

# Rhenium-Osmium Isotope Measurements of Geological Reference Material BIR-1a: Evaluation of Homogeneity and Implications for Method Validation and Quality Control

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To evaluate the homogeneity of geological reference material BIR-1a (basalt; United States Geological Survey, USGS) for Re-Os isotopic studies at the 0.2–1.0 g test portion size level, sixty-three precise measurement results of Re and Os mass fractions and isotope amount ratios were obtained over an 18-month period. These data reveal that the reference material has higher Re ( $0.691 \pm 0.022 \text{ ng g}^{-1}$ ,  $2s$ ,  $n = 63$ ) and lower Os mass fractions ( $0.343 \pm 0.089 \text{ ng g}^{-1}$ ,  $2s$ ,  $n = 63$ ) than UB-N (serpentinite, CRPG) and is homogeneous in  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratio ( $0.13371 \pm 0.00092$ ,  $2s$ ,  $n = 63$ ) at the 0.2–1.0 g test portion size level. The results are essentially consistent with previous views indicating that BIR-1a gives precise measurement results for Re-Os isotope amount ratio measurements at the 1 g test portion size level (Ishikawa *et al.*, *Chemical Geology*, 2014, 384, 27–46; Meisel and Horan, *Reviews in Mineralogy and Geochemistry*, 2016, 81, 89–106). Based on these new Re-Os data and previous studies, we propose BIR-1a as a useful reference material that can be used in method validation and quality control and interlaboratory comparisons for studies dealing with mafic geological samples at test portion sizes of  $> 0.4 \text{ g}$ .

Keywords: BIR-1a, Re-Os isotope, determination, reference material, quality control.

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The Re-Os isotopic system is based on the  $\beta^-$  decay of  $^{187}\text{Re}$  to  $^{187}\text{Os}$  with a half-life of 41.6 Ga (Smoliar *et al.* 1996). Rhenium and osmium are variably chalcophile and siderophile elements, meaning they preferentially partition into metal and sulfide. In addition, during mantle partial melting, Os behaves compatibly, whereas Re is moderately incompatible during mantle melting (e.g., Shirey and Walker 1998). This unique isotopic system has therefore been exploited to address a wide variety of geochemical and cosmochemical questions (Shirey and Walker 1998, Peucker-Ehrenbrink and Jahn 2001, Day *et al.* 2010, 2016a, b, Harvey *et al.* 2016, Lorand and Luguet 2016).

Over the last two decades, the increasing application of the Re-Os system has been spurred by new achievements in sample preparation, chemical separation techniques and

instrumentation (e.g., Creaser *et al.* 1991, Völkening *et al.* 1991, Shirey and Walker 1995, Birck *et al.* 1997, Pearson and Woodland 2000, Meisel *et al.* 2001b, Reisberg and Meisel 2002, Ishikawa *et al.* 2014, Meisel and Horan 2016). The development of high-sensitivity negative-thermal ionisation mass spectrometry (N-TIMS) (Creaser *et al.* 1991, Völkening *et al.* 1991, Walczyk *et al.* 1991, Liu and Pearson 2014) has provided the appropriate measurement precision to fully exploit the system. Several advanced techniques have been developed to dissolve a diverse range of geological materials, including acid digestion in reducing media (Walker 1988, Birck *et al.* 1997), alkali fusion (Morgan and Walker 1989), nickel sulfide fire assay (Hoffman *et al.* 1978, Ravizza and Pyle 1997), microwave dissolution (Suzuki *et al.* 1992), Carius tube (CT) dissolution (Shirey and Walker 1995), and high-pressure asher system

digestion (HPA-S) (Meisel *et al.* 2001a, 2003). Among these analytical techniques, N-TIMS coupled with sample digestion using inverse *aqua regia* in CT (Shirey and Walker 1995) or an HPA-S (Meisel *et al.* 2001a) has become the most commonly used measurement protocol in many Re-Os isotope laboratories. The limitation of this protocol is the propensity for ineffective breakdown of most silicate minerals, although it is highly effective at dissolving the sulfides and noble-metal alloys that are the primary hosts of Re and Os in silicate rocks. To liberate the Re and Os in residual silicate minerals, two recent studies proposed a modified method for basaltic samples, employing a desilicification step with HF prior to or after a reverse *aqua regia* digestion in CT or HPA-S (Ishikawa *et al.* 2014, Li *et al.* 2015b).

Although the precision of measurement results of Re-Os isotopes has improved significantly in the last two decades, there are still considerable uncertainties in the accurate determination of Re-Os isotope amount ratios in some geological materials. This can be demonstrated by the large variance in  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratios reported for some reference materials (RMs), such as NIM-D (Meisel and Moser 2004a), TDB-1 (Ishikawa *et al.* 2014), WGB-1 (Chu *et al.* 2015) and BHVO-2 (Li *et al.* 2015a, b). This may be attributed to test portion sizes, which were not large enough, or difficulty in the complete liberation of Os or Re that may have occurred in an irreproducible manner, leading to a lack of reproducibility in the measurement results (Meisel *et al.* 2001a, Ishikawa *et al.* 2014, Wang and Becker 2014, Chu *et al.* 2015, Li *et al.* 2015a, b). For example, the measurement results of replicate analyses of basaltic RM BHVO-2 (USGS) for  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratios vary from 0.14 to 0.17 with an average of  $0.158 \pm 0.018$  ( $2s$ ,  $n = 17$ ; Li *et al.* 2015a). For RM BHVO-2, it is difficult to discriminate the cause of the observed discrepancies in Re-Os isotopic data, which may be attributed to incomplete mineral dissolution, contamination, spectral interferences, laboratory-induced artefacts or sample heterogeneity.

To ensure data quality and avoid analytical artefacts, it is common practice to analyse well-characterised geological RMs during the course of routine analyses. Reference materials should be homogenous, meaning that the contribution of sample heterogeneity must be very small compared with the measurement uncertainty at a given minimum test portion size. However, the identification of geological RM with homogenous Re-Os isotope compositions is still limited at a given sample mass, for example  $\sim 2$  g. Only the RM UB-N (serpentinite, CRPG) has been accepted as a reference material for validating measurement procedures of Re and Os mass fractions and  $^{187}\text{Os}/^{188}\text{Os}$  ratios in peridotites (Meisel *et al.* 2003, Luguet *et al.* 2004, Becker

*et al.* 2006, Puchtel *et al.* 2008, Fischer-Gödde *et al.* 2011, Ishikawa *et al.* 2014). However, the serpentinite RM UB-N is not a suitable material for use as a validation and quality control material for mafic geological samples (e.g., basalts) with higher Re, but low Os abundances, because matrix-matched RMs are required to validate a particular measurement procedure (Meisel and Moser 2004b, Meisel and Horan 2016). Until recently, there has been only a limited number of RMs appropriate for use in the study of mafic rocks. A number of studies have suggested the use of some well-characterised mafic rock RMs, such as basalt BHVO-2/BIR-1a, diabase TDB-1, and gabbro WGB-1 (e.g., Meisel and Moser 2004b, Meisel *et al.* 2009, Dale *et al.* 2012, Ishikawa *et al.* 2014, Chu *et al.* 2015, Li *et al.* 2015a, b, Ackerman *et al.* 2016, Day *et al.* 2016b). However, these RMs provide extremely low intermediate precision in Re-Os isotopic composition except for BIR-1a (Ishikawa *et al.* 2014, Meisel and Horan 2016); consequently, BIR-1a may be a potential candidate RM as a validation and quality control standard for geological samples with low Re-Os abundances.

In this study, we present precise Re and Os mass fractions and Os isotopic compositions for the reference material BIR-1a, determined by both inverse *aqua regia* digestion using a Carius tube and by HF desilicification prior to CT digestion. The intermediate precision of the Re-Os isotopic data of BIR-1a over an 18-month period reveals that for  $\sim 0.2$ – $1.0$  g test portion sizes, this RM is more homogeneous in Re and Os mass fractions and Os isotopic compositions than previously thought. We propose that BIR-1a (USGS) may be used as a well-characterised RM in routine Re-Os isotope analysis and that this RM will be suitable for quality control and interlaboratory comparisons in future analytical methodology studies.

## Experimental method

### Materials and reagents

Basalt reference material BIR-1a (a coarse-grained olivine tholeiite from Reykjavik, Iceland) was purchased from the USGS. The powder of RM BIR-1a was shaken vigorously in a glass bottle before weighing to achieve a random distribution of particles.

The acids used in this study ( $14 \text{ mol l}^{-1} \text{ HNO}_3$ ,  $12 \text{ mol l}^{-1} \text{ HCl}$ ,  $9 \text{ mol l}^{-1} \text{ HBr}$  and  $29 \text{ mol l}^{-1} \text{ HF}$ ; GR grade) were further purified by sub-boiling distillation using a DST-1000 PFA apparatus (Saville Corporation, Eden Prairie, MN, USA). In particular, because of the relatively high levels of Os in  $\text{HNO}_3$ , before sub-boiling distillation the

HNO<sub>3</sub> used for sample digestion was heated on a hot plate at 400 °C to volatilise OsO<sub>4</sub> and purged with clean air for 2 h. Carbon tetrachloride (CCl<sub>4</sub>) (HPLC grade, Tianjin, China) was used in the Os extraction procedure without additional treatment. The oxidising solution CrO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>, which is CrO<sub>3</sub> (8% *m/v*) dissolved in 6 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, was purified by heating to 100 °C, with clean air bubbling, to remove Os as OsO<sub>4</sub> gas.

The borosilicate Carius tubes used in this study were 3 mm thick, with a volume of ~ 210 ml and were similar to those used by Shirey and Walker (1995). Fluoropolymer (PFA; Savillex) vials were cleaned with 50% *v/v* aqua regia and subsequently with Milli-Q water, filled with concentrated HBr and heated overnight at 100 °C to ensure a minimum Os blank interference during separation and micro-distillation (Li *et al.* 2014). Finally, all the vials were rinsed with Milli-Q water and air-dried.

## Measurement procedure

The Carius tube (CT), together with an inverse aqua regia digestion technique, was employed in this study for Re-Os chemistry (Shirey and Walker 1995, Shen *et al.* 1996). The CT digestion allows nearly complete liberation of platinum-group element (PGE) from rock samples at 240 °C for 24 h, with relatively low procedural blanks. However, previous studies observed that some Re and Os could still remain in the residue of the HCl-HNO<sub>3</sub> digestion for certain basaltic samples, primarily in silicate minerals, and that an additional digestion step using HF acid can attack the residue and liberate the remaining Re and Os (e.g., Dale *et al.* 2009, 2012, Meisel *et al.* 2009, Ishikawa *et al.* 2014, Li *et al.* 2015b, Day *et al.* 2016b). To test the possible effects of incomplete recovery of Re and Os from basalt BIR-1a, CT digestions with HF-HBr pre-attack (HF-CT) were performed for comparison.

For the regular Carius tube digestion method, about 0.2–1.0 g of BIR-1a sample powder was digested and equilibrated with <sup>185</sup>Re- and <sup>190</sup>Os-enriched spikes in reverse aqua regia (7.5 ml concentrated HNO<sub>3</sub> + 2.5 ml concentrated HCl) for 24 h at 240 °C in sealed Carius tubes. Osmium tetroxide was extracted by solvent extraction into CCl<sub>4</sub> and back-extraction into concentrated HBr, with subsequent clean-up by micro-distillation (Birck *et al.* 1997). The Re fraction was separated and purified using anion column chromatography (AG1X8, Eichrom Technologies, Lisle, IL, USA).

For HF-desilicification digestion, desilicification prior to Os extraction was done using HF-HBr instead of HF-HCl, which can suppress the volatile loss of Os during desilicification or

incomplete attack (Ishikawa *et al.* 2014). Powder samples were dissolved in 4 ml HF and 4 ml HBr and equilibrated with <sup>185</sup>Re- and <sup>190</sup>Os-enriched spikes in Teflon vials for 24 h at 120 °C, followed by drying and redissolution in 1 ml HCl. After evaporation to dryness again, the residues were then redissolved in 2.5 ml HCl and transferred into Carius tubes. In order to assess the effect of HF-HBr attack on the volatile loss of Os, we applied an additional protocol of desilicification by addition of spikes after HF-HBr attack. As a comparison, powder subsamples were processed with no spikes added during the HF digestion step. After the sample residues were transferred into Carius tubes by redissolving in HCl, the spikes were added to the tubes. The subsequent steps in the CT digestion and Re-Os separation and purification are the same as the regular CT digestion, which is described above.

The technique of determining Os isotope amount ratios by mass spectrometry employed in this study is described by Li *et al.* (2014, 2015a). The Os-bearing fraction was loaded onto Pt filaments and measured as OsO<sub>3</sub><sup>-</sup> by negative-thermal ionisation mass spectrometry (N-TIMS) using the electron multiplier mode on a Thermo-Finnigan Triton (Thermo Fisher Scientific, Waltham, MA, USA) (Creaser *et al.* 1991, Völkering *et al.* 1991) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, and on a Thermo-Finnigan Triton plus at Northwest University, Xi'an, China. The OsO<sub>3</sub><sup>-</sup> intensity measurements followed a six-peak switch mass scan including 240 (<sup>192</sup>Os<sup>16</sup>O<sub>3</sub><sup>-</sup>), 238 (<sup>190</sup>Os<sup>16</sup>O<sub>3</sub><sup>-</sup>), 237 (<sup>189</sup>Os<sup>16</sup>O<sub>3</sub><sup>-</sup>), 236 (<sup>188</sup>Os<sup>16</sup>O<sub>3</sub><sup>-</sup>), 235 (<sup>187</sup>Os<sup>16</sup>O<sub>3</sub><sup>-</sup>) and 233 (<sup>185</sup>Re<sup>16</sup>O<sub>3</sub><sup>-</sup>). Interference from <sup>185</sup>Re<sup>16</sup>O<sub>3</sub><sup>-</sup> was corrected for potential <sup>187</sup>Re<sup>16</sup>O<sub>3</sub><sup>-</sup> interference on the <sup>187</sup>Os<sup>16</sup>O<sub>3</sub><sup>-</sup>, and the interference on the <sup>187</sup>Os<sup>16</sup>O<sub>3</sub><sup>-</sup> was insignificant. Measured raw intensity data were corrected for oxygen isotope amount ratios using <sup>17</sup>O/<sup>16</sup>O = 0.0003749 and <sup>18</sup>O/<sup>16</sup>O = 0.0020439 (Nier 1950) and for mass fractionation using <sup>192</sup>Os/<sup>188</sup>Os = 3.08271 (Creaser *et al.* 1991). Rhenium mass fractions were determined using an inductively coupled plasma-mass spectrometry (ICP-MS) (Thermo Elemental X2 Series; Thermo Fisher Scientific, Waltham, MA, USA) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry. The details of measurements by ICP-MS are described by Li *et al.* (2014).

## Results and discussion

### Procedural blanks

The total procedural blanks (TPBs) of Re and Os were monitored in each batch analysis, and these data are listed

in Table 1. During the course of our experiments, we found that the use of HF for desilicification in Carius tube digestion did not systematically increase the blank for Re or for Os. The average TPB for the regular CT method was  $5.3 \pm 3.0$  pg,  $0.43 \pm 0.12$  pg, and  $0.274 \pm 0.087$  ( $n = 16$ , 1s) for Re, Os, and  $^{187}\text{Os}/^{188}\text{Os}$ , respectively. For the CT method with HF desilicification, the average TPB yield was  $4.9 \pm 1.6$  pg,  $0.58 \pm 0.34$  pg and  $0.235 \pm 0.050$  ( $n = 6$ , 1s) for Re, Os and  $^{187}\text{Os}/^{188}\text{Os}$ , respectively. We applied a blank correction to all analyses and the influence of the TPB on the accuracy of the analyses for RM BIR-1a was generally insignificant.

### Rhenium mass fraction

Table 2 lists the Re data of BIR-1a obtained with CT digestion vials in the present study, and the Re measurement results from previous studies. Figure 1a shows the Re mass fraction data obtained from the literature (Ishikawa *et al.* 2014, Chu *et al.* 2015, Li *et al.* 2015a, Ackerman *et al.* 2016), compared with our measurement results for CT digestions of 0.2–1.0 g test portions. Our CT digestion method provides highly reproducible results (RSD < 2%)

with an average value of  $0.689 \pm 0.023$  ng g<sup>-1</sup> (2s,  $n = 43$ ), and the results show good agreement with previously published values obtained by the same digestion method (Ishikawa *et al.* 2014, Chu *et al.* 2015, Li *et al.* 2015a, Ackerman *et al.* 2016).

To further verify the Re extraction efficiency for BIR-1a powder, we compared the extraction efficiency of Re using the regular CT method, and the method using HF desilicification prior to CT digestion (Table 2, Figure 1a,d). The average Re mass fraction for non-desilicified analyses ( $0.689 \pm 0.023$  ng g<sup>-1</sup>) is within 2 standard deviations of that for desilicified digestion ( $0.696 \pm 0.017$  ng g<sup>-1</sup>, 2s,  $n = 20$ ). The mean values of Re mass fraction obtained by non-desilicified and desilicified digestions are also in agreement with previous data obtained for HPA digestion ( $0.678 \pm 0.013$  ng g<sup>-1</sup>, 2s,  $n = 4$ ; Ishikawa *et al.* 2014). These results reflect the efficiency of Re extraction from BIR-1a powder, regardless of the use of HF or HPA digestions, and that the Re in BIR-1a is dominated probably by non-silicate phases such as Fe-Ti oxide and homogeneously distributed within the test samples, despite the samples ranging in size from 0.2 to 1.0 g.

**Table 1.**  
Procedural blanks during the Re-Os determinations

No.	Method	Re (pg)	2SE	Os (pg)	2SE	$^{187}\text{Os}/^{188}\text{Os}$	2SE
1	CT	4.5	2.3	0.582	0.050	0.2647	0.0099
2	CT	2.3	2.8	0.149	0.080	0.2354	0.0235
3	CT	2.5	0.3	0.384	0.017	0.3114	0.0112
4	CT	9.5	0.4	0.521	0.017	0.4334	0.0257
5	CT	4.2	1.9	0.454	0.040	0.3632	0.0094
6	CT	4.3	2.7	0.375	0.050	0.2878	0.0128
7	CT	9.4	1.0	0.414	0.004	0.2321	0.0066
8	CT	8.9	0.7	0.599	0.010	0.2552	0.0054
9	CT	1.6	1.8	0.544	0.017	0.2126	0.0070
10	CT	2.5	1.0	0.591	0.009	0.1872	0.0033
11	CT	5.8	2.4	0.454	0.012	0.1709	0.0027
12	CT	3.8	2.1	0.446	0.021	0.1999	0.0065
13	CT	9.7	1.6	0.322	0.005	0.3421	0.0072
14	CT	9.4	3.1	0.324	0.009	0.2272	0.0058
15	CT	2.9	1.6	0.373	0.007	0.4654	0.0062
16	CT	3.5	2.0	0.359	0.004	0.2061	0.0039
<b>Mean (<math>n = 16</math>, 1s)</b>		<b>5.3</b>	<b>3.0<sup>a</sup></b>	<b>0.431</b>	<b>0.120<sup>a</sup></b>	<b>0.2747</b>	<b>0.0872<sup>a</sup></b>
1	HF-CT	6.2	0.0	0.806	0.002	0.2779	0.0179
2	HF-CT	3.2	0.6	1.109	0.010	0.2524	0.0152
3	HF-CT	5.1	0.0	0.305	0.043	0.2910	0.0057
4	HF-CT	4.2	0.5	0.663	0.004	0.1688	0.0022
5	HF-CT	7.4	0.8	0.290	0.007	0.2408	0.0100
6	HF-CT	3.6	0.6	0.317	0.009	0.1805	0.0047
<b>Mean (<math>n = 16</math>, 1s)</b>		<b>4.9</b>	<b>1.6<sup>a</sup></b>	<b>0.582</b>	<b>0.337<sup>a</sup></b>	<b>0.2352</b>	<b>0.0503<sup>a</sup></b>

CT, Carius tube digestion technique; HF-CT, HF desilicification prior to Carius tube digestion. Uncertainties on each blank analysis are 2SE (standard error). 2SE was estimated by error propagation of measurement uncertainties in N-TIMS (for forty runs of Os isotope amount ratios) and ICP-MS (for nine runs of Re isotope amount ratios). <sup>a</sup>Uncertainties are standard deviation (1s) for the mean values.

**Table 2.**  
Re-Os isotope and mass fraction data for BIR-1a obtained with and without desilicification combined with Carius tube digestion

No.	Mass (g)	Digestion method	Re (ng g <sup>-1</sup> )	2SE	Os (ng g <sup>-1</sup> )	2SE	<sup>187</sup> Os/ <sup>188</sup> Os	2SE	<sup>187</sup> Re/ <sup>188</sup> Os	2SE
1	0.2016	CT	0.689	0.011	0.3640	0.0004	0.13384	0.00029	9.12	0.14
2	0.2020	CT	0.693	0.009	0.4789	0.0014	0.13392	0.00092	6.98	0.09
3	0.2137	CT	0.686	0.013	0.3592	0.0003	0.13395	0.00045	9.20	0.17
4	0.2542	CT	0.705	0.011	0.4815	0.0006	0.13348	0.00038	7.05	0.11
5	0.2559	CT	0.680	0.008	0.3314	0.0002	0.13374	0.00035	9.89	0.12
6	0.2605	CT	0.690	0.011	0.4426	0.0007	0.13275	0.00041	7.51	0.12
7	0.2850	CT	0.679	0.009	0.3011	0.0002	0.13587	0.00035	10.87	0.14
8	0.2897	CT	0.692	0.012	0.3514	0.0011	0.13398	0.00054	9.49	0.17
9	0.2994	CT	0.691	0.012	0.3245	0.0004	0.13460	0.00047	10.26	0.18
10	0.3024	CT	0.698	0.016	0.2308	0.0004	0.13368	0.00049	14.57	0.34
11	0.3497	CT	0.689	0.012	0.2968	0.0003	0.13307	0.00041	11.18	0.19
12	0.3534	CT	0.695	0.011	0.3195	0.0005	0.13395	0.00041	10.49	0.16
13	0.3683	CT	0.699	0.020	0.3572	0.0005	0.13294	0.00065	9.43	0.26
14	0.3743	CT	0.713	0.013	0.3600	0.0018	0.13408	0.00086	9.54	0.17
15	0.3882	CT	0.688	0.002	0.3400	0.0006	0.13330	0.00033	9.75	0.04
16	0.4256	CT	0.692	0.010	0.3649	0.0011	0.13344	0.00027	9.13	0.14
17	0.4536	CT	0.698	0.007	0.3083	0.0008	0.13406	0.00026	10.91	0.11
18	0.4780	CT	0.683	0.011	0.3212	0.0006	0.13339	0.00034	10.25	0.17
19	0.4802	CT	0.679	0.012	0.3259	0.0009	0.13359	0.00038	10.04	0.19
20	0.4871	CT	0.690	0.007	0.3356	0.0017	0.13352	0.00050	9.90	0.11
21	0.4920	CT	0.686	0.016	0.3488	0.0016	0.13362	0.00035	9.48	0.23
22	0.4986	CT	0.691	0.013	0.3460	0.0012	0.13417	0.00057	9.62	0.18
23	0.5175	CT	0.693	0.006	0.3421	0.0018	0.13389	0.00023	9.76	0.10
24	0.5273	CT	0.683	0.008	0.3646	0.0018	0.13322	0.00056	9.02	0.12
25	0.5402	CT	0.668	0.006	0.3545	0.0015	0.13342	0.00051	9.08	0.09
26	0.5451	CT	0.641	0.003	0.3666	0.0005	0.13363	0.00012	8.43	0.05
27	0.5471	CT	0.682	0.016	0.3716	0.0008	0.13421	0.00025	8.84	0.21
28	0.5492	CT	0.689	0.006	0.3691	0.0014	0.13448	0.00044	9.00	0.08
29	0.5693	CT	0.698	0.030	0.3375	0.0016	0.13368	0.00032	9.97	0.42
30	0.5869	CT	0.685	0.008	0.3517	0.0006	0.13345	0.00034	9.39	0.11
31	0.6505	CT	0.695	0.006	0.3273	0.0010	0.13315	0.00029	10.23	0.09
32	0.6904	CT	0.693	0.005	0.3432	0.0007	0.13400	0.00036	9.73	0.07
33	0.8034	CT	0.692	0.037	0.3978	0.0015	0.13359	0.00052	8.38	0.44
34	0.8484	CT	0.696	0.005	0.3071	0.0010	0.13365	0.00043	10.92	0.09
35	0.9725	CT	0.690	0.005	0.3584	0.0017	0.13329	0.00031	9.28	0.08
36	1.0073	CT	0.681	0.008	0.3403	0.0009	0.13366	0.00031	9.65	0.11
37	1.0324	CT	0.685	0.005	0.3422	0.0018	0.13386	0.00037	9.65	0.09
38	1.0637	CT	0.690	0.005	0.3336	0.0019	0.13396	0.00042	9.97	0.09
39	1.0695	CT	0.692	0.036	0.3531	0.0081	0.13334	0.00073	9.45	0.54
40	1.0740	CT	0.683	0.030	0.3354	0.0017	0.13334	0.00029	9.81	0.44
41	1.0909	CT	0.692	0.004	0.3646	0.0023	0.13330	0.00030	9.15	0.08
42	1.0956	CT	0.689	0.031	0.3312	0.0026	0.13327	0.00042	10.02	0.46
43	1.1224	CT	0.715	0.033	0.3497	0.0018	0.13379	0.00036	10.15	0.48
44	0.3019	HF-CT	0.699	0.016	0.2472	0.0005	0.13425	0.00032	13.63	0.31
45 <sup>o</sup>	0.3535	HF-CT	0.679	0.017	0.3286	0.0011	0.13379	0.00057	9.96	0.25
46	0.3979	HF-CT	0.703	0.031	0.2425	0.0004	0.13412	0.00032	13.96	0.61
47	0.4235	HF-CT	0.708	0.011	0.4007	0.0009	0.13399	0.00029	8.52	0.13
48	0.4630	HF-CT	0.702	0.013	0.3318	0.0005	0.13371	0.00029	10.19	0.19
49 <sup>o</sup>	0.4930	HF-CT	0.688	0.009	0.3196	0.0004	0.13384	0.00024	10.37	0.14
50	0.5044	HF-CT	0.703	0.013	0.3205	0.0008	0.13319	0.00025	10.57	0.20
51	0.5197	HF-CT	0.688	0.014	0.2946	0.0007	0.13386	0.00036	11.26	0.23
52 <sup>o</sup>	0.5413	HF-CT	0.697	0.010	0.3181	0.0004	0.13370	0.00024	10.56	0.15
53 <sup>o</sup>	0.5727	HF-CT	0.693	0.009	0.3890	0.0006	0.13370	0.00019	8.59	0.11
54	0.5886	HF-CT	0.709	0.013	0.2752	0.0004	0.13395	0.00025	12.41	0.23
55	0.6035	HF-CT	0.708	0.018	0.3655	0.0010	0.13376	0.00035	9.33	0.24
56	0.6171	HF-CT	0.682	0.009	0.3145	0.0004	0.13377	0.00023	10.46	0.14
57 <sup>o</sup>	0.6660	HF-CT	0.689	0.008	0.2878	0.0003	0.13409	0.00023	11.54	0.14
58	0.7335	HF-CT	0.700	0.016	0.3283	0.0013	0.13390	0.00034	10.27	0.24
59	0.7924	HF-CT	0.687	0.020	0.3368	0.0011	0.13338	0.00029	9.84	0.29

Table 2 (continued).

Re-Os isotope and mass fraction data for BIR-1a obtained with and without desilicification combined with Carius tube digestion

No.	Mass (g)	Digestion method	Re (ng g <sup>-1</sup> )	2SE	Os (ng g <sup>-1</sup> )	2SE	<sup>187</sup> Os/ <sup>188</sup> Os	2SE	<sup>187</sup> Re/ <sup>188</sup> Os	2SE
60 <sup>a</sup>	0.8163	HF-CT	0.694	0.009	0.3628	0.0009	0.13310	0.00021	9.22	0.12
61	0.8302	HF-CT	0.697	0.004	0.3564	0.0010	0.13372	0.00027	9.42	0.06
62	0.8494	HF-CT	0.693	0.027	0.3471	0.0021	0.13336	0.00035	9.62	0.37
63	0.9978	HF-CT	0.701	0.002	0.4170	0.0017	0.13328	0.00017	8.11	0.04
Mean for CT (n = 43, 2s)			0.689 (1.6)	0.023 <sup>b</sup>	0.349 (12.1)	0.085 <sup>b</sup>	0.13370 (0.4)	0.00103 <sup>b</sup>	9.6 (12.3)	2.4 <sup>b</sup>
Mean for HF-CT (n = 20, 2s)			0.696 (1.2)	0.017 <sup>b</sup>	0.329 (14.0)	0.092 <sup>b</sup>	0.13372 (0.2)	0.00063 <sup>b</sup>	10.4 (15.0)	3.1 <sup>b</sup>
Mean for all (n = 63, 2s)			0.691 (1.6)	0.022 <sup>b</sup>	0.343 (12.9)	0.089 <sup>b</sup>	0.13371 (0.3)	0.00092 <sup>b</sup>	9.9 (13.6)	2.7 <sup>b</sup>
Mean for mass < 0.4 g (n = 18, 2s)			0.693 (1.3)	0.018 <sup>b</sup>	0.342 (20.8)	0.142 <sup>b</sup>	0.13385 (0.5)	0.00138 <sup>b</sup>	10.2 (21.1)	4.3 <sup>b</sup>
Mean for mass > 0.4 g (n = 45, 2s)			0.691 (1.7)	0.023 <sup>b</sup>	0.343 (8.3)	0.057 <sup>b</sup>	0.13365 (0.2)	0.00064 <sup>b</sup>	9.8 (8.8)	1.7 <sup>b</sup>
Ishikawa <i>et al.</i> 2014 (n = 8, 1s)		CT	0.675	0.007 <sup>b</sup>	0.355	0.020 <sup>b</sup>	0.13372	0.00040 <sup>b</sup>	9.2	0.5 <sup>b</sup>
Chu <i>et al.</i> 2015 (n = 2, 1s)		CT	0.661	0.005 <sup>b</sup>	0.385	0.026 <sup>b</sup>	0.13347	0.00004 <sup>b</sup>		
Li <i>et al.</i> , 2015a (n = 9, 1s)		CT	0.680	0.022 <sup>b</sup>	0.341	0.039 <sup>b</sup>	0.13369	0.00047 <sup>b</sup>	9.7	0.13 <sup>b</sup>
Ackeman <i>et al.</i> (2016) (n = 3, 1s)		CT	0.675	0.004 <sup>b</sup>	0.383	0.025 <sup>b</sup>	0.13246	0.00048 <sup>b</sup>		
Ishikawa <i>et al.</i> (2014) (n = 3, 1s)		Pre-HF-CT			0.305	0.026 <sup>b</sup>	0.13637	0.00026 <sup>b</sup>		
Ishikawa <i>et al.</i> (2014) (n = 9, 1s)		Post-HF-CT	0.685	0.005 <sup>b</sup>	0.345	0.024 <sup>b</sup>	0.13299	0.00074 <sup>b</sup>	9.6	0.6 <sup>b</sup>

CT, Carius tube digestion technique; HF-CT, HF desilicification prior to Carius tube digestion technique. Uncertainties on each digestion are 2SE (standard error). 2SE was estimated by error propagation of measurement uncertainties in N-TIMS (for forty runs of Os isotope amount ratios) and ICP-MS (for nine runs of Re isotope amount ratios). Relative standard deviations (% RSD) are shown in parentheses. <sup>a</sup>Re and Os spikes were added after HF-HBr desilicification.

<sup>b</sup>Uncertainties are standard deviation (s) for the mean values obtained in this study (2s) and for the literature data (1s).

## Osmium mass fraction

The Os mass fractions determined in this study, together with data from the literature, are listed in Table 2 and shown in Figure 1b, e. The mean value for all measurement results (0.343 ± 0.089 ng g<sup>-1</sup>, 2s, n = 63) is nearly identical to our previous value (0.341 ± 0.078 ng g<sup>-1</sup>, 2s, n = 9; Li *et al.* 2015a), and these values are also in good agreement with the analyses by Ishikawa *et al.* (2014) (0.342 ± 0.056 ng g<sup>-1</sup>, 2s, n = 17) obtained by non-desilicified and desilicified digestions. Our data for sample sizes of 0.2–1.0 g of BIR-1a with CT digestion, with and without hydrofluoric acid, do not display any systematic differences in Os mass fractions, thereby supporting the efficiency of *aqua regia* attack and the insignificance of the HF treatment for digesting BIR-1a. Moreover, our protocols of desilicification by addition of spikes before and after HF-HBr attack provides consistent average Os values of 0.33 ± 0.10 ng g<sup>-1</sup> (2s, n = 14) and 0.334 ± 0.072 ng g<sup>-1</sup> (2s, n = 6), respectively. This suggests that there is no loss of Os during HF and HBr attack. From these observations, we conclude that the additional HF step is not required for the extraction of Re and Os from BIR-1a.

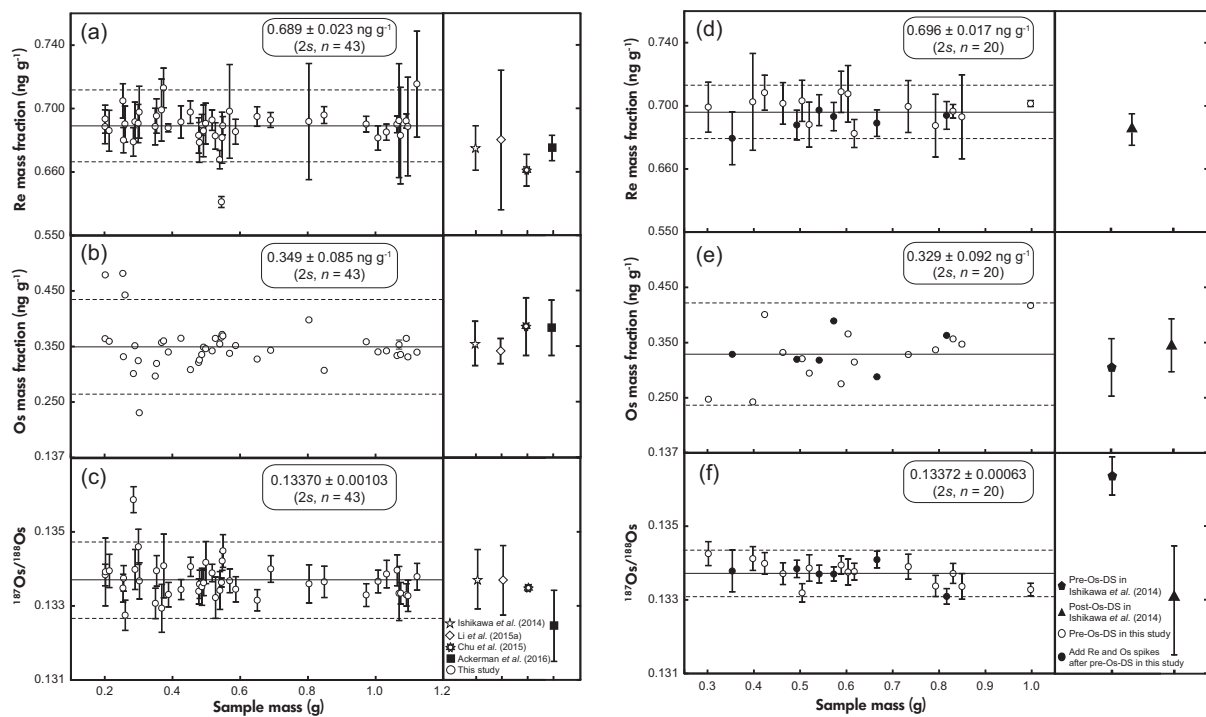
The intermediate precision of the Os mass fraction analyses (RSD = 12.9%, Table 1) is slightly poorer than that for Re. This could be attributed to the relatively

heterogeneous distribution of the Os host minerals in BIR-1a, which is apparent with small test portion sizes (0.2–1.0 g). We examine this possibility in the ‘Sample homogeneity’ section, by comparing the results from different test portion sizes of BIR-1a.

## <sup>187</sup>Os/<sup>188</sup>Os ratios

As shown in Figure 1c, f, there are no systematic differences in the <sup>187</sup>Os/<sup>188</sup>Os isotope amount ratio of BIR-1a using CT digestion, with or without HF desilicification. As for Os mass fraction, measured data of <sup>187</sup>Os/<sup>188</sup>Os isotope amount ratio show no apparent difference between the two protocols of desilicification (Table 2 and Figure 1f). The <sup>187</sup>Os/<sup>188</sup>Os isotope amount ratios for all analyses show high intermediate precision (RSD ≤ 0.3%) with an average value of 0.13371 ± 0.00092 (2s, n = 63), which is indistinguishable from published values for BIR-1a (Chu *et al.* 2015, Li *et al.* 2015a), and the post-Os desilicification data reported by Ishikawa *et al.* (2014). However, Ishikawa *et al.* (2014) reported a significantly higher mean value of the <sup>187</sup>Os/<sup>188</sup>Os isotope amount ratio (0.13637 ± 0.00052, 2s, n = 3) than our value (0.13372 ± 0.00063, 2s, n = 20), obtained by the same pre-Os desilicification digestion (Table 2, Figure 1f). Considering the significantly lower average of the Os mass fraction (0.305 ± 0.026 ng g<sup>-1</sup>) in





**Figure 1.** Rhenium and Os mass fractions, and  $^{187}\text{Os}/^{188}\text{Os}$  ratios for BIR-1a determined using the regular CT digestion are illustrated in (a), (b) and (c), respectively. Rhenium and Os mass fractions, and  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratios for BIR-1a obtained using the regular CT digestion with HF desilicification are plotted in (d), (e) and (f), respectively. Error bars are 2 standard error (2SE) for data obtained in this study and 2 standard deviation (2s) for the literature data. The solid lines represent the mean values, and the dotted lines represent the 2s of the mean value obtained in this study.

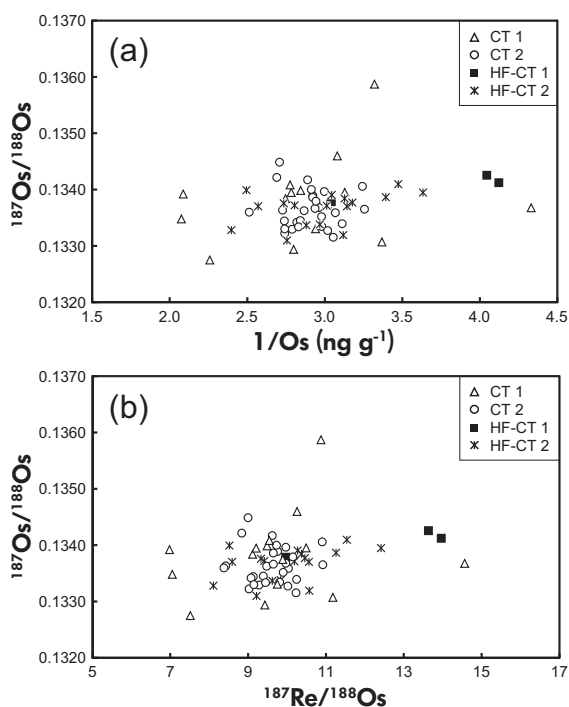
the pre-Os data of Ishikawa *et al.* (2014) compared with our pre-Os data ( $0.343 \pm 0.089 \text{ ng g}^{-1}$ ) and that there were only three replicated pre-Os analyses reported by Ishikawa *et al.* (2014), this unreasonably high mean value of  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratio is likely attributed to an analytical artefact caused during the initial HF step.

### Sample homogeneity

Relatively small test portion sizes (typically < 2 g) can be digested effectively in Carius tubes. However, this can lead to a ‘nugget effect’, which arises from small-sample bias and from the heterogeneous distribution of mineral hosts for Re and Os in the bulk rock, not effectively homogenised when sample size is small. Sample heterogeneity, which can be expressed by Ingamells’ (1974) sampling constant, is expected to increase with decreasing test portion size. The nugget effect can compromise both intermediate measurement repeatability and measurement reproducibility (Meisel *et al.* 2001a). However, this limitation can generally be overcome, especially in basaltic igneous rocks, by increasing the sample size. To further evaluate the sample

homogeneity, we examined the influence of test portion size (0.2–1.0 g) on the Re-Os isotopic composition of BIR-1a.

For all measurements, Re mass fractions showed better intermediate precision for BIR-1a (RSD = 1.6%) than did Os mass fractions (RSD = 12.9%) at test portion sizes of 0.2–1.0 g (Table 1). Our new BIR-1a data obtained for ~ 0.2–1.0 g aliquots span a slightly wider range of Os mass fractions, from 0.231 to  $0.482 \text{ ng g}^{-1}$  (Table 2), indicating that Os may not be homogeneously distributed throughout this finely ground RM sample powder. The mean value of the Os mass fraction for 0.4–1.0 g test portion sizes shows relatively small intermediate precision (RSD = 8.3%) with a mean value of  $0.343 \pm 0.057 \text{ ng g}^{-1}$  (2s,  $n = 45$ ). In contrast, the data for 0.2–0.4 g test portion sizes show much lower intermediate precision (RSD = 20.8%) with a mean value of  $0.342 \pm 0.142 \text{ ng g}^{-1}$  (2s,  $n = 18$ ). Differences between various sample test portion sizes are presented in plots of  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratio vs. inverse Os mass fractions (Figure 2a) and  $^{187}\text{Re}/^{188}\text{Os}$  ratio (Figure 2b). These plots illustrate that the data sets are not correlated and that the data for 0.2–0.4 g test portion sizes



**Figure 2.** Plots of (a)  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratio vs.  $1/\text{Os}$  ( $\text{ng g}^{-1}$ ) and (b)  $^{187}\text{Os}/^{188}\text{Os}$  ratio vs.  $^{187}\text{Re}/^{188}\text{Os}$  ratio of replicates of BIR-1a, showing no obvious correlations. CT1 and HF-CT1 representative of 0.2–0.4 g test portion sizes using regular CT and CT digestion with HF desilicification digestions, respectively. CT2 and HF-CT2 representative of 0.4–1.0 g test portion sizes using regular CT and CT digestion with HF desilicification digestions, respectively.

are more discrete in  $^{187}\text{Os}/^{188}\text{Os}$  vs.  $1/\text{Os}$  and  $^{187}\text{Re}/^{188}\text{Os}$  space (Figures 2a, b).

These observations suggest that the intermediate precision of Os mass fractions is poorer than the intermediate precision of the Re mass fraction measurement results for RM BIR-1a and that this poor precision can be attributed to sample heterogeneity in small samples ( $< 0.4$  g), rather than from some other analytical issue.

## Summary

The Re-Os isotopic composition of replicate samples of BIR-1a was determined by a Carius tube method with and without HF desilicification prior to Carius tube digestion method. The mean Re and Os mass fractions, and the  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratios for all measurement results in this study are  $0.691 \pm 0.022 \text{ ng g}^{-1}$ ,  $0.343 \pm 0.089 \text{ ng g}^{-1}$  and  $0.13371 \pm 0.00092$  ( $2s$ ,  $n = 63$ ), respectively. We found no systematic trends in

Re mass fractions, Os mass fractions or  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratios as determined by either the Carius tube method or the HF desilicification prior to Carius tube digestion method, indicating that an HF-desilicification step is not required to obtain reliable Re and Os mass fractions. The Os mass fractions display a relatively large degree of variation at 0.2–0.4 g test portion sizes because of sample heterogeneity, but Re mass fractions and  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratios are very constant. A higher precision in Re-Os data can be obtained for test portion sizes of  $> 0.4$  g, which yield mean values of  $0.691 \pm 0.023$  ( $2s$ ,  $n = 45$ ),  $0.343 \pm 0.057$  ( $2s$ ,  $n = 45$ ) and  $0.13365 \pm 0.00064$  ( $2s$ ,  $n = 45$ ) for Re, Os and  $^{187}\text{Os}/^{188}\text{Os}$  isotope amount ratio, respectively. The obtained data in this study are in good agreement with previous results (Ishikawa *et al.* 2014, Chu *et al.* 2015, Li *et al.* 2015a, Ackerman *et al.* 2016). Based on these observations, we conclude that BIR-1a is a relatively homogeneous basaltic reference material in terms of Re-Os isotopic compositions for test portion sizes of  $> 0.4$  g. It is therefore recommended as a quality control material for mafic geological samples.

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