Method of Data Reduction and Uncertainty Estimation for Platinum-Group Element Data Using Inductively Coupled Plasma-Mass Spectrometry

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A data reduction method is described for determining platinum-group element (PGE) abundances by inductively coupled plasma-mass spectrometry (ICP-MS) using external calibration or the method of standard addition. Gravimetric measurement of volumes, the analysis of reference materials and the use of procedural blanks were all used to minimise systematic errors. Internal standards were used to correct for instrument drift. A linear least squares regression model was used to calculate concentrations from drift-corrected counts per second (cps). Furthermore, mathematical manipulations also contribute to the uncertainty estimates of a procedure. Typical uncertainty estimate calculations for ICP-MS data manipulations involve: (1) Carrying standard deviations from the raw cps through the data reduction or (2) calculating a standard deviation from multiple final concentration calculations. It is demonstrated that method 2 may underestimate the uncertainty estimate of the calculated data. Methods 1 and 2 do not typically include an uncertainty estimate component from a regression model. As such models contribute to the uncertainty estimates affecting the calculated data, an uncertainty estimate component from the regression must be included in any final error calculations. Confidence intervals are used to account for uncertainty estimates from the regression model. These confidence intervals are simpler to calculate than uncertainty estimates from method 1, for example. The data reduction and uncertainty estimation method described here addresses problems of reporting PGE data from an article in the literature and addresses both precision and accuracy. The method can be applied to any analytical technique where drift corrections or regression models are used.

Cet article présente une méthode de traitement des données permettant de déterminer les concentrations des Eléments de la Mine du Platine (PGE) analysés par ICP-MS avec calibration externe et addition de standard interne. La mesure des volumes par gravimétrie, l'analyse de matériaux de référence et de blancs de procédure ont été utilisées pour minimiser les erreurs systématiques. Les standards internes ont été utilisés pour corriger les signaux mesurés (coups par second, cps) de la dérive instrumentale. De plus, les calculs mathématiques eux-mêmes peuvent contribuer à l'estimation de l'incertitude sur une procédure. Typiquement, un calcul des incertitudes estimées liées à l'analyse par ICP-MS repose: (1) Sur la propagation d'erreur lors de la transformation des nombres de coups bruts par seconde au résultat final; (2) Sur le calcul d'une déviation standard pour plusieurs calculs de concentrations finales. Il a été démontré que dans cette phase, on peut sous-estimer l'incertitude sur les valeurs calculées. Les méthodes (1) et (2) ne prennent généralement pas en compte un coefficient d'erreur estimée donné par un modèle de régression. Etant donné que de tels modèles participent aux estimations des incertitudes affectant les données calculées, un coefficient d'erreur estimée provenant de la régression doit être inclus dans tout calcul d'erreur finale. Les intervalles de confiance sont utilisés pour prendre en compte les incertitudes estimées du modèle de régression. Ces intervalles de confiance sont plus simples à calculer que les incertitudes estimées avec la méthode 1, par exemple. Le traitement des données et la méthode d'estimation des incertitudes décrite ici posent le problème de l'utilisation de données de la littérature sur les PGE et celui de leur précision et de leur justesse. La méthode peut être appliquée à toute analytique technique où des corrections de dérive et des modèles de régression sont utilisés.

Calculation of uncertainty of measurement is a critical component of any analytical procedure. Uncertainty of measurement is the result of the evaluation aimed at characterizing the range within which the true value is estimated to lie, generally with a given confidence (Potts 1997 and references therein). This generally takes the form of a confidence interval and has implications for both the precision (the closeness of agreement between independent test results) and the accuracy (the closeness of the measured value to the true value) of the data. Uncertainty of measurement calculations should incorporate all significant random error components, both from the procedure and subsequent mathematical manipulation, in order to allow the reader the opportunity to readily assess the quality of the data. Random error is the result of a measurement minus the mean that would result from an infinite number of measurements carried out under the same conditions (Potts 1997 and references therein). In practice, random errors are those errors that result from small changes in variables such as temperature or mass of reagent; these errors vary unpredictably between measurements of different aliquots. Systematic error is equal to the error minus the random error (Potts 1997). In practice, systematic errors are attributable to instrumentation or the method used; these errors do not vary between repeated measurements and cannot be fully known. Systematic errors can be minimised through gravimetric measurement of volumes, procedural blanks and the use of reference materials of well-constrained composition.

McDonald (1998) pointed out that much of the ever-increasing platinum-group element (PGE: Ru, Rh, Pd, Os, Ir and Pt) data now available in the literature lack adequate uncertainty estimates. Such uncertainty estimates are crucial since the PGE data, often in the form of PGE element/element ratios or normalized patterns, are being used to interpret fundamental geochemical/geological processes. Without adequate uncertainty estimates, it is impossible for the reader to determine the validity of such interpretations. This paper addresses the following points made by McDonald (1998): (1) Inadequate sampling protocols addressing the heterogeneous distribution of PGEs in geological samples (i.e., the "nugget effect"); (2) Lack of uncertainty estimates for PGE element/element ratios or PGE-normalized patterns and the necessity for these uncertainty estimates to be reported in order to validate geochemical interpretations from ratio or normalized data; (3) Reproducibility of results and the problems with using indirect methods to estimate uncertainty. A method for calculating uncertainty estimates for PGE data obtained using ICP-MS is proposed and demonstrated. All formulae are based on statistical concepts presented in Strobel and Heineman (1989), Neter et al. (1990) and Skoog et al. (1996).

Previous work

Sampling protocols

It has been well documented that PGEs occur heterogeneously in most geological samples (Cabri 1976, 1981, Allegré and Luck 1980, Mitchell and Keays 1981, Hall and Bonham-Carter 1988, Hall and Pelchat 1994). Therefore, great care has to be taken in the sampling protocol, so that obtained PGE abundances are representative of the whole rock composition. In the past, the problem of representative analyses has been solved commonly by taking large amounts of test portion (10-100 g) for analysis in order to average out the PGE heterogeneities of the sample (Hall and Bonham-Carter 1988, Jarvis et al. 1992). However, with the ever-increasing sophistication of analytical instrumentation, the point has been reached where the amount of sample must be reduced in order to reduce the quantity of reagents involved in sample preparation, thus lowering blank levels, so that advantage can be taken of lower instrument detection limits. Therefore, a sampling protocol that uses small sample sizes (≤ 250 mg), but still accounts for potential heterogeneities in the sample is necessary. Such a sampling protocol for PGE analyses of geological samples (with subsequent lower blank levels) has been developed and described by Ely et al. (1999). This protocol involves rolling the sample powder on a rock tumbler for 24 hours to rehomogenise the powder, since the PGEs have a tendency to settle out of the sample powder over time. A 1-20 g aliquot of this rolled sample powder is then further rehomogenised in an alumina ball mill for 15-30 minutes. A 250 mg aliquot (or less) is taken

from this rehomogenised sample powder and is analysed. Several authors have correctly pointed out that some samples are naturally more heterogeneous than others, based on PGE grain size and type of rock (McDonald 1998, Plessen and Erzinger 1998, Pearson and Woodland 2000). However, our rehomogenisation protocol minimises the effects of this inherent heterogeneity on analytical reproducibility as much as is possible. This is demonstrated by looking at coefficients of variation [=100*(standard deviation/mean)] for various types of samples. For the reference material UMT-1, which is produced from Ni-Cu ultramafic ore mine tailings composed of mostly silicates with minor ore minerals, twenty two analyses of 250 mg test portions produced coefficients of variation from 2-3% for the PGE concentration range of 8-129 ng g^{-1}. However, sixteen analyses of roadside soils from northern Indiana, which are much more heterogeneous in nature than UMT-1 (Ely *et al.* 2001), produced coefficients of variation in the range 10-26% using the rehomogenisation protocol with 250 mg test portions with a lower PGE concentration range of 0.09-73 ng g^{-1}. The increased coefficients of variation for the soils are due to both the larger original heterogeneity of the samples and the lower concentration range. It is evident that the concentration range of the samples, and its proximity to the detection limits, is as large a factor in the quality of the uncertainty estimate as the heterogeneity of the sample for the same sample size, instrumentation and methodology.

Ratios, reproducibility and estimates of precision

Calculating PGE element/element ratios magnifies the uncertainty estimate on the given elemental abundances. Therefore, having a firm understanding of the individual elemental uncertainty estimates allows simple assessment of calculated ratios used in petrogenetic modelling, and thus, on the validity of geochemical interpretations based on these ratios or patterns.

McDonald (1998) noted that the analysis of a single test portion does not measure all possible sources of error involved, especially sample heterogeneity. Ideally, analysis of replicate test portions is needed to characterise sample heterogeneity and to give an estimate of precision. McDonald (1998) concluded that estimating precision using indirect methods has serious limitations. He demonstrated, for example, that counting statistics for INAA data grossly underestimate errors for Rh, Ir and Au. Analyses of reference materials

can only be used as an indirect *estimate* of precision for sample (i.e., unknown) PGE abundances if both the reference material and the sample are matched in terms of rock type and matrix, and exhibit similar heterogeneities and PGE concentrations. As many well-characterized PGE reference materials are derived from PGE ores, it is difficult to use this method to estimate precision realistically in the majority of geological analyses. Therefore, a direct method that addresses precision and is applicable to a wide variety of samples is necessary.

An important point not mentioned by McDonald (1998) is that uncertainty is also produced by the mathematical manipulation of the raw data to compute final concentrations. This uncertainty is not included in the final concentrations when using indirect methods, such as counting statistics (INAA) or relative standard deviations (RSD's), but must be included to give the reader the most comprehensive uncertainty estimate for the final concentrations. Estimation of uncertainty produced by the mathematical manipulation of raw data can be calculated by three methods. Method 1 moves the standard deviation of the raw cps (counts per second from multiple powder replicates) through the data reduction using appropriate mathematical formulae (e.g., taking the square root of the sum of squares of the standard deviations when adding two values together to obtain the new standard deviation, etc.). For a complete discussion of these formulae, see Skoog *et al.* (1996). Method 1 is illustrated in Figure 1a for external calibration and in Figure 1d for standard addition. Method 2 calculates the concentration of each powder replicate separately and simply determines a standard deviation from these multiple concentrations. This is illustrated in Figure 1b for external calibration and in Figure 1e for standard addition. Method 3 calculates uncertainty estimates from the regression model, which is illustrated in Figure 1c for external calibration and in Figure 1f for standard addition.

Method

The method is described using a procedure to determine PGE concentrations of a basalt, but can be applied to any PGE-bearing sample. Data reduction can be performed relatively easily using spreadsheet software. All solutions were measured gravimetrically into a test tube to eliminate systematic errors associated with pipetting. Actual test tube concentrations of elements in the calibration standards (for external
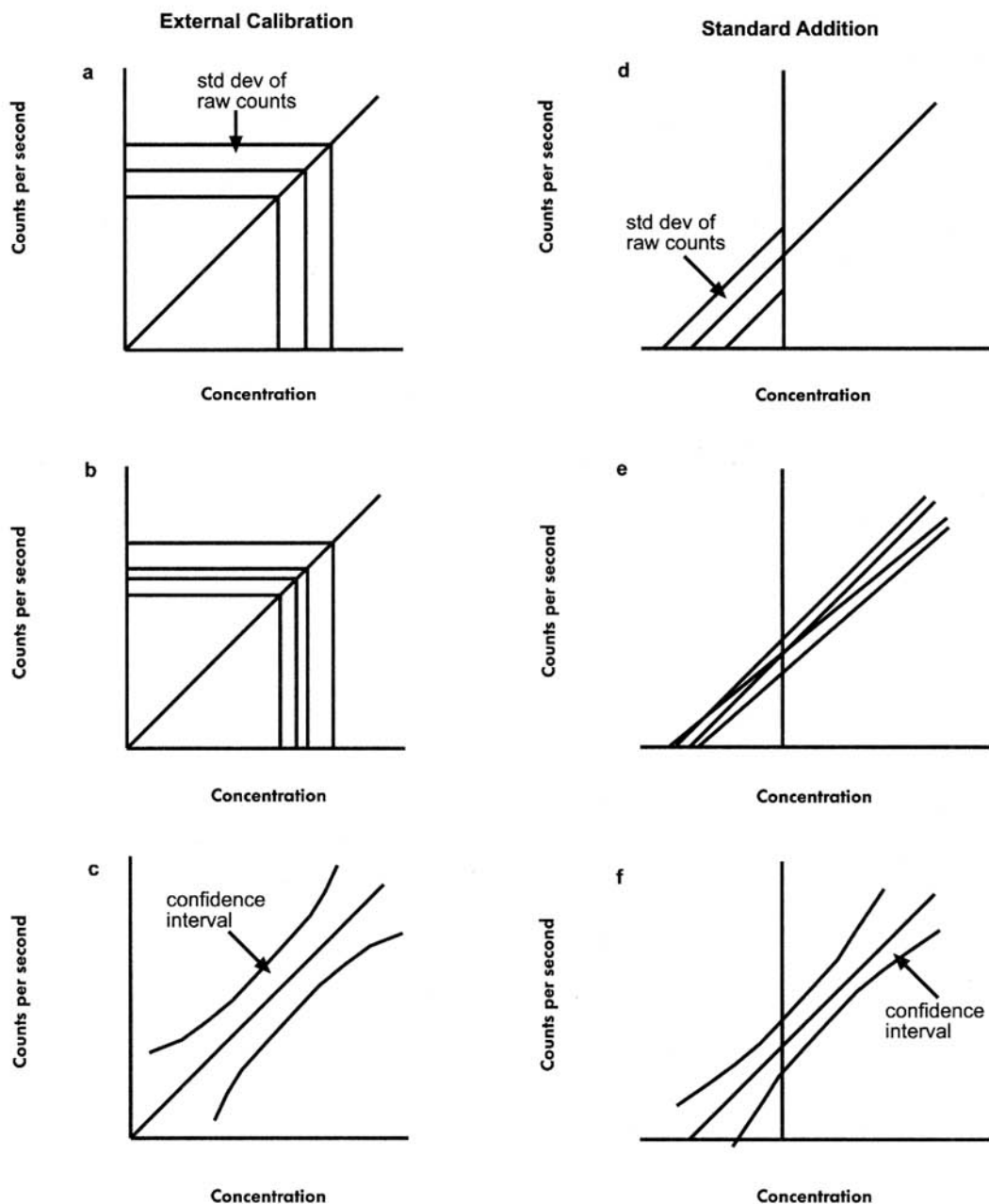
Figure 1. Graphical representation of uncertainty estimation methods. (a) external calibration data using the uncertainty estimation method of carrying the standard deviations of the raw data through the calculations; (b) external calibration data using the uncertainty estimation method of calculating each powder replicate concentration separately and determining a standard deviation from the final concentrations; (c) external calibration data using the uncertainty estimation method of calculating uncertainty estimates from a regression model; (d) standard addition data using the uncertainty estimation method of carrying the standard deviations of the raw data through the calculations; (e) standard addition data using the uncertainty estimation method of calculating each powder replicate concentration separately and determining a standard deviation from the final concentrations; (f) standard addition data using the uncertainty estimation method of calculating uncertainty estimates from a regression model.

calibration) and spike concentrations (for standard addition) were calculated by equation (1):

$$\text{actual concentration} = \frac{\text{stock concentration} \times \text{weight stock added}}{\text{total weight}} \quad (1)$$

As the stock solutions and internal standards were pipetted into the analyte solution test tube, the weight of added solution was slightly different for each tube. Correction factors (weight of internal standard added/total weight) for this internal standard variability were calculated and the cps were normalized to those of the first solution in the run. The raw cps of the internal standards in each sample, calibration solution and blank were multiplied by these correction factors to produce internal standards of uniform concentration throughout the analytical run.

The raw cps produced for each sample were the mean of six duplicate analyses on the same solution; this method can be adapted to four duplicate analyses and still calculate valid statistical variables. Blank subtraction for the internal standards was not required in this example, because the PGEs had very low background cps (i.e., not statistically different from zero) and because the internal standards were normalized to the first sample in the run. If blank subtraction were necessary, it should be the first function performed on the raw data.

Normalisation of internal standard cps to the first aliquot analysed produced ratios that were used to correct for instrument drift. For drift correction, the atomic masses of the internal standards must encompass the mass range of the "unknown" elements to be quantified and must have drift ratios that change together (i.e., all increase or all decrease from aliquot to aliquot). These ratios were used to correct the raw cps of the elements of interest between each set of internal standards using equation (2):

$$C_c = \frac{C_r (i_u - i_L)}{r_u (w - i_L) + r_L (i_u - w)} \quad (2)$$

where C_c = corrected counts of element of interest; C_r = raw counts of element of interest; w = measured isotopic mass of element of interest; i_u = measured isotopic mass of upper internal standard; i_L = measured isotopic mass of lower internal standard; r_u = drift ratio of upper internal standard; r_L = drift ratio of lower internal standard; and where drift ratio

$$= \frac{\text{internal standard cps in sample}}{\text{internal standard cps in first aliquot analysed}}$$

By bracketing the elements of interest with internal standards that had similar physiochemical properties, mass dependent drift could be corrected by the linear interpolation given by equation (2). Barwick et al. (1999) showed that in ICP-MS procedures, the two factors that contributed the most to the uncertainty estimate budget were method precision and instrument drift. The method of drift correction using internal standards effectively minimised uncertainty due to instrument drift.

After correcting for drift, the actual concentrations (calculated gravimetrically) of the elements of interest in the calibration samples (external calibration) or the actual spike concentrations (standard addition) were used with the corrected cps of those elements to define a calibration curve using a linear least squares regression model given by equation (3):

$$Y_h = \beta_o + \beta_1 X_h \quad (3)$$

where Y_h is the concentration of element h; X_h is the corrected cps of element h, and β_o and β_1 are calculated parameters. β_o and β_1 are calculated using equations (4) and (5):

$$\beta_1 = \frac{\sum X_i Y_i - \dfrac{\sum X_i \sum Y_i}{n}}{\sum X_i^2 - \dfrac{(\sum X_i)^2}{n}} = (n \sum X_i Y_i - \sum X_i \sum Y) \frac{1}{n \sum (X_i - \overline{X})^2} \quad (4)$$

$$\beta_o = \overline{Y} - \beta_1 \overline{X} \quad (5)$$

where , $\overline{X}$, $\overline{Y}$ are the means of the X_i and Y_i data, respectively; n is the number of data points used in the regression.

To calculate β_1, the equation on the right hand side in (4) should be used. In order to minimise rounding errors, either a large number of significant figures (e.g., > 10) should be used or the division operation should be performed last.

Once the regression line was fitted to the calibration sample data, for external calibration the regression model was used to find the concentration Y_h of the sample solution based on the corrected cps X_h in the sample, using equation (3).

For standard addition, the y intercept of the regression line (where the line crosses the y-axis, β_o) is the negative of the unspiked sample concentration for the element of interest.

After unknown sample concentrations were determined using the regression, the concentrations were corrected for the dilution factor (weight of solution/weight of sample) used during sample preparation. That is, the dilution factor multiplied by the sample solution concentration (Y_h) gave the actual (rock) concentrations of the element in the original sample.

Comparison of errors

Every regression model has an uncertainty estimate component that is a function of how well the regression line fits the data. If the regression line were a poor fit, it would result in a large uncertainty estimate component. Methods 1 and 2 make the assumption that there is a negligible uncertainty estimate component associated with the regression model; whether the regression line is a good or a poor fit to the data is not taken into account in the final uncertainty estimate reported. Therefore, the reader has incomplete information and cannot judge the true magnitude of the uncertainty estimates presented with the final data produced by these methods.

While the assumption that the uncertainty estimate component caused by the regression model is negligible may be valid for higher concentrations (i.e., $\mu g\ g^{-1}$ rock concentrations), it is not valid for lower concentrations that approach the detection limits (i.e., low- to sub-ng g^{-1} rock concentrations). At these lower concentrations the uncertainty estimate component of the regression model is as large a factor as the uncertainty estimate component of the raw data. Therefore, it is imperative to include this in the uncertainty estimate reported on the final concentrations, since it allows the reader a more complete evaluation of the total error associated with the data.

Calculating the uncertainty estimate from a regression model involves just two equations (6 and 7, below) that use information already calculated in determining the regression through the calibration data. Method 3 is the most simple, yet the most complete of the three methods, for the uncertainty estimate calculation for the mathematical manipulation of the raw data.

The uncertainty estimate on each value of Y_h (the calculated sample solution concentration) is determined by method 3 from the regression and is usually expressed in the form of a 1-α confidence interval using equation (6):

$$Y_h \pm t\left(1 - \frac{\alpha}{2}; n - 2\right) s\ (Y_h) \qquad (6)$$

where

$$t\left(1 - \frac{\alpha}{2}; n - 2\right)$$

is the t value from a Student's t distribution with n-2 degrees of freedom and $s(Y_h)$ is the calculated standard deviation for the value Y_h, which is calculated using equation (7):

$$s\ (Y_h) = \sqrt{MSE\left[\frac{1}{n} + \frac{(X_h - \overline{X})^2}{\Sigma\ (X_i - \overline{X})^2}\right]} \qquad (7)$$

where MSE (the mean square error)

$$= \frac{\Sigma Y_i^2 - \beta_0\ \Sigma Y_i - \beta_i\ \Sigma X_i Y_i}{n-2}$$

For example, a 95% confidence interval would give an α = 0.05 so

$$t\left(1 - \frac{\alpha}{2}; n - 2\right)$$

would require a t value from the t table of t (0.975; n-2). Also, n-2 degrees of freedom are used because the sample concentration Y_h and the standard deviation $s(Y_h)$ have been estimated, thus reducing n degrees of freedom to n-2.

As the Student's t distribution is dependent on the degree of freedom, increasing the number of calibration samples (external calibration) or the number of aliquots (standard addition) will, in general, decrease (i.e., improve) the size of the confidence interval. Conversely, the size of the confidence interval will increase with increasing distance from the mean of the regression line (i.e., concentrations on the ends of the regression line will have larger uncertainty estimates than concentrations from the middle of the regression line - see Figures 1c and 1f). Therefore, the greatest number of calibration samples that is feasible and that spans the concentration range of interest, should be run to minimise the confidence interval size.

Errors calculated by methods 1, 2, and 3 for a basalt sample (SGB-25 from the Ontong Java Plateau) are presented in Table 1 for external calibration and in Table 2 for standard addition. The concentration data were averaged from multiple analyses (six for external calibration and twenty one for standard addition), but the uncertainty estimates were calculated for

Table 1.
External calibration data for Ontong Java
Plateau basalt SGB-25 from the southwest Pacific

Element	Concentration	Method 1 error	Method 2 error	Method 3 error
[102]Ru	0.33	0.35	0.04	0.72
[103]Rh	bdl	0.37	0.03	0.78
[105]Pd	3.88	0.29	0.05	0.44
[193]Ir	3.88*	0.26	0.14	0.14
[195]Pt	12.3*	0.62	0.55	0.27

Six analyses were used to calculate the concentration data. Errors are calculated for a single representative
analysis by data reduction methods: (1) Carrying standard deviations of raw data through the data reduction;
(2) Calculating each powder replicate concentration separately and determining a standard deviation;
and (3) Error from regression model. All units are ng g^{-1}.   bdl   below detection limit.
*   Note: These concentrations are due to oxide polyatomic interferences of Hf on these elements, which
resulted in the development of the standard addition technique for these samples. See Ely et al. (1999)
for a full discussion.

Table 2.
Standard addition data for Ontong Java
Plateau basalt SGB-25 from the southwest Pacific

Element	Concentration	Method 1 error	Method 2 error	Method 3 error
[102]Ru	0.75	0.83	0.08	0.12
[103]Rh	0.22	0.72	0.05	0.16
[105]Pd	6.44	0.67	0.66	1.22
[191]Ir	0.22	0.14	0.06	0.11
[198]Pt	5.86	1.86	0.58	0.98

Twenty one analyses were used to calculate the concentration values. Errors are calculated for a single
representative analysis by data reduction methods: (1) Carrying standard deviations of raw data through the
data reduction; (2) Calculating each powder replicate concentration separately and determining a standard
deviation; and (3) Error from regression model. All units are ng g^{-1}.

a single representative analysis to demonstrate the differences between the methods. The standard addition concentration data more accurately reflect the true concentrations of SGB-25, because standard addition is less subject to interferences, is overall more precise and has a greater number of analyses relative to external calibration (i.e., better statistics). As seen in both Tables 1 and 2, method 2 generally gives the smallest uncertainty estimates. This is not surprising because this method does not include any uncertainty estimate component from the regression model and only accounts for the variation in the final concentrations. The calculated uncertainty is, therefore, not a true reflection of the total uncertainty.

Method 1 produces smaller uncertainty estimates for Ru, Rh, and Pd in Table 1 (external calibration), but this shows that the regression model in method 3 used to calculate uncertainty estimates was a worse fit, resulting in larger uncertainty estimates than for the regression model used for Ir and Pt. Method 1 does not give the reader any indication of the poor fit of the regression model used to calculate Ru, Rh and Pd.

The fit of the regression model for the standard addition samples in Table 2 is critical since the concentration value is given by the y intercept. For standard addition, the uncertainty estimate component of the regression model is crucial for the magnitude of the uncertainty estimates on the final data. Uncertainty estimates from method 1 are larger than those for method 3 in Table 2 for Ru, Rh, Ir and Pt. This indicates that method 1 would give a false sense of *larger* uncertainty in the final data than is truly there, since method 3 demonstrates that the regression fits for these elements were good. Only Pd gives an uncertainty estimate in method 3 larger than using method 1. Therefore, method 3 includes the uncertainty estimate component from the regression model and, as such, gives a more complete representation of the uncertainty estimates of the final concentrations, which is critical for standard addition data.
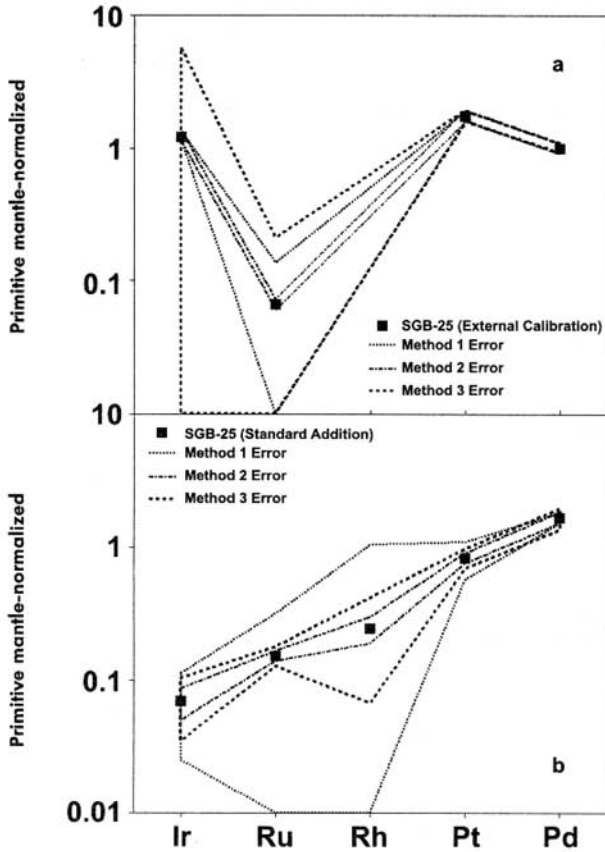
Figure 2. Primitive mantle-normalized PGE patterns for SGB-25, comparing uncertainty estimates from methods 1, 2 and 3. (a) External calibration PGE data with methods 1, 2 and 3 uncertainty estimates shown as fields. Note the exceedingly small (and incomplete) uncertainty estimates produced by method 2. (b) Standard addition PGE data with methods 1, 2 and 3 uncertainty estimates shown as fields. Primitive mantle PGE abundances are from McDonough and Sun (1995).

Summary and conclusions

McDonald (1998) demonstrated the problems inherent in uncertainty estimation in current PGE literature data. Random errors and non-representative analyses due to heterogeneous distribution of PGEs in the sample (i.e., the "nugget effect") can be minimised using the sampling protocol of Ely *et al.* (1999). Existing indirect methods of precision estimation are difficult to apply due to problems in determining how accurately they represent the uncertainty of the data. Direct methods via duplicate analyses provide the best method to estimate uncertainty. However, mathematical

manipulation of the raw data to final concentrations introduces an additional uncertainty component to the data that is often ignored. This uncertainty component becomes more significant at lower concentrations (low- to sub-ng g^{-1}) that approach instrument detection limits.

The data reduction method described here provides a simple way to apply internal standards for drift correction and to use a linear least squares regression model to calculate concentration data produced by the ICP-MS. Ideally, all possible sources of uncertainty should be included in any analysis of raw data, including uncertainty from the data reduction method itself; methods 1 and 2, described above, do not account for this uncertainty. Method 3, which calculates 95% confidence intervals from the regression model, does include uncertainty caused by the regression model itself and is the method used to reduce PGE data from the University of Notre Dame ICP-MS laboratory. The method is illustrated in Figure 1c (for external calibration) and Figure 1f (for standard addition) and also in Figure 2. Method 3 gives the reader a more comprehensive assessment of the uncertainty estimates of the calculated concentrations. Furthermore, these uncertainty estimates are relatively simple to calculate. This data reduction method provides a coherent, reproducible way to reduce and interpret ICP-MS data and can be applied to other analytical techniques (e.g., atomic absorption spectroscopy), where drift corrections and regression models are used to calculate concentration data.

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