical isolation and mass spectrometric

measurement have been presented in detail elsewhere (Xie *et al.* 2005, Yang *et al.* 2010, 2011, 2012, 2014, Chu *et al.* 2014, 2015, Li *et al.* 2015, 2016) and will be only briefly described here.

CGSG glass and rock powder reference materials

CGSG glass and rock powder reference materials CGSG-1, CGSG-2, CGSG-4 and CGSG-5 glass chips are produced by the National Research Centre of Geoanalysis (NRCG) in Beijing. The glasses were melted and fused (as described detail in Hu *et al.* 2011), and Li, Rb, Sr, Sm, Nd, Lu, Hf and Pb contents of the CGSG materials are summarised in Table 1. CGSG-1, CGSG-2, CGSG-4 and CGSG-5 respectively comprise an alkali basalt from Tibet, a Chinese geological reference syenite (made from GSR-7 also named after GSR-7G), a soil sample from Beijing and a Chinese geological reference andesite (made from GSR-2 also named after GSR-2G). For comparative purposes, Chinese rock powder reference materials (GSR-2 andesite, GSR-3 basalt and GSR-7 syenite from NRCG), as well as CGSG glasses, were also analysed with Sr, Nd, Hf and Pb isotopes as targets (Table 1). Additionally, BCR-2 (basalt), BHVO-2 (basalt) and AGV-2 (andesite) rock reference powders from the USGS were used as quality control materials in our measurement sessions.

Sample digestion

About 100 mg of glass chip or rock powder test portions was weighed into 7-ml round-bottomed Savillex™ PFA screw-top beakers. Concentrated HF, HNO₃ and HClO₄ (2, 1 and 0.2 ml, respectively) were added, and the beakers were capped and then heated on a hot plate at about 120 °C for 1 week. After cooling, the capsules were opened and then heated to evaporate HClO₄. One millilitre of 6 mol l⁻¹ HCl was added to the residue and subsequently evaporated. This procedure was then repeated. After cooling, the residue was dissolved in 5 ml of 3 mol l⁻¹ HCl. The beaker was again sealed and placed on a hot plate at about 100 °C overnight to redissolve the residues prior to chemical isolation of Sr-Nd-Hf. For Pb isotopic isolation using Sr-specific resin, the samples were redissolved using 1.0 ml of 3 mol l⁻¹ HNO₃ on a hot plate at about 100 °C overnight.

Chromatographic separation

The 3 mol l⁻¹ HCl sample solution was centrifuged and then loaded onto preconditioned Ln-Spec resin (100–150 μm particle size, ca. 2 ml Ln-Spec resin, ca. 0.8 cm × 4 cm). Firstly, the matrix elements, including light

Table 1.
Rubidium, Sr, Sm, Nd, Lu, Hf and Pb contents of CGSG reference material and corresponding rock reference materials

Sample	Note	Li ($\pm 2s$) [$\mu\text{g g}^{-1}$]	Rb ($\pm 2s$) [$\mu\text{g g}^{-1}$]	Sr ($\pm 2s$) [$\mu\text{g g}^{-1}$]	Sm ($\pm 2s$) [$\mu\text{g g}^{-1}$]	Nd ($\pm 2s$) [$\mu\text{g g}^{-1}$]	Lu ($\pm 2s$) [$\mu\text{g g}^{-1}$]	Hf ($\pm 2s$) [$\mu\text{g g}^{-1}$]	Pb ($\pm 2s$) [$\mu\text{g g}^{-1}$]
CGSG-1	a		106 \pm 5	1317 \pm 32	18.1 \pm 0.8	132 \pm 5	0.25 \pm 0.02	11.6 \pm 1.4	32.6 \pm 1.3
	b	23.1 \pm 5.2	104 \pm 3	1316 \pm 21	18.5 \pm 2.0	131 \pm 5	0.245 \pm 0.085	11.2 \pm 1.2	29.1 \pm 1.2
	c	23.6 \pm 1.7	108 \pm 2	1287 \pm 23	17.4 \pm 0.4	131 \pm 3	0.246 \pm 0.035	11.0 \pm 0.5	28.9 \pm 0.7
CGSG-2 [GSR-7G]	a		125 \pm 7	1200 \pm 41	9.65 \pm 0.34	72.5 \pm 2.7	0.39 \pm 0.02	35.5 \pm 3.3	138 \pm 12
	b	425 \pm 15	124 \pm 4	1200 \pm 13	9.99 \pm 1.08	71.7 \pm 3.6	0.396 \pm 0.090	34.0 \pm 2.0	138 \pm 4
	c	437 \pm 9	129 \pm 2	1172 \pm 21	9.32 \pm 0.32	70.1 \pm 2.4	0.382 \pm 0.032	33.4 \pm 1.2	133 \pm 2
GSR-7	c	411	124	1161	9.75	74.6	0.42	35.4	129
	e		130 \pm 5	1160 \pm 58	9.7 \pm 0.7	65.1 \pm 4.1	0.43 \pm 0.09	34.0 \pm 4.6	196
	f	32.9	130	1160	9.7	65.1	0.43	34	196
CGSG-4	a		85 \pm 4	390 \pm 14	5.43 \pm 0.29	30.6 \pm 1.3	0.36 \pm 0.02	6.83 \pm 0.48	47 \pm 3
	b	1144 \pm 23	86.1 \pm 2.1	384 \pm 8	5.30 \pm 0.71	29.4 \pm 2.2	0.353 \pm 0.087	6.56 \pm 0.70	47.3 \pm 1.5
	c	1143 \pm 21	88.3 \pm 0.9	380 \pm 4	5.06 \pm 0.26	28.9 \pm 1.0	0.338 \pm 0.023	6.50 \pm 0.37	44.9 \pm 1.3
	d	1120	84.9	386	5.49	30.8	0.37	6.72	44.8
CGSG-5 [GSR-2G]	a		39 \pm 2	795 \pm 31	3.62 \pm 0.12	22.3 \pm 0.7	0.12 \pm 0.01	4.77 \pm 0.26	20.8 \pm 1.3
	b	2048 \pm 83	38.6 \pm 2.2	826 \pm 66	3.96 \pm 0.70	21.7 \pm 2.3		4.85 \pm 1.04	21.7 \pm 9.3
	c	2001 \pm 45	38.8 \pm 1.5	788 \pm 10	3.37 \pm 0.41	21.1 \pm 0.6	0.116 \pm 0.022	4.44 \pm 0.17	22.0 \pm 9.5
GSR-2	e		38 \pm 3	790 \pm 35	3.4 \pm 0.2	19 \pm 2	0.12 \pm 0.03	2.9 \pm 0.5	11.3
	f	18.3	38	851	3.4	19	0.12	2.9	11.3
	g	22.6 \pm 0.3	33.0 \pm 1.2	785 \pm 15	3.11 \pm 0.10	17.5 \pm 0.08	0.11 \pm 0.01	2.71 \pm 0.08	9.92 \pm 0.17

^a Data from Hu *et al.* (2011); ^{b,c} Data from Wu *et al.* (2016); ^d Data from Jochum and Enzweiler (2014); ^e Data from Chi and Yan (2007); ^f Data from GeoReM (<http://georem.mpch-mainz.gwdg.de>); ^g Data from Qi and Grégoire (2000).

and middle rare earth elements (LMREEs), were sequentially eluted with 3 and 4 mol l⁻¹ HCl and were collected in a 30-ml PFA beaker for further purification in the following second- and third-column purifications. The heavy rare earth element (HREE) fraction was eluted in sequence with 4 mol l⁻¹ HCl and 6 mol l⁻¹ HCl, in order to minimise the isobaric interference of ¹⁷⁶Lu and ¹⁷⁶Yb on ¹⁷⁶Hf. Titanium was separated from Hf using a freshly prepared 4 mol l⁻¹ HCl + 0.5% H₂O₂ mixture. Finally, Hf (+Zr) was extracted from the column with 5 ml 2 mol l⁻¹ HF, collected in a 10-ml PFA beaker and gently evaporated to dryness.

The solution collected from the first Ln column, consisting of matrix elements, including the LMREE, was gently evaporated to dryness and diluted with 1 ml 2.5 mol l⁻¹ HCl prior to cation-exchange resin purification. After centrifuging, the solution was loaded into a quartz column packed with AG50W-X12 (200–400 mesh size, ca. 2 ml cation resin, ca. 0.5 cm \times 10 cm) preconditioned with 2 ml of 2.5 mol l⁻¹ HCl. The resin was washed with 2 ml of 2.5 mol l⁻¹ HCl, followed by 2.5 ml of 5 mol l⁻¹ HCl to remove the most unwanted elements. Following this, Rb was eluted with 1.5 ml of 5 mol l⁻¹ HCl. In order to minimise the isobaric interference of ⁸⁷Rb on ⁸⁷Sr, the resin was rinsed with 4 ml of 5 mol l⁻¹ HCl to remove residual Rb. Finally, the Sr fraction was eluted using 3 ml of 5 mol l⁻¹ HCl and gently evaporated to dryness prior to further isolation, whereas the LMREE fraction was eluted with 6 ml of 6 mol l⁻¹ HCl for the Ln resin column purification for Nd.

Considering the strong retention of Sr-specific resin, the Sr sample solution obtained from the cation-exchange resin was taken up in a 1 ml 3.0 mol l⁻¹ HNO₃ medium prior to chemical isolation. The 1 ml 3 mol l⁻¹ HNO₃ sample solution was loaded into a Bio-Rad polypropylene column (1-ml columns with an internal diameter of 6 mm) freshly packed with Sr-specific resin (100–150 μm particle size, ca. 0.2 ml Sr resin). Subsequently, the resin was rinsed with 20 ml of 3 mol l⁻¹ HNO₃. Finally, Sr and Pb were stripped from the column with a small volume of 0.05 mol l⁻¹ HNO₃. The first millilitre was discarded, and the next 5 ml was collected for MC-ICP-MS or TIMS analysis.

The separation of Nd and Sm was achieved using another commercial Ln-Spec resin (only for Sm and Nd isolation loading LMREE) column. The LMREE fraction collected in the second column was gently evaporated to dryness, taken up with 0.5 ml of 0.25 mol l⁻¹ HCl and loaded onto Ln-Spec resin. Lanthanum, Ce and Pr were removed with a 6 ml, 0.25 mol l⁻¹ HCl wash. Then, the fraction containing Nd was eluted with 6 ml of 0.25 mol l⁻¹ HCl for Nd determination using the MC-ICP-MS.

Mass spectrometric measurement

Strontium isotopic compositions were measured on two different Thermo Fisher Scientific instruments (Triton Plus TIMS and Neptune MC-ICP-MS), whereas Nd, Hf and Pb isotopic

compositions were entirely determined on the Neptune MC-ICP-MS.

MC-ICP-MS: Prior to Sr-Nd-Hf-Pb isotopic measurements, the Neptune MC-ICP-MS was allowed to stabilise for at least 1 h under normal operating conditions. A summary of the typical instrumental parameters is presented in Table 2. Sr-Nd-Hf-Pb isotopic data were acquired in static multi-collector mode at low resolution (400). During the Sr-Nd-Hf-Pb isotope measurement session, an aliquot of 200 $\mu\text{g l}^{-1}$ NIST SRM 987, JNdi-1, Alfa Hf or NIST SRM 981 was used regularly for optimising the operational parameters and evaluating the reproducibility and accuracy of the instrument. NIST SRM 987, JNdi-1, Alfa Hf or NIST SRM 981 was analysed for data monitoring after every ten actual samples were analysed. After the chemical isolation mentioned above, the Sr-Nd-Hf-Pb fractions were taken up with 2% HNO_3 and aspirated into the ICP source using a Micromist PFA nebuliser in a free aspiration (Xie *et al.* 2005, Wu *et al.* 2006, Yang *et al.* 2010, 2011, 2012, Li *et al.* 2015). The isotopic results were corrected online for mass fractionation using natural stable ratios (Sr, Hf and Nd) or using a Tl spike for Pb. All Sr, Nd and Hf isotope ratios were internally corrected for mass fractionation using constant values of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$, respectively, by the exponential law. During this measurement session, the NIST SRM 987, JNdi-1 and Alfa Hf reference solutions yielded mean $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.710245 ± 18 ($2s$, $n = 22$), 0.512110 ± 13 ($2s$,

$n = 24$) and 0.282190 ± 12 ($2s$, $n = 24$), respectively, consistent within our long-term mean and other, previously reported, data (Li *et al.* 2007, 2015, 2016). During the course of data acquisition in this study, the mean of the measured Pb standard NIST SRM 981 (200 ng g^{-1} Pb doped with 50 ng g^{-1} Tl of NIST SRM 997), corrected online for mass fractionation using $^{205}\text{Tl}/^{203}\text{Tl} = 2.3871$, was $^{208}\text{Pb}/^{204}\text{Pb} = 36.7018 \pm 0.0019$ ($2s$, $n = 7$), $^{207}\text{Pb}/^{204}\text{Pb} = 15.4826 \pm 0.0005$ ($2s$, $n = 7$) and $^{206}\text{Pb}/^{204}\text{Pb} = 16.9298 \pm 0.0006$ ($2s$, $n = 7$), respectively, which is consistent with our previous data and other colleagues' reported data by MC-ICP-MS or TIMS (Xie *et al.* 2005, Chen *et al.* 2014, Li *et al.* 2016).

Furthermore, USGS BCR-1, BHVO-2 and AGV-2 were also processed for Sr-Nd-Hf isotopic measurement and gave values of 0.704998 ± 14 ($2s$, $n = 3$), 0.703485 ± 13 ($2s$, $n = 2$) and 0.703984 ± 13 ($2s$, $n = 3$) for $^{87}\text{Sr}/^{86}\text{Sr}$; 0.512640 ± 08 ($2s$, $n = 3$), 0.512984 ± 10 ($2s$, $n = 2$) and 0.512800 ± 11 ($2s$, $n = 3$) for $^{143}\text{Nd}/^{144}\text{Nd}$; and 0.282866 ± 08 ($2s$, $n = 3$), 0.283100 ± 9 ($2s$, $n = 2$) and 0.282980 ± 08 ($2s$, $n = 3$) for $^{176}\text{Hf}/^{177}\text{Hf}$, respectively, which are identical, within analytical uncertainties with the recommended values (Weis *et al.* 2005, 2006, 2007). In the meantime, GSR-3 together with CGSG glasses was analysed for Pb isotopic measurement and gave values of 37.8269 ± 0.0122 ($2s$, $n = 4$) for $^{208}\text{Pb}/^{204}\text{Pb}$, 15.4783 ± 0.0013 ($2s$, $n = 4$) for $^{207}\text{Pb}/^{204}\text{Pb}$ and 17.7519 ± 0.0159 ($2s$, $n = 4$) for $^{206}\text{Pb}/^{204}\text{Pb}$, respectively, also consistent, within analytical uncertainties, with previously reported data by Nu MC-ICP-MS (Fourny *et al.* 2016).

Table 2.
Typical operating parameters for Sr, Nd, Hf and Pb isotopic measurements using the Neptune MC-ICP-MS

Parameter	Setting
RF forward power	~1300 W
Cooling gas	16l min^{-1}
Auxiliary gas	0.8l min^{-1}
Sample gas	~1.00 l min^{-1} (optimised daily)
Extraction	-2000 V
Focus	-645 V
Detection system	Nine Faraday collectors
Acceleration voltage	10 kV
Interface cones	Standard nickel cone
Nebuliser type	Micromist PFA nebuliser
Sample uptake rate	50 $\mu\text{l min}^{-1}$
Uptake mode	Free aspiration
Instrument resolution	~ 400 (low)
Typical sensitivity on ^{88}Sr , ^{146}Nd , ^{180}Hf and ^{208}Pb	~ 40, 10, 20, 33 V per $\mu\text{g g}^{-1}$ (10^{-11} Ω resistors)
Integration time	4 s
Baseline/background determination	ca. 1 min on peak in 2% HNO_3

TIMS: Strontium isotopic measurements were performed on a Triton Plus TIMS. A single W filament geometry was used to obtain Sr^+ ion beams. All data were acquired by static multi-collection with the collector array of ^{84}Sr , ^{85}Rb , ^{86}Sr , ^{87}Sr and ^{88}Sr . A standard solution of NIST SRM 987 for Sr was measured during the same TIMS runs as the samples. Prior to sample measurement, the Sr fraction was dissolved using 2 μl of 2.5 mol l^{-1} HCl, loaded with a 2 μl of TaF_5 onto a degassed W filament (0.03 mm thick, 0.72 mm wide) assembly, dried on a clean bench at low temperature, and subsequently loaded and dried again. After final drying, the filament was heated slowly until it glowed dull red for about three seconds (Chu *et al.* 2014, Li *et al.* 2016). For the mass spectrometric measurement, the W filament was first heated at 300 mA min^{-1} until a signal of ^{88}Sr reached 30 mV. The beam was peak-centred and roughly focused, and the filament was slowly heated to obtain 4 V for ^{88}Sr . When the signal intensity of ^{88}Sr reached 5 V, data acquisition commenced. Fifteen scans with an integration time of 4 s and an idle time of 3 s made up one block. For

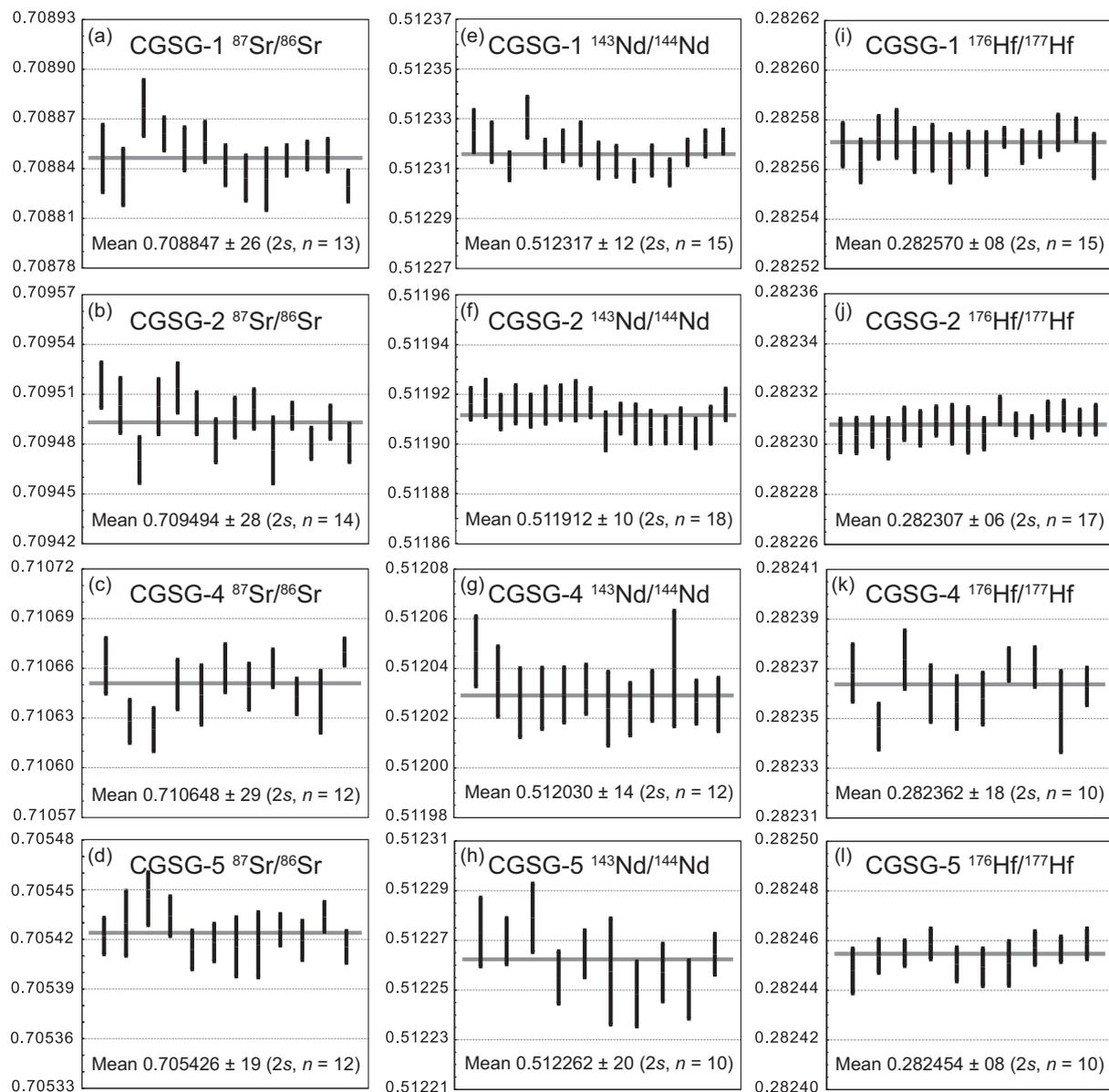


Figure 1. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values for CGSG-1, CGSG-2, CGSG-4 and CGSG-5 glass samples measured using the Neptune MC-ICP-MS and Triton Plus TIMS instruments. The bars shown for each measured value represent 2s, and the solid horizontal line represents mean of all measurements.

each sample, twelve blocks were run. Prior to mass fractionation correction, the ^{87}Sr signal intensity had been corrected for the potential bias caused by the remaining isobaric overlap of ^{87}Rb on ^{87}Sr using an $^{85}\text{Rb}/^{87}\text{Rb}$ value of 2.59265. After Sr-specific resin purification chemistry, the $^{85}\text{Rb}/^{86}\text{Sr}$ ratios obtained were $\leq 10^{-5}$ for the analysis of natural silicate samples, showing negligible isobaric interferences. Then, the corrected $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ using the exponential law. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ value of the NIST SRM 987 reference solution, during all measurement sessions of our

data collection, was 0.710250 ± 16 (2s, $n = 8$), showing good agreement with previously published data (Chu *et al.* 2014, Li *et al.* 2016).

Results and discussion

The Sr-Nd-Hf-Pb isotope measurement results for six different aliquots (chips) of CGSG materials using different instruments acquired in the last 3 years are presented in Figures 1 and 2, and Tables 3, 4 and 5. There was insignificant difference between the Sr-Nd-Hf-Pb isotope

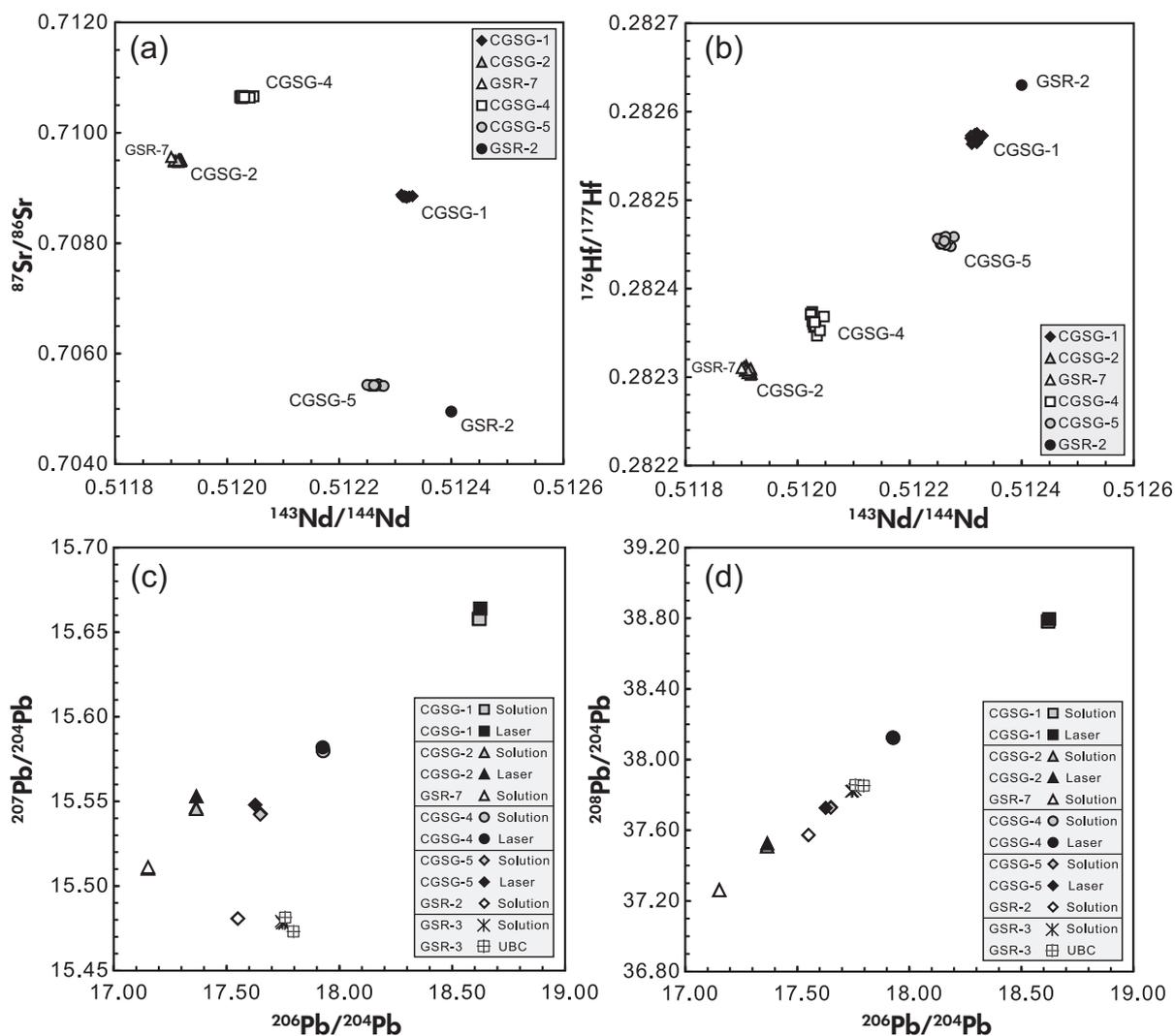


Figure 2. Comparison of the Sr-Nd-Hf-Pb isotopic variation in CGSG-1, CGSG-2, CGSG-4 and CGSG-5 glasses and GSR-2, GSR-3 and GSR-7 rock reference materials. (a) $^{87}\text{Sr}/^{86}\text{Sr}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$. (b) $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$. (c) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. (d) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$. Sr-Nd-Hf isotopic data are from this study, while Pb isotope data are from this study, Fourny *et al.* (2016) (Solution, University of British Columbia (UBC), Canada) and Chen *et al.* (2014; Laser, Northwest University, China), respectively. Error bars are smaller than the symbols.

ratios obtained during different measurement sessions, along with their individual repeatability. This demonstrates that the chemical fraction was of adequate purity for mass spectrometric measurements. Comparative isotopic ratios from the literature are reported here only when the number of duplicates was greater than one (Tables 4 and 5; Li *et al.* 2007, Cheng *et al.* 2015, Fourny *et al.* 2016). There are some obvious Sr-Nd-Hf-Pb isotopic differences between the glasses and the original powdered rock reference materials (CGSG-2 and GSR-7, especially CGSG-5 and GSR-2). A possible reason is discussed in the following sections.

Strontium isotopic composition

Although the 'internal' uncertainty of Sr isotope data obtained in the first batch analysis is a little larger than that of the other two batch measurements, our obtained $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for CGSG-1, CGSG-2, CGSG-4 and CGSG-5 for six aliquot chips were 0.708847 ± 26 ($2s$, $n = 13$), 0.709494 ± 28 ($2s$, $n = 14$), 0.710648 ± 29 ($2s$, $n = 12$) and 0.705426 ± 20 ($2s$, $n = 12$), respectively (Figure 1a–d), indicating relatively homogeneous Sr isotopic compositions varying from 0.7054 to 0.7106 for the four CGSG glass materials. Considering their relatively narrow

Table 3.
Strontium, Nd and Hf isotopic compositions of CGSG glass, and GSR-2 and GSR-7 rock reference materials in this work

Sample	Aliquots	$^{87}\text{Sr}/^{86}\text{Sr} (\pm 2s)$		$^{143}\text{Nd}/^{144}\text{Nd} (\pm 2s)$		$^{176}\text{Hf}/^{177}\text{Hf} (\pm 2s)$	
		Analysis	Re-analysis	Analysis	Re-analysis	Analysis	Re-analysis
CGSG-1	a61 01 ^a	0.708846 (± 20)	0.708835 (± 17)	0.512325 (± 08)	0.512321 (± 08)	0.282570 (± 09)	
	a61 02 ^a	0.708877 (± 17)	0.708861 (± 10)	0.512311 (± 06)		0.282563 (± 09)	
	a61 03 ^a	0.708852 (± 13)*	0.708856 (± 12)*	0.512331 (± 08)		0.282573 (± 09)	0.282574 (± 10)
	a61 04 ^a	0.708842 (± 12)		0.512316 (± 06)	0.512319 (± 06)	0.282568 (± 09)	0.282569 (± 09)
	a13 01 ^b	0.708834 (± 14)	0.708834 (± 19)	0.512320 (± 09)		0.282565 (± 10)	
	a11 01 ^c	0.708845 (± 09)		0.512313 (± 07)	0.512313 (± 06)	0.282568 (± 07)	0.282566 (± 09)
	a15 01 ^c	0.708848 (± 08)		0.512309 (± 04)	0.512313 (± 06)	0.282573 (± 04)	0.282569 (± 07)
	a17 01 ^c	0.708848 (± 10)		0.512308 (± 05)	0.512317 (± 07)	0.282570 (± 05)	0.282575 (± 07)
	a19 01 ^c	0.708830 (± 09)		0.512320 (± 05)	0.512321 (± 05)	0.282576 (± 04)	0.282565 (± 09)
Mean [$\pm 2s$]	0.708847 \pm [26] ($n = 13$)		0.512317 \pm [12] ($n = 15$)		0.282570 \pm [08] ($n = 15$)		
CGSG-2 [GSR-7G]	B61 01 ^a	0.709516 (± 14)	0.709503 (± 17)	0.511916 (± 06)	0.511918 (± 07)	0.282304 (± 07)	0.282303 (± 07)
	B61 02 ^a	0.709470 (± 14)	0.709503 (± 17)	0.511913 (± 07)	0.511916 (± 08)	0.282305 (± 06)	0.282302 (± 08)
	B61 03 ^a	0.709514 (± 15)	0.709499 (± 13)	0.511913 (± 06)	0.511916 (± 07)	0.282308 (± 06)	0.282306 (± 07)
	B61 04 ^a	0.709482 (± 13)*	0.709496 (± 12)*	0.511917 (± 07)	0.511917 (± 08)	0.282309 (± 06)	0.282308 (± 08)
	B03 01 ^b	0.709501 (± 12)	0.709476 (± 20)	0.511917 (± 07)	0.511905 (± 08)	0.282306 (± 09)	
	B01 01 ^c	0.709496 (± 08)		0.511910 (± 06)	0.511908 (± 08)	0.282304 (± 07)	0.282313 (± 07)
	B05 01 ^c	0.709482 (± 09)		0.511907 (± 07)	0.511906 (± 05)	0.282308 (± 07)	0.282307 (± 07)
	B07 01 ^c	0.709493 (± 10)		0.511907 (± 07)	0.511904 (± 06)	0.282311 (± 07)	0.282311 (± 07)
	B09 01 ^c	0.709481 (± 12)		0.511908 (± 07)	0.511916 (± 06)	0.282309 (± 07)	0.282310 (± 07)
Mean [$\pm 2s$]	0.709494 \pm [28] ($n = 14$)		0.511912 \pm [10] ($n = 18$)		0.282307 \pm [06] ($n = 17$)		
GSR-7	0.709544 \pm (16)		0.511832 \pm (10)		0.282310 \pm (08)		
CGSG-4	d116 01 ^a	0.710662 (± 17)		0.512047 (± 14)	0.512035 (± 14)	0.282368 (± 12)	0.282347 (± 09)
	d116 02 ^a	0.710628 (± 13)	0.710623 (± 13)	0.512026 (± 14)		0.282374 (± 12)	
	d116 03 ^a	0.710650 (± 15)*	0.710644 (± 18)*	0.512028 (± 12)		0.282360 (± 11)	
	d03 01 ^b	0.710660 (± 14)	0.710649 (± 14)	0.512029 (± 11)	0.512032 (± 10)	0.282356 (± 11)	0.282358 (± 10)
	d01 01 ^c	0.710660 (± 11)		0.512024 (± 15)		0.282372 (± 07)	
	d05 01 ^c	0.710643 (± 11)		0.512024 (± 11)	0.512029 (± 11)	0.282371 (± 08)	
	d07 01 ^c	0.710640 (± 19)		0.512040 (± 23)		0.282353 (± 16)	
	d09 01 ^c	0.710670 (± 08)		0.512027 (± 09)	0.512026 (± 11)	0.282363 (± 08)	
Mean [$\pm 2s$]	0.710648 \pm [29] ($n = 12$)		0.512030 \pm [14] ($n = 12$)		0.282362 \pm [18] ($n = 10$)		
CGSG-5 [GSR-2G]	E33 01 ^a	0.705424 (± 11)	0.705432 (± 20)	0.512273 (± 14)		0.282448 (± 09)	0.282454 (± 07)
	E33 02 ^a	0.705447 (± 16)	0.705436 (± 12)	0.512270 (± 09)		0.282455 (± 05)	
	E33 03 ^a	0.705416 (± 12)*	0.705420 (± 11)*	0.512279 (± 14)		0.282459 (± 06)	
	E77 01 ^b	0.705417 (± 18)	0.705419 (± 20)	0.512255 (± 11)	0.512265 (± 09)	0.282450 (± 07)	0.282449 (± 08)
	E67 01 ^c	0.705428 (± 09)		0.512257 (± 21)	0.512248 (± 13)	0.282451 (± 09)	
	E88 01 ^c	0.705421 (± 12)		0.512257 (± 12)		0.282457 (± 07)	
	E91 01 ^c	0.705436 (± 09)		0.512250 (± 12)		0.282457 (± 05)	
	E98 01 ^c	0.705417 (± 10)		0.512264 (± 08)		0.282459 (± 06)	
Mean [$\pm 2s$]	0.705426 \pm [20] ($n = 12$)		0.512262 \pm [15] ($n = 10$)		0.282454 \pm [08] ($n = 10$)		
GSR-2	0.704914 \pm (15)		0.512382 \pm (10)		0.282645 \pm (08)		

^a 1st batch analysis of 2015, ^b 2nd batch analysis of 2017, ^c 3rd batch analysis of 2018, *measurement by Triton Plus TIMS. ($\pm 2s$) is the absolute error value of the individual analysis and reported as times 10^6 , and [$\pm 2s$] means the standard deviation value of the individual analysis and is reported as times 10^6 .

Rb/Sr ratio (0.05–0.1) with moderate Sr mass fraction ranging from 390 to 1300 $\mu\text{g g}^{-1}$, CGSG glass materials can also be used as a potential secondary RMs in method development for *in situ* Sr isotopic measurement by LA-MC-ICP-MS, comparable to the USGS and MPI-DING glasses (e.g., BIR-1G, BCR-2G, BHVO-2G, KL2-G and ML3B-G; Tong *et al.* 2015, Zhang *et al.* 2018). As mentioned above,

CGSG-2 (GSR-7G) and CGSG-5 (GSR-2G) materials were made from the original rock reference material GSR-7 and GSR-2, which are Chinese syenite and andesite geochemical reference materials, respectively (Xie *et al.* 1985, 1989, Qi and Grégoire 2000). For comparison, GSR-7 and GSR-2 rock powders were also processed for Sr isotope determination in the same way as the CGSG materials. Our

Table 4.
Comparison of Sr, Nd and Hf isotopic composition of CGSG glass, GSR-2 and GSR-7 obtained in this study with published values

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$ ($\pm 2s$)	<i>n</i>	$^{143}\text{Nd}/^{144}\text{Nd}$ ($\pm 2s$)	<i>n</i>	$^{176}\text{Hf}/^{177}\text{Hf}$ ($\pm 2s$)	<i>n</i>	Reference
CGSG-1	0.708847 (± 26)	13	0.512317 (± 12)	15	0.282570 (± 08)	15	This study
CGSG-2 [GSR-7G]	0.709494 (± 28)	14	0.511912 (± 10)	18	0.282307 (± 06)	17	This study
GSR-7	0.709544 (± 16)	1	0.511832 (± 10)	1	0.282310 (± 08)	1	This study
			0.511820 (± 10)	4	0.282309 (± 06)	4	Li <i>et al.</i> (2007)
CGSG-4	0.710648 (± 29)	12	0.512030 (± 14)	12	0.282362 (± 18)	10	This study
CGSG-5 [GSR-2G]	0.705426 (± 20)	12	0.512262 (± 15)	10	0.282454 (± 08)	10	This study
GSR-2	0.704914 (± 15)	1	0.512382 (± 10)	1	0.282645 (± 08)	1	This study
					0.282641 (± 06)	10	Cheng <i>et al.</i> (2015)

($\pm 2s$) is the standard deviation value of the individual analyses and reported as times 10^6 .

$^{87}\text{Sr}/^{86}\text{Sr}$ value for GSR-7 was 0.709544 ± 16 (2s), which is slightly higher than that of CGSG-2. Similarly, our obtained $^{87}\text{Sr}/^{86}\text{Sr}$ value for GSR-2 was 0.704914 ± 15 (2s), which is obviously lower than that of CGSG-5.

Neodymium isotopic composition

The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for CGSG-1, CGSG-2, CGSG-4 and CGSG-5 for the six aliquot chips were 0.512317 ± 12 (2s, $n = 15$), 0.511912 ± 10 (2s, $n = 18$), 0.512030 ± 14 (2s, $n = 12$) and 0.512262 ± 15 (2s, $n = 10$), respectively (Figure 1e–h), indicating relatively homogeneous Nd isotopic compositions of the individual CGSG materials. For the purpose of comparison, GSR-7 and GSR-2 rock powders were also analysed for Nd isotopes in the same way as for the CGSG materials. For GSR-7, our $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.511832 ± 10 (2s) agrees well with 0.511820 ± 10 (2s, $n = 04$) obtained by Li *et al.* (2007) using TIMS. This value is slightly lower than that of CGSG-2. Similarly, our $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.512382 ± 10 (2s) for GSR-2 is obviously higher than that of CGSG-5.

Hafnium isotopic composition

During different measurement sessions spanning the last 3 years, our obtained $^{176}\text{Hf}/^{177}\text{Hf}$ values for CGSG-1, CGSG-2, CGSG-4 and CGSG-5 for six aliquot chips were 0.282570 ± 08 (2s, $n = 15$), 0.282307 ± 06 (2s, $n = 17$), 0.282362 ± 18 (2s, $n = 10$) and 0.282454 ± 08 (2s, $n = 10$), respectively (Figure 1i–l), indicating relatively homogeneous Hf isotopic compositions of individual CGSG materials. For comparison, GSR-7 and GSR-2 rock powders were also analysed for Hf isotopes. Our obtained $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282310 ± 08 (2s) for GSR-7 is identical to the value (0.282309 ± 06 , 2s, $n = 4$) previously reported by Li

et al. (2007) and also agrees well with that of sample 09JH80 (0.282301 ± 08 , 2s) from the Sima alkaline complex, north-east China (Zhu *et al.* 2016). Similarly, our obtained $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.282645 ± 08 (2s) for GSR-2 is in good agreement with 0.282641 ± 06 (2s, $n = 10$) recently reported by Cheng *et al.* (2015).

Lead isotopic composition

For Pb isotopes, to assess the analytical reliability and accuracy of our procedure for CGSG glasses, we analysed the Chinese rock reference materials GSR-2 (andesite), GSR-3 (basalt) and GSR-7 (syenite) during the measurement sessions. Data for GSR-3 from Fourny *et al.* (2016) and CGSG glass data from Chen *et al.* (2014) are also shown for comparison. The results from replicate analyses of these samples are summarised in Table 5 and illustrated in Figure 2. Measurement reproducibility for the samples is satisfactory, though that for GSR-3 is slightly lower than that of Fourny *et al.* (2016). Additionally, we also compared our results with those utilising the fs-LA-MC-ICP-MS technique by Chen *et al.* (2014) for CGSG glasses, although their analytical reproducibility is significantly worse than our solution data. Additionally, Pb isotopic ratios of the solid glasses and the unfused Chinese reference material powders (i.e., CGSG-2 and GSR-7, and CGSG-5 and GSR-2, respectively) are not identical in all instances (Figure 2).

Isotopic discrepancy between CGSG-2 and GSR-7, and CGSG-5 and GSR-2

As already known, the major and trace element, and isotopic compositions of the USGS glass materials BCR-2G, BHVO-2G and BIR-1G are identical to those of the original USGS powdered rock reference materials (BCR-2, BHVO-2 and BIR-1; Elburg *et al.* 2005, Jochum and Nohl 2008). For

Table 5.
Comparison of Pb isotopic compositions of CGSG glass, GSR-2, GSR-3 and GSR-7 measured in this work and the literature

Sample	$^{208}\text{Pb}/^{204}\text{Pb}$ ($\pm 2s$)#	$^{207}\text{Pb}/^{204}\text{Pb}$ ($\pm 2s$)#	$^{206}\text{Pb}/^{204}\text{Pb}$ ($\pm 2s$)#	$^{208}\text{Pb}/^{206}\text{Pb}$ ($\pm 2s$)*	$^{207}\text{Pb}/^{206}\text{Pb}$ ($\pm 2s$)*	n	Method	Reference
CGSG-1								
$\alpha 15$	38.7830 (± 11)	15.6578 (± 04)	18.6191 (± 05)	2.08297 (± 02)	0.84095 (± 01)	1	Sol. MC	This study
$\alpha 17$	38.7810 (± 07)	15.6579 (± 03)	18.6201 (± 03)	2.08278 (± 01)	0.84092 (± 01)	1	Sol. MC	This study
Mean [$\pm 2s$]	38.7820 [± 28]	15.6579 [± 01]	18.6196 [± 15]	2.08287 [± 27]	0.84093 [± 04]	2	Sol. MC	This study
Mean [$\pm 2s$]	38.7950 [± 80]	15.6640 [± 30]	18.6240 [± 40]	2.08330 [± 10]	0.84114 [± 04]		fs-LA-MC	Chen <i>et al.</i> (2014)
CGSG-2 [GSR-7G]								
B05	37.5106 (± 09)	15.5464 (± 04)	17.3646 (± 04)	2.16016 (± 02)	0.89528 (± 01)	1	Sol. MC	This study
B07	37.5092 (± 09)	15.5455 (± 03)	17.3658 (± 04)	2.16000 (± 02)	0.89519 (± 01)	1	Sol. MC	This study
Mean [$\pm 2s$]	37.5099 [± 19]	15.5460 [± 13]	17.3652 [± 16]	2.16008 [± 23]	0.89524 [± 13]	2	Sol. MC	This study
Mean [$\pm 2s$]	37.5260 [± 30]	15.5530 [± 30]	17.3660 [± 10]	2.16090 [± 00]	0.89559 [± 02]		fs-LA-MC	Chen <i>et al.</i> (2014)
GSR-7								
1	37.2610 (± 08)	15.5102 (± 03)	17.1519 (± 03)	2.17238 (± 02)	0.90428 (± 01)	1	Sol. MC	This study
2	37.2613 (± 08)	15.5111 (± 03)	17.1525 (± 03)	2.17236 (± 02)	0.90430 (± 01)	1	Sol. MC	This study
Mean [$\pm 2s$]	37.2611 [± 05]	15.5107 [± 12]	17.1522 [± 09]	2.17237 [± 02]	0.90429 [± 02]	2	Sol. MC	This study
CGSG-4								
d05	38.1222 (± 08)	15.5798 (± 03)	17.9287 (± 03)	2.12633 (± 02)	0.86900 (± 01)	1	Sol. MC	This study
d07	38.1235 (± 09)	15.5797 (± 03)	17.9277 (± 03)	2.12652 (± 02)	0.86903 (± 01)	1	Sol. MC	This study
Mean [$\pm 2s$]	38.1228 [± 18]	15.5798 [± 02]	17.9282 [± 14]	2.12642 [± 26]	0.86901 [± 05]	2	Sol. MC	This study
Mean [$\pm 2s$]	38.1260 [± 80]	15.5820 [± 30]	17.9260 [± 40]	2.12700 [± 10]	0.86930 [± 03]		fs-LA-MC	Chen <i>et al.</i> (2014)
CGSG-5 [GSR-2G]								
E88	37.7309 (± 12)	15.5428 (± 05)	17.6507 (± 05)	2.13764 (± 02)	0.88058 (± 01)	1	Sol. MC	This study
E91	37.7280 (± 07)	15.5422 (± 03)	17.6490 (± 03)	2.13769 (± 02)	0.88062 (± 01)	1	Sol. MC	This study
Mean [$\pm 2s$]	37.7295 [± 41]	15.5425 [± 08]	17.6499 [± 24]	2.13766 [± 07]	0.88060 [± 07]	2	Sol. MC	This study
Mean [$\pm 2s$]	37.7270 [± 160]	15.5480 [± 60]	17.6270 [± 70]	2.13990 [± 10]	0.88203 [± 05]		fs-LA-MC	Chen <i>et al.</i> (2014)
GSR-2								
1	37.5725 (± 10)	15.4808 (± 04)	17.5494 (± 04)	2.14098 (± 02)	0.88213 (± 01)	1	Sol. MC	This study
2	37.5730 (± 09)	15.4808 (± 04)	17.5505 (± 04)	2.14089 (± 02)	0.88207 (± 01)	1	Sol. MC	This study
Mean [$\pm 2s$]	37.5728 [± 07]	15.4808 [± 00]	17.5500 [± 15]	2.14093 [± 13]	0.88210 [± 07]	2	Sol. MC	This study
GSR-3								
1	37.8205 (± 14)	15.4793 (± 06)	17.7433 (± 06)	2.13152 (± 02)	0.87240 (± 01)	1	Sol. MC	This study
2	37.8229 (± 15)	15.4780 (± 06)	17.7470 (± 07)	2.13121 (± 02)	0.87215 (± 01)	1	Sol. MC	This study
3	37.8328 (± 15)	15.4781 (± 06)	17.7592 (± 06)	2.13033 (± 02)	0.87155 (± 01)	1	Sol. MC	This study
4	37.8314 (± 11)	15.4778 (± 04)	17.7580 (± 05)	2.13044 (± 02)	0.87159 (± 01)	1	Sol. MC	This study
Mean [$\pm 2s$]	37.8269 [± 122]	15.4783 [± 13]	17.7519 [± 159]	2.13087 [± 116]	0.87192 [± 84]	4	Sol. MC	This study
Mean [$\pm 2s$]	37.8562 [± 20]	15.4814 [± 08]	17.7595 [± 45]			5	Sol. MC	Fourny <i>et al.</i> (2016)
Mean [$\pm 2s$]	37.8526 [± 75]	15.4731 [± 33]	17.7961 [± 61]			5	Sol. MC	Fourny <i>et al.</i> (2016)

($\pm 2s$)# means the absolute error value of the individual $^{208,7,6}\text{Pb}/^{204}\text{Pb}$ sample analyses and is reported as times 10^4 , and ($\pm 2s$)* means the absolute error value of the individual $^{208,7}\text{Pb}/^{206}\text{Pb}$ sample analyses and is reported as times 10^5 . [$\pm 2s$] means the standard deviation value of the individual $^{208,7,6}\text{Pb}/^{204}\text{Pb}$ sample analyses and is reported as times 10^4 , and [$\pm 2s$] means the standard deviation value of the individual $^{208,7}\text{Pb}/^{206}\text{Pb}$ sample analyses and is reported as times 10^5 . Sol. MC means solution MC-ICP-MS while fs-LA-MC means femtosecond laser ablation MC-ICP-MS.

example, both the Sr isotopic composition and the Rb and Sr contents of BHVO-2G are indistinguishable from those of BHVO-2. No obvious differences were observed between the Sr isotopic compositions of the powdered rock and the solid glass materials (Elburg *et al.* 2005). Similarly, there are insignificant differences in the Sr-Nd-Hf isotopic composition between BCR-2 and BIR-1, and BCR-2G and BIR-1G, respectively (Weis *et al.* 2005, 2006, 2007).

However, unlike the USGS glass reference materials, significant discrepancies of Sr-Nd-Hf-Pb isotopic

compositions between CGSG-5 and GSR-2 are clearly illustrated in Figure 2, indicating flux contamination during glass preparation (Tables 1 and 4). For the CGSG-5 glass, all the Hf isotope compositions are identical within measurement reproducibility with a calculated $^{176}\text{Hf}/^{177}\text{Hf}$ mean of 0.282454 ± 08 ($2s$, $n = 10$), but lower than the 0.282645 ± 08 ($2s$) in this work and 0.282641 ± 06 ($2s$, $n = 10$) for GSR-2 powdered rock obtained by Cheng *et al.* (2015). Furthermore, our $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values of CGSG-5 glass are 0.705426 ± 20 ($2s$, $n = 12$) and 0.512262 ± 15 ($2s$, $n = 10$), respectively, which are

significantly higher than the Sr value of 0.704914 ± 15 (2s) and Nd value of 0.512382 ± 10 (2s) for the GSR-2 powdered sample. The probable reason for the isotopic difference between CGSG-5 and GSR-2 could be that the impurity arising from the addition of Na_2CO_3 and $\text{Li}_2\text{B}_4\text{O}_7$ flux during the preparation of the glass (Hu *et al.* 2011) might have changed the isotopic compositions (Table 1). Actually, these differences are also supported and demonstrated by the Li, Sr, Nd, Hf and Pb contents in Table 1. For example, the Pb content of GSR-7 decreased from 196 to $138 \mu\text{g g}^{-1}$ Pb of CGSG-2, indicating volatilisation of Pb during the high-temperature preparation of the glass. In contrast to CGSG-2, the Pb mass fraction of CGSG-2 dramatically increased up to $\sim 21 \mu\text{g g}^{-1}$ from $\sim 11 \mu\text{g g}^{-1}$ Pb of GSR-2, indicating significant Pb contamination from the flux agent (Bao *et al.*, 2011).

Similarly, there are slight differences in the Sr and Nd isotopic compositions between GSR-7 (rock powder) and CGSG-2 (solid glass), although their $^{176}\text{Hf}/^{177}\text{Hf}$ values agree well within analytical uncertainty. The $^{143}\text{Nd}/^{144}\text{Nd}$ value of 0.511832 ± 10 (2s) for GSR-7 (powdered sample) obtained in this study is consistent with 0.511820 ± 10 (2s, $n = 4$) measured on a Finnigan MAT 262 TIMS (Li *et al.* 2007) and, however, is apparently lowered by 0.000080 than the mean value of 0.511912 ± 10 (2s, $n = 18$) for the solid glass following duplicate measurements (Table 3). The $^{176}\text{Hf}/^{177}\text{Hf}$ values for the CGSG-2 glass and GSR-7 powder are 0.282307 ± 06 (2s, $n = 17$) and 0.282310 ± 08 (2s), respectively, which agree well with each other within analytical uncertainty, and are also consistent with 0.282309 ± 06 (2s, $n = 4$; Li *et al.* 2007). Nevertheless, the significant discrepancy between our Pb isotope data for CGSG-2 and that for GSR-7 (powder) is clearly illustrated in Figure 2, making it therefore more susceptible to contamination of any kind (Table 5).

Conclusions

In this study, a series of Sr-Nd-Hf-Pb isotopic ratio determinations were performed on four available CGSG reference materials. The results were obtained by high-precision bulk techniques, such as MC-ICP-MS and TIMS. Our investigation indicates that these reference glass materials have homogenous Sr-Nd-Hf-Pb compositions, which are therefore suitable reference materials for Sr-Nd-Hf-Pb isotope measurements. Considering the relatively narrow Rb/Sr ratios (0.05–0.1) with moderate Sr mass fraction ranging from 390 to $1300 \mu\text{g g}^{-1}$ for the CGSG glass materials, they can potentially be used as primary or secondary glass reference materials for LA-MC-ICP-MS measurement of Sr isotopes. Furthermore, the Hf isotopic

composition of the CGSG-2 glass sample is identical, within uncertainty, to its unfused counterpart and there are relatively significant isotopic discrepancies in the isotopic composition of Sr, Nd and Pb between the glass and the original rock powder reference material, indicating possible contamination of Sr, Nd and Pb from the flux agent. In contrast, the Sr-Nd-Hf-Pb isotopic data of the CGSG-5 glass are significantly different from its unfused counterpart, indicating the contamination of Sr, Nd, Hf and Pb from the flux agent. Based on these duplicate analyses in different measurement sessions over a 3-year period, preferred values are provided for the Sr, Nd, Hf and Pb isotopic compositions of the CGSG-1, CGSG-2, CGSG-4 and CGSG-5 samples. These data are now available to the geochemical community for use in future analyses for Sr-Nd-Hf-Pb isotopes.

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