GEOSTANDARDS and GEOANALYTICAL RESEARCH

Comparative Determination of Mass Fractions of Elements with Variable Chalcophile Affinities in Geological Reference Materials with and without HF-desilicification

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Desilicification elevates extraction of Re and platinum-group elements (PGEs) from many geological reference materials (RMs), but the extent to which it affects less chalcophile elements has been investigated rarely. To further evaluate the effect of desilicification, mass fractions of elements with variable chalcophile affinities (In, Cd, Cu, Ag, S, Se, Te, Re and PGEs) in different RMs were obtained by isotope dilution and digestion procedures involving HF-HNO_3 in bombs versus HNO_3-HCl in Carius tubes. The results show that the extraction efficiencies of HF-desilicification vary in different RMs and for different elements. HF-desilicification led to a significant increase (30–70%) for In and Cd mass fractions in all analysed RMs, but it played a negligible role in other strongly chalcophile elements in many samples (e.g., UB-N and WGB-1). Noticeably, desilicification led to a 10–30% increase in the mass fractions of Cu, Ag, S, Se and Te in BHVO-2 and BIR-1a, but less so in BCR-2. These results could be attributed mainly to the variable chalcophile affinities of elements and their relative budget in sulfides, alloys and silicates. Desilicification should thus be preferred to determine chalcophile elements for most samples, except in cases where they are negligibly hosted in silicates.

Keywords: chalcophile elements, desilicification, reverse *aqua regia*, isotope dilution, sample heterogeneity, geological reference materials.

Received 27 Nov 19 – Accepted 31 Mar 20

Chalcophile elements are not only economically important but also useful in understanding numerous planetary and geological processes, such as terrestrial core formation and late accretion (e.g., Wood *et al.* 2006, Rose-Weston *et al.* 2009, Rubie *et al.* 2011, Wang and Becker 2013), mantle processes (e.g., Yi *et al.* 2000, Kiseeva and Wood 2013, Nielsen *et al.* 2014, Lorand and Luguet 2016) and mantle-crust differentiation and interaction (e.g., Jenner *et al.* 2010, Lee *et al.* 2012, Jenner 2017, Wang *et al.* 2018, Chen *et al.* 2019, 2020, Cox *et al.* 2019). These broad applications require high-quality mass fraction data for chalcophile elements in geological samples. A combination of acid digestion and the isotope dilution method has been commonly used to obtain high-quality mass fraction data of low-abundance chalcophile elements (e.g., PGE, Re, S, Se, Te and Ag; Makishima and Nakamura 2001, 2009, Meisel *et al.* 2001a, Reisberg and Meisel 2002, Qi *et al.* 2007, Savard *et al.* 2010, Fischer-Gödde *et al.* 2011, König *et al.* 2012, Erdman *et al.* 2013, Ishikawa *et al.* 2014, Wang and Becker 2014, Li *et al.* 2014a, Chu *et al.* 2015, Day *et al.* 2016, Yierpan *et al.* 2018, Zhou *et al.* 2019).

Because of the high partition coefficients between sulfides/alloys and silicates (up to 10^4; Kiseeva *et al.* 2017, Lorand *et al.* 2010, Mungall and Brenan 2014, Patten *et al.* 2013), PGEs are predominantly hosted in sulfides/alloys and they are thus thought to be efficiently extracted from geological samples by *aqua regia* or reverse *aqua regia* (the mixture of concentrated HCl and HNO_3) in closed systems such as high pressure asher and Carius tubes at elevated temperatures and pressure (e.g., > 230 °C for > 72 h; Shirey and Walker 1995, Rehkämper *et al.* 1998, Meisel *et al.* 2003, Becker *et al.* 2006, Qi *et al.* 2007, Ishikawa *et al.* 2014, Wang and Becker 2014, Chu *et al.*

doi: 10.1111/ggr.12328

2015, Cheng *et al.* 2019). The mass fractions of PGEs and the less chalcophile Re in peridotites obtained after digestions by HF-desilicification or *aqua regia* are indistinguishable (Meisel *et al.* 2009, Ishikawa *et al.* 2014, Li *et al.* 2014b, Day *et al.* 2016, Zhou *et al.* 2019), indicating the negligible effect of HF-desilicification. However, HF-desilicification has been documented to increase the extraction efficiency of Ru for some RMs such as TDB-1 and BIR-1 (Meisel *et al.* 2009, Ishikawa *et al.* 2014, Li *et al.* 2014b, Day *et al.* 2016, Meisel and Horan 2016, Zhou *et al.* 2019). Although the release of Re from some samples benefits from the prolonged duration of digestion by *aqua regia* (Ishikawa *et al.* 2014), HF-desilicification does yield higher Re mass fractions in many rock types than those obtained from *aqua regia* digestion, for example, by 10–20% for TDB-1 (Meisel *et al.* 2009, Ishikawa *et al.* 2014, Li *et al.* 2014b, Day *et al.* 2016, Meisel and Horan 2016, Zhang and Hu 2019, Zhou *et al.* 2019). These previous studies thus have indicated that desilicification is of great importance in achieving complete liberation of some (not all) chalcophile elements from geological samples.

Chalcophile elements include a large group of elements with different affinities to sulfides, and their behaviour is thus variably controlled by sulfides during magmatic processes (Yi *et al.* 2000, Li and Audétat 2012, Patten *et al.* 2013, Li 2014, Brenan 2015, Wang and Becker 2015a, Brenan *et al.* 2016, Kiseeva *et al.* 2017). Most of them show lower chalcophilic affinities compared with PGEs and Re, and partition into the silicate phases in a larger proportion, implying the importance of desilicification for efficient extraction of the elements less chalcophile than PGEs and Re from geological samples. However, the extent to which desilicification affects these chalcophile elements has been investigated rarely, but the limited available data for Se and Te probably suggest the necessity of desilicification in some cases (Yierpan *et al.* 2018). The mass fractions of Se and Te in UB-N (peridotite) obtained after digestions by HF-desilicification (König *et al.* 2012, Wang *et al.* 2015) do not show differences from those by *aqua regia* (Wang and Becker 2013, Wang *et al.* 2013). However, HF-desilicification noticeably elevates the mass fractions of Se and Te in basalts (BHVO-2) by ~ 12–25% (Yierpan *et al.* 2018). The specific reason for such a difference is unclear and may result from the incomplete dissolution of Se and Te from silicate glasses or micro-sulfide inclusions hosted in silicates (Yierpan *et al.* 2018). In probability, these observations indicate that the sample compositions also play a key role.

In order to better understand the effect of desilicification on the extraction efficiency of chalcophile elements, comparative digestion experiments with and without HF-desilicification (HF-HNO_3 + HNO_3-HCl in bombs versus HNO_3-HCl alone in Carius tubes) for a variety of chalcophile elements (In, Cd, Cu, Ag, S, Se, Te, Re and PGEs, as well as Tl from HF-desilicification) in different types of geological RMs (from ultramafic to felsic igneous rocks) are presented here. These elements display variable chalcophile affinities (Yi *et al.* 2000, Li and Audétat 2012, Patten *et al.* 2013, Li 2014, Brenan 2015, Wang and Becker 2015a, Brenan *et al.* 2016, Kiseeva *et al.* 2017), and obtaining their mass fractions from the same test portion could be suitable to address the effect of HF-desilicification. Based on isotope dilution methods, we combined and updated previously established chemical separation procedures for multiple chalcophile elements (Wang and Becker 2014, Wang *et al.* 2015) and Re-PGEs (Rehkämper and Halliday 1997), and obtained the mass fractions of these chalcophile elements from the same sample aliquot. These data could be also useful to compare the variable extents of sample heterogeneity on different chalcophile elements at a given test portion size.

Geological reference materials

HF-desilicification results in variable effects on the same chalcophile elements (such as Re, Ru, Se and Te) in crystalline or mafic–ultramafic rocks, as mentioned above. Therefore, geological RMs with a wide range of petrographical types and chemical compositions were selected. The rock types of the studied RMs are peridotites (serpentinized lherzolite UB-N, Centre de Recherches Pétrographiques et Géochimiques – CRPG; serpentinized harzburgite MUH-1, International Association of Geoanalysts – IAG), intrusive mafic–ultramafic rocks (diabase TDB-1 and gabbro WGB-1, Canadian Certified Reference Material Programme – CCRMP) and extrusive mafic–ultramafic rocks (basalts BHVO-2, BCR-2 and BIR-1a, United States Geological Survey – USGS; komatiite OKUM, IAG). The granodiorite GSP-2 (USGS) was also analysed. These RMs represent variable extents of crystallinity with different sulfide modes; a large proportion of chalcophile elements may not be hosted in sulfides but silicate glasses or the crystal lattice of some RMs such as basalts. They are suitable to aid understanding of the effect of HF-desilicification on chalcophile elements in different geological samples.

Experimental procedure

Instrumentation and reagents

All the elements determined in this study were measured by high-sensitivity sector field ICP-MS Element XR (Thermo Fisher Scientific Inc. Waltham, MA, USA) at the State Key

Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. Concentrated HCl (12 mol l^{-1}), HNO_3 (14 mol l^{-1}) and HF (24 mol l^{-1}) used in this study were purified twice from reagent grade concentrated acids by sub-boiling distillation in Savillex PFA stills. High-purity water (resistivity, 18.2 MΩ cm) from a Milli-Q purification system (Millipore Corporation, Molsheim, France) was used throughout. Hydrogen peroxide (30 g 100 g^{-1}; Fisher Chemical, USA) and L-ascorbic acid (Bio-Ultra, Dorset, UK), ≥ 99.5 g 100 g^{-1}, RT, Sigma-Aldrich, Dorset, UK) were used in the study.

Except for the sulfur calibration solution, other calibration solutions (In, Cd, Tl, Cu, Ag, Se, Te, Re and PGEs standard solutions) that were used to correct instrumental mass drift were prepared by dilution from *ca.* 10000 µg ml^{-1} NIST standard reference materials. The sulfur calibration solution was dissolved from K_2SO_4 powder (> 99%, *m/m*; Merck company, Darmstadt, Germany; $\delta^{34}S$: 10.70 ± 0.15‰) (Wang and Becker 2014). The borosilicate Carius tubes used (2 mm thick and a volume of about 50 ml) were pre-cleaned in sub-boiling *aqua regia* diluted with high-purity water (1:1 by volume; 48 h) and water. Ion exchange resins (Bio-Rad AG 1-X8, 100–200 mesh and Eichrom 50W-X8, 100–200 mesh) were pre-cleaned in high-purity water, HCl and HNO_3 of different concentrations (1 and 6 mol l^{-1}, three times). Savillex PFA beakers were used for sample solutions and, after use, sequentially cleaned with diluted *aqua regia* (1:1 by volume), HNO_3, HCl and high-purity water on hot plate overnight at 120 °C.

Non-desilicification digestion by HNO_3-HCl

In this study, RMs were attacked by reverse *aqua regia* (a mixture of concentrated HNO_3 and HCl in a volume ratio of 5:2) in borosilicate Carius tubes, which followed the procedures described in Cheng *et al.* (2019). About 1–2 g test portions of RM powder and appropriate amounts of spike solutions (^{34}S, ^{77}Se-^{125}Te, ^{65}Cu-^{109}Ag-^{113}In-^{110}Cd, ^{185}Re, ^{99}Ru-^{105}Pd-^{191}Ir-^{194}Pt, the same stock spike solutions as in Wang and Becker (2014) and Wang *et al.* (2015), and see the details therein) were weighed into pre-cleaned Carius tubes. Individual Carius tubes were sealed and placed into steel jackets. The RMs were digested in an electric oven at 220–270 °C for 96 h. Such a long digestion time was expected to yield the highest extent of extraction efficiency for the chalcophile elements of interest in this study as indicated previously (Ishikawa *et al.* 2014). After digestion, the sample solutions were transferred to centrifuge tubes, and 6 mol l^{-1} HCl was used to rinse the Carius tubes and combined with the sample solution. After centrifugation, part of the supernatant solution equivalent to 0.2 g of the sample was transferred to pre-cleaned Savillex PFA beakers. The sample solution was evaporated to dryness, followed by addition and evaporation of concentrated HCl twice at 80–90 °C. Finally, samples were dissolved in 1.5 ml 4.5 mol l^{-1} HCl for analyte–matrix separation.

Desilicification digestion by HF-HNO_3 and HNO_3-HCl

Since the chalcophile elements hosted in silicate minerals and/or glasses are likely to be incompletely released by reverse *aqua regia*, digestion experiments with desilicification by HF-HNO_3 and HNO_3-HCl were also performed for comparison. An in-house PTFE-lined magnalium bomb that consisted of a 15 ml volume inner PTFE vessel and an outer magnalium pressure jacket was used to digest RMs by HF-HNO_3. About 0.2–0.4 g test portions of RM powder and appropriate amounts of spike solutions (^{34}S, ^{77}Se-^{125}Te, ^{65}Cu-^{109}Ag-^{113}In-^{110}Cd, ^{203}Tl, ^{185}Re, ^{99}Ru-^{105}Pd-^{191}Ir-^{194}Pt, as in Wang and Becker (2014) and Wang *et al.* (2015)) were weighed into pre-cleaned PTFE vessels, followed by 2 ml of concentrated HNO_3 and 4 ml of concentrated HF. The PTFE-lined magnalium bombs were then placed in an electric oven and heated to 190 °C for 48 h. After cooling, the bombs were opened, and the sample solutions were evaporated to dryness on the hot plate at 80–90 °C. Then, 2 ml of concentrated HNO_3 was added and evaporated to further convert fluorides into nitrates. In order to completely dissolve the potential remaining phases such as spinels or alloys and ensure spike-sample equilibration, considering the high dissolubility of PGEs and PGE minerals in *aqua regia*, the residue was then dissolved by adding a mixture of 4 ml reverse *aqua regia* (3 ml concentrated HNO_3 + 1 ml concentrated HCl) and the beakers were closed for digestion on the hot plate at 140 °C for 24 h. Dissolution of minerals was confirmed visually by clear solutions; white fluoride precipitates occasionally existed. Such precipitates would not affect the results because spike-sample equilibration is achieved during sample digestion (Wang *et al.* 2015). Sample solutions were then dried down, followed by repeated addition of concentrated HCl and evaporation at 80 °C three times. Finally, samples were dissolved in 3 ml 4.5 mol l^{-1} HCl and transferred to centrifuge tubes for 15 min of centrifugation. To avoid exceeding the capacity of the resin, supernatant solution equivalent to around 0.2 g of sample was taken for analyte–matrix separation.

Analyte–matrix separation

The chemical separation and purification procedure for sample solutions (Table 1 and Table S1) were combined and modified from previously described methods (Rehkämper and Halliday 1997, Wang and Becker 2014, Wang *et al.* 2015). The main modification was the additional step to elute Re-PGE elements based on the procedure of Wang *et al.* (2015). Bio-Rad Poly-Prep columns containing 2 ml of pre-cleaned Bio-Rad AG1-X8 (100–200 mesh, chloride form) anion resin were used to remove the potential interfering ions. The Bio-Rad AG1-X8 anion resin was discarded after use. The S-Se, Cu-In-Te, Ag, Cd-Tl and Re-PGE fractions were separated from each other in this column separation (Table 1). This procedure can avoid possible strong interferences from the elements of ions, for example, In-Cd-Pd (Table S2). After collecting other chalcophile ions, Re-PGE ions were strongly retained on anion resins and eluted by 14 ml of concentrated HNO_3 and 14 ml of concentrated HCl (Rehkämper and Halliday 1997, Pearson and Woodland 2000, Meisel and Horan 2016).

The collected solutions of different fractions were evaporated to dryness on a hot plate. To avoid the possible loss of volatile chalcophile elements (König *et al.* 2012, Kurzawa *et al.* 2017) and liquid sputtering from decomposing reverse *aqua regia*, the temperature of the hot plate was initially held at 60 °C and increased to 80–90 °C later. The Ag, Cd-Tl and Re-PGEs fractions were dissolved in 4 ml 2% *v/v* HNO_3 ready for ICP-MS measurement. Because of the presence of much matrix in the S-Se fraction and Cu-In-Te fraction, a further purification step was carried out, respectively (Table S1). The S-Se fraction was dried down and dissolved in 2 ml 0.1 mol l^{-1} HNO_3, and after centrifugation, it was loaded on 2 ml cation exchange ion resin for the analyte–matrix separation (Table S1). The Cu-In-Te fraction was dissolved in 0.5 ml 9 mol l^{-1} HCl, followed by 0.5 ml 0.15 g ml^{-1} ascorbic acid in high-purity water (Wang *et al.* 2015). Then, the solution of Cu-In-Te fraction was loaded onto 1 ml anion resin for further chemical separation as in Table S1 to remove the Fe matrix (Wang *et al.* 2015).

Measurements and data reduction

Intensities of all chalcophile elements of this study were measured by a high-sensitivity sector field ICP-MS (Element XR), equipped with a quartz spray chamber. The oxide formation rates during measurement were less than 3% (CeO^+/Ce^+). Sulfur and Cu were measured in medium mass resolution mode ($M/\Delta M$ = 4000, MR) and other elements in low mass resolution mode. The measurements of In, Cd, Tl, Cu, Ag, S and Te intensities followed the methods outlined in Wang *et al.* (2015). The Re-PGE elements were measured following the methods outlined in Wang and Becker (2014). A continuous flow system hydride generator (assembled by components from PerkinElmer, Shelton, CT, USA) was used to measure Se of a few samples. The hydride generation occurred for the generation of Se hydrides, and the sample solution was mixed with 1 mol l^{-1} HCl with 0.5 g per 100 g $NaBH_4$ and 0.5 g per 100 g NaOH (Rouxel *et al.* 2002, Elwaer and Hintelmann 2008).

The monitored signals at a given mass-to-charge ratio of analytes and interferences for the elements of In, Cd, Tl, Cu, Ag, S, Se, Te, Re and PGE are listed in Table S2. Oxide ion interferences could be ignored (< 0.01) at the oxide formation rates of < 3% (CeO^+/Ce^+). After the purification, the contribution from isobaric interferences to the measured analyte ions was negligible for most samples (< 1%) and was also subtracted. For example, after analyte–matrix separation, the intensity ratios of isobaric ion compound/ion were < 0.01 for In and < 0.0001 for Cd for most samples. The blank solutions (the diluted acids) were measured before and after each sample to monitor the background intensities and memory effect. The intensities of blank solutions were negligible and always subtracted (< 0.5%). The isotopic intensity ratios used for calculations are listed in Table S2. For Cd, S, Se, Ru, Pt and Pd, the results calculated from different isotopic ratios were used for comparison (Table S2), and the differences were < 1–3% in most cases.

Detection limits and total procedural blanks

The detection limits of the Element XR ICP-MS were calculated from three times the standard deviation of the reagent blank (dilute HCl or HNO_3) in counts per second. The results indicate very low detection limits for elements measured in this study (Table S3). For each digestion batch of samples, a total procedural blank (TPB) was treated as samples and obtained by isotope dilution ICP-MS methods (see details in Table S3; Yu *et al.* 2002). The total procedural blanks are listed in Table S3 and were negligible (mostly < 1%) for In, Cd, Tl, S, Ag, Cu, Se, Te, Re and PGEs mass fractions of the measured RMs, but larger for the RMs with extremely low mass fractions of some chalcophile elements, for example, ~ 20% S blanks for BIR-1a (5.26 ± 0.56 µg g^{-1}). The procedural blanks of non-desilicification digestion in Carius tubes for Re-PGE elements have been reported in Cheng *et al.* (2019), a level similar to procedural blanks of desilicification digestion obtained in this study. All results presented in Table S4 were subtracted by the mean values of the total procedural blanks. The measurement uncertainties (2 standard deviations, 2*s*) of the reported individual values in Table S4 were calculated by error propagation, which includes uncertainties of isotope ratio, spike mass fraction and blank correction, and the uncertainties of mean values of replicates of the RMs

Table 1.
Chemical separation procedure using 2 ml AG 1-X8 anion exchange resin (100–200 mesh) on a Bio-Rad Poly-Prep column

	Eluent	Volume (ml)	Following steps
	High-purity water	5	
Resin cleaning	14 mol l^{-1} HNO_3	5 + 5 + 5	
	1 mol l^{-1} HNO_3	10	
	High-purity water	4	
Resin conditioning	4.5 mol l^{-1} HCl	2 + 2	
Load sample and collect S-Se in major matrix	Sample in 4.5 mol l^{-1} HCl	1.5	Evaporate to dryness and dissolve in 2 ml 0.1 mol l^{-1} HNO_3 for secondary S-Se separation on 1 ml cation anion (Table S1)
	4.5 mol l^{-1} HCl	1 + 1 + 1	
Cu-In-Te in matrix	0.4 mol l^{-1} HCl	2 + 3 + 3	1) Evaporate to dryness 2) Dissolve in 0.5 ml 9 mol l^{-1} HCl and followed by 0.5 ml 0.15 g ml^{-1} ascorbic acid in high-purity water. 3) Ready for secondary Cu-In-Te separation on 1 ml anion resin separation (Table S1)
Discard	0.05 mol l^{-1} HCl	5 + 5	
Ag fraction	9 mol l^{-1} HCl	3 + 3	Evaporate to dryness and dissolve in 0.28 mol l^{-1} HNO_3 for analysis
Discard	High-purity water	2	
Cd-Tl fraction	0.7 mol l^{-1} HNO_3 + 1% H_2O_2	3 + 5*5	Evaporate to dryness and dissolve in 0.28 mol l^{-1} HNO_3 for analysis
Re-Ru-Pt-Ir-Pd fraction	14 mol l^{-1} HNO_3	5 + 5 + 4	Evaporate to dryness and dissolve in 0.28 mol l^{-1} HNO_3 for analysis
	12 mol l^{-1} HCl	5 + 5 + 4	

The chemical separation procedure was combined and modified from the methods described by Rehkämper and Halliday (1997), Wang and Becker (2014) and Wang *et al.* (2015).

(intermediate precision of several digestions) are 2 standard deviations of the repeated measurements (Table 2).

Measurement results and discussion

Except for MUH-1 and GSP-2, which were only digested in bombs with HF-desilicification, other RMs were attacked by methods with and without HF-desilicification. The detailed results obtained in this study are listed in Table S4, and the compiled literature values are also presented for comparison. The Re and PGE data underlined in Table S4 are previously published non-desilicified data from Cheng *et al.* (2019), and other chalcophile elements, if reported in the same lines of Table S4, were from the same digestion aliquot as Re and the PGEs. The mean mass fractions of chalcophile elements in reference materials of this study are collated in Table 2.

Variable effects of sample heterogeneity on chalcophile elements

The affinities to sulfides/alloys for chalcophile elements (Lorand *et al.* 2010, Patten *et al.* 2013, Mungall and Brenan 2014, Kiseeva *et al.* 2017) and the heterogeneous distribution of some accessory minerals (e.g., sulfides and alloys; often called the nugget effect) have significant effects on the uncertainties of measurement results (intermediate precision) of chalcophile elements (Meisel *et al.* 2001b, Meisel and Moser 2004a). Thus, the sample heterogeneity should be evaluated before the comparison of digestion methods. Besides sample inhomogeneity, other factors such as sample preparation and measurement may also contribute to the uncertainties of measurement results for chalcophile elements (Meisel *et al.* 2001b). Thus, the relative standard deviation of replicated measurement results of RMs is used here to represent the maximum effect of the sample inhomogeneity, at a 0.2–0.4 g level test portion size for the data obtained by HF-desilicification. Because many values were also obtained by *aqua regia* digestion (see section: Non-desilicification digestion by HNO_3-HCl), the nugget effect at a 2 g test portion size could be further compared for strongly chalcophile elements, including PGEs.

Effect of sample heterogeneity on PGEs: Because of the extremely high affinities to sulfides and alloys (Lorand *et al.* 2010, Patten *et al.* 2013, Mungall and Brenan 2014, Kiseeva *et al.* 2017), a test portion size of 0.2–0.4 g for the method with HF-desilicification has been considered to be too small for PGE determination (Meisel *et al.* 2001b, Meisel and Moser 2004a). Indeed, as Figure 1 shows, the PGEs for

Table 2.
Mean mass fractions of chalcophile elements in reference materials from this study

RM	Digestion technique	In			Cd			Tl			Cu			Ag			S			Se			Te			Re			Ir			Ru			Pt			Pd		
		ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	µg g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	µg g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*	ng g^{-1}	2*s*	*n*
TDB-1	Bomb-HF	97.6	8.8	9	231	13	9	90.6	5.2	9	327	36	9	153	12	10	294	18	10	364	14	2	6.85	0.48	8	1.07	0.06	10	0.063	0.019	8	0.334	0.153	9	5.40	1.12	9	22.8	3.2	9
	CT	48.7	17.6	2	161	19	2				314	4	2	156	19	21	313	6.1	4				6.51	0.66	2	1.04	0.10	23	0.077	0.025	21	0.224	0.062	13	5.14	1.00	21	22.8	1.9	11
WGB-1	Bomb-HF	57.7	3.7	7	101	12	6	380	16	6	108	16	7	54.2	14.9	7	193	20	6	64.7	4.0	2	12.2	5.5	7	1.23	0.05	6	0.182	0.034	4	0.231	0.211	5	4.88	4.80	5	12.0	4.8	5
	CT										93.5	15.4	2	54.5	9.7	7	196	4	4				12.6	3.9	3	1.19	0.05	7	0.203	0.052	4	0.192	0.064	2	5.14	0.69	4	14.0	8.8	2
BHVO-2	Bomb-HF	81.4	6.0	9	94.8	3.4	8	19.9	1.4	6	126	8	9	44.1	0.9	9	169	10	9	169	9	4	14.2	0.7	9	0.624	0.034	10	0.045	0.009	8	0.360	0.159	9	13.6	20.0	9	3.49	0.46	9
	CT	22.5	0.7	3	31.2	15.9	3				88.6	5.2	5	32.9	3.8	13	136	1	5				12.2	0.3	3	0.537	0.044	14	0.073	0.019	14	0.129	0.036	11	8.76	7.05	14	3.12	0.54	9
BCR-2	Bomb-HF				215	24	6	262	32	6	16.0	1.9	6	30.7	2.4	5	316	12	6	77.8	10.5	4				12.3	0.4	6	0.008	0.006	5	0.029	0.012	2	1.20	3.0	6	0.290	0.227	3
	CT				109	42	3				16.0	0.5	3	25.6	2.5	2	315	1	3							12.0	0.5	3	0.039	0.082	3				1.04	1.12	3			
BIR-1a	Bomb-HF	57.0	1.0	4	97.7	4.0	4	1.14	0.07	4	119	7	4	29.7	0.4	4	5.26	0.56	4				5.65	0.47	4	0.819	0.066	4	0.083	0.008	4	0.519	0.012	4	4.65	0.26	4	6.02	0.12	4
	CT	15.7	0.2	1	37.7	0.5	1				99.1	9.8	3	21.7	2.1	3	5.33	0.49	3				3.10	0.4	1	0.713	0.025	2	0.124	0.007	1	0.290	0.035	1	4.49	0.18	1	6.51	0.19	1
OKUM	Bomb-HF	30.9	1.5	5	49.0	1.2	5	15.4	0.8	5	42.2	3.0	5	4.21	3.59	5	220	20	5	151	7	2	24.0	0.5	5	0.523	0.022	5	0.929	0.044	4	4.77	0.93	4	12.6	0.1	4	13.1	0.7	4
	CT													4.15	1.40	14	240	10	1							0.488	0.117	14	0.914	0.137	14	4.71	0.14	7	11.9	0.6	14	12.0	0.2	7
UB-N	Bomb-HF	10.7	0.3	4	34.1	2.0	4	38.8	2.6	4	24.4	1.1	4	44.2	1.5	4	143	12	3	128	7	2	9.87	0.28	4	0.214	0.012	4	2.39	0.79	4	5.73	1.11	4	6.84	1.09	4	6.14	0.54	4
	CT													43.8	4.4	5	146	6	4							0.188	0.027	5	3.35	0.59	5	6.60	0.710	5	7.20	0.65	5	6.11	0.40	5
MUH-1	Bomb-HF	5.77	0.2	4	17.5	0.4	4	3.66	0.09	3	17.7	2.3	4	9.86	3.0	4	132	15	4	81.8	2.6	2	11.6	2.0	4	0.231	0.068	4	2.42	2.02	3	10.2	12.2	3	9.42	9.46	3	7.67	1.50	3
GSP-2	Bomb-HF	46.4	0.5	3	89.7	2.1	3	1214	336	3	41.5	1.5	3	87.1	9.4	3	433	13	3	78.4	1.1	3	33.8	2.2	3	0.331	0.017	3							0.852	0.241	2	2.20	0.47	2

CT, digested by *aqua regia*/reverse *aqua regia* in Carius tube; Bomb-HF, desilicification digestion by HF-HNO_3 and HNO_3-HCl in high-pressure bomb. The mean values are calculated from Table S4; except for BIR-1a and BCR-2, the non-desilicified Re-PGE data in this study and previously published in Cheng *et al.* (2019) were used to calculate the mean values. Uncertainties (2*s*) of mean values are calculated from repeated measurements (*n*) of different digestion aliquots.

most samples such as BHVO-2, UB-N and MUH-1 display larger variances at the 0.2–0.4 g level than at the 2 g level (e.g., RSD of 60% versus 20% for Ru in MUH-1; Figure 1 and Table S4). Test portion sizes up to 2 g also remain to show a certain level of variance (mostly 10–20%), indicating the strong effect of sample heterogeneity on PGEs. However, the experiments with HF-desilicification show that the mass fractions of PGEs in OKUM and BIR-1a show less variance at the 0.2–0.4 g level (RSD < 5%), except for Ru in OKUM (RSD = 10%, Figure 1). Such a value is similar to the results of reverse *aqua regia* at a 1–2 g level (Figure 1 and Table S4; Meisel and Moser 2004b, Savard *et al.* 2010, Cheng *et al.* 2019, Zhou *et al.* 2019). Additionally, apart from WGB-1 (RSD = 20%), the variance of the measurement results, mainly caused by heterogeneity, of Pd in other RMs seems to be similar at a 0.2–0.4 g level or at a 2 g level (about 4–10% RSD, Figure 1 and Table S4). Therefore, the mass fractions of PGEs in OKUM and BIR-1a and at least Pd in most RMs in this study can be used to evaluate the extraction efficiency of HF-desilicification.

Effect of sample heterogeneity on other chalcophile elements: As chalcophile elements, the mass fractions of In, Cd, Tl, Cu, Ag, S, Se, Te and Re are potentially affected by the heterogeneous distribution of sulfides or alloys. However, given limited available data, the nugget effects on most of these elements in studied RMs have been poorly understood. As Figure 1 displays, 0.2–0.4 g of sample powder achieved very reproducible results for Cu, Ag, S, Te and Re, particularly In, Cd and Tl in most RMs (Figure 1 and Table S4, mostly RSD < 5%). These strongly chalcophile elements are obviously more homogeneously distributed than the PGEs in most RMs (Figure 1 and Table S4).

In only a few cases, the results show a larger variance, such as Re, Cu, Ag and Te in MUH-1 and WGB-1 (RSD = 7%–22.5%, Figures 1 and 2), and Ag in OKUM (RSD = 43%). Considering the obvious heterogeneity of PGEs in WGB-1 and MUH-1 (Figure 1 and Table S4), the variable mass fractions of Cu, Ag and Te in MUH-1 and WGB-1 and Re in MUH-1 could be the result of the heterogeneous distribution of sulfides or alloys at a 0.2–0.4 g level. For example, six replicates of WGB-1 showed a variable range of mass fractions of Cu, Ag, S and Te, but much lower extents for the ratios of Cu/Ag and Te/Ag (Figure 2), supporting the heterogeneous distribution of sulfides in the crystalline gabbro. However, sulfide is difficult to account for the decoupling of heterogeneous Ag (RSD of 43% for 0.4 g and 17% for 2 g) and homogenous S, Cu, Se, Te and PGEs in OKUM (RSD mostly less than 10%, Figure 1 and Table S4). Even if the outlier is removed, the RSD (15%) for Ag in OKUM is still higher than those for other chalcophile elements (Figure 1). OKUM was sampled from the komatiite spinifex zone with a pronounced bluish-grey weathered surface (Richardson 1995). It has been shown that alteration processes have a strong effect on Ag and may lead to its redistribution (Theis *et al.* 2013, Wang and Becker 2015b). The anomalous variances of Ag in OKUM could be interpreted to result from the effect of alteration, especially when its mass fraction is rather low (3.08–7.33 ng g^{-1} Ag). Therefore, apart from these occasional cases, the mass fractions of In, Cd, Tl, Cu, Ag, S, Se, Te and Re in the studied RMs display small variances (RSD < 5%, Figure 1) at the 0.2–0.4 g level and are useful to evaluate the extraction efficiencies for chalcophile elements of methods with and without HF-desilicification.

Comparison of the digestion methods with and without HF-desilicification

Previous comparative experiments with and without HF-desilicification on igneous rocks for Se, Te and Re-PGEs show significant bias for some RMs (e.g., Re and Te in basalt; Meisel *et al.* 2009, Ishikawa *et al.* 2014, Li *et al.* 2014b, Day *et al.* 2016, Meisel and Horan 2016, Yierpan *et al.* 2018). The PGE mineral/sulfide-bearing oxides (e.g., spinel), PGE alloys, potential existence of micro-sulfide inclusions and undissolved silicates after reverse *aqua regia* attack potentially affect the complete release of chalcophile elements (Meisel *et al.* 2003, 2009, Ishikawa *et al.* 2014, Li *et al.* 2014b, Meisel and Horan 2016, Yierpan *et al.* 2018). In this study, the complete digestion of silicates by the mixture of HNO_3 and HF was achieved, and the subsequent use of *aqua regia* ensured the complete extraction of chalcophile elements such as PGEs from samples. Thus, the data obtained by methods with and without HF-desilicification in this study, combined with results from previous studies, are used to evaluate HF-desilicification for the effectiveness of extraction.

Extraction efficiency of PGEs: Iridium, Ru and Pt are more likely to be affected by the nugget effect compared with Pd, in which Ir, Ru and Pt can be enriched in alloys if the sample is sulfide-undersaturated (Mungall and Brenan 2014, Brenan *et al.* 2016, Meisel and Horan 2016). In this study, the variabilities of Ir and Pt are not resolvable from sample powder heterogeneity for most RMs (see Effect of sample heterogeneity on PGEs; Figure 1 and Table S4). Thus, here we mainly use Ru and Pd as representatives of the IPGE and the PPGE, respectively, to compare the extraction efficiencies by acid digestion with and without HF-desilicification.

In this study, HF-desilicification had a negligible effect on PGEs in peridotites (UB-N and MUH-1) and other mafic–

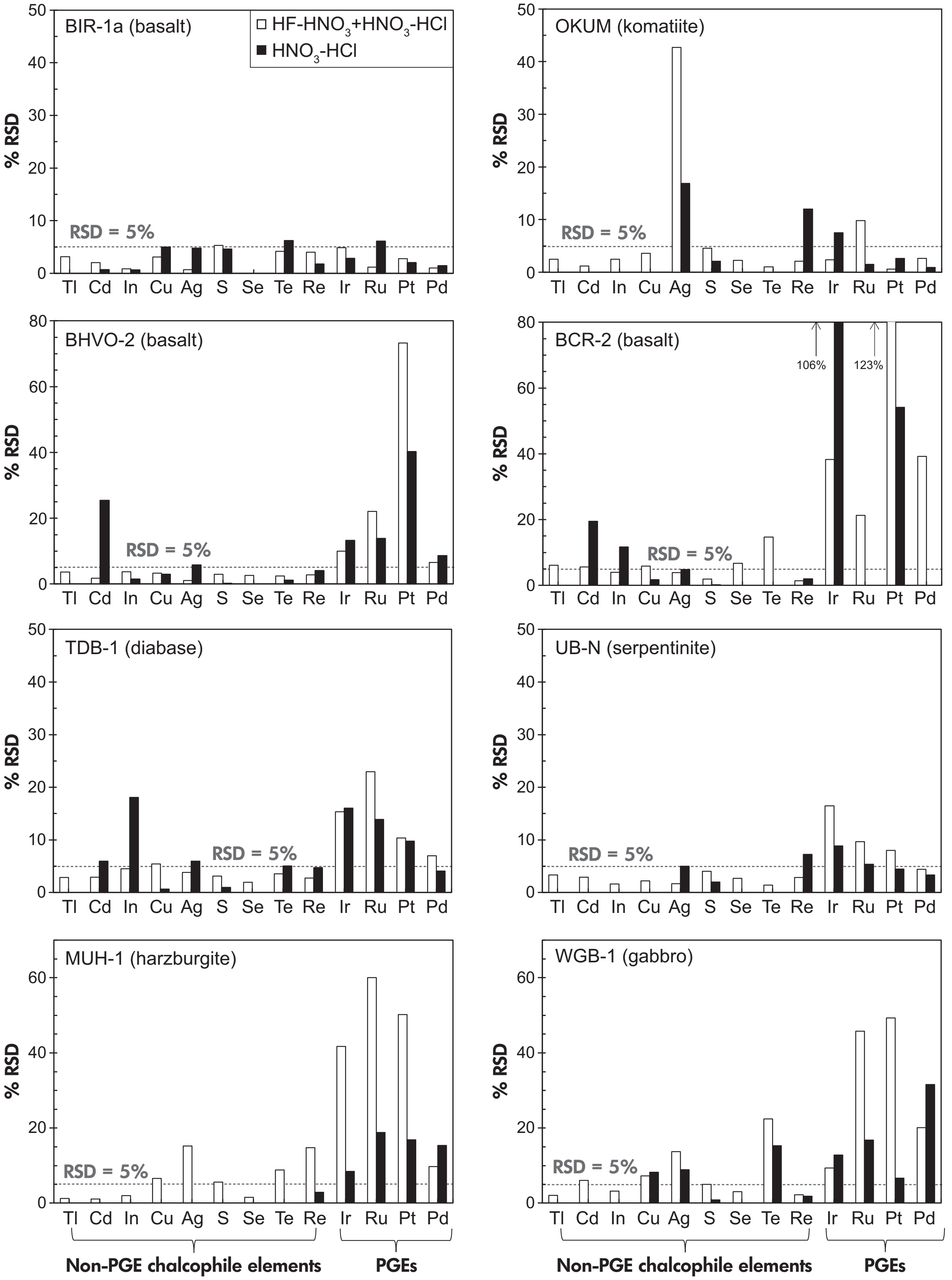
BIR-1a (basalt)
☐ HF-HNO$_3$+HNO$_3$-HCl
■ HNO$_3$-HCl
OKUM (komatiite)
BHVO-2 (basalt)
BCR-2 (basalt)
106%
123%
TDB-1 (diabase)
UB-N (serpentinite)
MUH-1 (harzburgite)
WGB-1 (gabbro)
% RSD
RSD = 5%
0
10
20
30
40
50
60
80
Tl Cd In Cu Ag S Se Te Re Ir Ru Pt Pd
Non-PGE chalcophile elements
PGEs

Figure 1. The relative standard deviation (% RSD) of replicated digestions of reference materials. Note that the intermediate precision was obtained from 0.2–0.4 g test portion sizes for HF-HNO_3 + HNO_3-HCl digestion, but a 2 g level for *aqua regia* digestion (HNO_3-HCl). The grey dashed lines represent RSD = 5%. The non-desilicified literature values for Re and PGEs from MUH-1 are used for comparison (Zhou *et al*. 2019). Non-PGE chalcophile elements show less variance at a 0.2–0.4 g level, with RSD much lower than the PGEs. Note that the RSDs for non-PGE chalcophile elements are potentially affected by incompletely dissolved minerals following *aqua regia* digestion, especially for the elements that are also lithophile (e.g., In, Tl and Cd).

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ultramafic rocks (WGB-1 and OKUM and BCR-2; Figures 3 and 4 and Table S4). Similar results have been reported in previous studies (Figure 3 and Table S4; Meisel and Moser 2004b, Dale *et al.* 2012, Ishikawa *et al.* 2014, Li *et al.* 2014a, Day *et al.* 2016, Zhou *et al.* 2019). The complete extraction of Pd from TDB-1 and BIR-1a was achieved after reverse *aqua regia* attack. However, HF-desilicification led to a noticeable increase by ~ 33% and ~ 44% for Ru in TDB-1 and BIR-1a, respectively (Figures 3 and 4 and Table S4), which is fully consistent with previous studies (Ishikawa *et al.* 2014, Meisel and Horan 2016, Zhou *et al.* 2019). For BHVO-2, the mean mass fractions of Ru and Pd obtained by digestion with reverse *aqua regia* showed values ~ 64% and ~ 11% lower than those of desilicified values, respectively (Figure 4 and Table S4). It is interesting to note that the desilicified mean mass fractions of Ir in BHVO-2 and BIR-1a are 38% and 33% lower than those non-desilicified values, respectively (Figure 4). The mean mass fraction of Ir in BIR-1a is also noticeably lower than those desilicified values obtained in a previous study (Figure 4 and Table S4; Ishikawa *et al.* 2014). The specific reason is unclear and may reflect undigested Ir-bearing minerals or alloys of this sample under lower digestion temperature and pressure in bombs than in Carius tubes.

The PGEs budgets are predominantly hosted in sulfides, chalcogenide and/or alloys (Lorand *et al.* 2010, Li and Audétat 2012, Patten *et al.* 2013, Mungall and Brenan 2014, Brenan *et al.* 2016, Kiseeva *et al.* 2017). Base metal sulfide phases have been reported in the matrices of WGB-1 and TDB-1 (Canada 1994a, 1994b). Thus, the complete release of PGEs from peridotites and the other mafic–ultramafic rocks may be attributed to the predominant distribution of PGEs in sulfides and alloys. In contrast, HF-desilicification led to the greater release of Ru and Pd for some basalts such as BHVO-2 and BIR-1a (Figure 4), which may reflect the presence of PGE alloys when base metal sulfides are absent, or the dissolution of these metals in silicate glasses. We also note the negligible effect of HF-desilicification on PGEs for other mafic–ultramafic rocks such as BCR-2 and OKUM. These results indicate the variable effects of HF-desilicification on PGEs from sample to sample.

Extraction efficiency of strongly chalcophile elements (Cu, Ag, S, Se, Te and Re): Copper, Ag, S, Se, Te and Re are less chalcophile than PGEs but overall strongly chalcophile ($D_{\text{sulfide-silicate melt}}$ = 200–3800, 22–10^4 for Re; Kiseeva *et al.* 2017, Li and Audétat 2012). Unlike most PGEs, these elements hardly form alloys and are predominantly hosted in sulfides if present. A comprehensive study of these elements could provide valuable information to evaluate the effect of HF-desilicification. Since the Se mass fractions for non-desilicified analyses for RMs were not determined in this study, the available literature data (Table S4; Wang and Becker 2013, 2014, Wang *et al.* 2013, Kurzawa *et al.* 2017, Yierpan *et al.* 2018) were used for comparison in the discussion below.

In Figures 5 and 6, it is remarkable to show indistinguishable mass fractions of strongly chalcophile elements obtained by either HF-HNO_3 + HNO_3-HCl digestion or *aqua regia* digestion for most RMs, except basalts of BHVO-2 and BIR-1a. The results indicate that HF-desilicification plays a negligible effect on Cu, Ag, S, Se, Te and Re in most cases, including peridotite (UB-N) and mafic–ultramafic rocks (TDB-1, OKUM and WGB-1; Figures 5 and 6). Chalcophile elements are concentrated in sulfides if present, depending on their partitioning between sulfides and silicate phases. Sulfides have been reported in the matrices of these highly crystalline mafic–ultramafic rocks (OKUM, TDB-1 and WGB-1; IAGeo Limited, http://iageo.com/okum-komatiite-ontario/, Canada 1994a, 1994b). Thus, the results for Cu, Ag, S, Se, Te and Re in this study, together with complete release of PGEs from peridotites (e.g., serpentinized UB-N) by experiments with and without HF digestion in previous studies (e.g., König *et al.* 2012, Wang and Becker 2013, 2015a, Ishikawa *et al.* 2014, Yierpan *et al.* 2018), suggest that these strongly chalcophile elements are negligibly hosted in silicates of peridotites and crystalline mafic–ultramafic rocks.

In contrast, the extraction efficiency varies in other studied mafic samples and for different elements. For the basalt BHVO-2, the sample digestion by reverse *aqua regia* led to the systemically incomplete liberation of Cu, Ag,

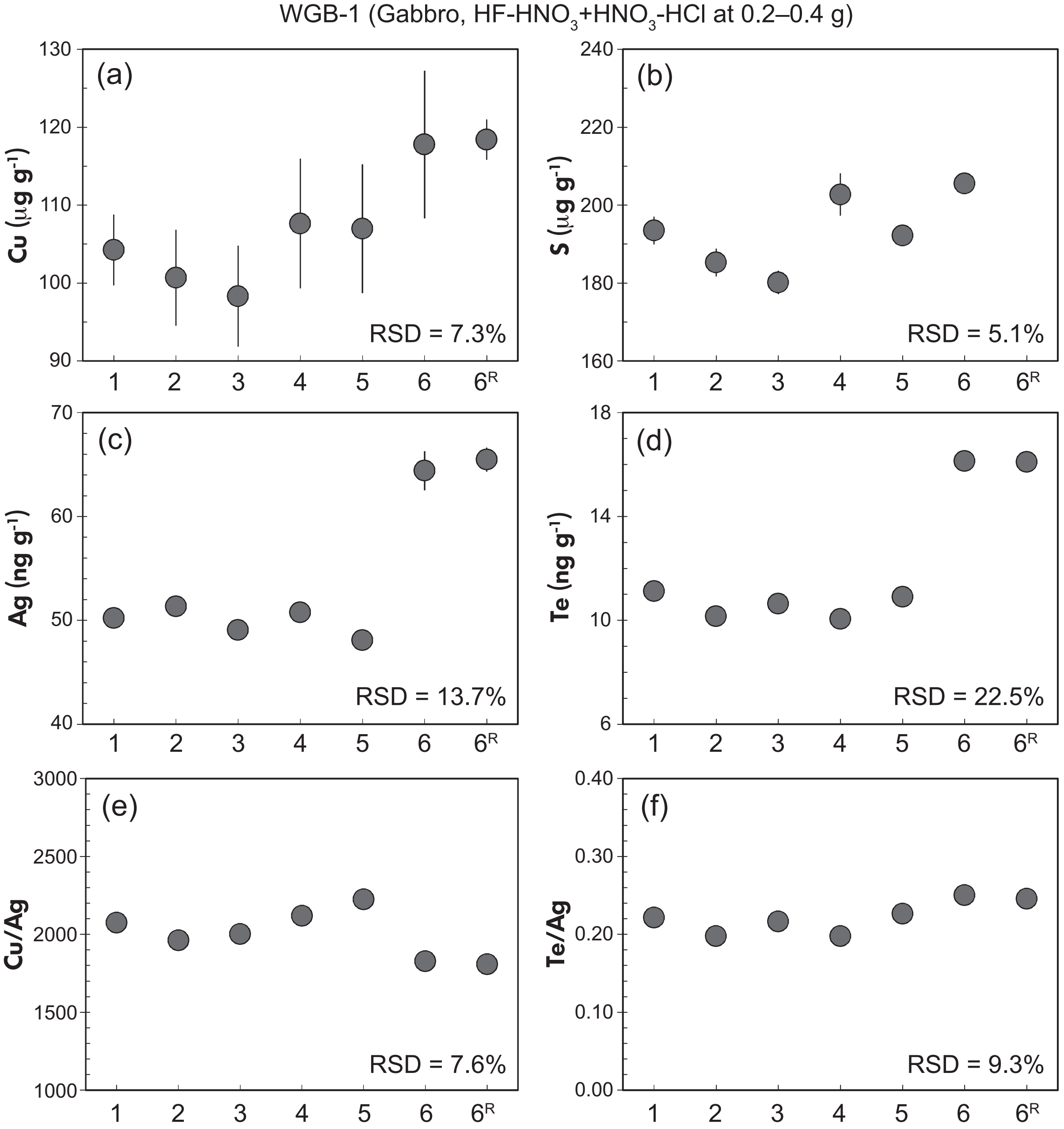

Figure 2. Mass fractions of Cu, Ag, S and Te and their ratios for the gabbro WGB-1 obtained by experiments with HF-desilicification in this study. The higher precision of the element ratios than those of mass fractions indicates the heterogeneous distribution of sulfides or alloys. The range bars for mass fractions represent uncertainties (2*s*), and most are within the symbol size. R represents the repeated measurement of the same digestion aliquot after a different analyte–matrix separation.

S, Se, Te and Re (Figure 6), as well as PGEs mentioned above. Overall, these chalcophile elements displayed variably lower values (10–30%) than those of experiments with HF digestion. Such results are fully consistent with previous comparative experiments (Figure 6 and Table S4), which have indicated that HF digestion increases the mass fractions of Re, Se and Te by ~ 10–25% (Li *et al.* 2014b, Yierpan *et al.* 2018). These results suggest that a considerable fraction of Cu, Ag, S, Se, Te and Re budgets is hosted in the undigested silicate matrix of basalts. However, these chalcophile elements in basalts of BCR-2 and BIR-1a are decoupled. HF-desilicification did not improve the

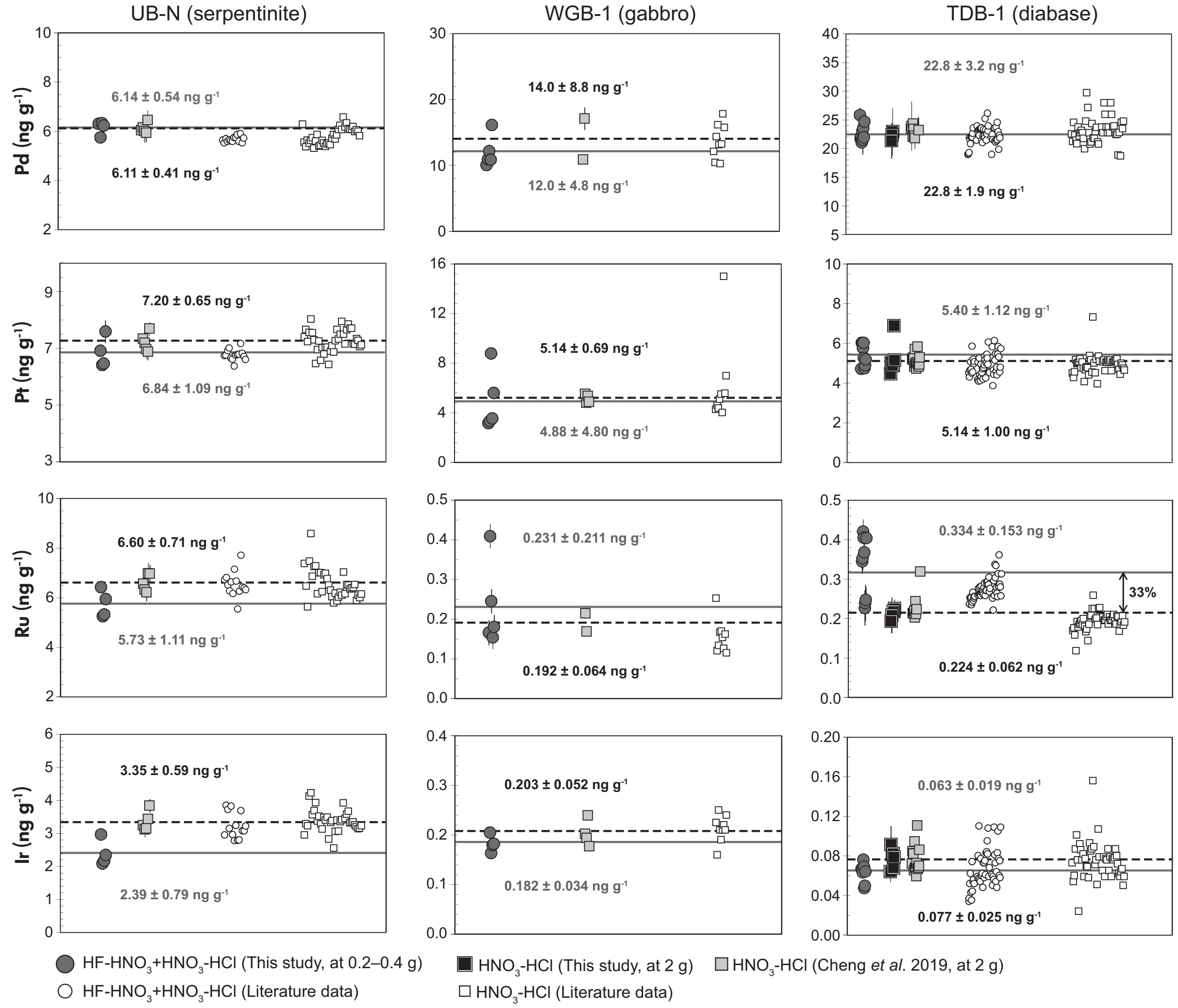

Figure 3. Comparison of PGE data from crystalline rocks UB-N, WGB-1 and TDB-1 obtained by experiments with and without HF-desilicification. The circles are the data analysed from desilicification digestion. The squares represent the non-desilicified results. The range bars for mass fractions represent uncertainties (2*s*), and most are within the symbol size. The published non-desilicified data (Cheng *et al.* 2019) from the same laboratory as this study are presented here for comparison (filled grey squares). The literature data are included for comparison as well (open square and circle). The continuous grey lines and dashed black lines represent the mean mass fractions obtained by methods with and without HF-desilicification, respectively, and the percentages are their relative differences. The literature data are compiled from those listed in Table S4 and the GeoReM database (http://georem.mpch-mainz.gwdg.de/).

liberation of S and Pd (as mentioned above) from BIR-1a, but HF-desilicification elevated the mean mass fractions of Cu, Ag, Te and Re in BIR-1a by ~ 17%, ~ 27%, 45% and 13% (Figure 6). In addition, the Cu, S and Re mass fractions of BCR-2 are identical after desilicified and non-desilicified digestion (Figure 6). However, HF-desilicification led to an increase of Ag mass fractions in BCR-2 by 17% (Figure 6). Furthermore, it was unclear that the chalcophile elements are dissolved in silicates or exist as micro-sulfide inclusions (< 0.5 μg g^{-1}) hosted in silicates (Yierpan *et al.* 2018). The decoupling of Ag and other chalcophile elements further supports that the unextracted budgets of chalcophile elements are more likely to be dissolved in silicates, consistent with experimental predictions (Zajacz *et al.* 2013, Yin and Zajacz 2018).

The mean mass fractions of S obtained from the methods with HF-desilicification are slightly lower (~ 6% for TDB-1 and ~ 8% for OKUM) than those obtained from *aqua regia* digestion in closed systems in this and previous studies (e.g.,

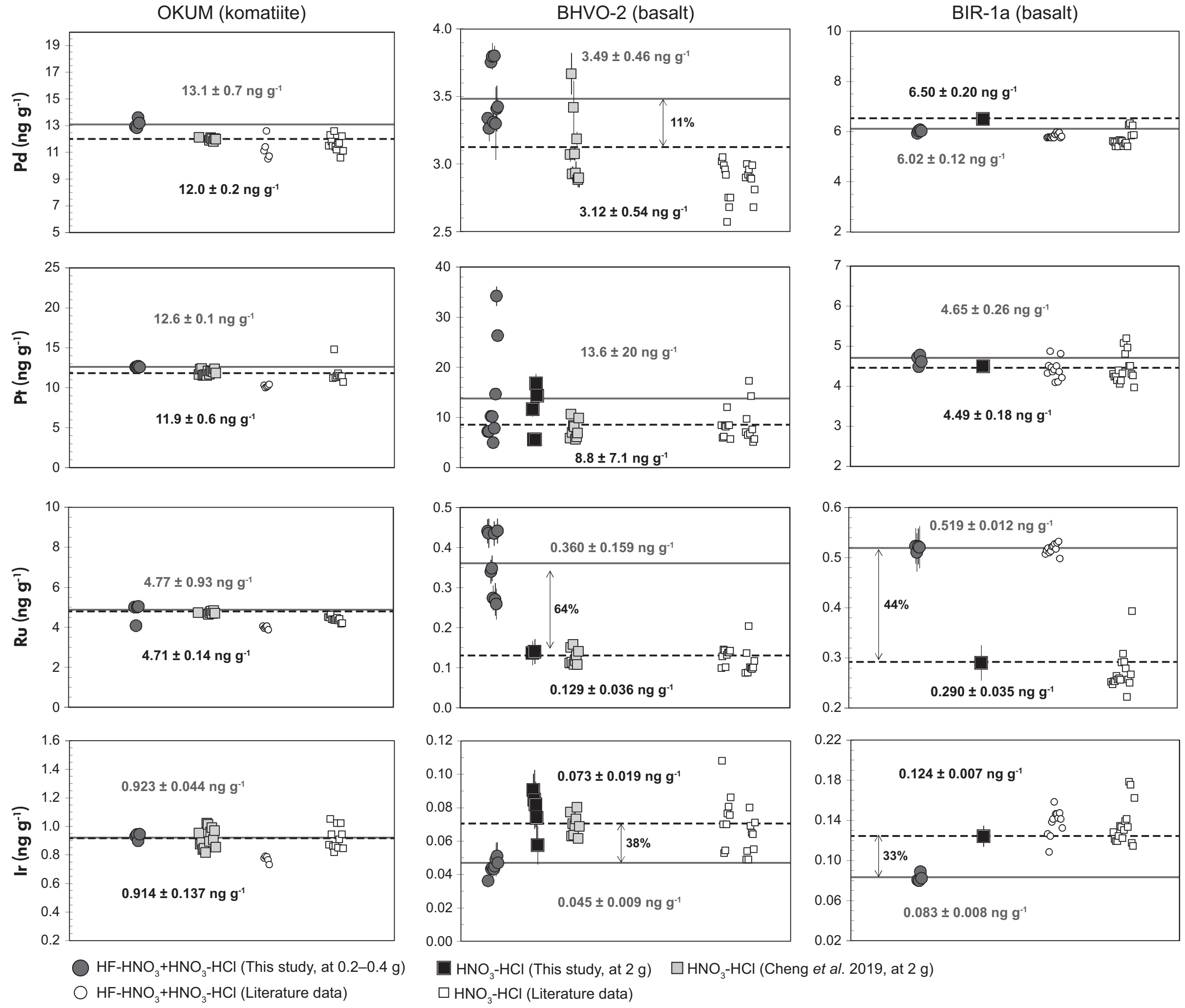

Figure 4. Comparison of PGE data from mafic–ultramafic rocks OKUM, BHVO-2 and BIR-1a obtained by methods with and without HF-desilicification. The symbols and literature data sources are the same as Figure 3. The test portion sizes for digestions of HNO_3-HCl in this study were at a 2 g level, except for several digestions for basalts that were at a 1 g level. The larger ranges of PGEs for BHVO-2 digested by HF-HNO_3 + HNO_3-HCl reflect the strong effect of sample heterogeneity (0.2–0.4 g test portion).

Bédard *et al.* 2008, Wang and Becker 2014). Given the relatively homogenous Cu, S, Se and Te in TDB-1 and OKUM (Figure 1), such minor differences could be ascribed to the partial loss of sulfur during the acid digestion (Okai *et al.* 2001, Wang and Becker 2014). Besides, we note that the mean Re mass fraction of MUH-1 obtained in this study is significantly higher than the desilicified value (34%) and no-desilicified value (27%) reported in Zhou *et al.* (2019) (Table S4). The desilicified (0.819 ± 0.066 ng g^{-1}) and non-desilicified Re (0.713 ± 0.025 ng g^{-1}) mass fractions of BIR-1a in this study are higher than the previously reported values (0.661–0.682 ng g^{-1}; Chu *et al.* 2015, Ishikawa *et al.* 2014, Li *et al.* 2014a). It is unclear whether the prolonged digestion time in this study or nugget effect affected the results.

These results indicate that like PGEs, the complete extraction of Cu, Ag, S, Se, Te and Re from peridotites and sulfide-bearing crystalline rocks could be achieved by *aqua regia* digestion at high temperature (220–270 °C) (Figures 5 and 6). However, the extraction efficiencies of strongly chalcophile elements are variable and depend on the chemical and mineralogical compositions (Figure 6). Thus, if a fraction of chalcophile elements are incorporated in the silicate crystal lattice (such as basaltic rocks), HF-desilicification is mandatory.

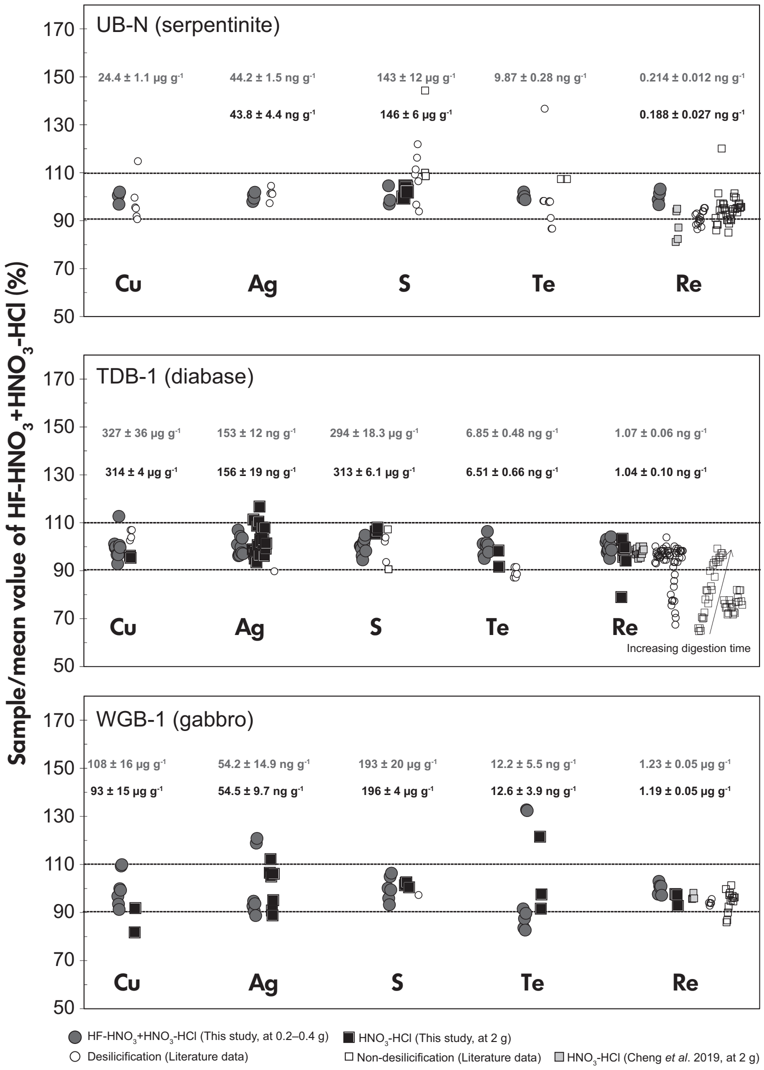

Figure 5. Comparison of Cu, Ag, S, Te and Re mass fractions from crystalline rocks UB-N, WGB-1 and TDB-1 obtained by methods with and without desilicification, normalised to the mean desilicified values by digestion of HF-HNO$_3$ + HNO$_3$-HCl in this study. The dark grey circle (desilicified) and black square (non-desilicified) symbols represent the values of mean mass fractions of elements in this study. Note that the longer digestion time by *aqua regia* could lead to a higher extraction of Re (Ishikawa *et al.* 2014). The literature data are compiled from those listed in Table S4 and the GeoReM database (http://georem.mpch-mainz.gwdg.de/).

Extraction efficiency of weakly chalcophile elements: Although In ($D_{\text{sulfide-silicate melt}}$ = 8–24) and Cd ($D_{\text{sulfide-silicate melt}}$ = 42–98) are chalcophile elements (Kiseeva *et al.* 2017), most of them can be hosted by silicates, and they behave like the lithophile elements during partial melting and magma differentiation (e.g., Yi *et al.* 2000, Wang *et al.* 2016, Greaney *et al.* 2017). Thus, it is not surprising that their mass fractions in all studied RMs obtained by *aqua regia* digestion are significantly lower than those by HF-desilicification digestion (Figures 7 and 8). For example, the unextracted fractions of In and Cd for TDB-1 in remnants represent ~ 50% and ~ 30% of the bulk-rock budgets, respectively (Figure 7). For basalts of BHVO-2 and BIR-1a, the non-desilicified mass fractions of Cd and In were on average 60–70% lower than those desilicified values (Figure 7 and Table S4).

These results clearly indicate that silicate phases host significant budgets of In and Cd, suggesting the necessity of HF-desilicification for these weakly chalcophile elements. Different samples display variable differences between the results with and without HF-desilicification and may reflect their different compositions and the relative proportion in sulfides and silicates. Since there are no Tl data for non-desilicification digestion by HNO$_3$-HCl, the extraction

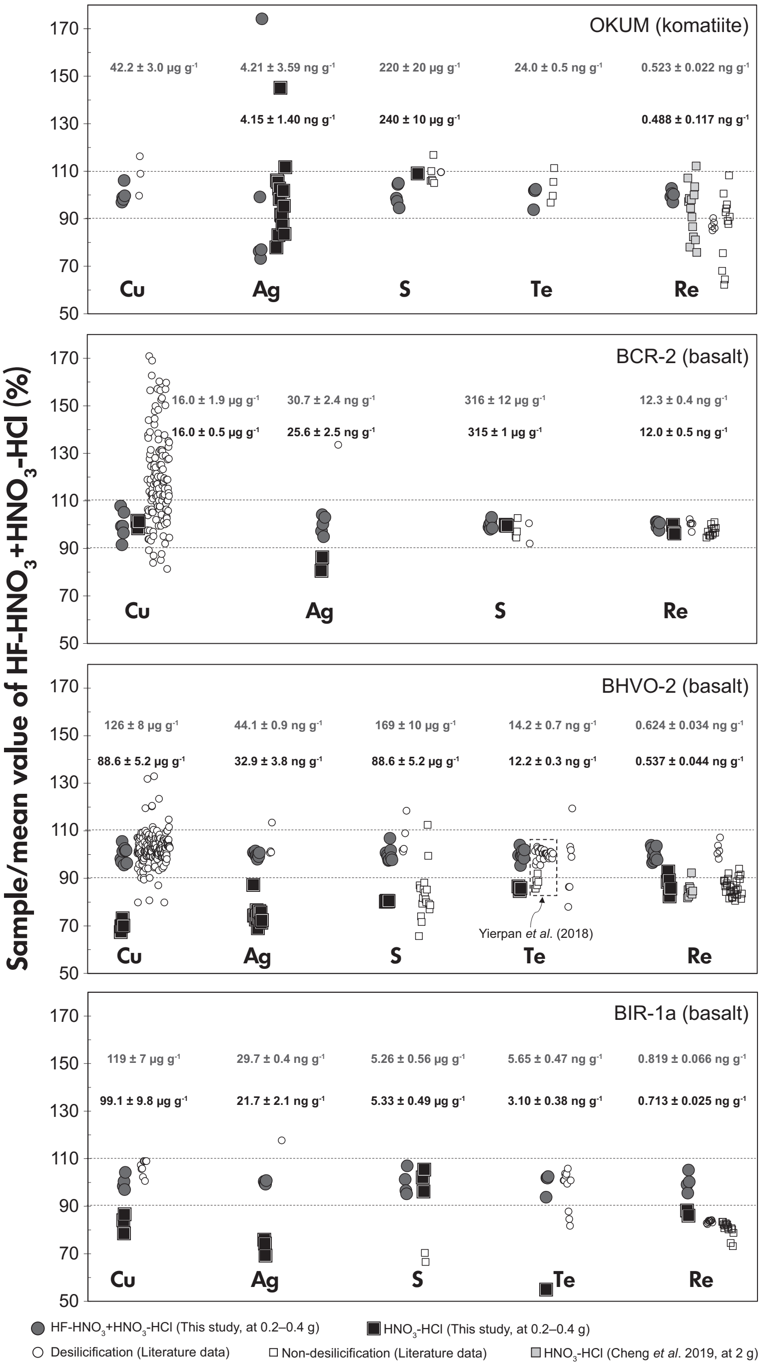

Figure 6. Comparison of Cu, Ag, S, Te and Re mass fractions of basaltic rocks of OKUM, BCR-2, BHVO-2 and BIR-1a obtained by methods with and without desilicification, normalised to mean desilicified (HF-HNO$_3$ + HNO$_3$-HCl) values in this study. The test portion sizes for digestions of HNO$_3$-HCl in this study were at a 2 g level, except for several digestions for basalts that were at a 1 g level. The labels are the same as Figure 5. The literature data are compiled from the literature listed in Table S4 and GeoReM database (http://georem.mpch-mainz.gwdg.de/).

efficiency of Tl is not discussed here. Similarly, Tl is a weakly chalcophile element ($D_{\text{sulfide-silicate melt}}$ = 8–24), and like In and Cd, it also behaves as a lithophile element during partial melting and magma differentiation (Yi *et al.* 2000, Nielsen *et al.* 2014, Wang *et al.* 2016, Greaney *et al.* 2017). Thus, the mass fractions of Tl obtained by HF-desilicification in this study should reflect an approximation of the true values in the RMs (Table S4).

Summary and implications

In this study, mass fractions of elements with variable chalcophile affinities (e.g., Cd, In, Tl, Cu, Ag, S, Se, Te, Re and PGEs) were obtained from the same test portions of geological RMs with variable chemical and mineralogical compositions. We have evaluated the extraction efficiencies of these different chalcophile elements by acid digestion methods with and without HF-desilicification. At the 0.2–0.4 g sample test portion size for most RMs, mass fractions of Cu, Ag, S, Se, Te, Re, Cd, In and Tl showed little variance (mostly < 5%, RSD), and hence, the influence of heterogeneity is small, much better than the highly chalcophile PGEs.

The results indicate that complete extraction of Cu, Ag, S, Se, Te, Re and PGEs from peridotites (e.g., UB-N) and intrusive crystalline rocks (e.g., WGB-1 and TDB-1) was achieved by *aqua regia* digestion in Carius tubes at 220–227 °C for > 96 h (Figure 8). This was also supported by previous comparative experiments (Meisel *et al.* 2009, Ishikawa *et al.* 2014, Li *et al.* 2014b, Day *et al.* 2016, Zhou *et al.* 2019). HF-desilicification followed by HNO_3-HCl digestion in PFA beakers led to indistinguishable results for these samples. This is probably due to the predominant control of these chalcophile elements by sulfides and/or alloys.

However, the extraction efficiencies of these elements vary for different basalts (e.g., BHVO-2, BCR-2 and BIR-1a; Figure 8). This probably reflects that a variable fraction of chalcophile elements (a few per cent to up to 30%) is dissolved in silicate phases, thus requiring HF-desilicification to completely liberate them. Noticeably, the HF-desilicification step led to an increase (by 30–70%) for mass fractions of weakly chalcophile elements such as Cd and In in all analysed samples, irrespective of crystalline rocks and basalts. The lack of systematic links between the chalcophile affinity of elements and their extraction efficiencies for these

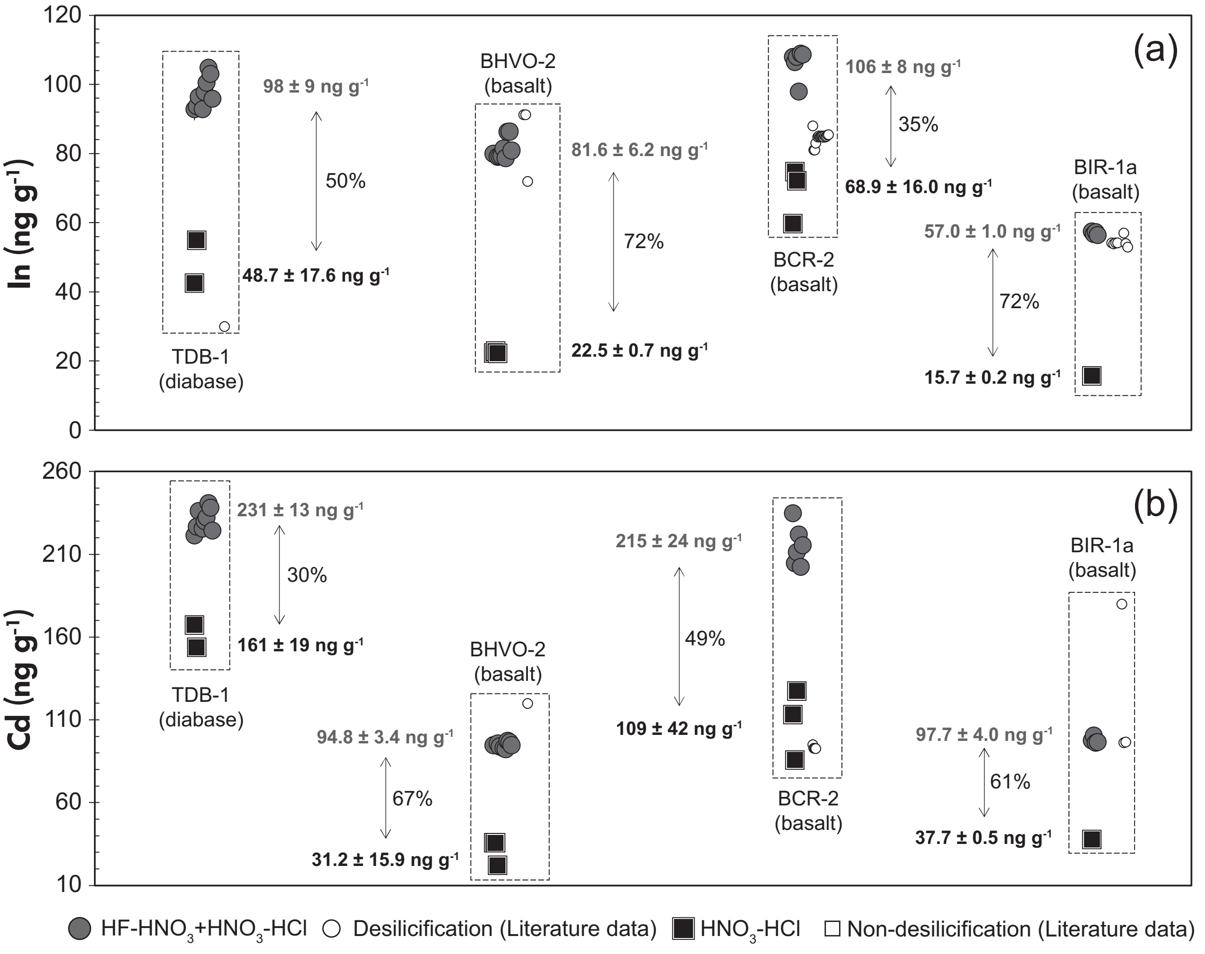

Figure 7. Comparison of In and Cd mass fractions of TDB-1, BCR-2, BHVO-2 and BIR-1a obtained by methods with and without desilicification. The labels are the same as Figure 5. The literature data are compiled from those listed in Table S4 and the GeoReM database (http://georem.mpch-mainz.gwdg.de/).

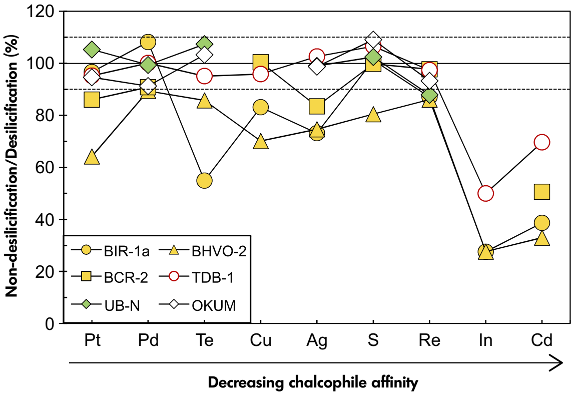

Figure 8. The comparative extraction efficiencies for variable chalcophile elements of geological RMs obtained by methods with and without HF-desilicification. The sequence of elements from left to right follows the decreasing partition coefficients between sulfide liquid and silicate melts (Kiseeva *et al.* 2017). Extraction efficiencies for different chalcophile elements in the RMs are variable.

basalts (Figure 8) probably results from the variable extents of dissolution and extraction of chalcophile elements from the basaltic matrix.

Therefore, the strategy of sample digestion to determine mass fractions of chalcophile elements should be flexible and consider at least sample types, the elements of interest and the effect of sample heterogeneity. In general, the HF-desilicification step is recommended for complete extraction of Cu, Ag, S, Se, Te, Re, Cd, In, Tl and other weakly chalcophile elements from geological samples (especially extrusive rocks such as basalts and andesites). Considering the obvious effect of sample heterogeneity on PGEs that requires a large amount of material for digestion (Figure 1) and the predominant control of sulfides/alloys, *aqua regia* digestion in closed HPA-S or Carius tubes for test portions of 2 g or greater is more suitable for PGEs, particularly in sulfide-bearing samples. The complete extraction of strongly chalcophile elements such as Cu, Ag, S, Se, Te and Re from sulfide-bearing crystalline rocks such as peridotites and gabbros could be also achieved by *aqua regia* digestion under high temperature conditions.

Acknowledgements

We thank Xiang Wang, Aiqing Ren and Haihong Chen for their kind support during the development of the analytical methods. This study was supported by China National Space Administration (No. D020205), National Natural Science Foundation of China (No. 41673027, 41722302, 41703034). Many thanks go to two anonymous reviewers for the constructive comments and to Thomas Meisel for careful editorial handling.

Data availability statement

The data that support the findings of this study are available in the Tables S1–S4 of this article.

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Supporting information

The following supporting information may be found in the online version of this article:

Table S1. Secondary chemical separation procedure.

Table S2. Monitored signals, isobaric and potential polyatomic interferences for chalcophile element measurements by ICP-MS.

Table S3. Detection limits and total procedural blanks (TPB) in the study.

Table S4. Mass fractions of chalcophile elements in reference materials from this study and comparison with literature results.

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