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RESEARCH

Determination of Ga, Ge, Mo, Ag, Cd, In, Sn, Sb, W, Tl and Bi in USGS Whole-Rock Reference Materials by Standard Addition ICP-MS

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A procedure for determining a wide range of chalcophile and siderophile elements in typical crustal rocks using standard addition and ICP-SFMS (inductively coupled plasma sector field mass spectrometry) is presented. New results for Ga, Ge, Mo, Ag, Cd, In, Sn, Sb, W, Tl and Bi abundances in USGS whole-rock reference materials AGV-2, BHVO-1, BIR-1, G-2, GSP-1 and W-2 are reported using this analytical procedure. Intermediate precision of means based on multiple dissolved aliquots of each USGS reference material was 10% RSD or better for Ga, Ge, In and Sn in all, and similarly good for Ag, Cd, Sb, Tl and Bi in most reference materials. Poorer intermediate precision of Mo and W measurements in several reference materials is probably due to higher analytical blanks on these elements and powder heterogeneity due to a sulfide-related nugget effect in the specific case of Mo in GSP-1. Results for all elements fell within the range of available published data with the exception of Ag, which yielded systematically higher concentrations than found in the literature for five of the six reference materials, likely reflecting interference from unresolved polyatomic species.

Keywords: siderophile elements, chalcophile elements, trace elements, reference material data, recommended value, standard additions, inductively coupled plasma-mass spectrometry.

Une procédure analytique pour déterminer un large éventail d'éléments chalcophiles et sidérophiles dans des roches typiques de la croûte en utilisant l'ajout d'un standard et un ICP-SFMS est présentée. Des résultats nouveaux pour les abondances du Ga, Ge, Mo, Ag, Cd, In, Sn, Sb, W, Tl et du Bi sur roches totales dans les matériaux de référence USGS AGV-2, BHVO-1, BIR-1, G-2, du GSP-1 et W-2 obtenus en utilisant cette procédure analytique sont présentés. La précision intermédiaire sur la moyenne basée sur l'analyse de plusieurs aliquotes dissous de chaque matériel de référence USGS était de 10% (1 RSD) voire meilleure pour Ga, Ge, In et Sn, et aussi bonne pour Ag, Cd, Sb, Tl et Bi dans la plupart des matériaux de référence. Des précisions intermédiaires plus basses pour les mesures de Mo et W dans plusieurs matériaux de référence sont probablement dues à des blancs analytiques plus élevés pour ces éléments et à l'hétérogénéité de la poudre dans le cas spécifique du Mo dans GSP-1 en relation avec un effet de pépite lié aux sulfures. Les résultats pour tous les éléments sont dans la fourchette des données publiées disponibles à l'exception de ceux pour Ag, qui correspondent systématiquement à des concentrations plus élevées que celles de la littérature pour cinq des six matériaux de référence, reflétant probablement des interférences provenant d'espèces polyatomiques non résolues.

Mots-clés : éléments sidérophiles, éléments chalcophiles, éléments traces, données de matériaux de référence, valeur recommandée, ajouts de standard, spectrométrie de masse à source plasma.

Inductively coupled plasma-mass spectrometry (ICP-MS) trace element analysis of geological materials commonly relies on the use of whole-rock geological reference materials as calibrators, but small uncertainties on the elements of interest in the reference materials is a prerequisite to accurate analysis of samples. Several USGS whole-rock reference materials have been thoroughly characterised for the abundances of elements of common

petrological interest such as the rare earth elements. For example, the GeoReM database (http://georem.mpch-mainz.gwdg.de; accessed 08/2014) contains 162 individual values for La in BHVO-1 and the relative standard deviation of the mean is less than 4%. In contrast, many other elements, particularly chalcophile and siderophile elements, are poorly constrained in these reference materials, either due to a small number of published values and/or large differences in published values. For example, only four values for In have been published for BHVO-1, and the highest and lowest values for Cd for BHVO-1 differ by more than a factor of four.

Chalcophile and siderophile elements play an important role in efforts to understand the Earth's differentiation and crustal evolution, in addition to having economic importance. Many of these elements are 'doubly incompatible' in the silicate Earth, in that they will partition into a metallic phase during core formation and silicate melt phase during mantle melting and crust formation. Consequently, studies of the distribution of chalcophile and siderophile elements in mantle-derived basalts have been used to study core formation and the relationship between the continental crust and mantle (e.g., Newsom and Palme 1984, Sims *et al.* 1990, Jochum *et al.* 1993, Jochum and Hofmann 1997, Yi *et al.* 2000, Arevalo and McDonough 2008, 2010, Righter *et al.* 2010, 2011, Jenner *et al.* 2012). Several of these elements have also been used as tracers in studies of subduction zone processes (e.g., Bali *et al.* 2012, Prytulak *et al.* 2013).

This paper presents a procedure for the determination of eleven poorly characterised chalcophile and siderophile elements (Ga, Ge, Mo, Ag, Cd, In, Sn, Sb, W, Tl and Bi) in typical crustal rocks using standard addition coupled with ICP-SFMS. We report new results for these elements in USGS reference materials AGV-2, BHVO-1, BIR-1, G-2, GSP-1 and W-2 (Table 1). The standard addition approach has the potential to produce concentration data second only to isotope dilution in accuracy because it does not rely on imperfectly characterised calibrators and is resistant to matrix effects (e.g., Ratzlaff 1979, Abbyad *et al.* 2001, Ellison and Thompson 2008). The method entails the analysis of a series of solution aliquots with identical amounts of dissolved sample solution but differing amounts of spike containing the elements of interest. The instrumental responses are then plotted against the concentrations of the spike in the aliquots and regressed (Figure 1). The absolute value of the x-intercept of the regression provides the concentration of the element of interest in the sample (when corrected for dilution).

Methods

Sample decomposition

Sample dissolution methods closely follow those of Zhang *et al.* (2012). Fifty milligram aliquots of the USGS reference materials were dispensed into Teflon® Parr bombs. One millilitre of concentrated quartz-distilled HNO_3 (Sigma–Aldrich®, St. Louis, MO, USA) and 3 ml of concentrated Teflon-distilled HF (BDH Aristar®) were added to the bombs, which were then sealed and placed in an oven at 180 °C for at least 4 d. Bombs were then opened and the acids were evaporated on a hot plate. Two ml of concentrated HNO_3 were added to the dry salts and evaporated. One millilitre of concentrated HNO_3 and 2 ml of Milli-Q® (18 $M\Omega$) were then added to the salts, and the bombs were sealed and placed in an oven overnight at 150 °C. The sample solutions were then transferred to centrifuge capsules and diluted to a total of 15 ml with 2% HNO_3 plus a trace of HF. These solutions will be referred to as the *master solutions* below.

Standard addition preparation

Due to the potential for interference from both the elements of interest (e.g., ^{115}Sn on ^{115}In) and their polyatomic products (e.g., $^{95}Mo^{16}O$ on ^{111}Cd) and the large difference in the expected mass fractions of different analytes, two separate mixed standard addition spikes were

Table 1.
Summary of reference materials analysed in this study

| Reference material	Lithology	Location	References
AGV-2	Andesite	Guano Valley, OR, USA	http://crustal.usgs.gov/geochemical_reference_standards/andesite2.html
BHVO-1	Basalt	Kilauea Caldera, HI, USA	Flanagan *et al.* (1976)
BIR-1	Basalt/dolerite	Iceland	Flanagan (1984)
G-2	Granodiorite	Bradford, RI, USA	Flanagan (1967)
GSP-1	Granodiorite	Silver Plume, CO, USA	Flanagan (1967)
W-2	Diabase	Centreville, VA, USA	Flanagan (1984)
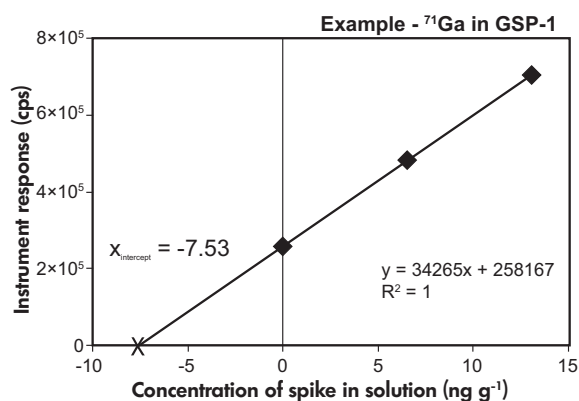
Figure 1. Example of standard addition analysis for ^{71}Ga in GSP-1, showing counts per second (in medium resolution) versus the concentration of Ga added from the spike. The absolute value of the x-intercept is divided by the dilution factor in order to calculate the natural concentration of the Ga in the sample.

Table 2.
Final concentrations of elements in the spikes

Element	Concentration (ng g^{-1})
Spike A	
Ga	130
Ge	12.0
Mo	8.96
Sn	17.7
W	8.90
Spike B	
Ag	0.58
Cd	0.577
In	0.487
Sb	1.98
Tl	0.974
Bi	0.974

produced. Spike A contained Ga, Ge, Sn, Mo and W and Spike B contained Ag, Cd, In, Sb, Tl and Bi. Spikes were made from Alfa Aesar Specpure® and SPEX Certiprep Claritas® pure single element solutions, which were combined in proportions that are typical of crustal rocks. These spike solutions were then diluted so that the element concentrations were roughly double those of the USGS reference materials. Final concentrations of elements in the spikes are given in Table 2.

For each dissolved USGS reference material, multiple solution aliquots were prepared for analysis. All aliquots were prepared gravimetrically. The first solution contained 1 g of master solution and 1 g of a purified Rh solution

Table 3.
Mean concentrations of the analytes of interest in the blank solutions from different analytical sessions

Element	Mean concentration in total analytical blank solutions (pg g^{-1})
Ga	2
Ge	5
Mo	13
Ag	0.8
Cd	1
In	0.4
Sn	12
Sb	1
W	11
Tl	0.1
Bi	3

($\sim$ 50 ng g^{-1} Rh), which was used as an internal standard for drift correction. The second solution contained 1 g of master solution, 1 g of Rh solution and 0.5 g of spike A. The third solution contained 1 g of master solution, 1 g of Rh and 1 g of spike A. All aliquots were then diluted to a total of 10 g with 2% HNO$_3$. A separate group of analogous aliquots was prepared with spike B. A total analytical blank was also prepared, containing the Rh solution. The mean concentrations (in picograms per gram) of the analytes of interest in the blank solutions from different analytical sessions are given in Table 3.

Table 4.
Instrumental operating parameters for the Thermo-Finnigan Element2 HR-ICP-MS

RF power	1350 W
HV	10 kV
Cool gas flow rate	16 l min^{-1} Ar
Auxiliary gas flow rate	1.05 l min^{-1} Ar
Sample gas flow rate	0.9 l min^{-1} Ar
UO$^+$/U$^+$	0.8–0.6%
Nebuliser	Microflow PFA
Spray chamber	Apex IR desolvation system
Torch	Quartz glass torch
Sample uptake rate	0.05 ml min^{-1}
Sample cone	Aluminium, 1.0 mm aperture
Skimmer cone	Aluminium, 0.5 mm aperture
Detector mode	Dual
Dwell time/mass	Variable (10–30 ms)
Scan type	Electronic sweep through selected masses, 10 samples per peak in 120% mass window for low 20 per peak in 125% mass window for medium resolution
Mass resolution	Low (300) and medium (4000)
Isotopes	^{69}Ga, ^{71}Ga, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{95}Mo, ^{97}Mo, ^{98}Mo, ^{107}Ag, ^{109}Ag, ^{111}Cd, ^{114}Cd, ^{115}In, ^{117}Sn, ^{118}Sn, ^{119}Sn, ^{121}Sb, ^{123}Sb, ^{181}W, ^{183}W, ^{184}W, ^{203}Tl, ^{205}Tl, ^{209}Bi

ICP-MS analysis

Samples were analysed on a Thermo-Finnigan Element2 inductively coupled plasma sector field mass spectrometer (ICP-SFMS) with solutions being introduced using an ESI Apex desolvation system. Operating parameters are given in Table 4. The instrument was tuned to simultaneously maximise sensitivity and hold oxide production to 0.6–0.8% for $^{238}U^{16}O/^{238}U$. Multiple isotopes of each element (with the exception of mono-isotopic Bi) were determined in both low ($M/\Delta M = 300$) and medium mass resolution ($M/\Delta M = 4000$) modes, the latter of which was able to filter out many potentially problematic oxide and argide interferences. The values reported in this paper are for ^{109}Ag, ^{111}Cd, ^{121}Sb, ^{205}Tl and ^{209}Bi in low resolution and ^{71}Ga, ^{74}Ge, ^{95}Mo, ^{115}In, ^{117}Sn and ^{183}W in medium resolution. Due to the larger signal size and no difference in the determined value, low-resolution concentration data for Ag, Cd, Sb, Tl and Bi are reported because they yielded greater precision than the medium resolution analyses. For In measurements, ^{117}Sn was used to correct for interference of ^{115}Sn on ^{115}In.

Results

A graphic example of the standard addition approach is shown in Figure 1. Concentration of the element of interest is derived from the x-intercept of a York regression (York 1966) through results for spiked and unspiked aliquots of a given test portion. Mean values for the elements of interest are shown in Table 5 with concentrations given in µg g^{-1}. These means were derived from standard addition analyses of separately dissolved aliquots of the reference materials conducted over the course of a year, and n is the number of dissolved test portions (with associated spiked and unspiked aliquots) for which results were used to calculate the means. Intermediate precision and comparison with existing GeoReM values are shown in Figures 2 and 3.

Gallium

All six reference materials gave intermediate precision for Ga ranging from 2 to 7% relative standard deviation (RSD, 1s). Mean results for Ga in all reference materials fell within one standard deviation of the mean value found in the GeoReM database.

Germanium

All six reference materials show intermediate precision for Ge ranging from 3 to 6% RSD. Mean results for AGV-2, BHVO-1, BIR-1 and W-2 fell within one standard deviation

Table 5.
Standard addition ICP-SFMS results for six USGS reference materials*

	AGV-2			BHVO-1			BIR-1			G-2			GSP-1			W-2		
	Mean	% RSD	n	Mean	% RSD	n	Mean	% RSD	n	Mean	% RSD	n	Mean	% RSD	n	Mean	% RSD	n
Ga	20.2	2.0	6	21.8	5.5	7	15.1	2.4	5	22.9	6.9	6	21.6	3.6	8	17.5	4.5	7
Ge	1.15	3.4	6	1.61	5.8	8	1.45	4.1	5	0.960	3.1	6	1.23	4.4	9	1.55	4.1	8
Mo	1.93	2.4	6	1.1	11.3	8	0.12	18.4	5	0.37	15.4	6	0.45	38.3	9	0.464	8.4	8
Ag	0.174	3.9	6	0.202	6.5	6	0.0378	9.0	5	0.118	6.6	6	0.29	12.9	6	0.106	3.6	7
Cd	0.136	3.6	6	0.140	7.1	6	0.0947	2.4	5	0.0843	4.9	6	0.191	11.8	6	0.0987	7.0	7
In	0.0453	2.0	6	0.0886	3.2	6	0.0559	3.9	5	0.0277	0.7	6	0.0448	1.6	6	0.0585	5.9	7
Sn	1.90	3.2	6	1.91	3.9	7	0.700	3.1	5	1.71	5.2	6	7.11	5.6	8	1.72	3.8	7
Sb	0.579	8.0	6	0.195	5.3	6	0.634	4.6	5	0.069	10.8	6	4.6	10.0	6	1.03	7.5	7
W	0.489	4.2	6	0.24	12.2	8	0.059	18.9	5	0.18	14.2	6	0.31	11.5	9	0.273	7.0	8
Tl	0.276	5.6	6	0.0420	2.7	6	0.0014	10.5	5	0.890	2.5	6	1.3	14.1	6	0.0918	4.3	7
Bi	0.0510	9.0	6	0.0119	14.4	5	0.00606	5.5	4	0.0389	5.1	6	0.0329	3.5	5	0.0287	9.4	7

n = number of dissolved test portions.
* Values in bold type are recommended new working values. All mean values in µg g^{-1}.
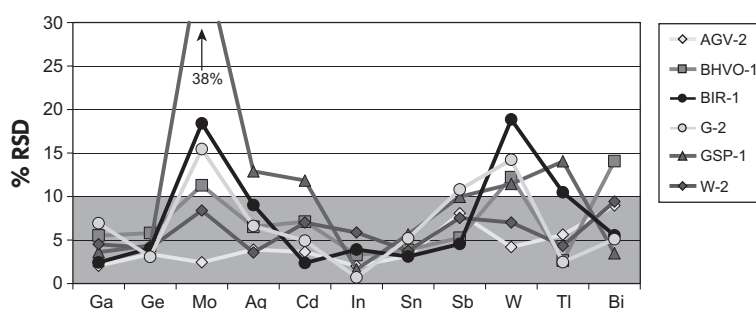
Figure 2. Intermediate precision of measured elements in six USGS reference materials. Intermediate precision is defined as % relative standard deviation (1s) for analysis of multiple separately dissolved powder aliquots.

of the mean GeoReM value, but the mean Ge concentration for G-2 determined here is slightly below the GeoReM value. For Ge in GSP-1, there are little grounds for comparison, as only one published value exists (the compiled value in Govindaraju 1994).

Molybdenum

Intermediate precision of Mo was highly variable amongst the six reference materials, ranging from 2% RSD in the case of AGV-2 to 38% in the case of GSP-1. Mean results fell within one standard deviation of the GeoReM means for all reference materials except GSP-1, although the large % RSD of our GSP-1 mean overlaps with the GeoReM range.

Silver

Intermediate precision for Ag was variable amongst the reference materials, ranging from 4% RSD in AGV-2 and W-2 to 13% in GSP-1. Although few published values exist for Ag in the reference materials, our mean values are significantly beyond one standard deviation of the GeoReM means (or sole value in the case of GSP-1 from Govindaraju 1994) for all reference materials except BIR-1.

Cadmium

Intermediate precision of Cd was variable amongst the reference materials, ranging from 2% RSD in BIR-1 to 12% in GSP-1. Mean values fell within one standard deviation of the GeoReM means for all reference materials except GSP-1, for which only one published value exists (Govindaraju 1994).

Indium

Intermediate precision for In was the best of any element, ranging from 1 to 6% RSD. Means fell within one standard deviation of the GeoReM means for all RMs except AGV-2

and GSP-1, each of which has only one published value (Govindaraju 1994).

Tin

Intermediate precision for Sn in all reference materials ranged from 3 to 6% RSD. Means fell within one standard deviation of the GeoReM means, with the exception of GSP-1, for which only one published value exists (Govindaraju 1994).

Antimony

Intermediate precision for Sb ranged from 5 to 11% RSD in the reference materials. Mean values in AGV-2 and BHVO-1 fell within one standard deviation of the mean GeoReM values, but our mean BIR-1, GSP-1 and W-2 values are higher. Only one published value exists for G-2 (Govindaraju 1994), and our mean value is quite similar to this.

Tungsten

Intermediate precision of W was highly variable amongst the six reference materials, ranging from 4% RSD in the case of AGV-2 to 19% in the case of BIR-1. Means fell within one standard deviation of the GeoReM means.

Thallium

Intermediate precision of Tl was variable in the reference materials, ranging from 3% RSD in BHVO-1 and G-2 to 14% in GSP-1. Means fell within one standard deviation of the GeoReM means, with the exception of GSP-1, for which only one published value exists (Govindaraju 1994).

Bismuth

Intermediate precision of Bi was variable in the reference materials, ranging from 4% RSD in GSP-1 to 14% in BHVO-
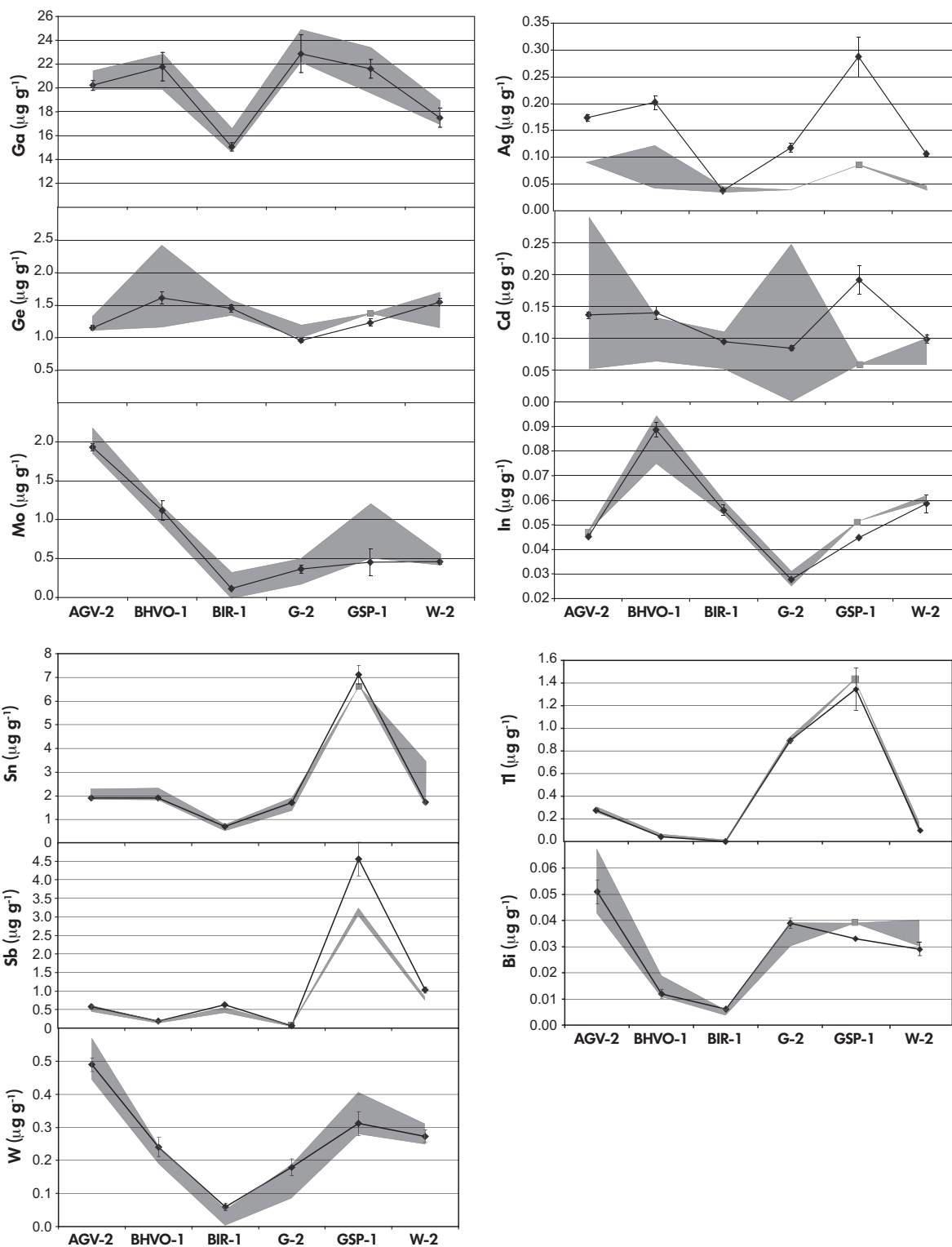
Figure 3. Mean values (diamonds) with one standard deviation error bars (which are often smaller than symbols) for measured elements in each RM compared with the mean and one standard deviation (indicated by the shaded envelope) of the values found in the GeoReM database. A few of the individual values reported in GeoReM for a given element in a given reference material were filtered out in cases where they fall far outside the range of all other values. (For example, a value of 63 μg g^{-1} for Ga in BHVO-1 was excluded since all other published values fall between 18 and 26 μg g^{-1}). Several elements in RMs have only one published value, indicated by square symbols.

1. Means fell within one standard deviation of the GeoReM means, with the exception of GSP-1, for which only one published value exists (Govindaraju 1994).

Discussion

Figures 2 and 3 show that acceptable intermediate precision (< 10% RSD) was obtained within the published range for Ga, Ge, In and Sn in all six reference materials, for most reference materials in the case of Cd, Sb, Tl and Bi, and for two reference materials in the case of Mo and W. The more problematic elements and RMs are discussed in detail below.

Poor intermediate precision of Tl, Sb, Mo, Ag and Cd in GSP-1

Our results yielded unsatisfactory (i.e., > 10% RSD) intermediate precision for more elements in GSP-1 than any other reference material. The causes of the poor intermediate precision of Tl and Sb are easily attributable to the unusually high concentration of these elements compared with the other reference materials, which resulted in under-spiking. The two spikes used in this study were designed for use on a broad range of crustal rocks so elements were added in concentrations and proportions typical of the average continental crust. When added to GSP-1, the high intrinsic levels of Tl and Sb resulted in much smaller increases in signal strength for the spiked aliquots, leading to less leverage on the linear regressions, poorer measurement repeatability ('internal error') on the individual concentration determinations, and the potential for greater scatter in the calculated means.

Determinations of Mo in GSP-1 yielded unusually poor intermediate precision (38% RSD), and the causes are less clear. One possible explanation is a nugget effect, wherein one mineral with low modal abundance but high concentration of an element exerts overwhelming leverage on that element's budget in the rock, leading to powder heterogeneity at small test portion masses, such as the 0.05 g used here. Molybdenum exhibits chalcophile (in addition to siderophile and lithophile) characteristics and may be expected to concentrate more heavily in sulfides, when present, in igneous rocks. The granodiorite material from which GSP-1 was prepared was reported to contain pyrite (Flanagan 1967), which may be a reservoir for Mo. More importantly, however, molybdenite (MoS_2) has also been reported in the Silver Plume pluton from which the RM was derived (Neuerburg *et al.* 1974). If a molybdenite nugget effect is the cause of the poor intermediate precision of Mo, it may also be responsible for the poor (albeit less severe)

intermediate precision of Ag and Cd, which are also chalcophile elements.

Poor intermediate precision of Mo and W in several RMs

The intermediate precision of Mo and W in BHVO-1, BIR-1, G-2 and GSP-1 was generally inferior (10–20%, with the exception of the already discussed Mo in GSP-1) to other elements in these reference materials, and all elements in the other two reference materials. The probable cause of this is the higher total analytical blank (Table 3) for Mo and W compared with the other elements (except Sn), resulting in a lower analyte/background ratio. BIR-1, which gave the poorest intermediate precision, is especially susceptible to this effect because it contains roughly four times less W than the other RMs and also has the least Mo. Consequently, the analyte/background ratio was low in the unspiked aliquots, by about a factor of two in the case of W and five in the case of Mo, magnifying the effect of any minor variability in the blank contribution between the blank solution and sample solution. In contrast, the analyte/background ratio was typically one to several orders of magnitude for the other elements of interest. These results, in addition to the possible Mo nugget effect documented above in GSP-1, suggest that 50 mg may not be an appropriate test portion size to produce precise results for Mo and W. Larger test portions may be needed.

Anomalously high Ag concentrations

Evaluating the potential accuracy of Ag determinations is difficult because little published data exist for this element, and in the case of AGV-2, G-2 and GSP-1, only one published quantitative value exists. Nevertheless, the values determined here for Ag are systematically higher than the highest published value by a factor of 2–4 for all of the reference materials but BIR-1. We attribute this to polyatomic interfering species. Oxides, hydroxides, and fluorides of Y, Zr and Nb can cause interferences on the two isotopes of silver that are unresolvable even in medium resolution mode, and although the instrument was tuned to a low oxide production ratio (0.6–0.8% for $^{238}U^{16}O/^{238}U$), the low (sub $\mu g\ g^{-1}$) abundance of Ag in all reference materials increases the likelihood that these species will influence the Ag results.

We tested this hypothesis by spiking an aliquot of G-2 with single element solutions of Zr and Nb at levels that increased the effective concentrations of these elements by about five and twenty-five times, respectively, and observing the effect on count rates of ^{109}Ag. In both cases, the count rates of ^{109}Ag increased significantly. The Nb addition had

a much larger effect on ^{109}Ag counts (20000 cps increase for every 1 ng g^{-1} increase in Nb concentration) than Zr (400 cps for every 1 ng g^{-1} increase in Zr concentration). These results indicate that the Ag concentration data has been compromised by interference from ^{93}Nb^{16}O and, to a lesser extent, either ^{91}Zr^{18}O, ^{92}Zr^{16}O^{1}H, ^{90}Zr^{18}O^{1}H, or ^{90}Zr^{19}F. BIR-1 appears to have been unaffected by these interferences because it has more than an order of magnitude less Nb and Zr than the other reference materials.

Conclusions

We have developed a procedure for the determination of select chalcophile and siderophile elements in typical crustal rocks using ICP-SFMS and standard addition. New values for the elements Ga, Ge, Mo, Cd, In, Sn, Sb, W, Tl and Bi in six USGS whole-rock reference materials are presented. Poor intermediate precision of Mo and Cd data in the GSP-1 reference material may be due to powder heterogeneity at the test size used due to a sulfide nugget effect, whereas > 10% RSD for Mo and W in several RMs is attributable to a higher analytical blank for these elements. Silver was also measured but results appear to be compromised by polyatomic interferences.

Acknowledgements

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