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Determination of Te, As, Bi, Sb and Se (TABS) in Geological Reference Materials and GeoPT Proficiency Test Materials by Hydride Generation-Atomic Fluorescence Spectrometry (HG-AFS)

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### Abstract

The study of Te, As, Bi, Sb and Se (TABS) has increased over the past years due to their use in the development of low-carbon energy technologies. However, there is a scarcity of mass fraction values of TABS in geological reference materials. This underlines the difficulty in undertaking routine determinations of these elements. The mass fractions of TABS were determined in geological reference materials using hydride generation-atomic fluorescence spectrometry (HG-AFS), calibrated with standard solutions. Comparisons with literature values were used to validate the method. Samples from the GeoPT proficiency test were also analysed. For most elements there are no assigned or even provisional values for many of the GeoPT and reference materials because of the wide range of results reported. For mass fractions above the quantification limit of the method our results are in good agreement with the median of GeoPT results. Thus, we propose GeoPT median values as informational values for these elements. In contrast, at mass fractions  $< 0.5 \mu\text{g g}^{-1}$  median values of Se from GeoPT are systematically higher than our results. Our Se results are in agreement with the reference materials down to  $0.02 \mu\text{g g}^{-1}$ , which suggest that many of the results for Se reported in GeoPT testing are too high.

Keywords: Te, As, Bi, Sb, Se, HG-AFS, geological reference materials, GeoPT.

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The determination of Te, As, Bi, Sb and Se (TABS; Barnes 2016) is critical for both environmental and economic reasons. These elements pose risks to the environment (especially As and Sb), such as through the contamination of soils, surface drainage and groundwater (e.g., Jamieson 2014, Singh *et al.* 2015). Consequently, most TABS are routinely monitored in various materials as elevated mass fractions can be highly toxic (Wu 2004, Duker *et al.* 2005, Sundar and Chakravarty 2010). On the other hand, TABS are also classified as critical raw materials for the development of low-carbon energy technologies (Zweibel 2010, Moss *et al.* 2013). Thus, the demand for analytical methods capable of quantifying these elements down to low levels is continually increasing.

Although most studies have focused on the importance of TABS in environmental and health issues over the past decades, there is a growing demand to understand their geochemical cycles (Hattori *et al.* 2002, Wang and Becker 2013, Brenan 2015). For example, TABS may be particularly important during the formation of platinum-group elements and gold deposits (Pitcairn *et al.* 2015, Barnes and Ripley 2016). However, there are very few values for TABS mass fractions in geological reference materials (especially of Bi, Se and Te), and consequently analytical protocols are difficult to validate. Therefore, the geological interpretations of the data are weakened by the uncertainty in the analytical results.

Atomic fluorescence spectrometry (AFS), coupled to hydride generation (HG), is an effective method for determining elements such as TABS that form covalent hydrides (Corns *et al.* 1993). Consequently, HG-AFS has been applied for monitoring trace amounts of TABS in materials such as food (Reyes *et al.* 2008, Zhang *et al.* 2011, Cava-Montesinos *et al.* 2013, Lai *et al.* 2016) and water (He *et al.* 1998, Yan *et al.* 2002). This technique has also been used by geologists to assess the behaviour of TABS during various geological processes (Pitcairn 2004, Pitcairn *et al.* 2015, Patten *et al.* 2016). The mass fractions of TABS in geological materials are variable (Hattori *et al.* 2002, Ketris and Yudovich 2009, Samalens *et*

*al.* 2017, Henrique-Pinto *et al.* 2015), and in some cases (especially for Se and Te), very low (Wang and Becker 2014, König *et al.* 2012, 2014, Lissner *et al.* 2014). The method appears suitable for studying the distribution of TABS in geological materials. However, to date HG-AFS has not been comprehensively tested using geological reference materials.

In this work we first establish the effectiveness of HG-AFS by determining the mass fractions of TABS in a series of geological reference materials and comparing the results with literature values. In addition, we report results for TABS in GeoPT proficiency test materials, and compare the results with GeoPT assigned and provisional values where available, and where not, with ranges of values reported by participating laboratories. We will show that our results mostly agree with the median values of results reported by GeoPT participating laboratories for Te, As, Bi and Sb and propose that these values could be used as informational values. However, the median values for the generally rather small Se datasets reported in GeoPT proficiency tests are elevated in comparison with our results. Because the values that we determined for Se in the reference materials are in agreement with certified or provisional values we suggest that many of the results contributed to the GeoPT tests are probably overestimations.

## **Experimental**

The analytical protocol is a slightly modified version of the method implemented by Pitcairn (2004).

### **Digestion of the rock samples**

Around 0.2 g of rock powder was mixed with 5 ml of *aqua regia* (1:3 HNO<sub>3</sub>:HCl; PlasmaPURE – SPC Science) in a 50 ml-disposable beaker (Digi TUBES – SCP Science). The closed-cap beaker was swirled and then placed in a digestion block for 2 h at room temperature, and further heated up to 80 °C for 22 h. The solution was then allowed to cool and diluted to 25 ml with distilled water (Figure 1). A different sample digest was prepared for each individual measurement.

The digestion of rock samples has to take into account the volatile behaviour of TABS (Corns *et al.* 1993, König *et al.* 2012, Wang and Becker 2014), and thus avoid a loss by volatilisation. The use of closed-cap beakers and low temperature are fundamental (Wang and Becker 2014). Previous studies indicate that heating the sample up to 80 °C in a closed system results in digestion without any analyte loss. In fact, heating the analytes to temperatures below 100 °C is a common step adopted in several analytical routines to ensure the reduction of TABS prior to analysis without any loss (Pitcairn 2004, He *et al.* 1998, Savard *et al.* 2006, 2009, König *et al.* 2012, Wang and Becker 2014).

### **Preparation of analytical solutions**

The hydride generation method makes use of the ability of TABS to form covalent gaseous hydrides (e.g., AsH<sub>3</sub>, SbH<sub>3</sub>). However, the formation of hydrides by these elements depends on them being in the reduced oxidation state (Corns *et al.* 1993). Consequently, the preparation of solutions for analysis requires a pre-reduction step, which varies for each element. Hence, As and Sb were measured in a different aliquot from Te, Se and Bi.

The aliquots were prepared by adding 10 ml of the digested rock solution to 30 ml of a reagent blank (Figure 1) in a 50 ml disposable beaker. For the As and Sb aliquot, the reagent blank was a solution of 6 mol l<sup>-1</sup> HCl, 13 g l<sup>-1</sup> potassium iodide (KI; VWR Chemicals), and 3.5 g l<sup>-1</sup> ascorbic acid (VWR Chemicals; Figure 1). The KI and the ascorbic acid are used to reduce the oxidation state of Sb<sup>V</sup> and As<sup>V</sup> to Sb<sup>III</sup> and As<sup>III</sup>, respectively (Nielsen and Hansen 1997, Potin-Gautier *et al.* 2005). For the Te, Se and Bi aliquot the reagent blank does not need any KI or ascorbic acid, and consists only of a 6 mol l<sup>-1</sup> HCl solution (Figure 1). The pre-reduction of Se and Te was achieved by heating the aliquot to 80 °C for 40 min in a water bath, in a closed-cap beaker (Cava-Montesinos *et al.* 2003, Savard *et al.* 2006). During this step, the Se<sup>VI</sup> and the Te<sup>VI</sup> are converted to Se<sup>IV</sup> and Te<sup>IV</sup>, respectively, which is necessary to ensure the formation of hydrides (Corns *et al.* 1993).

## Instrumentation

Analyses were performed at LabMaTer, Université du Québec à Chicoutimi (UQAC), using a continuous flow hydride generation-atomic fluorescence spectrometer, the PSA Millennium Excalibur 10.055 from PS Analytical. The instrument was equipped with boosted hollow cathode discharge (BHCD) lamps for As, Sb, Se, Te and Bi, and the primary currents were 27.5, 17.5, 20, 15 and 20 mA, respectively. The analytical solution was mixed with a reductant solution (Figure 1), at flow rates of 9 ml min<sup>-1</sup> and 4.5 ml min<sup>-1</sup>, respectively. The reductant solution was prepared by mixing 14 g of NaBH<sub>4</sub> and 8 g of NaOH with 2 l of distilled water. Hence, the gaseous hydrides were formed after the reaction between HCl and NaBH<sub>4</sub>, and further atomised using a hydrogen flame fed by excess H<sub>2</sub> gas created during the reaction. The BHCD lamp focussed on the flame provided the excitation source for the fluorescence of the element determined, which was then measured by an AFS detector. Atomic fluorescence signals were recorded and measured on the basis of the peak height of the signal.

## Calibration

Six calibration solutions with concentrations of 0.1, 0.25, 0.5, 1, 2.5 and 5 ng ml<sup>-1</sup> were prepared for each element of interest. These solutions were prepared from 1000 µg ml<sup>-1</sup> standard solutions of each element (PlasmaCAL, SPC Science). All the calibration solutions were mixed with the reagent blank prior to measurement, in the same proportion as sample aliquots (i.e., 10 ml of calibration solution and 30 ml of reagent blank). Calibration solutions were measured at the beginning and the end of each sequence of analysis to monitor fluctuations of the fluorescence signal. The calibration curves obtained were all linear.

## Detection limits of the method

As the detection limit (LoD) for each element we used three times the standard deviation (3s) of corresponding measurements on the blank solutions (Long and Winefordner 1983, Potts 1987). These values were calculated using the results for thirty blank solutions prepared in the same manner as the samples (total procedure). The detection limits obtained were 0.01, 0.019, 0.016, 0.026 and 0.002 µg g<sup>-1</sup> for Te, As, Bi, Sb and Se, respectively (Table 1). We chose to use ten times the standard deviation (10s) of the blank solutions to estimate limits of quantification for each element (LoQ; Potts 1987).

## Results and discussion

### Precision and accuracy based on geological reference materials

The average HG-AFS measurements, the standard deviations ( $1s$ ) and the relative standard deviations (% RSD) obtained for ten geological reference materials (CH-4, TDB-1, OKUM, WPR-1, WMG-1, AN-G, BE-N, BIR-1, W-2 and WGB-1) and one in-house reference material (KPT-1) are presented in Table 1. The full dataset is available in the online supporting information (Tables S1 and S2). Three reference materials (CH-4, TDB-1 and KPT-1) were measured in every round to monitor the reproducibility of the method. Only reference materials CH-4 and TDB-1 have been previously analysed using HG-AFS (Pitcairn *et al.* 2015, Patten *et al.* 2016), and the reported values for Te, Se, As and Sb are in the same range of our results (Tables S1 and S2).

The Horwitz function (Horwitz *et al.* 1980) was used to evaluate the acceptable variability of the measurements, which will vary following the mass fraction in the material. For example, according to the Horwitz function a relative uncertainty of 32% is acceptable at a mass fraction of  $0.01 \mu\text{g g}^{-1}$ , whereas the uncertainty should fall to 11.3% at a mass fraction of  $10 \mu\text{g g}^{-1}$ . The HG-AFS measurement results have % RSD values below the acceptable limits as derived from the Horwitz function (% RSD (Hwz); Table 1) for most samples. A characteristic of the Horwitz function is for greater variations in the % RSD to be obtained for lower mass fractions of an element. Moreover, individual measurements of the same sample digest for reference materials CH-4, TDB-1 and KPT-1 were carried out (Table 2), and were characterised by lower % RSD than those from different sample digests (Table 2). This suggests that the general variations in % RSD mostly reflect different mass fractions of TABS in the reference materials.

The only two HG-AFS measurements with % RSD greater than the acceptable variability were the Bi and Sb determinations for reference material TDB-1 (Table 1). High uncertainties reported for Bi and Sb in the certificate of analysis for TDB-1 suggest that high % RSD may reflect sample heterogeneity. In order to evaluate the problem, different sample masses were used in digestion of materials CH-4, TDB-1 and KPT-1 (i.e., 0.1, 0.2 and 0.4g). The HG-AFS results are recorded in Table 2. The % RSD are similar to slightly lower for sample digests of

0.4 g. However, for Bi and Sb determinations in TDB-1 the % RSD are significantly lower for sample digests of 0.4 g (Table 2). This supports the belief that % RSD values greater than the acceptable variability probably reflect minor heterogeneities of some elements. Therefore, for most reference materials 0.2 g is suitable, whereas measurements with high % RSD may be improved by preparing a sample of a greater sample mass.

The accuracy of the method was evaluated by comparing measured quantities for reference materials with literature values. The literature values of TABS for all the reference materials were compiled from the GeoReM database (Jochum *et al.* 2005), and are available in Tables S1 and S2. Comparisons are shown in Figure 2, where measured values mostly fall within the range of literature values.

All determinations of Sb and Se are above their respective limits of quantification, i.e., 0.088  $\mu\text{g g}^{-1}$  and 0.008  $\mu\text{g g}^{-1}$  (Table 1), and are within uncertainties with literature values for all the reference materials (Figure 2a and 2b). For five reference materials (TDB-1, OKUM, AN-G, BIR and BEN), Se measurements by the isotopic dilution method are available (König *et al.* 2012, 2014, Wang and Becker 2013, Tables S1 and S2). Our results are within uncertainties of the results for TDB-1, BIR and BEN, but are slightly lower compared with OKUM and AN-G. However, results obtained by other methods for these materials are within uncertainties of our results. Thus, the method is validated for Sb and Se down to 0.09  $\mu\text{g g}^{-1}$  and 0.008  $\mu\text{g g}^{-1}$ , respectively (the limits of quantification).

Arsenic and Bi mass fractions in most of the reference materials are above the limits of quantification (0.064 and 0.055  $\mu\text{g g}^{-1}$  respectively). Measured quantities of As are within the range of literature values except for the two samples (AN-G and BIR-1), which are below the limit of quantification, but above the limit of detection (Figure 2c). For these samples, the results are lower than literature values but still within range of literature results when the uncertainties of the literature values are considered. Therefore, we consider the method validated for As down to the limit of quantification. For Bi there is a more limited range of reference materials available and the results are variable. The results are in the same range as the literature values down to 0.2  $\mu\text{g g}^{-1}$  (Figure 2d), and we consider the method validated



down to this level. There are a number of reference materials with mass fractions close to the limit of quantification, for three of these the obtained values are higher than the literature values and for two they are lower than literature values. The source of the differences is not clear, but a weakness of the literature values is that all were determined by the same method (ICP-MS).

For Te, literature values are very sparse and variable making comparison problematic. For the six reference materials above the limits of quantification of  $0.032 \mu\text{g g}^{-1}$  the values fall within the range of literature values except for OKUM, where the value is slightly higher (Figure 2e). For the reference materials TDB-1, OKUM, AN-G, BIR and BEN, Te measurements by the isotopic dilution method are also available (König *et al.* 2012, 2014, Wang and Becker 2013, Tables S1 and S2). Obtained results are below the quantification limits for materials AN-G, BIR and BEN, which is in accord with isotopic dilution results lower than  $0.004 \mu\text{g g}^{-1}$  for these materials. For TDB-1 and OKUM our Te measurements ( $0.043 \mu\text{g g}^{-1}$  and  $0.053 \mu\text{g g}^{-1}$ , respectively) are higher than those obtained by isotopic dilution ( $0.006 \mu\text{g g}^{-1}$  and  $0.025 \mu\text{g g}^{-1}$ , respectively). However, our results are within uncertainties of literature values of TDB-1, including results by HG-AFS by Patten *et al.* (2016), obtained at a different laboratory. For the reference material OKUM, only a Te measurement by isotopic dilution data is available, not allowing a comparison with results from various studies, ideally using different analytical methods. The discrepancies of Te results for these two reference materials suggest that either the HG-AFS measurements (Patten *et al.* 2016 and this study) are slightly overestimated, or isotopic dilution results are slightly underestimated (Wang and Becker 2013, König *et al.* 2012, 2014).

In summary, the HG-AFS method is considered sufficiently accurate for measuring mass fractions of Te, As, Bi, Sb and Se above their respective limits of quantification (Table 1). The % RSD values are below the acceptable limits calculated from the Horwitz function in almost all of the reference materials, which demonstrates that the method is sufficiently precise to satisfy the analytical requirements.



## **IAG GeoPT proficiency test samples**

The International Association of Geoanalysts (IAG) conducts a proficiency testing programme, named *GeoPT*, designed to enable geoanalytical laboratories to routinely assess their analytical performance. In each round of *GeoPT*, participating laboratories analyse powders of the same test material (*GeoPT* samples), and report quantity values of major and trace element constituents to the *GeoPT* organisers. A detailed account of the proficiency testing programme and how proficiency testing values are obtained may be found in the *GeoPT* protocol (IAG 2018). To increase the dataset of measurement results for TABS in geological materials, thirty-four test samples from previous *GeoPT* rounds were analysed by HG-AFS (Table 3), and the results compared with values derived from the proficiency tests (Table 4).

The Horwitz function was calculated for the HG-AFS measurement results on each sample, and 85% of the results had % RSD values lower than those acceptable limits (Table 3), validating the precision of the method. For most results with % RSD values higher than the tolerance provided by the Horwitz function, the measurements are close to the LoD of the method, which may explain the discrepancy.

Whenever possible, assigned and provisional values from *GeoPT* reports were taken for comparison with measured values of each element (Table 4). For the materials for which neither assigned nor provisional values were available from *GeoPT* reports, median values of all mass fraction values reported by participants were used as a reference (Table 4). Figure 3 shows the comparison of our measurement results with *GeoPT* assigned, provisional and median values. Our results are also compared with all individual mass fractions reported by the participating laboratories, for each element in Figure 4.

**Antimony and bismuth:** Our Sb and Bi measurement results are in close agreement with assigned and provisional values for most of the test materials (Figures 3a and 3b; Tables 3 and 4). Exceptions are *GeoPT* samples 13, 29 and 33 for Sb, and *GeoPT* sample 36 for Bi. Although these four results do not agree with the assigned or provisional values, they fall well within the range of reported values (Figure 4a and b). For those samples that have

neither assigned nor provisional values, and which are above the respective limits of quantification, the Sb and Bi HG-AFS results are similar to the median values of the GeoPT contributed data (Figures 3a and 3b; Tables 3 and 4). Therefore, for most samples without assigned or provisional values, and for which HG-AFS results are above our quantification limits, we suggest that the median values for Bi and Sb could be used as informational values. Exceptions to this are for Bi in GeoPT samples 12, 16, 19, 23 and 29, and Sb for GeoPT sample 25, where our results fall within the range of reported results (Figure 4a and b), but differ from the median value. All of these samples contain less than  $0.2 \mu\text{g g}^{-1}$  Bi according to the HG-AFS determination. Below  $0.3 \mu\text{g g}^{-1}$  Bi, the range of values reported in some cases by GeoPT participants increases from one order of magnitude to over three, and in some cases too few data were reported, thus the median GeoPT values may not always be adequate, especially at low levels. Therefore, there appears to be considerable room for improvement in determination of Bi at low levels by the geoanalytical community.

**Arsenic:** Arsenic results are in good agreement with most of the assigned and provisional values (Figure 3c; Tables 3 and 4). The exceptions are results on GeoPT test samples 06 and 33. Our results are lower than assigned and provisional values for these two samples, and at the lower end of reported values (Figure 4c). The reasons for these discrepancies are not clear.

For samples with no assigned or provisional values, the medians of the GeoPT rounds are in agreement with our results for mass fractions above  $1 \mu\text{g g}^{-1}$  (Fig 3c, and Table 4). However, for samples with As mass fractions below  $1 \mu\text{g g}^{-1}$ , our results are lower than GeoPT median values (Figure 3c), although still within the range of reported values (Figure 4c). However, as discussed above we consider our method valid down to the limit of quantification ( $0.064 \mu\text{g g}^{-1}$ ), and all of these samples appear to contain more than  $0.1 \mu\text{g g}^{-1}$  As. Therefore, we suggest that the GeoPT median values for samples with As mass fractions below  $1 \mu\text{g g}^{-1}$  overestimate the As mass fractions. As in the case of Bi, the ranges of the results reported from the GeoPT tests are much wider for samples with less than  $1 \mu\text{g g}^{-1}$  As (2 to 3 orders of magnitude), than for samples above  $1 \mu\text{g g}^{-1}$  (generally 1 order of magnitude, Figure 4c). We suggest that median values for samples with As mass fractions greater than  $1 \mu\text{g g}^{-1}$  could be used as informational values.

**Selenium:** Among the GeoPT samples only KPT-1 (GeoPT-18) and DBC-1 (GeoPT-33) have assigned and provisional values for Se, respectively (Table 4). The HG-AFS results for these samples are in excellent agreement with these assigned and provisional values (Figure 3d). In addition, the median values for samples 36A and 40 are close to our determinations (Table 3 and 4). For the other samples, the values determined for Se by HG-AFS are lower than the GeoPT median values (Figure 4d; Tables 3 and 4), and below  $0.1 \mu\text{g g}^{-1}$  most of our results are less than GeoPT results by one to two orders of magnitude. All of the samples contain Se mass fractions above the HG-AFS detection limit, and all but four are above the quantification limit (i.e.,  $0.008 \mu\text{g g}^{-1}$ ). As discussed above, the method was demonstrated to be sufficiently accurate at these mass fractions as evidenced by measurement of geological reference materials (Figure 2b). Therefore, we must conclude that the majority of Se values reported in the GeoPT test (especially those below  $0.1 \mu\text{g g}^{-1}$ ) are significant overestimates (see especially Figure 4d).

**Tellurium:** The number of laboratories that have reported Te mass fractions for GeoPT test materials is low, and thus no assigned or provisional values are available (Table 4). Moreover, the median values are unlikely to be reliable unless a sufficient number of measurements have been reported. For samples above the limit of quantification ( $0.032 \mu\text{g g}^{-1}$ ) there is broadly a positive correlation (0.86) between the HG-AFS Te results and the median values of the GeoPT contributed values (Figure 3e). This observation suggests that the median results for the samples with Te mass fractions greater than  $0.032 \mu\text{g g}^{-1}$  approximate to the correct order of magnitude. However, the range of GeoPT test values reported by participants is very large ( $0.01$  to  $10 \mu\text{g g}^{-1}$ ; Figure 4e). Unlike the observations for As and Bi the variability did not change regardless of the median mass fraction. Based on the validation of the HG-AFS with reference materials (Figure 2e), we propose that our HG-AFS Te results, above the limit of quantification ( $0.032 \mu\text{g g}^{-1}$ ), could be used as informational values. Once again, this illustrates the lack of well-characterised reference materials for Te at sub  $\mu\text{g g}^{-1}$  levels, and reinforces the need of further studies.

## Variability of TABS values in GeoPT proficiency test results

The datasets of measurement results for TABS in GeoPT samples are, in some cases, extremely variable. The variability of results is greater for samples with low mass fractions of a given element. Such variability may be due to some participating laboratories reporting measurements close to their detection limits. These measurements may have consequently been overestimated, resulting in a wide range of measurements and in some cases overestimated median values. For less commonly determined elements such as Se and Te, precise and accurate measurements normally require a highly specialised analytical procedure (Savard *et al.* 2006, 2009, Wang and Becker 2014, König *et al.* 2012, 2014, Lissner *et al.* 2014). Therefore, the wide range of measurements may reflect analyses performed in routine analytical procedures, which may not properly account for properties such as the oxidation state, and volatile behaviour of these elements.

Another possible explanation for the wide variation observed in measurements of TABS in GeoPT proficiency tests is the presence of analytical interferences. An example would be the polyatomic interference from  $^{40}\text{Ar}^{35}\text{Cl}$  on  $^{75}\text{As}$ , during ICP-MS analysis (Sheppard *et al.* 1990, Branch *et al.* 1991, Komorowicz and Baralkiewicz 2011). Thus, the problem most likely arises because *aqua regia* digestion is a common procedure in most solution work, and ICP-MS is predominantly used for determining As. Therefore, as an example, it would be plausible that some of the variations in As measurements result from  $^{40}\text{Ar}^{35}\text{Cl}$  interferences on  $^{75}\text{As}$  in *aqua regia* digestion when followed by ICP-MS analysis. The analytical routine used by each laboratory for measuring various elements is not reported for the majority of GeoPT proficiency tests, thus it is not possible to verify whether interferences affect the results. However, the large range of variation in reported measurements suggests that specialised analytical protocols are critical for precise and accurate quantification of TABS mass fractions in geological materials.

A final consideration is the “nugget” effect. All of these elements are chalcophile and could be present in the samples only as minute sulfide grains, thus at low mass fractions nugget effects may be in part the source of the variation (Bédard *et al.* 2016). Tellurium, Bi and Se are strongly to highly chalcophile elements with partition coefficients into sulfides greater than 400 (Barnes and Ripley 2016), and their mass fractions are very low, thus they are particularly vulnerable to the nugget effect.

## Conclusions

The characterisation of TABS in geological reference materials is a subject that needs more attention, as illustrated by the paucity of information and wide variation of literature values. This work demonstrates that *aqua regia* digestion followed by HG-AFS is an appropriate method for determination of TABS in geological materials to sub  $\mu\text{g g}^{-1}$  level. The study provides results for TABS in ten international geological reference materials (CH-4, TDB-1, OKUM, WPR-1, WMG-1, AN-G, BE-N, BIR-1, W-2 and WGB-1) and thirty-four test materials from the GeoPT programme. The comparison between HG-AFS results and geological reference materials results validates the method for measuring Te, As, Bi, Sb and Se above their respective limits of quantification. Our results agree with GeoPT results for Sb, and we suggest that for those samples with no assigned or provisional values the GeoPT median values could be used as informational values. Above  $0.3 \mu\text{g g}^{-1}$  Bi, and  $1 \mu\text{g g}^{-1}$  As, our results agree with the GeoPT results, and for those samples with no assigned or provisional values the GeoPT median values could potentially be used as informational values. Below  $1 \mu\text{g g}^{-1}$  As the median GeoPT values are systematically higher than ours. For Se the median GeoPT values are systematically higher than our values. Considering that for these two elements the HG-AFS method was successful in determining the mass fractions in a range of geological reference materials, we consider that the median results from the GeoPT test overestimate As mass fractions below  $1 \mu\text{g g}^{-1}$  and Se in most samples. This overestimation is probably related with the fact that fewer and less reliable results are reported for materials with low mass fractions, and the medians may not be an appropriate estimate. The GeoPT dataset for Te is limited, but above the limit of quantification the median GeoPT test results correlate with the HG-AFS results. We suggest that the HG-AFS results could be used as informational values for As in GeoPT test samples with less than 1

$\mu\text{g g}^{-1}$ . The HG-AFS results could also be used as informational values for Se and Te in GeoPT materials with mass fractions above the quantification limits.

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## **Supporting information**

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

Table S1. Complete dataset for Te, As, Bi, Sb and Se results obtained in this study by HG-AFS.

Table S2. Published Te, As, Bi, Sb and Se values for international geological reference materials, compiled from the GeoReM database (Jochum *et al.* 2005), and respective references.

This material is available from:

<http://onlinelibrary.wiley.com/doi/10.1111/ggr.00000/abstract>

(This link will take you to the article abstract).

### Figure captions

Figure 1. Schematic flow diagram showing the main preparation steps for reagents and aliquots. See text for further explanation. HG-AFS – Hydride generation-atomic fluorescence spectrometry.

Figure 2. Comparison of new HG-AFS determinations and literature values (from Supplementary Materials) for (a) Sb, (b) Se, (c) As, (d) Bi and (e) Te. Uncertainties are shown by error bars at the  $1\sigma$  level. For materials with a compositional range, instead of a result, the range is plotted using an error bar. Dashed lines indicate the limits of detection (LoD) and quantification (LoQ) for HG-AFS.

Figure 3. Comparison of new HG-AFS determinations with assigned and provisional values from GeoPT reports and median values (this work, from Table 4) of GeoPT proficiency test materials for (a) Sb, (b) Bi, (c) As, (d) Se and (e) Te. Values with mass fractions below the detection limits (Table 3) are not plotted. Dashed lines indicate the limits of detection (LoD) and quantification (LoQ) for HG-AFS.

Figure 4. Comparison of new determinations and all previously reported results by other laboratories for GeoPT proficiency test materials for (a) Sb, (b) Bi, (c) As, (d) Se and (e) Te. Dashed lines indicate the limits of detection (LoD) and quantification (LoQ) for HG-AFS.

Table 1.								
Tellurium, As, Bi, Sb and Se results for geological reference materials by HG-AFS								
Sample ID	n *	Rock type		Te	As	Bi	Sb	Se
LoD		Blank	3s ( $\mu\text{g g}^{-1}$ )	0.010	0.019	0.016	0.026	0.002
LoQ		Blank	10s ( $\mu\text{g g}^{-1}$ )	0.032	0.064	0.055	0.088	0.0081
CH-4	7	Anorthosite	Mean ( $\mu\text{g g}^{-1}$ )	0.414	8.534	0.676	0.844	1.942
			1s	0.073	0.355	0.094	0.062	0.044
			% RSD	17.712	4.163	13.900	7.334	2.272
			% RSD (Hwz)	18.266	11.585	16.968	16.409	14.476
TDB-1	7	Diabase	Mean ( $\mu\text{g g}^{-1}$ )	0.043	2.127	0.064	1.034	0.344
			1s	0.006	0.207	0.024	0.176	0.029
			% RSD	12.961	9.717	37.609	16.984	8.494
			% RSD (Hwz)	25.656	14.279	24.186	15.916	18.785
KPT-1	7	Quartz diorite	Mean ( $\mu\text{g g}^{-1}$ )	0.498	2.151	0.907	11.077	2.959
			1s	0.060	0.280	0.085	0.247	0.113
			% RSD	11.959	13.041	9.361	2.232	3.832
			% RSD (Hwz)	17.768	14.255	16.234	11.139	13.587
OKUM	3	Komatiite	Mean ( $\mu\text{g g}^{-1}$ )	0.053	0.241	0.072	0.111	0.101
			1s	0.006	0.039	0.011	0.014	0.011
			% RSD	10.340	16.128	15.799	12.234	10.950
			% RSD (Hwz)	24.862	19.819	23.785	22.271	22.588
WPR-1	3	Peridotite	Mean ( $\mu\text{g g}^{-1}$ )	0.474	1.070	0.194	0.876	3.859
			1s	0.027	0.130	0.015	0.108	0.083
			% RSD	5.606	12.111	7.568	12.326	2.143
			% RSD (Hwz)	17.900	15.834	20.471	16.319	13.055
WMG-1	3	Gabbro	Mean ( $\mu\text{g g}^{-1}$ )	1.419	7.087	0.489	1.920	13.635
			1s	0.081	0.207	0.050	0.081	0.536
			% RSD	5.716	2.915	10.277	4.216	3.930
			% RSD (Hwz)	15.176	11.913	17.817	14.501	10.796
AN-G	3	Anorthosite	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	0.024	0.070	0.117	0.028
			1s	n.a.	0.003	0.014	0.007	0.005
			% RSD	n.a.	12.633	20.204	6.278	17.726
			% RSD (Hwz)	n.a.	28.069	23.893	22.096	27.430
BEN	3	Basalt	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	1.808	< 0.016	0.294	0.070
			1s	n.a.	0.045	n.a.	0.006	0.006
			% RSD	n.a.	2.473	n.a.	1.894	8.975
			% RSD (Hwz)	n.a.	14.633	n.a.	19.238	23.895
BIR-1	3	Basalt	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	0.054	0.017	0.543	0.016
			1s	n.a.	0.005	0.002	0.024	0.002
			% RSD	n.a.	8.968	14.280	4.428	14.863
			% RSD (Hwz)	n.a.	24.801	29.449	17.539	29.689
W-2	3	Diabase	Mean ( $\mu\text{g g}^{-1}$ )	0.011	0.767	0.073	0.786	0.087
			1s	0.001	0.048	0.016	0.037	0.004
			% RSD	4.660	6.259	21.623	4.659	4.981
			% RSD (Hwz)	31.379	16.650	23.731	16.588	23.121
WGB-1	3	Gabbro	Mean ( $\mu\text{g g}^{-1}$ )	0.013	1.595	0.052	1.810	0.092
			1s	0.002	0.047	0.009	0.040	0.008
			% RSD	18.085	2.946	17.925	2.184	8.549
			% RSD (Hwz)	30.674	14.911	24.934	14.630	22.903

LoD = limit of detection; LoQ = limit of quantification; % RSD (Hwz) = Target % RSD calculated using the Horwitz function; n.a. = non applicable; \* Number of individual determinations.

	Sample mass (g)	N	CH-4				TDB-1				KPT-1			
			Anorthosite				Diabase				Quartz diorite			
			Mean ( $\mu\text{g g}^{-1}$ )	1s	% RSD	% RSD (Hwz)	Mean ( $\mu\text{g g}^{-1}$ )	1s	% RSD	% RSD (Hwz)	Mean ( $\mu\text{g g}^{-1}$ )	1s	% RSD	% RSD (Hwz)
Te	0.1 (n = 4)	4	0.369	0.094	25.4	18.6	0.047	0.006	13.6	25.3	0.533	0.070	13.2	17.6
	0.2 (n = 7)	7	0.414	0.073	17.7	18.3	0.043	0.006	13.0	25.7	0.498	0.060	12.0	17.8
	0.4 (n = 4)	4	0.43	0.04	8.1	18.2	0.030	0.004	14.6	27.1	0.49	0.04	8.2	17.8
	0.2 (n = 3)	1	0.469	0.035	7.4	17.9	0.047	0.004	8.5	25.4	0.533	0.048	9.1	17.6
As	0.1 (n = 4)	4	8.773	0.245	2.8	11.5	2.210	0.270	12.2	14.2	1.878	0.131	7.0	14.5
	0.2 (n = 7)	7	8.534	0.355	4.2	11.6	2.127	0.207	9.7	14.3	2.151	0.280	13.0	14.3
	0.4 (n = 4)	4	8.400	0.219	2.6	11.6	2.041	0.213	10.4	14.4	2.246	0.111	4.9	14.2
	0.2 (n = 3)	1	8.455	0.320	3.8	11.6	2.210	0.196	8.9	14.2	1.878	0.100	5.3	14.5
Bi	0.1 (n = 4)	4	0.610	0.092	15.1	17.2	0.062	0.030	48.9	24.3	0.847	0.068	8.1	16.4
	0.2 (n = 7)	7	0.676	0.094	13.9	17.0	0.064	0.024	37.6	24.2	0.907	0.085	9.4	16.2
	0.4 (n = 4)	4	0.800	0.074	9.2	16.5	0.084	0.005	6.0	23.2	0.943	0.075	7.9	16.1
	0.2 (n = 3)	1	0.748	0.063	8.4	16.7	0.046	0.002	5.1	25.4	0.847	0.048	5.6	16.4
Sb	0.1 (n = 4)	4	0.876	0.068	7.8	16.3	0.857	0.136	15.8	16.4	11.113	0.240	2.2	11.1
	0.2 (n = 7)	7	0.844	0.062	7.3	16.4	1.034	0.176	17.0	15.9	11.077	0.247	2.2	11.1
	0.4 (n = 4)	4	0.877	0.082	9.4	16.3	0.931	0.064	6.9	16.2	11.031	0.153	1.4	11.1
	0.2 (n = 3)	1	0.790	0.019	2.4	16.6	0.857	0.018	2.1	16.4	11.113	0.173	1.6	11.1
Se	0.1 (n = 4)	4	1.944	0.057	3.0	14.5	0.343	0.026	7.5	18.8	3.029	0.134	4.4	13.5
	0.2 (n = 7)	7	1.942	0.044	2.3	14.5	0.344	0.029	8.5	18.8	2.959	0.113	3.8	13.6
	0.4 (n = 4)	4	1.928	0.039	2.0	14.5	0.394	0.071	13.1	18.4	2.934	0.054	1.8	13.6
	0.2 (n = 3)	1	1.936	0.044	2.3	14.5	0.343	0.020	5.8	18.8	3.029	0.102	3.4	13.5

Abbreviations: % RSD (Hwz) = Target % RSD calculated using the Horwitz function; n = number of individual determinations; N = number of sample digests.

Table 3. Tellurium, As, Bi, Sb and Se results for GeoPT proficiency test samples by HG-AFS

Sample ID	n *	Rock type		Te	As	Bi	Sb	Se
LoD		blank	3s ( $\mu\text{g g}^{-1}$ )	0.010	0.019	0.016	0.026	0.002
LoQ		blank	10s ( $\mu\text{g g}^{-1}$ )	0.032	0.064	0.055	0.088	0.0081
GeoPT-06 (OU-3)	4	Nanhoron microgranite	Mean ( $\mu\text{g g}^{-1}$ )	0.020	0.917	0.227	0.221	0.028
			1s	0.007	0.052	0.085	0.018	0.011
			% RSD	31.9	5.6	37.7	8.1	39.6
			% RSD (Hwz)	28.7	16.2	20.0	20.1	27.4
GeoPT-08 (OU-4)	4	Penmaenmawr microdiorite	Mean ( $\mu\text{g g}^{-1}$ )	0.019	1.317	0.090	0.289	0.019
			1s	0.010	0.071	0.017	0.038	0.004
			% RSD	53.7	5.4	18.7	13.2	20.3
			% RSD (Hwz)	29.1	15.3	23.0	19.3	29.1
GeoPT-10 (CH-1)	4	Marine sediment	Mean ( $\mu\text{g g}^{-1}$ )	0.080	3.648	0.309	0.960	0.543
			1s	0.009	0.184	0.033	0.022	0.019
			% RSD	11.3	5.1	10.6	2.3	3.6
			% RSD (Hwz)	23.4	13.2	19.1	16.1	17.5
GeoPT-11 (OU-5)	4	Leiton dolerite	Mean ( $\mu\text{g g}^{-1}$ )	0.028	2.413	0.073	0.470	0.021
			1s	0.017	0.046	0.023	0.031	0.001
			% RSD	58.8	1.9	31.1	6.6	6.3
			% RSD (Hwz)	27.4	14.0	23.7	17.9	28.7
GeoPT-12 (GAS)	4	Serpentine	Mean ( $\mu\text{g g}^{-1}$ )	0.027	115.628	0.141	12.304	0.029
			1s	0.008	3.514	0.046	0.340	0.003
			% RSD	30.9	3.0	32.8	2.8	11.4
			% RSD (Hwz)	27.6	7.8	21.5	11.0	27.2
GeoPT-13 (UoK Loess)	4	Köln loess	Mean ( $\mu\text{g g}^{-1}$ )	0.016	6.470	0.159	0.350	0.029
			1s	0.008	0.230	0.020	0.056	0.001
			% RSD	51.9	3.6	12.7	16.0	3.7
			% RSD (Hwz)	29.7	12.1	21.1	18.7	27.3
GeoPT-15 (MSAN)	4	Ocean Floor sediment	Mean ( $\mu\text{g g}^{-1}$ )	0.078	7.161	0.112	0.457	0.533
			1s	0.006	0.301	0.041	0.066	0.049
			% RSD	7.3	4.2	36.6	14.5	9.1
			% RSD (Hwz)	23.5	11.9	22.2	18.0	17.6
GeoPT-16 (BNV-1)	4	Nevada basalt	Mean ( $\mu\text{g g}^{-1}$ )	0.023	2.358	0.063	0.164	0.025
			1s	0.013	0.112	0.002	0.019	0.004
			% RSD	58.9	4.7	3.0	11.5	15.5
			% RSD (Hwz)	28.3	14.1	24.3	21.0	27.9
GeoPT-17 (OU-8)	4	Calcareous sandstone	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	0.963	0.058	0.165	0.007
			1s	n.a.	0.076	0.016	0.022	0.002
			% RSD	n.a.	7.9	27.7	13.2	28.4
			% RSD (Hwz)	n.a.	16.1	24.5	21.0	34.0
GeoPT-18 (KPT-1)	4	Quartz diorite	Mean ( $\mu\text{g g}^{-1}$ )	0.500	2.199	0.854	10.720	2.988
			1s	0.021	0.158	0.078	0.353	0.085
			% RSD	4.1	7.2	9.1	3.3	2.9
			% RSD (Hwz)	17.8	14.2	16.4	11.2	13.6
GeoPT-19 (MGR-N)	4	Gabbro	Mean ( $\mu\text{g g}^{-1}$ )	0.082	1.764	0.162	0.151	0.500
			1s	0.009	0.070	0.013	0.008	0.055
			% RSD	11.4	4.0	7.9	5.1	11.0
			% RSD (Hwz)	23.3	14.7	21.0	21.3	17.8
GeoPT-20 (OPY-1)	4	Ultramafic rock	Mean ( $\mu\text{g g}^{-1}$ )	0.037	0.324	< 0.016	0.188	0.105
			1s	0.005	0.047	n.a.	0.028	0.009
			% RSD	13.1	14.4	n.a.	14.8	8.3
			% RSD (Hwz)	26.3	19.0	n.a.	20.6	22.4



GeoPT-21 (MGT-1)	4	Granite	Mean ( $\mu\text{g g}^{-1}$ )	0.043	2.080	1.102	0.244	0.009
			1s	0.020	0.115	0.041	0.033	0.005
			% RSD	46.0	5.5	3.7	13.6	54.5
			% RSD (Hwz)	25.7	14.3	15.8	19.8	32.6
GeoPT-22 (MBL-1)	4	Basalt	Mean ( $\mu\text{g g}^{-1}$ )	0.208	1.624	0.092	0.224	0.028
			1s	0.036	0.089	0.010	0.022	0.008
			% RSD	17.3	5.5	10.3	9.9	30.3
			% RSD (Hwz)	20.3	14.9	22.9	20.0	27.4
GeoPT-23 (OU-9)	4	Separation Lake pegmatite	Mean ( $\mu\text{g g}^{-1}$ )	0.211	2.670	0.064	6.443	0.006
			1s	0.017	0.073	0.028	0.437	0.000
			% RSD	8.1	2.7	43.8	6.8	6.7
			% RSD (Hwz)	20.2	13.8	24.2	12.1	34.5
GeoPT-24 (OU-10)	4	Longmyndian greywacke	Mean ( $\mu\text{g g}^{-1}$ )	0.186	1.769	0.143	0.242	0.010
			1s	0.036	0.015	0.016	0.027	0.002
			% RSD	19.1	0.9	11.0	11.2	20.3
			% RSD (Hwz)	20.6	14.7	21.4	19.8	32.0
GeoPT-25 (HTB-1)	4	Basalt	Mean ( $\mu\text{g g}^{-1}$ )	0.226	0.203	0.054	0.233	0.173
			1s	0.040	0.014	0.027	0.021	0.031
			% RSD	17.9	6.8	50.2	9.2	18.1
			% RSD (Hwz)	20.0	20.3	24.8	19.9	20.8
GeoPT-27 (MGL-AND)	4	Andesite	Mean ( $\mu\text{g g}^{-1}$ )	0.198	2.004	0.074	0.230	0.003
			1s	0.025	0.084	0.018	0.012	0.001
			% RSD	12.8	4.2	24.2	5.0	17.1
			% RSD (Hwz)	20.4	14.4	23.7	20.0	38.0
GeoPT-29 (NKT-1)	4	Nephelinite	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	1.836	0.052	0.358	0.035
			1s	n.a.	0.064	0.016	0.019	0.002
			% RSD	n.a.	3.5	31.1	5.4	5.0
			% RSD (Hwz)	n.a.	14.6	24.9	18.7	26.6
GeoPT-30 (CG-2)	4	Syenite	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	4.244	0.169	0.819	0.011
			1s	n.a.	0.138	0.021	0.046	0.001
			% RSD	n.a.	3.2	12.5	5.7	9.9
			% RSD (Hwz)	n.a.	12.9	20.9	16.5	31.4
GeoPT-31 (SdAR-1)	4	Modified River Sediment	Mean ( $\mu\text{g g}^{-1}$ )	0.399	35.139	1.775	5.923	0.300
			1s	0.031	0.538	0.066	0.384	0.020
			% RSD	7.9	1.5	3.7	6.5	6.6
			% RSD (Hwz)	18.4	9.4	14.7	12.2	19.2
GeoPT-32 (WG-1)	4	Woodstock basalt	Mean ( $\mu\text{g g}^{-1}$ )	0.016	0.575	0.052	0.071	0.021
			1s	0.009	0.065	0.018	0.014	0.001
			% RSD	60.2	11.3	35.2	19.6	4.4
			% RSD (Hwz)	29.9	17.4	24.9	23.8	28.6
GeoPT-33 (DBC-1)	4	Ball Clay	Mean ( $\mu\text{g g}^{-1}$ )	0.259	3.285	1.683	1.587	2.442
			1s	0.037	0.093	0.150	0.054	0.091
			% RSD	14.3	2.8	8.9	3.4	3.7
			% RSD (Hwz)	19.6	13.4	14.8	14.9	14.0
GeoPT-34 (GRI-1)	4	Granite	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	1.044	0.057	0.204	0.049
			1s	n.a.	0.088	0.010	0.015	0.003
			% RSD	n.a.	8.5	17.1	7.4	6.7
			% RSD (Hwz)	n.a.	15.9	24.6	20.3	25.2
GeoPT-35 (TLM-1)	4	Tonalite	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	2.295	0.092	1.556	0.010
			1s	n.a.	0.100	0.025	0.062	0.001
			% RSD	n.a.	4.4	27.4	4.0	5.7
			% RSD (Hwz)	n.a.	14.1	22.9	15.0	31.9
GeoPT-36 (GSM-1)	4	Gabbro	Mean ( $\mu\text{g g}^{-1}$ )	0.032	2.470	0.116	1.934	0.213
			1s	0.007	0.214	0.015	0.038	0.015
			% RSD	23.3	8.6	12.9	2.0	6.9
			% RSD (Hwz)	26.8	14.0	22.1	14.5	20.2
GeoPT-36A (SdAR-M2)	4	Metal-rich sediment	Mean ( $\mu\text{g g}^{-1}$ )	1.096	72.972	1.051	111.793	3.321
			1s	0.084	2.455	0.108	2.520	0.268
			% RSD	7.7	3.4	10.3	2.3	8.1
			% RSD (Hwz)	15.8	8.4	15.9	7.9	13.4
GeoPT-37 (ORPT-1)	4	Rhyolite	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	0.423	0.063	0.253	0.005
			1s	n.a.	0.025	0.021	0.042	0.003
			% RSD	n.a.	5.9	33.1	16.7	53.8
			% RSD (Hwz)	n.a.	18.2	24.2	19.7	35.3
GeoPT-38 (OU-7)	4	Ardnamurchan gabbro	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	0.152	0.032	0.059	0.082
			1s	n.a.	0.008	0.008	0.014	0.003
			% RSD	n.a.	5.3	24.8	24.5	3.2
			% RSD (Hwz)	n.a.	21.2	26.8	24.5	23.3
GeoPT-38A (HARZ01)	4	Modified harzburgite	Mean ( $\mu\text{g g}^{-1}$ )	0.014	0.282	0.077	1.175	0.031
			1s	0.004	0.029	0.018	0.050	0.005
			% RSD	26.4	10.4	23.1	4.3	14.9
			% RSD (Hwz)	30.5	19.4	23.5	15.6	26.9
GeoPT-39 (SyMP-1)	4	Syenite	Mean ( $\mu\text{g g}^{-1}$ )	0.138	3.666	0.800	0.231	0.182
			1s	0.011	0.117	0.028	0.012	0.004
			% RSD	7.6	3.2	3.5	5.2	2.1
			% RSD (Hwz)	21.6	13.2	16.5	19.9	20.7
GeoPT-39A (MNS-1)	4	Nepheline syenite	Mean ( $\mu\text{g g}^{-1}$ )	0.020	22.144	1.062	3.176	0.035
			1s	0.004	0.971	0.081	0.196	0.003
			% RSD	18.6	4.4	7.6	6.2	9.9
			% RSD (Hwz)	28.8	10.0	15.9	13.4	26.5
GeoPT-40 (ShWYO-1)	4	Silty marine shale	Mean ( $\mu\text{g g}^{-1}$ )	0.071	10.275	0.334	0.907	0.565
			1s	0.010	0.722	0.008	0.056	0.022
			% RSD	14.3	7.0	2.3	6.2	3.9
			% RSD (Hwz)	23.8	11.3	18.9	16.2	17.4
GeoPT-41 (ORA-1)	4	Andesite	Mean ( $\mu\text{g g}^{-1}$ )	< 0.01	0.258	0.050	0.975	0.004
			1s	n.a.	0.020	0.011	0.050	0.001
			% RSD	n.a.	7.8	21.8	5.1	34.9
			% RSD (Hwz)	n.a.	19.6	25.1	16.1	37.3

LoD = limit of detection; LoQ = limit of quantification; % RSD (Hwz) = Target % RSD calculated using the Horwitz function; n.a. = non applicable; \* Number of individual determinations

Table 4.  
Assigned, provisional and median values for GeoPT proficiency test samples

Sample ID	Assigned, provisional and median values ( $\mu\text{g g}^{-1}$ )					Reference
	Te	As	Bi	Sb	Se	
GeoPT-06	0.17	<b>3.379</b>	0.2	<b>0.305</b>	8	Potts <i>et al.</i> (2000)
GeoPT-08	0.32	1.85	0.098	<b>0.302</b>	4	Potts <i>et al.</i> (2000b)
GeoPT-10	n.r.	4.465	<b>0.31</b>	<b>1.05</b>	0.9	Potts <i>et al.</i> (2001)
GeoPT-11	0.30	<u>2.45</u>	0.067	<b>0.42</b>	1.5	Potts <i>et al.</i> (2002)
GeoPT-12	n.r.	<b>121.1</b>	0.07	<b>12.29</b>	1.8	Potts <i>et al.</i> (2003)
GeoPT-13	n.r.	<b>6.746</b>	0.13	<b>0.58</b>	1.1	Potts <i>et al.</i> (2003b)
GeoPT-15	0.22	<b>7.32</b>	0.11	<u>0.49</u>	1.05	Potts <i>et al.</i> (2004)
GeoPT-16	13.5	<u>2.328</u>	0.4	<u>0.13</u>	2	Potts <i>et al.</i> (2005)
GeoPT-17	0.04	1.214	<u>0.043</u>	<u>0.215</u>	0.414	Potts <i>et al.</i> (2005b)
GeoPT-18	0.35	2.21	<b>0.945</b>	<b>10.005</b>	<b>2.93</b>	Webb <i>et al.</i> (2006)
GeoPT-19	0.072	<u>1.75</u>	0.068	<u>0.124</u>	1	Webb <i>et al.</i> (2006b)
GeoPT-20	0.03	0.8	0.1	0.145	0.31	Webb <i>et al.</i> (2007)
GeoPT-21	0.036	<u>2.315</u>	<b>1.06</b>	<u>0.2</u>	n.r.	Webb <i>et al.</i> (2007b)
GeoPT-22	0.502	1.8	0.069	<u>0.29</u>	0.07	Webb <i>et al.</i> (2008)
GeoPT-23	0.24	2.82	0.19	<b>7.669</b>	0.25	Webb <i>et al.</i> (2008b)
GeoPT-24	0.05	2.02	0.1	0.287	0.238	Webb <i>et al.</i> (2009)
GeoPT-25	0.09	1.915	0.053	0.1	0.329	Webb <i>et al.</i> (2009b)
GeoPT-27	1	<u>2.346</u>	<b>0.106</b>	<u>0.237</u>	0.31	Webb <i>et al.</i> (2010)
GeoPT-29	0.03	2.2	0.023	<u>0.12</u>	0.2	Webb <i>et al.</i> (2011)
GeoPT-30	0.041	5.85	<u>0.17</u>	<b>1.054</b>	1.5	Webb <i>et al.</i> (2012)
GeoPT-31	0.825	<u>36.43</u>	<u>1.77</u>	<b>6.667</b>	1.48	Webb <i>et al.</i> (2012b)
GeoPT-32	0.1	1.486	0.07	0.12	0.556	Webb <i>et al.</i> (2013)
GeoPT-33	0.101	<u>9</u>	<u>2.04</u>	<u>2.809</u>	<u>3.006</u>	Webb <i>et al.</i> (2013b)
GeoPT-34	0.07	0.99	<u>0.057</u>	0.205	0.158	Webb <i>et al.</i> (2014)
GeoPT-35	0.023	3.255	<u>0.083</u>	<u>1.49</u>	1	Webb <i>et al.</i> (2014b)
GeoPT-36	0.836	2.86	<u>0.079</u>	<u>1.83</u>	0.41	Webb <i>et al.</i> (2015)
GeoPT-36A	2.12	<u>75.82</u>	<b>1.05</b>	<u>106.6</u>	2.5	Webb <i>et al.</i> (2015b)
GeoPT-37	0.19	1	<b>0.09</b>	0.27	1.8	Webb <i>et al.</i> (2015c)
GeoPT-38	0.424	0.7	0.013	0.079	0.153	Webb <i>et al.</i> (2016)
GeoPT-38A	0.03	0.39	0.1	<u>1.473</u>	0.05	Webb <i>et al.</i> (2016b)
GeoPT-39	0.439	7.1	<b>0.79</b>	<u>0.194</u>	0.8	Webb <i>et al.</i> (2016c)
GeoPT-39A	0.4	<b>22.94</b>	<b>1.086</b>	<b>2.8</b>	1.02	Webb <i>et al.</i> (2016d)
GeoPT-40	0.085	<b>11.75</b>	<u>0.3</u>	<b>0.9</b>	0.784	Webb <i>et al.</i> (2017)
GeoPT-41	0.048	1.35	0.04	0.858	0.801	Webb <i>et al.</i> (2017b)

Assigned values in bold type; Provisional values in underlined italic type; Median values in Roman type.







