Reassessment of Hydrofluoric Acid Desilicification in the Carius Tube Digestion Technique for Re–Os Isotopic Determination in Geological Samples

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In this study, Re and Os isotopes were systematically determined in six geological reference materials (RMs; covering a wide range of lithologies) using the Carius tube (CT) digestion technique with and without hydrofluoric acid desilicification. Our results show that the HF desilicification increased the Re extraction efficiency (by 9–15%) evidenced from basaltic and andesitic rocks (e.g., BHVO-2, TDB-1 and AGV-2). This implies that a small proportion of Re resides in silicate phases. For mafic–ultramafic rocks (e.g., BCR-2, WGB-1 and WPR-1), Re extraction efficiencies obtained by the CT digestion with and without HF desilicification were similar. This may indicate that Re in these rocks may dominantly reside in some phases (e.g., magnetite and sulfides) that could be completely dissolved in *aqua regia* solutions without the aid of HF desilicification. Our results also show that the HF desilicification increased Os extraction efficiency (by 13–99%) in some RMs (e.g., BHVO-2, WGB-1 and AGV-2). This observation suggests that a portion of Os-rich trace phases may occur as inclusions in the silicate phases that act as isolators at ~ 200 mesh sizes. This study demonstrates that the HF desilicification step prior to CT digestion is important for complete extraction of Re and Os in geological samples.

Keywords: Re–Os isotopes, Carius tube digestion, desilicification, extraction efficiency, sample heterogeneity.

Dans cette étude, les isotopes du Re et de l'Os ont été systématiquement déterminés pour six matériaux géologiques de référence (RMs, couvrant un large éventail de lithologies) en utilisant la technique de digestion avec tube de Carius (CT) avec et sans désilicification avec de l'acide fluorhydrique (HF). Nos résultats montrent à partir de l'étude de roches basaltiques et andésitiques (par exemple, BHVO-2, TDB-1 et AGV-2) que la désilicification avec l'HF augmente l'efficacité d'extraction du Re (de 9-15 %). Cela implique qu'une petite proportion du Re réside dans les phases silicatées. Pour les roches mafiques-ultramafiques (par exemple, BCR-2, WGB-1 et WPR-1), les rendements d'extraction obtenus pour le Re par la digestion CT avec et sans désilicification avec de l'HF son similaires. Ceci semble indiquer que le Re dans ces roches peut résider principalement dans certaines phases (par exemple, la magnétite et les sulfures) qui pourraient être complètement dissoutes dans des solutions d'aqua regia sans l'aide de la désilicification avec de l'HF. Nos résultats montrent également que la désilicification avec de l'HF augmente l'efficacité d'extraction de l'Os (de 13-99 %) dans certains RMs (par exemple, BHVO-2, WGB -1 et AGV-2). Cette observation suggère qu'une partie des phases traces riches en Os peuvent être présentes sous forme d'inclusions dans les phases silicatées qui agissent comme des isolateurs au maillage à ~ 200. Cette étude démontre que la désilicification avec de l'HF avant la digestion CT est importante pour l'extraction complète du Re et de l'Os dans des échantillons géologiques.

Mots-clés : isotopes Re-Os, digestion par tube de Carius, désilicification, efficacité de l'extraction, hétérogénéité des échantillons.

The Re–Os isotopic system is based on the β⁻ decay of ^{187}Re to ^{187}Os with a half-life of 41.6 Ga (Smoliar *et al.* 1996). Rhenium and osmium are chalcophile and siderophile and, hence, preferentially partition into base metal sulfide and metal. In addition, during mantle partial melting, Os behaves compatibly, whereas Re is moderately incompatible (e.g., Shirey and Walker 1998). This unique isotopic system therefore provides distinct constraints on geochemical processes compared with most other long-lived isotopic systems such as Rb-Sr, Sm-Nd, Lu-Hf and U-Pb, of which the parent and daughter elements are both incompatible lithophile (or chalcophile in case of Pb) trace elements and concentrated mostly in silicate minerals. As such, the Re–Os isotopic system has triggered numerous novel applications in a broad range of geological fields including, for example, cosmochemistry (e.g., Horan *et al.* 1992, Shirey and Walker 1998), mantle geochemistry and geochronology (e.g., Rudnick and Walker 2009, Pearson and Wittig 2014), surficial continental processes (e.g., Levasseur *et al.* 1998, Peucker-Ehrenbrink and Blum 1998), and ore deposits and organic-rich samples (e.g., Marques 2012, Qu *et al.* 2013).

Over the last two decades, the increasing application of the Re–Os system has been spurred by advances in measurement sensitivity, precision and accuracy (Reisberg and Meisel 2002). Development of high-sensitivity negative thermal ionisation mass spectrometry (N-TIMS) (Creaser *et al.* 1991, Vökening *et al.* 1991, Walczyk *et al.* 1991, Liu and Pearson 2014) provides appropriate analytical precision and accuracy to fully exploit the system. At present, N-TIMS is most commonly used for the determination of Os isotopic ratios in geological samples, while Re isotopic ratios are normally determined by inductively coupled plasma-mass spectrometry (ICP-MS). For precise isotopic ratio measurements on most geological samples that have relatively low mass fractions (pg g^{-1} to ng g^{-1}; i.e., ppt to ppb) of Re and Os, it is necessary to chemically extract and purify Re and Os from geological samples. One of the largest challenges in Re–Os chemical extraction is to find a suitable digestion technique (Reisberg and Meisel 2002). Considering that Os is easily oxidised to volatile OsO$_4$ under oxidising conditions and relatively low temperatures (130 °C) (Weast 1973), samples cannot be simply dissolved in oxidising solutions (e.g., using HF/HNO$_3$ mixtures) in open-system Teflon beakers, as routinely carried out for Sr, Nd, Hf and Pb determinations. Furthermore, because of the low mass fractions of Re and Os in most geological samples, the level of blank contribution must be kept to a minimum throughout the decomposition procedure. Consequently, digestion of large samples (one to several grams) is often required to yield sufficient Re and Os for precise determination and to approach representative sampling, due to the 'nugget effect' (a description of the

heterogeneous distribution of Re and Os in high quantities hosted in trace mineral phases within a barren matrix). In addition, the Os released from samples during the digestion step may not easily equilibrate with spikes used in the isotope dilution technique, provided that Os can take many oxidation states (Papanastassiou *et al.* 1994).

Several advanced techniques have been developed to dissolve diverse 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 digestion (HPA-S) (Meisel *et al.* 2001a, 2003a). Among these digestion techniques, high-temperature oxidising acid (reverse *aqua regia*) digestion in the CT (Shirey and Walker 1995) or HPA-S (Meisel *et al.* 2001a, 2003a) has proved superior, in many ways, to be a commonly used technique. For instance, the CT method achieves efficient digestion of Os-bearing phases with lower procedural blank and achievement of spike/sample equilibration under oxidising conditions and high temperatures (≥ 240 °C), while loss of the volatile Os is prevented (use of glass, rather than PFA). Nevertheless, it has been argued that the CT digestion, though much more efficient than low temperature digestions, is perhaps incomplete in some cases (Shirey and Walker 1995). For instance, the observation of substantial residues left behind in the CT after acid attack (i.e., undigested mineral particles that are dominantly composed of silicate phases) raises some doubts about the complete liberation of Re and Os. In order to completely dissolve silicates, the alternative technique was adopted: pre-dissolution of silicates using reduced hydrofluoric acid (referred to as HF desilicification) prior to reverse *aqua regia* digestion in CT or HPA-S (Meisel *et al.* 2003b, Dale *et al.* 2012). Earlier investigation of UB-N (a serpentinised peridotite reference material) showed no difference in the measured Re and Os mass fraction among the digestion procedures with or without HF desilicification (Meisel *et al.* 2003b). However, Meisel *et al.* (2009) and Dale *et al.* (2012) recently demonstrated a more effective extraction of Re, but not Os, from basaltic sample powders TDB-1 with HF desilicification, suggesting that Re may commonly reside in silicate phases in both mantle and magmatic systems. Such contrasting observations indicated that the HF desilicification step is necessary to achieve a more effective extraction of Re and Os for basaltic samples, but not for serpentinised ultramafic samples such as UB-N. Considering that, partially, Re may reside in silicate phases in some geological materials (Righter and Hauri 1998, Burton *et al.* 1999, 2000), it may be difficult to completely leach out of Re under regular

CT or HPA-S digestions. In this study, we systematically investigated CT dissolutions with or without HF desilicification in geochemical reference materials (RMs) that span a wide range of lithologies. The aim of this work was to reassess whether a HF desilicification step is required prior to a regular CT digestion for Re–Os isotope determination.

Experiments

Geological materials, reagents and labware

Six geological RMs were analysed for Re and Os mass fractions and Os isotopic compositions. The rock types of these RMs range from ultramafic (altered peridotite WPR-1, CAN-MET-CCRMP), mafic (basalts BHVO-2 and BCR-2, USGS; diabase TDB-1, CANMET-CCRMP; gabbro WGB-1, CAN-MET-CCRMP) to intermediate (andesite AGV-2, USGS).

All the acids (HF, HNO_3, HBr and HCl) used in this study were purified by DST-1000 sub-boiling stills (Savillex Corporation, Eden Prairie, MN, USA). Before sub-boiling distillation of HNO_3, the reagent HNO_3 was heated on a hot plate at 350 °C and purged with clean air for *ca.* 2 hr in order to reduce its Os blank. De-ionised water (18.2 MΩ cm) from a Millipore purification system was used. Ultrapure CCl_4 (HPLC grade, Tianjin, China) was used in the chemistry without further purification. The oxidising solution $Cr^{VI}O_3$-H_2SO_4 was prepared by dissolving 8 g of $Cr^{VI}O_3$ (Puratronic®, Alfa Aesar, Johnson Matthey Co., Ltd. UK) in 92 g of 6 mol l^{-1} H_2SO_4 (ACS grade, Thermo Fisher Scientific Inc. Waltham, MA, USA). This solution was purified by heating to *ca.* 100 °C and bubbling clean air through the solution to remove volatile OsO_4.

The Carius tubes used were made of borosilicate glass material similar to those described by Shirey and Walker (1995). These tubes had an inner volume of *ca.* 76 ml. The tubes were pre-cleaned with *aqua regia* (50% *v/v*) and heated on a hot plate at 300 °C for 6 hr. After rinsing with Milli-Q water, the tubes were dried. All the labware that the samples were exposed to was made of PFA (Savillex Corporation). PFA vials were cleaned with 50% *v/v aqua regia* and Milli-Q water and then filled with concentrated HBr and heated overnight at 100 °C. This step helped to further clean the PFA and ensured that the vials did not contribute Os blank during separation and microdistillation. Finally, all the vials were rinsed with Milli-Q water and air-dried.

Regular Carius tube digestion without desilicification (CT)

Test portions (0.5–2 g) of each sample powder were weighed and placed in Carius tubes. Appropriate amounts of the individual Re and Os spike solutions were accurately weighed and carefully added to each sample tube. While the tubes were chilled in a bath containing a freezing mixture of liquid N_2 and ethanol, 2.5 ml of concentrated HCl and 7.5 ml of concentrated HNO_3 were then successively added to each. The Carius tubes were carefully sealed and heated in an oven at 230 °C for 24 hr. After decomposition, the glass tubes were again chilled in a bath of liquid N_2 and ethanol and then opened. After thawing, the contents were poured into 20 ml centrifugation tubes, and after the residual solids were precipitated through centrifugation, the supernatant solutions were transferred into 30 ml PFA vials and subjected to Os solvent extraction by CCl_4 followed by back-extraction into concentrated HBr. The detailed solvent extraction procedure and conditions were described in prior studies (Cohen and Waters 1996, Pearson and Woodland 2000). The extracted Os fraction was further purified by microdistillation (Birck *et al.* 1997) and was then ready for N-TIMS measurement. Osmium was loaded in HBr on 99.999% Pt filaments (H. Cross Company, USA), and $Ba(OH)_2$ emitter solution was loaded on top of the sample to enhance ion emission. Osmium isotope ratios were measured as the trioxide negative ion (OsO_3^-) on a Thermo Finnigan Triton N-TIMS in negative ion mode. The detector used was a secondary electron multiplier operated in ion counting mode. High purity O_2 gas was introduced into the ion source via a leak valve to maintain a pressure of ~ 3 × 10^{-7} mbar. The OsO_3^- analyses followed a six-peak switch mass scan including: 240 ($^{192}Os^{16}O_3^-$), 238 ($^{190}Os^{16}O_3^-$), 237 ($^{189}Os^{16}O_3^-$), 236 ($^{188}Os^{16}O_3^-$), 235 ($^{187}Os^{16}O_3^-$) and 233 ($^{185}Re^{16}O_3^-$). Mass 233 ($^{185}Re^{16}O_3^-$) was monitored to correct for potential $^{187}Re^{16}O_3^-$ interference on the $^{187}Os^{16}O_3^-$ mass, and the interference contribution on the $^{187}Os^{16}O_3^-$ was typically < 0.2%. During measurements, the typical intensity of 235 ($^{187}Os^{16}O_3^-$) was > 3000 counts per s (cps). Measured raw ratios were corrected for oxygen isotope ratios using $^{17}O/^{16}O = 0.0003749$ and $^{18}O/^{16}O = 0.0020439$ (Nier 1950) and for mass fractionation using $^{192}Os/^{188}Os = 3.083$ (Walker *et al.* 2005).

The remaining solutions after Os extraction were evaporated to dryness, and the residues were dissolved in 1 ml of 6 mol l^{-1} HCl. After evaporation to dryness again, the residues were re-dissolved in 1 ml of 6 mol l^{-1} HCl. The solutions were again evaporated to dryness, and the residues were re-dissolved in 10 ml of 1 mol l^{-1} HCl on a hot plate at 120 °C. Bio-Rad Poly-Prep columns filled with 1.8 ml pre-cleaned anion exchange resin (Bio-Rad, AG1X8, 100–200 mesh) were used for the separation and purification of Re (Morgan and Walker 1989). Finally, Re mass fractions were determined by ID-ICP-MS (Thermo Elemental

X2 series; Thermo Fisher Scientific, Waltham, MA, USA). The details of measurement by ICP-MS are described elsewhere (Li *et al.* 2014). Total procedural blanks (TPB) for this technique were 0.32 ± 0.14 pg with the $^{187}Os/^{188}Os$ ratio of 0.284 ± 0.049 (n = 6, 1s) on average for Os and between 6 and 8 pg for Re. Blank contributions were typically (with highest blank contribution in brackets) < 1% (2%) for Re and < 2% (5%) for Os, respectively.

Carius tube digestion with HF desilicification (HF-CT)

Test portions (0.5–2 g) of each powdered sample were weighed and transferred together with Re and Os spikes into 30 ml PFA vials. Detailed procedures of desilicification with HF are available in Dale *et al.* (2009, 2012). After the HF digestion step, the residues were transferred by 2.5 ml of concentrated HCl to Carius tubes. After freezing of the test portions, concentrated HNO_3 (7.5 ml) was added, and the remaining procedure followed the method described above. TPB for this technique were 0.3 pg on average for Os and between 7 and 10 pg for Re.

Results and discussion

Comparison between CT and HF-CT

Rhenium and Os mass fractions and $^{187}Os/^{188}Os$ ratios (all corrected for the blank contributions), averages (X), the medians (M), the standard deviations (s) and the relative standard deviations (RSD) obtained by regular Carius tube digestion without HF desilicification (CT) and with HF desilicification (HF-CT), for the six geological RMs are presented in Table 1. To estimate whether or not there were significant differences among these results, the relative difference (RD in percent) was calculated (Equation 1) to quantify the relative differences of the average results between HF-CT digestion and regular CT digestion:

$$RD = (x_1 - X_0)/X_0 * 100 \qquad (1)$$

where X_0 is the average Re and Os mass fraction obtained by the regular CT digestion without desilicification, and x_1 is the average result obtained by HF-CT and is considered as the data to be evaluated (Figure 1).

Rhenium mass fractions

The RMs analysed here mostly have low and different Re mass fractions, ranging from pg g^{-1} to ng g^{-1} levels (Table 1). The intermediate precisions of repeated Re mass fraction determinations within one digestion scheme for each RM were smaller than 4% RSD, indicating that there was

at least one Re-bearing phase that was easy to digest and homogeneously distributed in the test portion masses (~ 1–2 g) within the sample units. An exception was the andesite AGV-2, which, with regular CT digestion, showed a relatively high RSD (10.5%) of Re mass fraction that is mainly attributed to the abnormally high Re mass fraction of one analysis (332 pg g^{-1} significantly higher than mean (267 ± 4 pg g^{-1}) of the other points). This abnormally high Re determination may indicate the heterogeneity of Re in this RM powder at ~ 2 g test portion size, provided by the correspondingly high Os mass fraction (Figure 2; Table 1).

With the exception of AGV-2, Re mass fractions of the other five RMs (BHVO-2, BCR-2, TDB-1, WGB-1 and WPR-1) have been well determined in previous studies (e.g., Brooks *et al.* 1999, Meisel and Moser 2004a,b, Qi and Zhou 2008, Dale *et al.* 2009, 2012, Savard *et al.* 2010, Schaefer *et al.* 2010, Li *et al.* 2014). In this study, duplicate analyses (n ≥ 4) of Re mass fractions by regular CT digestion for these RMs agreed well with the literature values obtained using regular CT or HPA-S digestions (Table 1). Although our Re results (758 ± 28 pg g^{-1}) in TDB-1 were consistent with the range of literature values (721–835 pg g^{-1}) obtained using regular CT or HPA-S digestions (Meisel and Moser 2004b, Qi and Zhou 2008, Dale *et al.* 2009, 2012, Savard *et al.* 2010), Re mass fractions (mean of 820 ± 20 pg g^{-1}) obtained in this study using the regular CT digestion with HF desilicification were about 18% lower than those reported by Dale *et al.* (2012) (mean of 1012 ± 40 pg g^{-1}) using HPA-S and HF digestion. In spite of the large variation in the literature data (721–835 pg g^{-1}), the cause for such substantial disparity between our Re data and those of Dale *et al.* (2012) using HF desilicification is unclear.

Among the six RMs, the RD values obtained from Re data of three samples (altered peridotite WPR-1, gabbro WGB-1 and basalt BCR-2) were within ± 2% (Figure 1a), suggesting similar yields between the regular CT digestion and that with HF desilicification, while the other three samples (basalt BHVO-2, diabase TDB-1 and andesite AGV-2) had RD values > 9% (Figure 1a), indicating that higher Re mass fractions in these rocks were obtained by the HF desilicification procedure. Further, the samples having RD values within ± 2% generally had significantly higher Re mass fractions (> 1 ng g^{-1}) than the others (< 1 ng g^{-1}), which had higher positive RD values (Figure 1a).

Os mass fractions and $^{187}Os/^{188}Os$ ratios

Osmium mass fractions in some RMs (AGV-2, BHVO-2 and WGB-1) obtained after repeated digestion and

Table 1.
Replicate determinations of Re-Os isotopes obtained with and without desilicification-combined Carius tube digestion for geological reference materials and literature data

AGV-2 (Andesite)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	$^{187}Os/^{188}Os$	2SE	$^{187}Re/^{188}Os$	2SE
1	2.0368	Regular CT	272	7	3.54	0.01	0.4409	0.0016	386	10
2	2.051		265	6	3.34	0.01	0.4627	0.0020	400	8
3	2.1148		267	5	3.57	0.01	0.4335	0.0019	374	8
4	2.0146		262	2	3.49	0.01	0.4441	0.0023	377	2
5	2.0530		332	7	4.35	0.01	0.4664	0.0024	384	9
Average			279.7		3.65		0.4495		384	
Median			266.7		3.54		0.4441		384	
s			29.3		0.4		0.01		10	
% RSD			10.5		10.9		3.2		3	
1	1.5647	HF-CT	307	4	3.95	0.01	0.4543	0.0017	389	5
2	1.5133		310	8	5.37	0.01	0.4399	0.0012	289	8
3	1.5172		303	5	4.27	0.01	0.4244	0.0017	355	5
4	1.5414		308	5	4.77	0.01	0.4312	0.0018	323	6
5	1.2267		299	8	5.3	0.01	0.4235	0.0016	282	8
Average			305.4		4.73		0.4347		328	
Median			306.5		4.77		0.4312		323	
s			4.3		0.6		0.01		45	
% RSD			1.4		13.2		2.9		14	

BCR-2 (Basalt)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	$^{187}Os/^{188}Os$	2SE	$^{187}Re/^{188}Os$	2SE
1	0.8117	Regular CT	11840	220	20.85	0.03	27.51	0.07	12509	236
2	0.7948		12090	220	22.90	0.15	20.25	0.13	9224	176
3	0.8016		12390	310	21.70	0.04	26.18	0.09	12097	308
4	0.8031		11850	160	20.82	0.05	27.37	0.11	12486	172
5	0.7980		12100	350	21.36	0.04	26.74	0.07	12203	356
Average			12054		21.52		25.61		11704	
Median			12090		21.36		26.73		12203	
s			226		0.9		3		1398	
% RSD			1.9		4		11.9		12	
1	1.0644	HF-CT	12550	810	23.15	0.03	20.86	0.06	9676	621
2	1.1085		12310	500	22.01	0.08	23.03	0.05	10741	434
3	0.9806		12340	570	22.66	0.03	21.34	0.05	9881	454
4	1.1546		11890	950	21.44	0.03	27.14	0.07	12087	967
5	0.8234		12320	320	22.28	0.07	25.14	0.05	11357	294
Average			12282		22.31		23.5		10748	
Median			12320		22.28		23.03		10741	
s			240		0.6		2.6		1008	
% RSD			2		2.9		11.2		9	
Meisel and Moser (2004a)		HPA-S	12030		30					

BHVO-2 (Basalt)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	$^{187}Os/^{188}Os$	2SE	$^{187}Re/^{188}Os$	2SE
1	0.8077	Regular CT	556	10	68.2	0.1	0.15615	0.00036	39.4	0.7
2	0.9107		554	8	70.4	0.1	0.15727	0.00037	38.1	0.5
3	1.0026		541	3	69.9	0.1	0.15519	0.00036	37.4	0.2
4	1.1038		526	8	96.6	0.1	0.14586	0.00031	26.3	0.4
5	1.2056		549	6	73.5	0.1	0.15646	0.00039	36.1	0.4
6[a]	1.0352		561	7	72.4	0.1	0.15560	0.00061	37.4	0.4
7[a]	1.0447		575	9	107.9	0.2	0.14983	0.00032	25.7	0.4
8[a]	1.0139		544	5	155.4	0.2	0.14109	0.00022	16.9	0.2
Average			550.7		89.3		0.1522		32.2	
Median			551.8		73		0.1554		36.8	
s			14.6		30.4		0.0060		8.2	

Table 1 (continued).
Replicate determinations of Re-Os isotopes obtained with and without desilicification-combined Carius tube digestion for geological reference materials and literature data

BHVO-2 (Basalt)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	^{187}Os/^{188}Os	2SE	^{187}Re/^{188}Os	2SE
% RSD			2.7		34.1		3.9		25.4	
1	0.8039	HF-CT	627	4	177.4	0.3	0.14474	0.00032	17.1	0.1
2	0.9015		648	11	319.2	0.7	0.13505	0.00024	9.8	0.2
3	1.0021		613	13	168.4	0.2	0.13785	0.00022	17.5	0.4
4	1.1141		634	16	97.0	0.1	0.15075	0.00023	31.6	0.8
5	1.1934		669	9	125.0	0.2	0.14900	0.00050	25.8	0.4
Average			638.1		177.4		0.14348		20.4	
Median			634.4		168.4		0.14474		17.5	
s			21.2		85.7		0.007		8.5	
% RSD			3.3		48.3		4.8		41.6	
Meisel and Moser (2004a)		HPA-S	543		101					
Li et al. (2014)		Regular CT	550		76		0.154			

TDB-1 (Diabase)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	^{187}Os/^{188}Os	2SE	^{187}Re/^{188}Os	2SE
1	0.9323	Regular CT	721	7	86.5	0.1	1.0341	0.0016	44.9	0.4
2	0.9781		752	12	83.2	0.1	1.0824	0.0018	48.9	0.8
3	0.9148		772	10	83.4	0.1	1.1069	0.0024	50.3	0.8
4	1.0033		787	7	87.5	0.4	1.073	0.0041	48.7	0.5
Average			758		85.2		1.0741		48.2	
Median			762		85		1.0777		48.8	
s			28.5		2.2		0.03		2.3	
% RSD			3.8		2.6		2.8		4.8	
1	0.9031	HF-CT	855	4	82.2	0.1	1.4291	0.0027	58.6	0.3
2	1.0048		807	3	90.5	0.1	1.1553	0.0019	48.7	0.2
3	1.1060		827	3	92.8	0.3	1.1274	0.0030	48.7	0.3
4	1.2037		830	6	93.9	0.2	1.1063	0.0023	47.8	0.4
Average			829.6		89.8		1.2045		50.9	
Median			828.1		91.6		1.1413		48.7	
s			19.8		5.3		0.15		5.1	
% RSD			2.4		5.9		12.5		10.1	
Meisel and Moser (2004b)		HPA-S	794		117		0.916			
Qi and Zhou (2008)		CT	770		153					
Savard et al. (2010)		HPA-S	721		50					
Dale et al. (2009)		HPA-S	809		104		0.9688			
Dale et al. (2012)		HPA-S	835		114		0.9374			
Dale et al. (2012)		HPA-S+HF	1010		106		0.973			

WGB-1 (Gabbro)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	^{187}Os/^{188}Os	2SE	^{187}Re/^{188}Os	2SE
1	1.0200	Regular CT	1184	20	440.8	0.9	0.18722	0.00029	13	0.2
2	1.0150		1195	19	605.9	1.8	0.17769	0.00025	9.6	0.2
3	1.1561		1167	21	433.7	1	0.18826	0.00029	13.1	0.2
4	1.0434		1187	18	400.5	1.1	0.19658	0.00038	14.4	0.2
5	0.9789		1188	21	587.8	3.4	0.17765	0.00031	9.8	0.2
Average			1184		493.7		0.18548		12	
Median			1187		440.8		0.18722		13	

Table 1 (continued).
Replicate determinations of Re–Os isotopes obtained with and without desilicification-combined Carius tube digestion for geological reference materials and literature data

WGB-1 (Gabbro)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	^{187}Os/^{188}Os	2SE	^{187}Re/^{188}Os	2SE
s			10.6		95.6		0.01		2.2	
% RSD			0.9		19.4		4.3		18.1	
1	0.9453	HF-CT	1160	24	686.4	2.3	0.17190	0.00037	8.2	0.2
2	1.2720		1145	24	470.8	1.3	0.17757	0.00023	11.8	0.3
3	1.0190		1159	17	459.2	1.2	0.18863	0.00026	12.2	0.2
4	1.0517		1158	9	660.4	3	0.17421	0.00036	8.5	0.1
5	1.0686		1179	12	524.6	1.9	0.18970	0.00030	10.9	0.1
Average			1160		560.3		0.18040		10.3	
Median			1159		524.6		0.17757		10.9	
s			12		106.6		0.01		1.9	
% RSD			1		19		4.6		18.2	
Meisel and Moser (2004b)		HPA-S	1150		540					
Savard et al. (2010)		HPA-S	1230		484					
Li et al. (2014)		Regular CT	1140		399		0.1858			

WPR-1 (Peridotite)	Test portion mass (g)	Digestion technique	Re (pg g⁻¹)	2SE	Os (pg g⁻¹)	2SE	^{187}Os/^{188}Os	2SE	^{187}Re/^{188}Os	2SE
1	0.5158	Regular CT	11160	70	15430	320	0.14446	0.00029	3.5	0.1
2	0.5608		11260	100	15570	470	0.14468	0.00026	3.5	0.1
3	0.6141		11140	80	14970	550	0.14506	0.00024	3.6	0.1
4	0.6724		11110	90	14950	680	0.14483	0.00020	3.6	0.2
5	0.7573		11270	140	14860	660	0.14506	0.00026	3.7	0.2
Average			11188		15156		0.14482		3.6	
Median			11160		14970		0.14483		3.6	
s			73		321		0.00026		0.1	
% RSD			0.7		2.1		0.2		2.1	
1	0.5370	HF-CT	10890	60	15430	410	0.14475	0.00026	3.3	0.1
2	0.5885		11210	50	15570	450	0.14469	0.00024	3.4	0.1
3	0.5407		10880	80	15850	520	0.14445	0.00025	3.3	0.1
4	0.5348		10900	130	15980	680	0.14420	0.00025	3.3	0.1
5	0.5622		10960	80	15810	660	0.14443	0.00027	3.3	0.1
6[b]	0.4623		11052	201	15862	399	0.14454	0.00018	3.4	0.1
7[c]	0.4462		10937	68	15446	295	0.14453	0.00016	3.4	0.1
Average			10976		15707		0.14451		3.3	
Median			10937		15810		0.14453		3.3	
s			119		221		0.00018		0.1	
% RSD			1.1		1.4		0.1		1.6	
Brooks et al. (1999)		Regular CT	11700		16800		0.14559			
Meisel and Moser (2004b)		HPA-S	10830		18550					
Schaefer et al. (2010)		Regular CT	10500		16890		0.1449			

[a] Digested at 230 °C for 72 hr.
[b] Os spike added during HF desilicification step.
[c] Os spike added during CT digestion step.

measurements showed low intermediate precision (RSD > 10%), indicating heterogeneous distribution of Os in these (~ 200 mesh sizes) RMs. By contrast, data of other RMs (BCR-2, TDB-1 and WPR-1) displayed good intermediate precision (RSD < 6%; Table 1) for Os mass fractions. The anomalously high and variable Os mass fractions in BHVO-2 obtained by HF desilicification compared with those without HF desilicification require closer
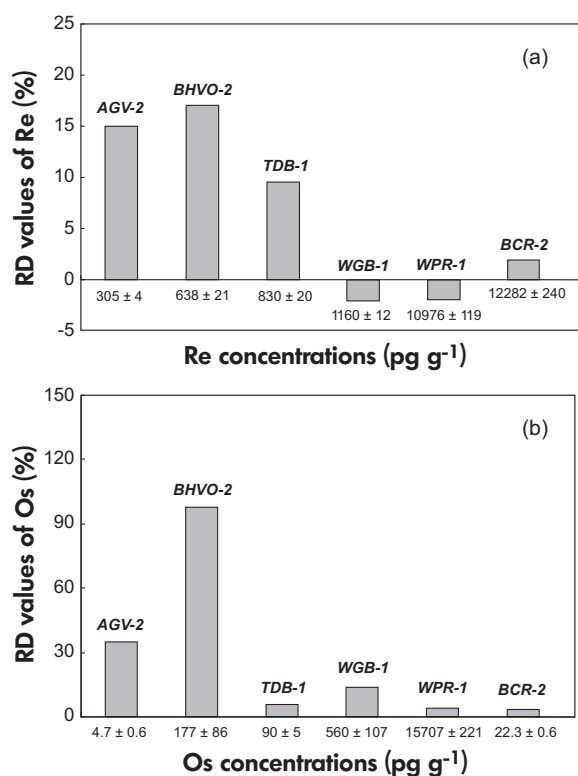
Figure 1. The relative difference (RD in %) values of Re (a) and Os (b) mass fractions of six geological reference materials. RD = $(x_1 - X_0)/X_0 * 100$, where X_0 is the average result obtained by the regular CT digestion without desilicification, and x_1 is the average result obtained by the CT digestion with HF desilicification. Average Re and Os mass fractions obtained by HF desilicification were also labelled on x axis in panel (a) and (b), respectively.

inspection. Replicates of BHVO-2 obtained by HF desilicification prior to CT attack had an average Os concentration of ~ 177 pg g^{-1}, much higher than those (~ 89 pg g^{-1}) obtained by the regular CT digestion without HF desilicification. This may be attributed to either loss of Os spike during HF desilicification prior to CT or increasing Os extraction efficiency using HF desilicification, or both. Through comparison of the Os data obtained by adding an Os spike prior to the HF desilicification step with those obtained by adding an Os spike prior to the CT digestion step, these two methods yielded identical Os mass fractions (Table 1), thus excluding the possibility of the loss of the Os spike during HF desilicification.

The RD values for Os among the RMs showed significantly larger variations, ranging from 3 to 99%, indicating that higher Os mass fractions were generally

obtained by the HF-CT procedure relative to the regular CT digestion (Figure 1b). Similar or smaller RD and RSD values of Os mass fractions between the regular CT and the CT with HF desilicification were observed in many other RMs (Figures 1b and 2).

Sample heterogeneity and the causes

Because of their chalcophile and siderophile geochemical behaviour, both Re and Os commonly occur in base metal sulfides (e.g., Luguet *et al.* 2004, Lorand *et al.* 2008, 2010, Piña *et al.* 2012). In particular, three-phase sulfide, garnet and magnetite have been identified to serve as hosts for Re in mantle melting (e.g., Roy-Barman and Allègre 1995, Righter and Hauri 1998, Righter *et al.* 1998). Osmium may be hosted in the form of micro-PGM (e.g., laurite–erlichmanite series RuS_2–OsS_2), alloy (Os–Ir–Ru alloys) and chromite. The heterogeneous distribution of these Re-rich and/or Os-rich tiny discrete mineral phases in the rock sample powder generates the so-called nugget effect, especially remarkable for samples with low mass fractions of these elements (Meisel *et al.* 2001b, Meisel and Moser 2004b, Savard *et al.* 2010). Gravitational settling and segregation of such high-density accessory trace phases can lead to the heterogeneous distribution of these phases in the powder and, therefore, the heterogeneous distribution of these elements if the mineral grains are large and small test aliquots are used (Meisel and Moser 2004b). In general, 0.5–2 g test portions achieved reproducible results for Re, given their RSD generally within 4% in most RMs regardless of the employment of HF desilicification (Table 1). By contrast, Os in the same test portion size showed much larger variations in most RMs. This observation is consistent with the results of previous studies (e.g., Meisel and Moser 2004a, b, Wang and Becker 2014) that the reproducibility of Re mass fractions is routinely better than that of Os mass fractions in geological samples. Such a contrasting feature indicates that Re and Os are not controlled by the same phases and/or that some Os-rich phases are isolated by silicate minerals.

As mentioned above, the high intermediate precision of Re mass fractions at RSD < 4% in 0.5–2 g test portions in each digestion scheme suggests that Re appears generally homogeneously distributed in such test portion sizes. Previous studies (Burton *et al.* 2000, Meisel *et al.* 2003b, Mallmann and O'Neill 2007, Dale *et al.* 2009, 2012) demonstrate that Re mass fractions of rock samples obtained using CT with HF desilicification were higher than, or similar to, those using CT without HF desilicification. This study confirms this conclusion that a small portion of Re may reside in silicate phases (that are not completely liberated by *aqua regia*
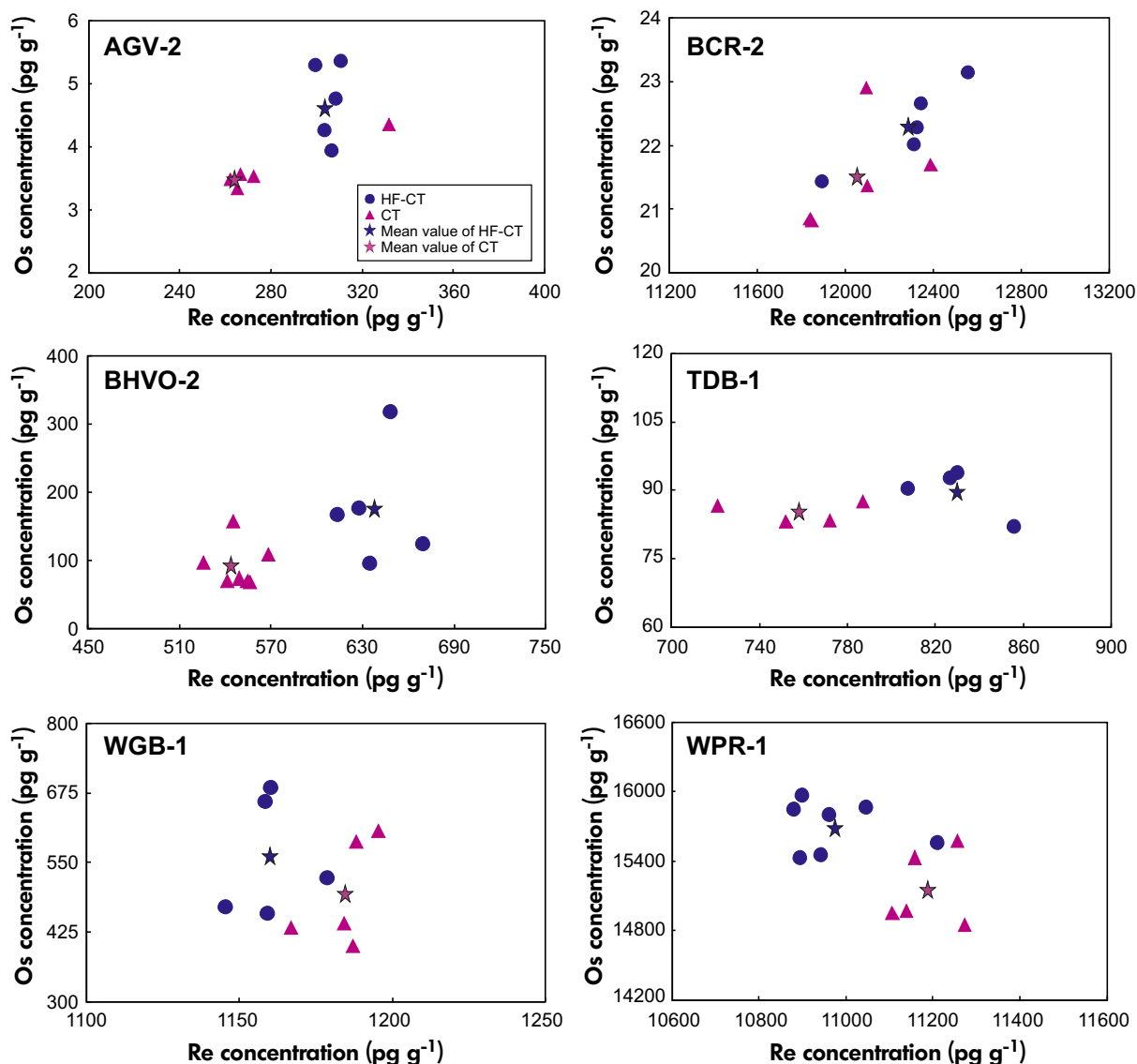
Figure 2. Plots of Re vs. Os mass fractions in replicates of geological reference materials.

solutions; Meisel *et al.* 2009, Dale *et al.* 2012) in some rock systems, particularly basaltic and andesitic rocks (e.g., BHVO-2, TDB-1 and AGV-2). For some mafic–ultramafic rocks (e.g., BCR-2, WGB-1 and WPR-1), complete Re liberation could be achieved by CT digestion without HF desilicification. This indicates that Re may be predominantly hosted in oxide minerals (e.g., magnetite; Righter *et al.* 1998) and/or the base metal sulfides, which can be completely dissolved in *aqua regia* solutions without the aid of HF desilicification.

In contrast to Re, the low intermediate precision (RSD > 10%) of Os mass fractions in some RMs (AGV-2, BHVO-2 and WGB-1) indicates that Os is more heterogeneously distributed in these rocks, which may be attributable

to the 'nugget effect', that is heterogeneous distribution of Os-bearing trace phases (alloy and sulfide) in 0.5–2 g test portions (Meisel *et al.* 2001b, Meisel and Moser 2004a, b, Savard *et al.* 2010, Li *et al.* 2014). The average Os mass fraction obtained using the CT digestion with HF desilicification was higher than the regular CT digestion. This observation implies that a complete digestion of silicate phases indeed increases Os extraction efficiency, because the employment of HF desilicification effectively breaks down strong Si–O bonds to expose all Os-hosted phases to *aqua regia* solution. This also suggests that a portion of Os-rich trace phases may occur as inclusions within the silicate phases that act as an isolator from regular *aqua regia* solutions. This may explain why replicates of BHVO-2 obtained by HF desilicification prior to CT attack had

anomalously high and variable Os mass fractions and less radiogenic $^{187}Os/^{188}Os$ ratios (Table 1). The occurrence of less radiogenic $^{187}Os/^{188}Os$ ratios coupled with higher Os mass fractions (Figure 3) indicates that the Os-rich trace phases are probably characterised by relatively low Re/Os ratios, typical characteristics of mantle-derived sulfides and alloys such as OsIr that are commonly preserved within silicate minerals (Harvey *et al.* 2011). Additionally, the Re–Os isotope system is highly sensitive to heterogeneous distribution of trace phases in sample powders (Meisel *et al.* 2001b). The positive 1/Os vs. $^{187}Os/^{188}Os$ correlations of replicate results of the RMs (Figure 3) provide solid evidence for the heterogeneous nature of both Os mass fractions and $^{187}Os/^{188}Os$ isotope ratios in 0.5–2 g powdered samples (~ 200 mesh sizes). Such a feature can be depicted by mixing of two end-member components with distinctive Os

mass fractions and Os isotope compositions (Vollmer 1976). Each individual analysis of a RM can be regarded as a mixture by random mixing of the two end-members. Plotting replicate results of the RMs simulates such a mixing process, which resulted in the trends in the Re–Os isochron diagrams (Figure 4).

Summary

Rhenium and Os mass fractions and Os isotopic compositions of geological RMs were determined using the Carius tube (CT) digestion with and without HF desilicification. Our results show that replicate measurements of RMs using CT digestion resulted in high intermediate precision (RSD < 4%), regardless of employment of HF desilicification. By contrast, Os mass fractions in the same
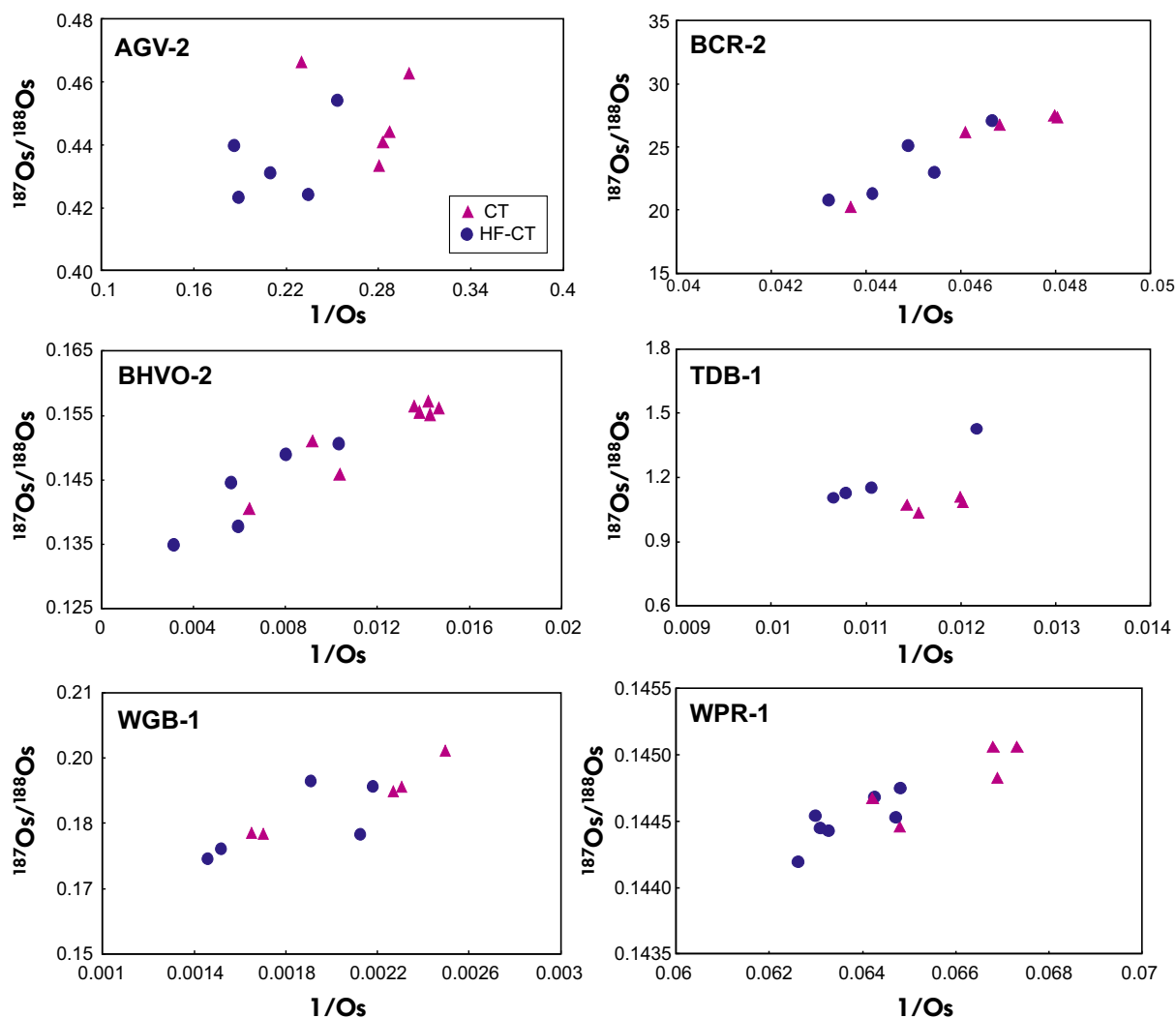

Figure 3. Plots of 1/Os (pg g^{-1}) vs. $^{187}Os/^{188}Os$ ratios of replicates of geological reference materials, showing good positive correlations for most of the RMs.
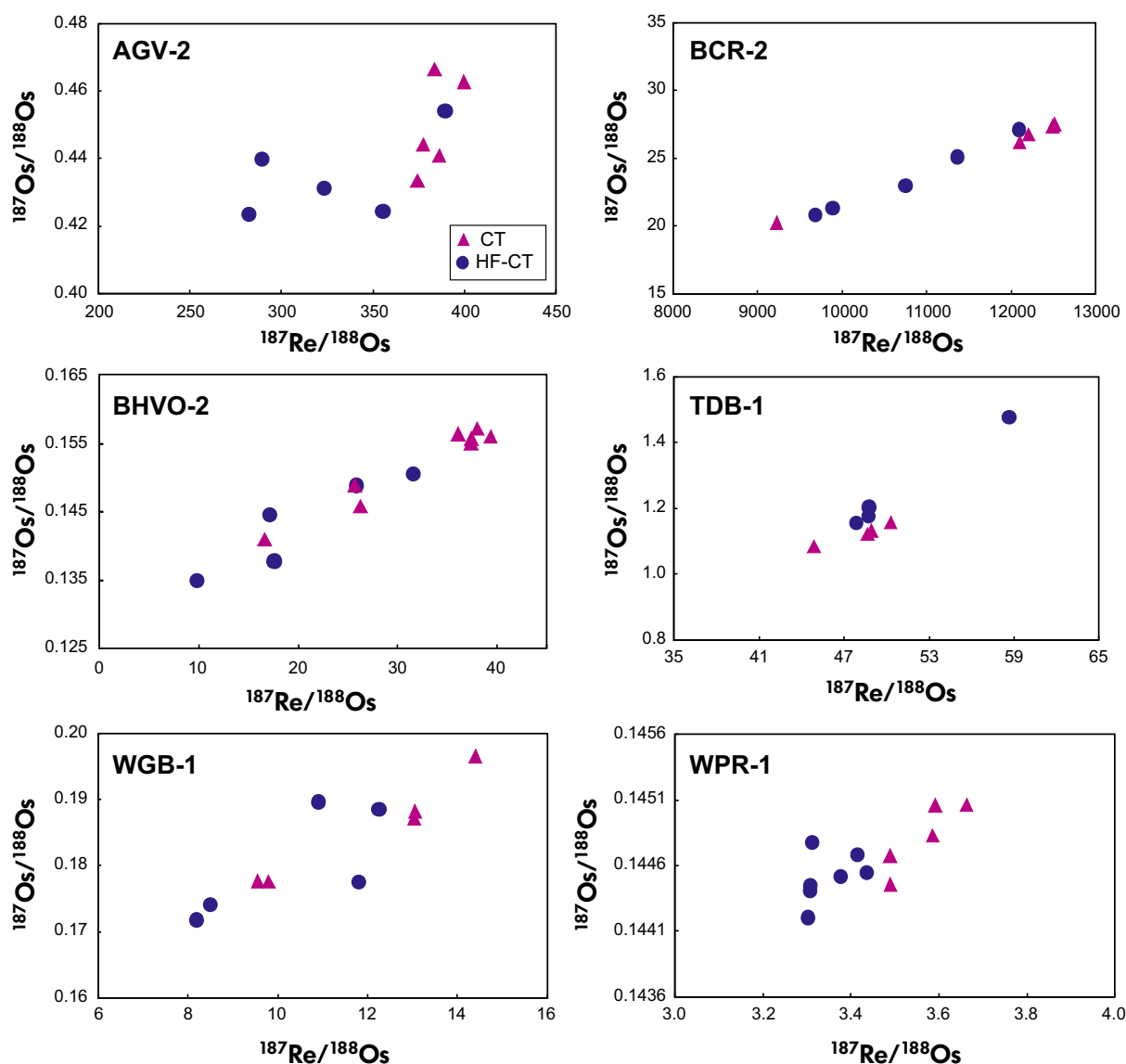
Figure 4. Plots of $^{187}Re/^{188}Os$ vs. $^{187}Os/^{188}Os$ in replicates of reference materials, typically showing mixing trends.

digestion aliquots of the RMs often displayed poor intermediate precision (RSD > 10%), especially in Os-poor samples. Such a feature implies that Re and Os are not controlled by the same phases. Our results also show that Re and Os mass fractions obtained with HF desilicification were higher than, or similar to, those without HF desilicification. Although the high-temperature (230 °C) *aqua regia* digestion can sufficiently decompose exposed sulfides and oxide minerals, the employment of HF desilicification, which effectively breaks down strong Si–O bonds to expose all the Re and Os host phases to acids, can improve the liberation of both the Re and Os that either are structurally bonded or occur as inclusions in silicate minerals. This study demonstrates that the HF desilicification step prior to CT digestion is important for complete extraction of Re and Os, particularly for basaltic and andesitic rocks.

Acknowledgements

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