

Improved concentration data in two international geochemical reference materials (USGS basalt BIR-1 and GSJ peridotite JP-1) by outlier rejection

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RESUMEN

Se examinaron los datos de elementos mayores y traza en dos materiales internacionales de referencia geoquímica (MIRG): basalto BIR-1 de la Comisión Geológica de los Estados Unidos de Norte América (USGS) y peridotita JP-1 del Consejo Geológico de Japón (GSJ). Después de la aplicación de un procedimiento estadístico para la detección y eliminación de valores desviados (basado en catorce pruebas estadísticas con treinta y cinco variantes), los valores promedios de la concentración y otros parámetros estadísticos fueron computados en estos dos materiales máficos difíciles, que contienen bajas concentraciones de la mayoría de los elementos traza, incluyendo los elementos de las tierras raras. Se emplearon dos métodos distintos para el procesado de los datos. En el método Opción (A), se trataron todos los datos de concentración disponibles para un elemento como una muestra estadística de una sola población. En el método Opción (B), se agruparon estos datos de acuerdo con el método analítico utilizado y luego se probaron por posibles diferencias significativas entre los diferentes grupos de métodos por medio de la prueba de hipótesis ANOVA, aplicada a un nivel estricto de confianza de 99%.

Para basalto BIR-1 de la USGS usando la Opción (A), fue posible obtener datos de valores promedios con alta calidad para cuatro elementos mayores (Ti, Fe⁺, Ca, and FeO) y cuatro traza (Cu, Eu, Sc, and Sr) caracterizados como *cve*, así como datos de calidad intermedia para cinco elementos mayores y dieciocho traza. De igual manera para la peridotita JP-1 del GSJ, tres elementos mayores (SiO₂, Fe₂O₃⁺, and CaO) y tres traza (Co, Ni, and Sc) tienen calidad *cve* y tres mayores y nueva traza son *rv*. La aplicación de la Opción (B) al material BIR-1 resultó en la calidad *cve* para dos elementos (Ti and Cu) y *rv* para once elementos. Para JP-1, dos elementos mayores (SiO₂ and CaO) fueron *cve* y tres traza (As, Yb, and Zn) *rv*. El resto de los elementos compilados en el presente trabajo sigue con la calidad provisional (*pv*).

Una comparación de estos resultados con los valores reportados en la literatura por los compiladores originales, quienes emplearon un método estadístico diferente, demuestra que el procedimiento estadístico presentado en el presente trabajo, que consiste en la aplicación de un gran número de pruebas para datos normales univariados, proporciona una mejor perspectiva de aplicación a este tipo de bases de datos geoquímicos.

PALABRAS CLAVE: Pruebas estadísticas para valores desviados, geoquímica, distribución normal, materiales internacionales de referencia geoquímica.

ABSTRACT

Concentration data for major and trace elements were examined in two international geochemical reference materials, basalt BIR-1 from the United States Geological Survey (USGS) and peridotite JP-1 from the Geological Survey of Japan (GSJ). After outlier rejection (based on fourteen different statistical tests with thirty-five variants), concentration means and other statistical parameters were computed in these two difficult mafic materials, which have low concentrations of most trace elements, including the rare-earth elements. Two distinct methods were used: (A) All available concentration data for a given element were treated as a statistical sample of a single population; (B) Data were grouped according to the analytical method used and tested for bias among method groups using ANOVA hypothesis test, at a confidence level of 99%.

For USGS basalt BIR-1 using Option (A), it was possible to derive high-quality data for four major elements (Ti, Fe⁺, Ca, and FeO) and four trace elements (Cu, Eu, Sc, and Sr), characterized as *cve* and intermediate-quality data for five major and eighteen trace elements as *rv*. Similarly in GSJ peridotite JP-1, three major (SiO₂, Fe₂O₃⁺, and CaO) and three trace elements (Co, Ni, and Sc) are at present of *cve* quality, and three major and nine trace elements are *rv*. The application of Option (B) resulted in *cve* quality for two elements (Ti and Cu) and *rv* for eleven elements in BIR-1. For JP-1 two major elements (SiO₂ and CaO) are *cve* quality and three trace elements (As, Yb, and Zn) *rv*. The remaining elements compiled here are still only provisional (*pv*) values.

A comparison of these results with literature values obtained by the original compilers using a different statistical method shows that the new statistical procedure involving a set of different tests for normal univariate data provides a better perspective of application to such geochemical databases.

KEY WORDS: Outlier statistical tests, geochemistry, normal distribution, international geochemical reference materials.

INTRODUCTION

Ever since the introduction of granite G-1 and diabase W-1 as geochemical reference materials for testing precision and accuracy of silicate rock analysis (Fairbairn, 1951; Flanagan, 1967), such international geochemical reference materials (RM) are widely employed in characterizing traceability, precision, accuracy, and sensitivity of routine analysis (e.g., Sutarno and Steger, 1985; Potts, 1987; Johnson, 1991; Kane, 1992; Verma, 1996, 1997) as well as in calibrations of analytical methods, such as X-ray fluorescence spectrometry (e.g., Verma *et al.*, 1992, 1993). Reliable concentration and statistical data for each constituent in the RM are therefore required. The rare-earth elements (REE) are very useful for solving many geological problems. In spite of the importance of these and other elements, their information in RM is still poorly evaluated (Kane, 1991; Velasco and Verma, 1998; Verma and Velasco, 1998). Reliable concentration and standard deviation values are required to evaluate new analytical methods, such as liquid chromatography (Cassidy, 1988; Verma, 1991a, b).

Some compilations on RM present only the average concentration values, without a mention of how they were actually derived (e.g., Govindaraju, 1989, 1994; Potts *et al.*, 1992). The mean values reported in these compilations should not be used in calibrations or method evaluations, without a reference to their standard deviations.

Various procedures to arrive at the mean concentration values and other statistical parameters have been reported (e.g., Abbey, 1977a, b, 1981, 1992; Abbey *et al.*, 1979; Dybczynsky, 1980; Lister, 1982; Abbey and Rousseau, 1985; Flanagan, 1986; Velasco and Verma, 1998). Recently, Verma (1997) presented an objective statistical procedure involving the application of sixteen different outlier detection and rejection tests for univariate sample population (Barnett and Lewis, 1987). He applied it successfully to a RM (microgabbro PM-S from Scotland) originally compiled by Govindaraju *et al.* (1994, 1995). Orduña-Galván and Verma (1997) and Verma *et al.* (1998) have developed a computer program (SIPVADE) to apply up to seventeen statistical tests for univariate data (a total of sixty-five single or multiple outlier versions of these tests) and used it to evaluate two other RM (dolerite WS-E from England processed earlier by Govindaraju *et al.*, 1994 and Soil-5 from Peru distributed by International Atomic Energy Agency and processed by Dybczynsky *et al.*, 1979).

I investigate if this procedure will work well for “difficult” RM, with low concentrations of many trace elements including the rare-earth elements, and if this will provide more reliable results than the method of two standard deviations from the mean as a criterion to identify outlier values used by several researchers (Stoch and Steele, 1978;

Ando *et al.*, 1987, 1989; Gladney and Roelandts, 1988, 1990; Gladney *et al.*, 1991; Itoh *et al.*, 1993; Imai *et al.*, 1995).

I also evaluate the value of fourteen statistical tests in the study of RM and report new average element concentration data of major and trace elements in two RM: basalt BIR-1 from the United States Geological Survey (USGS, U.S.A.; Flanagan, 1976, 1984) and peridotite JP-1 from the Geological Survey of Japan (GSJ, Japan; Ando *et al.*, 1987). These concentration values have been obtained by the application of fourteen tests, with thirtyfive variants, to the individual concentration data and estimation of statistical parameters from the final sample population. These particular samples, BIR-1 and JP-1, were chosen because they are among the worst characterized RM from USGS and of «igneous rock series» from GSJ. I show that an objective statistical procedure involving a large number of discordancy tests for normal univariate data can provide a useful way to process analytical data on RM.

STATISTICAL TESTS

Present methodology

Determination of most trace elements, including the REE and some major elements such as MnO, K₂O and P₂O₅, in basalt BIR-1 and peridotite JP-1, is a difficult analytical problem. These are respectively mafic and ultramafic rocks with very low concentrations of these difficult elements expected for such rock types. A large spread of analytical data from different laboratories is expected for most elements, with some results being outliers mainly due to the fact that the expected concentrations are close to the detection limits of many modern analytical methods and the presence of systematic errors or inadequate instrumental drift corrections or faulty calibrations in some participating laboratories. Their detection by objective criteria, without the need of extensive subjective judgements, is desirable to establish the more probable concentration values.

The discordancy tests for normal univariate samples used for the evaluation of these two RM are summarized in Table 1. The test labels and the nomenclature used are same as in Verma (1997) and Verma *et al.* (1998). The tests N5 and N6 that detect lower-upper data pair are not included in the present study, because they may detect a genuine lowest observation as an outlier if, as expected for these “difficult” RM, an extremely high discordant observation generally by a different analytical method is present in the database for that element. Similarly, although many more data values (k up to 10) can be tested simultaneously by variants of the different tests, the present application is restricted to a maximum of four observations (k=4) simultaneously tested. In fact, the test N16 is used only in its simplest form of k=1 observation, because for higher values of k this test is applied

Table 1

Discordancy tests for normal univariate samples used for the evaluation of USGS basalt BIR-1 and GSJ peridotite JP-1 (modified after Barnett and Lewis, 1987; Verma, 1997; and Orduña-Galván and Verma, 1997).

Test label	Description of test	Test statistic (T _{Ni} , i=1, 16)	Significance of test	Value(s) tested	Test applied		Ref	
					n _{min}	n _{max}		
N1	k=1 Upper	$(x_n - \bar{x}) / s$	<i>greater</i>	x_n	6	147	a	
	k=1 Lower	$(\bar{x} - x_1) / s$	<i>greater</i>	x_1	6	147	a	
N2	k=1 Extreme	$\max[(x_n - \bar{x}) / s, (\bar{x} - x_1) / s]$	<i>greater</i>	x_n <u>or</u> x_1	6	20	b	
N3	k=2 Upper	$(x_n + x_{n-1} - 2\bar{x}) / s$	<i>greater</i>	x_n, x_{n-1}	6	100	c	
	k=3 Upper	$(x_n + x_{n-1} + x_{n-2} - 3\bar{x}) / s$	<i>greater</i>	x_n, x_{n-1}, x_{n-2}	10	100	c	
	k=4 Upper	$(x_n + x_{n-1} + x_{n-2} + x_{n-3} - 4\bar{x}) / s$	<i>greater</i>	$x_n, x_{n-1}, x_{n-2}, x_{n-3}$	10	100	c	
	k=2 Lower	$(2\bar{x} - x_1 - x_2) / s$	<i>greater</i>	x_1, x_2	6	100	c	
	k=3 Lower	$(3\bar{x} - x_1 - x_2 - x_3) / s$	<i>greater</i>	x_1, x_2, x_3	10	100	c	
	k=4 Lower	$(4\bar{x} - x_1 - x_2 - x_3 - x_4) / s$	<i>greater</i>	x_1, x_2, x_3, x_4	10	100	c	
	N4	k=1 Upper	S_n^2 / S^2	<i>smaller</i>	x_n	6	50	d
		k=2 Upper	$S_{n,n-1}^2 / S^2$	<i>smaller</i>	x_n, x_{n-1}	6	149	a
k=2 Upper		$S_{n,n-1}^2 / S^2$	<i>smaller</i>	x_n, x_{n-1}	6	50	d	
k=3 Upper		$S_{n,n-1,n-2}^2 / S^2$	<i>smaller</i>	x_n, x_{n-1}, x_{n-2}	10	50	d	
k=4 Upper		$S_{n,n-1,n-2,n-3}^2 / S^2$	<i>smaller</i>	$x_n, x_{n-1}, x_{n-2}, x_{n-3}$	10	50	d	
k=1 Lower		$S_{1,1}^2 / S^2$	<i>smaller</i>	x_1	6	50	d	
k=2 Lower		$S_{1,2}^2 / S^2$	<i>smaller</i>	x_1, x_2	6	149	a	
k=2 Lower		$S_{1,2}^2 / S^2$	<i>smaller</i>	x_1, x_2	6	50	d	
k=3 Lower		$S_{1,2,3}^2 / S^2$	<i>smaller</i>	x_1, x_2, x_3	10	50	d	
k=4 Lower		$S_{1,2,3,4}^2 / S^2$	<i>smaller</i>	x_1, x_2, x_3, x_4	10	50	d	
N7	k=1 Upper	$(x_n - x_{n-1}) / (x_n - x_1)$	<i>greater</i>	x_n	6	30	e	
	k=1 Lower	$(x_2 - x_1) / (x_n - x_1)$	<i>greater</i>	x_1	6	30	e	
N8	k=1 Extreme	$\max[(x_n - x_{n-1}) / (x_n - x_1), (x_2 - x_1) / (x_n - x_1)]$	<i>greater</i>	x_n <u>or</u> x_1	6	30	c	
N9	k=1 Upper	$(x_n - x_{n-1}) / (x_n - x_2)$	<i>greater</i>	x_n	6	30	e	
	k=1 Lower	$(x_2 - x_1) / (x_{n-1} - x_1)$	<i>greater</i>	x_1	6	30	e	
N10	k=1 Upper	$(x_n - x_{n-1}) / (x_n - x_3)$	<i>greater</i>	x_n	6	30	e	
	k=1 Lower	$(x_2 - x_1) / (x_{n-2} - x_1)$	<i>greater</i>	x_1	6	30	e	
N11	k=2 Upper pair	$(x_n - x_{n-2}) / (x_n - x_1)$	<i>greater</i>	x_n, x_{n-1}	6	30	e	
	k=2 Lower pair	$(x_3 - x_1) / (x_n - x_1)$	<i>greater</i>	x_1, x_2	6	30	e	
N12	k=2 Upper pair	$(x_n - x_{n-2}) / (x_n - x_2)$	<i>greater</i>	x_n, x_{n-1}	6	30	e	
	k=2 Lower pair	$(x_3 - x_1) / (x_{n-1} - x_1)$	<i>greater</i>	x_1, x_2	6	30	e	
N13	k=2 Upper pair	$(x_n - x_{n-2}) / (x_n - x_3)$	<i>greater</i>	x_n, x_{n-1}	6	30	e	
	k=2 Lower pair	$(x_3 - x_1) / (x_{n-2} - x_1)$	<i>greater</i>	x_1, x_2	6	30	e	
N14	k=1 Extreme	$[\sum(x_j - \bar{x})^3] / ns^3$ for j=1 to n	<i>greater</i>	x_n <u>or</u> x_1	6	1000	b	
N15	k=1 Extreme	$[\{\sum(x_j - \bar{x})^4\} / ns^4] - 3$ for j=1 to n	<i>greater</i>	x_n <u>or</u> x_1	6	2000	b	
N16	k=1 Extreme	Tietjen and Moore's statistic	<i>smaller</i>	x_n <u>or</u> x_1	6	50	d, f	

Tests N6 and N7 were not included in the present application (see text for more details). k = number of value(s) tested; n_{min} = minimum number of observations to which a given test was applied; n_{max} = maximum number of observations to which a given test could be applied. References (Ref) to original source of tables of 1% critical values and description of the statistical tests are (besides Barnett and Lewis, 1987): a = Grubbs and Beck (1972); b = Pearson and Hartley (1966); c = Barnett and Lewis (1987); d = Tietjen and Moore (1972); e = Dixon (1951); f = Tietjen and Moore (1979).

as a direction-independent test with the danger of rejecting a valid observation as an outlier.

For the application of these tests, the minimum number of observations is set at 6, although in theory this can be done for a smaller number of data (Barnett and Lewis, 1987; Verma, 1997). This choice is compatible with the quality value (Q_v) characterization proposed by Potts and Kane (1992). The maximum number of observations that can be tested by a given test variant depends directly upon the availability of 1% critical values (99% confidence or significance level). The application of a more strict confidence level of 99%, rather than the 95% used by other workers in analytical geochemistry (e.g., Dybczynsky *et al.*, 1979; Dybczynsky, 1980) minimizes the danger of rejecting a valid observation as an outlier.

Method applied by US and Japanese scientists

As pointed out by Verma (1997), Ando *et al.* (1987, 1989), Gladney and Roelandts (1988, 1990), Gladney *et al.* (1991), Itoh *et al.* (1993), and Imai *et al.* (1995) applied a

simple statistical procedure involving rejection of all observations lying outside two standard deviations from the mean, irrespective of the total number of observations (called here two standard deviation method) to evaluate element concentration data in RM. This method seems to be in error due to a strong dependence of the critical value curves on the number of observations. In their procedure, it was also necessary to apply subjective judgements to eliminate data lying clearly beyond the “limits of acceptability”, prior to two standard deviation method. Figure 1 shows the reasons for the incorrectness of the approach of the two standard deviation method. Two critical value curves are included in Figure 1 for: 1% critical values (99% confidence or significance level; solid continuous curve) and 5% critical values (95% confidence level; dashed curve), both of which correspond to test N1 (Table 1). According to the theory of outliers in a normal univariate sample (Grubbs and Beck, 1972; Barnett and Lewis, 1987), an observation (x_n or x_1) for which the test statistic TN1 lies in the field D above both the 1% and 5% critical value curves should be rejected as an outlier at the 99% confidence level, whereas if this observation falls in the field C between the two curves, it

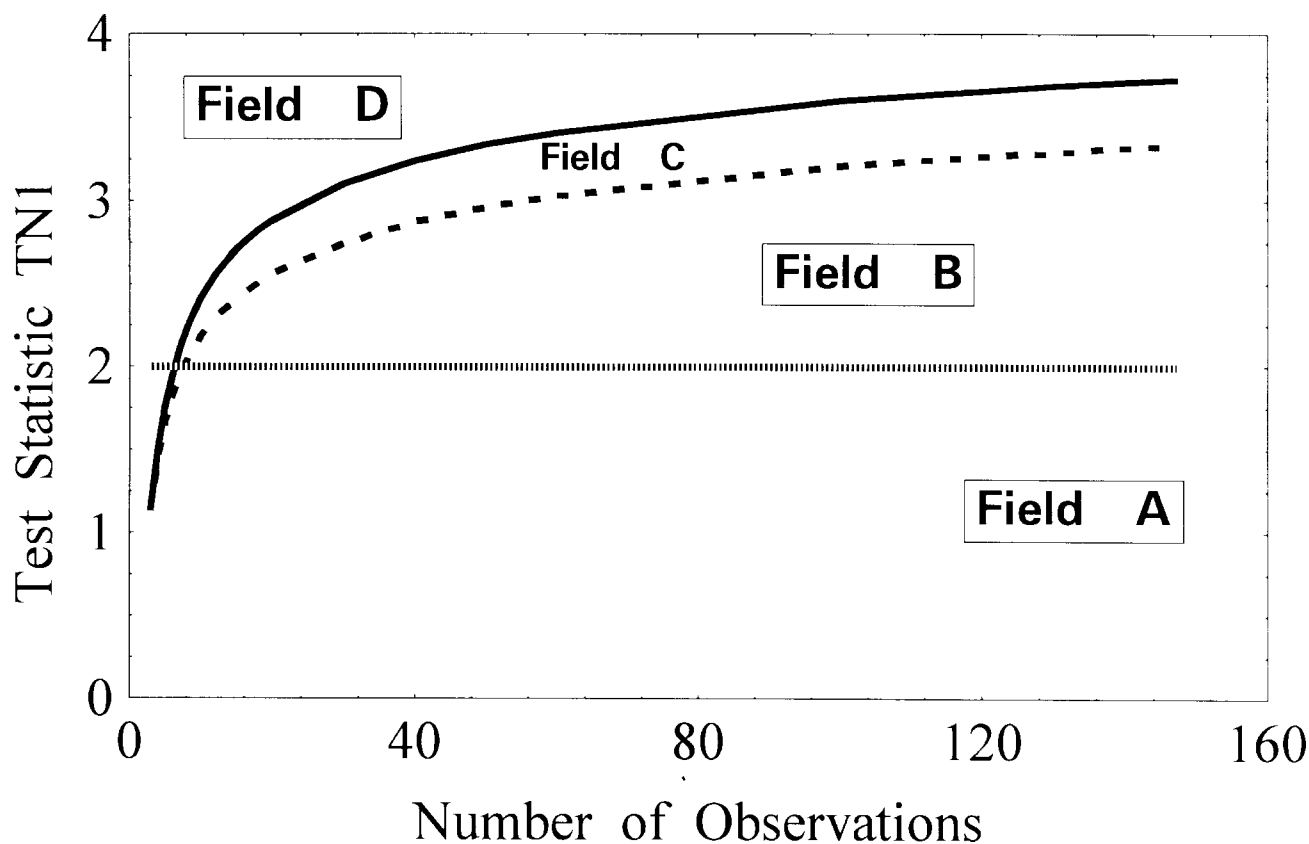


Fig. 1. Test statistic TN1 $[(x_n - \bar{x})/s]$; where \bar{x} =mean, and s =standard deviation of the sample] corresponding to the upper value (x_n) or $[(\bar{x}-x_1)/s]$ corresponding to the lower value (x_1) in a normal univariate sample plotted against the total number of observations. 1% critical value curve (99% confidence or significance level) for TN1 is included as a continuous curve; 5% critical value curve (95% confidence level) for TN1 is shown as a dashed line; and the dotted line represents the two standard deviation method. The fields A, B, C, and D are explained in the text.

will be identified as an outlier only at the 95% confidence level but as a valid observation at the more strict 99% level. On the other hand, if the observation to be tested lies below both these curves (in the fields A or B), it will be classified as a valid observation by test N1. The two standard deviation method (Gladney and Roelandts, 1988), on the other hand, will identify an observation as valid only if it falls in the field A but as an outlier if it lies in any of the fields B, C or D. Thus in contrast to the test N1 and the outlier theory, many more observations will be identified as outliers in the two standard deviation method. Some genuine and valid observations will be erroneously rejected, resulting in an artificial decrease of the final standard deviation of the remaining data.

DATA EVALUATION

Individual concentration data from Gladney and Roelandts (1988) on BIR-1 (Table 2) were established in a database, which enabled a direct comparison of the two statistical methods: the present method involving a large number of statistical tests and the two standard deviation method. More recent published data from this reference material were not included in this database, because my main objective was to compare two different statistical procedures. The individual major element data for BIR-1 were reported as elements and not as oxides (Gladney and Roelandts, 1988). They were not converted to oxides in our database, in order to permit a direct comparison of the final results. The analytical methods used to determine these individual data are also included using a METH code (Table 2). A group number (GR) was assigned to each individual observation following method grouping explained in the footnote of Table 2.

For the peridotite JP-1 the individual major element data were not available in printed form in the most recent publication (Imai *et al.*, 1995). Only the quantitative data (compiled in ascending order and summarized in Table 3) were taken from internet location <http://www.aist.go.jp/RIODB/geostand/welcome.html>, as recommended by Imai *et al.* (1996). Also included for the REE data in JP-1 were the results reported by Ionov *et al.* (1992), which were not included in the internet address for JP-1. The downloading of individual data from the internet was updated in February 1998 before revising an earlier version of this paper.

Elements with less than 6 individual observations were not compiled in the database. Examples of these elements in both RM include Ag, As, Au, B, Be, Bi, C, Cd, Hg, Ir, Pd, Pt, Rh, Se, Te, Tl, and W. An exception was Ho in JP-1, for which only five data were available. It was included because of the importance of the REE in the RM.

The individual entries in the database were checked for typographical errors, before processing the data files with

computer program "SIPVADE" (Orduña-Galván and Verma, 1997). This program automatically detects outliers, without the cumbersome spreadsheet calculations that were required earlier (Verma, 1997).

Two different options were applied to the compiled data. In Option (A), all the data for an element were tested for outliers, assuming no bias between the element concentration data obtained by different groups of analytical methods. In Option (B), the data sets according to method grouping were first tested for systematic differences using analysis of variance or ANOVA (e.g. Jensen *et al.*, 1997). ANOVA is robust to deviations from normality of the data tested. Therefore a prior normality test on individual groups was not considered necessary for this Option. If a group of data for an element differed significantly at 99% confidence level from all other remaining groups, that particular group was excluded from the data set for that element. Then the remaining data were treated as a statistical sample and outliers were detected using the SIPVADE program before the final computations of the mean and other statistical parameters. When no bias was detected in the data sets, the results of Option (A) were identical to Option (B).

The outliers for Option (A) are identified by solid diamonds in Tables 2 and 3 for BIR-1 and JP-1 respectively. Similarly for Option (B), the data from a particular group of analytical methods, which were considered significantly different from all other data for that element, are shown by solid circles and the outlier data by open circles in Tables 2 and 3. The tests applied and their relative efficiency for detecting outliers in BIR-1 and JP-1 are summarized in Tables 4 and 5 respectively for Option (A) and Tables 6 and 7 for Option (B).

For BIR-1 the tests were applied to thirteen major and thirty-two trace elements. Using Option (A) no outliers were detected for Mn, H₂O, Er, Ga, Sb, Ta, Th, Tm, and Y. For other elements, one or more outliers were detected by generally more than one test (Table 4). In Option (B), the application of ANOVA identified a method group giving significantly different mean values than all the other methods for the elements Ti, Mn, Co, Cr, Cu, Ga, Gd, Li, Lu, Nb, Nd, Ni, and Zn in BIR-1 (Table 6). The spark source mass spectrometry (SSMS) method gave significantly smaller concentration data for Ti, Mn, Co, Cr, Cu, Ga, and Ni (Table 2). X-ray fluorescence spectrometry (XRF) showed significant differences for Li and Zn, atomic absorption spectrometry (AA) for Gd, Lu, and Nd, and direct-current plasma atomic emission spectrometry (DCPES) for Nb. These data can be used to compute method mean values for these elements. After these data were eliminated from the database, the outlier tests for Option (B) detected outliers in data for ten elements, with the three remaining elements showing no outlying observation.

Table 2

Application of statistical tests on the sample population of analytical data for USGS BIR-1 (individual data are from compilation by Gladney and Roelandts, 1988 and are used for comparing Verma, 1997 and Gladney's methods as well as obtaining final statistical results). ♦=outlier detected by the present Option (A); ●=value excluded before outlier detection and ○=outlier detected by Option (B) (see footnotes for more details).

DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	
A		B		A		B		A		B		A		B		
Si (%)				Ti (ppm) Cont.				Al (%) Cont.				Fe^t (%) Cont.				
21.11	♦ ○	XRF	3	5678		CHEM	1	8.28		XRF	3	7.96		XRF	3	
21.7	♦ ○	TCGS	5	5690		WXRF	3	8.29		XRF	3	7.97		ITNA	5	
21.8		XRF	3	5690		AA	2	8.29		DCPES	4	7.98		COLOR	8	
21.81		XRF	3	5702		ICPES	4	8.29		XRF	3	8.02		ITNA	5	
21.88		AA	2	5750		COLOR	8	8.32		CHEM	1	8.04		PAA	5	
22.0		TCGS	5	5750		CHEM	1	8.32		AA	2	8.06		ITNA	5	
22.15		XRF	3	5750		WXRF	3	8.33		AA	2	8.12		WXRF	3	
22.16		CHEM	1	5750		XRF	3	8.37		WXRF	3	8.24		XRF	3	
22.22		ICPMS	6	5770		ITNA	5	8.39		AA	2	8.26		ITNA	5	
22.23		ITNA	5	5774		XRF	3	8.41		GRAV	1	8.26		ITNA	5	
22.27		XRF	3	5800		COLOR	8	8.41		ITNA	5					
22.30		MPOES	4	5800		ICPES	4	8.46		XRF	3					
22.31		GRAV	1	5800		XRF	3	8.47		CHEM	1					
22.35		CHEM	1	5800		ITNA	5	8.58		GRAV	1	7.85	♦ ○	VOLU	1	
22.35		GRAV	1	5810		XRF	3	8.89		XRF	3	8.28	♦ ○	TITR	1	
22.39		AA	2	5870		DCPES	4	9.63	♦ ○	XRF	3	8.30		TITR	1	
22.40		DCPES	4	5870		XRF	3					8.30		CHEM	1	
22.40		CHEM	1	5888		COLOR	8					8.32		TITR	1	
22.41		WXRF	3	5990		ITNA	5					8.35		CHEM	1	
22.42		CHEM	1	6038		ITNA	5	7.16	♦ ○	ITNA	5	8.37		CHEM	1	
22.45		WXRF	3	6050	○	MPOES	4	7.28	♦ ○	TCGS	5	8.4		CHEM	1	
22.45		XRF	3	6080	♦ ○	PAA	5	7.36	♦ ○	ITNA	5	8.44		COLOR	8	
22.46		XRF	3	6150	♦ ○	OES	4	7.4	♦ ○	DCPES	4	8.63		COLOR	8	
22.46		XRF	3	7300	♦ ○	DCPES	4	7.48		UU	8	8.72		AA	2	
22.50		XRF	3					7.5		TCGS	5					
22.55		GRAV	1			Al (%)		7.57		XRF	3					
22.66		XRF	3					7.59		ICPES	4			Mn (ppm)		
22.77		XRF	3	7.14		ITNA	5	7.69		ITNA	5	986		●	SSMS	6
23.0	♦ ○	UU	8	7.30		DCPES	4	7.69		ITNA	5	1000		●	SSMS	6
24	♦ ○	DCPES	4	7.35		UU	8	7.75		ITNA	5	1161			MPOES	4
				7.36		ITNA	5	7.77		XRF	3	1184			ITNA	5
				7.40		TCGS	5	7.79		AA	2	1200			OES	4
				7.66		AA	2	7.79		ITNA	5	1223			ICPES	4
3100	♦ ○	OES	4	7.66		ICPES	4	7.81		XRF	3	1238			XRF	3
3400	♦ ●	SSMS	6	7.72		XRF	3	7.84		XRF	3	1238			XRF	3
3457	♦ ●	SSMS	6	7.86		TCGS	5	7.86		TITR	1	1246			AA	2
3900	♦ ○	OES	4	7.90		ITNA	5	7.86		ITNA	5	1262			XRF	3
4253	♦ ○	XRF	3	7.90		XRF	3	7.87		ITNA	5	1262			XRF	3
5200	♦ ○	UU	8	7.92		AA	2	7.88		CHEM	1	1270			TCGS	5
5331		XRF	3	7.94		XRF	3	7.88		XRF	3	1290			AA	2
5460		TCGS	5	7.96		WXRF	3	7.90		TITR	1	1292			ITNA	5
5469		ITNA	5	7.99		AA	2	7.90		XRF	3	1300			COLOR	8
5499		XRF	3	8.04		ITNA	5	7.91		CALC	8	1300			DCPES	4
5511		AA	2	8.09		ITNA	5	7.92		WXRF	3	1300			XRF	3
5517		XRF	3	8.09		MPOES	4	7.93		AA	2	1300			TCGS	5
5600		XRF	3	8.12		XRF	3	7.93		ITNA	5	1300			AA	2
5600		COLOR	8	8.15		XRF	3	7.94		MPOES	4	1316			XRF	3
5600		TCGS	5	8.18		CHEM	1	7.95		DCPES	4	1316			XRF	3
5631		XRF	3	8.25		ICPES	4	7.95		XRF	3	1316			XRF	3
5631		AA	2	8.26		ICPES	4	7.95		XRF	3	1316			COLOR	8
5648		XRF	3	8.28		XRF	3	7.95		ICPES	4	1316			XRF	3

Table 2 (Contd.-1)

Application of statistical tests on the sample population of analytical data for USGS BIR-1 (individual data are from compilation by Gladney and Roelandts, 1988 and are used for comparing Verma, 1997 and Gladney's methods as well as obtaining final statistical results). ◆=outlier detected by the present Option (A); ●=value excluded before outlier detection and ○=outlier detected by Option (B) (see footnotes for more details).

DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR			
A		B		A		B		A		B		A		B				
Mn (ppm) Cont.				Mg (%) Cont.				Na (%) Cont.				K (ppm) Cont.						
1317		AA	2	6.33		UU	8	1.17		ITNA	5	249		XRF	3			
1320		COLOR	8	6.9	◆	○	ICPES	4	1.17		XRF	3	249		CHEM	1		
1331		XRF	3	7.01	◆	○	ITNA	5	1.18		XRF	3	249		MPOES	4		
1339		AA	2					1.19		AA	2	250		AA	2			
1354		COLOR	8			Ca (%)		1.21		ITNA	5	257		FE	2			
1362		PAA	5					1.24		TCGS	5	266		ICPES	4			
1378		WXRF	3	6.57	◆	○	ITNA	5	1.25		AA	2	266		DCPES	4		
1393		DCPES	4	8.66	◆	○	XRF	3	1.26		XRF	3	274		XRF	3		
1393		XRF	3	8.94	◆	○	ICPES	4	1.27		DCPES	4	280		TCGS	5		
1397		ITNA	5	9.01	◆	○	DCPES	4	1.3		UU	8	282		FE	2		
1400		ITNA	5	9.01			UU	8	1.31		AA	2	307		AA	2		
1450		IENA	5	9.05			TCGS	5	1.32		AE	2	330	◆	○	UU	8	
1476		ICPES	4	9.18			XRF	3	1.32		TCGS	5	357	◆	○	XRF	3	
1525	○	CHEM	1	9.2			TCGS	5	1.32		CHEM	1	581	◆	○	XRF	3	
1573	○	ITNA	5	9.22			MPOES	4	1.33		ITNA	5	1992	◆	○	XRF	3	
1573	○	ITNA	5	9.25			AA	2	1.33		ITNA	5						
1718	○	OES	4	9.34			CHEM	1	1.34		ITNA	5						
				9.38			XRF	3	1.34		AA	2			P (ppm)			
				9.41			PAA	5	1.34		FE	2	87		WXRF	3		
				9.45			ICPES	4	1.34		FE	2	87		CHEM	1		
4.64	◆	○	XRF	3	9.46		ITNA	5	1.34		ICPES	4	87		XRF	3		
5.09			XRF	3	9.47		ITNA	5	1.34		ITNA	5	87		COLOR	8		
5.18			TCGS	5	9.48		XRF	3	1.36		XRF	3	90		COLOR	8		
5.30			ITNA	5	9.48		XRF	3	1.36		AA	2	100		COLOR	8		
5.48			ICPES	4	9.49		XRF	3	1.37		FE	2	118		DCPES	4		
5.63			MPOES	4	9.51		CHEM	1	1.37		ITNA	5	130		UU	8		
5.66			XRF	3	9.51		GRAV	1	1.37		FE	2	131		XRF	3		
5.66			AA	2	9.51		GRAV	1	1.39		CHEM	1	161		CHEM	1		
5.68			AA	2	9.53		AA	2	1.40		MPOES	4	170		COLOR	8		
5.69			AA	2	9.54		XRF	3	1.40		AA	2	174		XRF	3		
5.7			TCGS	5	9.54		WXRF	3	1.40		ITNA	5	174		XRF	3		
5.72			XRF	3	9.54		AA	2	1.41		AA	2	187		CHEM	1		
5.76			XRF	3	9.55		XRF	3	1.41	◆	○	XRF	3	192	◆	○	XRF	3
5.77			WXRF	3	9.60		AA	2	1.42	◆	○	PAA	5	240	◆	○	XRF	3
5.78			GRAV	1	9.60		CHEM	1	1.53	◆	○	XRF	3	305	◆	○	XRF	3
5.80			AA	2	9.60		XRF	3	2.16	◆	○	XRF	3	392	◆	○	XRF	3
5.82			CHEM	1	9.60		XRF	3					423	◆	○	XRF	3	
5.87			PAA	5	9.61		XRF	3		K (ppm)			440	◆	○	XRF	3	
5.87			CHEM	1	9.68		ITNA	5					445	◆	○	AA	2	
5.89			XRF	3	9.7		ITNA	5	66		XRF	3	763	◆	○	ICPES	4	
5.89			DCPES	4	9.72		XRF	3	83		XRF	3						
5.89			XRF	3	9.80		WXRF	3	83		WXRF	3			H₂O⁺ (%)			
5.9			XRF	3	9.84		AA	2	83		AA	2	0.04		IR	8		
5.91			WXRF	3				133		AA	2	0.06		CHEM	1			
5.91			ITNA	5				140		TCGS	5	0.06		GRAV	1			
5.93			AA	2				141		AA	2	0.078		GRAV	1			
5.93			GRAV	1	1.05		WXRF	3	174		FE	2	0.09		KF	8		
5.93			CHEM	1	1.13		ITNA	5	175		AA	2	0.10		CEA	2		
6.05			XRF	3	1.13		ITNA	5	220		FE	2	0.10		COUL	8		
6.05			XRF	3	1.16		XRF	3	224		XRF	3	0.11		CHEM	1		
6.2			AA	2	1.17		ITNA	5	224		XRF	3						
6.23			XRF	3	1.17		ITNA	5	224		CHEM	1						

Table 3

Application of statistical tests on the sample population of analytical data for GSJ JP-1 (individual data are retrieved from internet <http://www.aist.go.jp/RIODB/geostand/welcome.html>, as suggested by Imai *et al.*, 1996 and are used for comparing Verma, 1997 and Imai *et al.* methods and obtaining final statistical results). ◆=outlier detected by the present Option (A); ●=value excluded before outlier detection and ○=outlier detected by Option (B).

DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR
A	B			A	B			A	B			A	B		
SiO₂ (%)				TiO₂ (%) Cont.				Fe₂O₃^t (%)				MnO (%) Cont.			
41.73		CHEM	1	0.02		XRF	3	7.78		INAA	5	0.119		XRF	3
41.78		XRF	3	0.02		CHEM	1	8.14		COLOR	8	0.12		AA	2
41.83		XRF	3	0.02		XRF	3	8.17		CHEM	1	0.12		XRF	3
41.83		XRF	3	0.02		AA	2	8.17		COLOR	8	0.12		ICPES	4
41.93		XRF	3	0.02		XRF	3	8.18		ICPES	4	0.12		AA	2
41.94		XRF	3	0.02		COLOR	8	8.20		XRF	3	0.12		XRF	3
42.00		XRF	3	0.03		XRF	3	8.22		AA	2	0.12		XRF	3
42.00		XRF	3	0.03		XRF	3	8.29		XRF	3	0.120		INAA	5
42.03		XRF	3					8.29		COLOR	8	0.121		AA	2
42.05		XRF	3			Al₂O₃ (%)		8.3		AA	2	0.122		XRF	3
42.07		COLOR	8					8.30		XRF	3	0.122		NAA	5
42.11		GRAV	1	0.07	◆ ○	VOLU	1	8.31		XRF	3	0.122		XRF	3
42.13		XRF	3	0.28	◆ ○	XRF	3	8.32		NAA	5	0.123		NAA	5
42.2		XRF	3	0.53	◆ ○	CHEM	1	8.34		AA	2	0.125		INAA	5
42.27		ICPES	4	0.54	◆ ○	AA	2	8.34		AA	2	0.125		XRF	3
42.34		ICPES	4	0.56		CHEM	1	8.34		XRF	3	0.125		NAA	5
42.39		GRAV	1	0.57		XRF	3	8.35		COLOR	8	0.125		INAA	5
42.39		XRF	3	0.57		INAA	5	8.35		INAA	5	0.125		INAA	5
42.50		XRF	3	0.58		XRF	3	8.35		NAA	5	0.126		XRF	3
42.53		XRF	3	0.58		ICPES	4	8.40		XRF	3	0.13		XRF	3
42.53		XRF	3	0.60		XRF	3	8.41		INAA	5	0.13		XRF	3
42.55		XRF	3	0.60		AA	2	8.41		XRF	3	0.13		AA	2
42.64		XRF	3	0.60		ICPES	4	8.50		XRF	3	0.13		XRF	3
42.66		XRF	3	0.60		XRF	3	8.53		XRF	3	0.13		XRF	3
42.68		XRF	3	0.61		AA	2	8.58		XRF	3	0.13		XRF	3
42.80		XRF	3	0.62		AA	2	8.60		XRF	3	0.13		CHEM	1
42.80		AA	2	0.62		XRF	3	8.67		XRF	3	0.13		XRF	3
43.15	◆ ○	AA	2	0.62		XRF	3	8.72		XRF	3	0.13		XRF	3
43.22	◆ ○	XRF	3	0.63		XRF	3	8.83		XRF	3	0.13		CHEM	1
43.79	◆ ○	XRF	3	0.63		INAA	5	8.89	◆ ○	XRF	3				
44.59	◆ ○	AA	2	0.65		XRF	3	9.13	◆ ○	XRF	3				
44.91	◆ ○	CHEM	1	0.66		XRF	3	9.16	◆ ○	XRF	3				
46.40	◆ ○	XRF	3	0.67		AA	2	9.25	◆ ○	XRF	3	41.12	◆ ○	CHEM	1
49.2	◆ ●	NAA	5	0.68		XRF	3	9.98	◆ ○	XRF	3	42.96		XRF	3
49.2	◆ ●	INAA	5	0.69		XRF	3	10.18	◆ ○	XRF	3	43.50		XRF	3
49.2	◆ ●	NAA	5	0.71		XRF	3					43.53		AA	2
				0.71		ICPES	4					43.9		CHEM	1
				0.72		XRF	3					43.91		XRF	3
				0.73		AA	2					44.06		AA	2
				0.77		XRF	3	0.09	◆ ○	XRF	3	44.08		AA	2
0.003		XRF	3	0.79		XRF	3	0.10	◆ ○	COLOR	8	44.26		XRF	3
0.009		COLOR	8	0.81		XRF	3	0.105	◆ ○	AA	2	44.30		XRF	3
0.01		XRF	3	0.83		XRF	3	0.108	◆ ○	AA	2	44.35		XRF	3
0.01		XRF	3	0.84		XRF	3	0.11		AA	2	44.38		XRF	3
0.01		XRF	3	0.88		INAA	5	0.110		INAA	5	44.50		AA	2
0.01		AA	2	0.88		NAA	5	0.11		ICPES	4	44.6		AA	2
0.01		XRF	3	0.90		XRF	3	0.11		XRF	3	44.61		XRF	3
0.01		XRF	3	0.99		XRF	3	0.116		AA	2	44.72		AA	2
0.013		XRF	3					0.116		AA	2	44.72		AA	2
0.02		XRF	3					0.116		AA	2	44.72		XRF	3

Table 3 (Contd.-3)

Application of statistical tests on the sample population of analytical data for GSJ JP-1 (individual data are retrieved from internet <http://www.aist.go.jp/RIODB/geostand/welcome.html>, as suggested by Imai *et al.*, 1996 and are used for comparing Verma, 1997 and Imai *et al.* methods and obtaining final statistical results). ◆=outlier detected by the present Option (A); ●=value excluded before outlier detection and ○=outlier detected by Option (B).

DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR
A	B			A	B			A	B			A	B		
Hf (ppm)				Lu (ppm) Cont.				Ni (ppm) Cont.				Rb (ppm) Cont.			
0.08		INAA	5	0.006		SSMS	6	2390		XRF	3	0.34		ICPMS	6
0.12		INAA	5	0.031		NAA	5	2397		XRF	3	0.36		SSMS	6
0.12		NAA	5	0.038		RNAA	5	2400		AA	2	0.4		XRF	3
0.13		INAA	5	0.038		NAA	5	2400		AA	2	0.5		XRF	3
0.13		ICPMS	6	0.051	◆ ○	NAA	5	2401		PAA	5	0.5		XRF	3
0.14		SSMS	6	4.2	◆ ○	RNAA	5	2402		XRF	3	1		XRF	3
0.14		INAA	5					2425		EXRF	3	1		XRF	3
0.14		INAA	5			Mo (ppm)		2450		XRF	3	1.0		XRF	3
0.149		INAA	5					2450		AA	2	1.0		AA	2
0.2		XRF	3	0.083		INAA	5	2452		XRF	3	1.8		XRF	3
0.26	◆ ○	NAA	5	0.09		ICPMS	6	2452		XRF	3	2		XRF	3
0.28	◆ ○	ICPMS	6	0.16		AA	2	2460		AA	2	2		XRF	3
0.3	◆ ○	INAA	5	0.58		OES	4	2460		XRF	3	2		XRF	3
0.603	◆ ○	NAA	5	0.58		OES	4	2461		XRF	3	2.1		XRF	3
				1		XRF	3	2483		XRF	3	2.7	◆ ○	XRF	3
		Ho (ppm)		1.6		XRF	3	2510		INAA	5	3	◆ ○	XRF	3
0.005		SSMS	6			Nb (ppm)		2513		XRF	3	3	◆ ○	XRF	3
0.005		MS	6					2519		XRF	3	7	◆ ○	XRF	3
0.018		NAA	5	0.058		SSMS	6	2530		XRF	3				
0.018		RNAA	5	0.075		ICPMS	6	2545		XRF	3			Sc (ppm)	
0.018		NAA	5	0.2		ICPMS	6	2550		AA	2	5.1	◆ ○	XRF	3
				0.3		XRF	3	2570		AA	2	6.7	◆ ○	OES	4
				0.9		XRF	3	2574		XRF	3	6.75	◆ ○	INAA	5
				1		XRF	3	2600		NAA	5	6.75	◆ ○	NAA	5
0.026		INAA	5	1		XRF	3	2693	◆ ○	XRF	3	7	◆ ○	ICPES	4
0.026		INAA	5	1		EXRF	3	2728	◆ ○	XRF	3	7.01		NAA	5
0.035		INAA	5	1.7		XRF	3	2877	◆ ○	CHEM	1	7.03		INAA	5
0.038		MS	6	2		XRF	3			Pb (ppm)		7.09		NAA	5
0.038		NM	5	2.1		XRF	3					7.1		XRF	3
0.04		SSMS	6	2.6		XRF	3	0.114		SIMS	8	7.12		INAA	5
0.042		INAA	5	3		XRF	3	0.12		SSMS	6	7.4		INAA	5
0.043		ICPMS	6			Nd (ppm)		0.12		FAA	2	7.44		INAA	5
0.09		INAA	5					0.21		ICPMS	6	7.5		INAA	5
0.11		IC	7					3		XRF	3	7.53		INAA	5
0.111		IC	7	0.039		MS	6	3		XRF	3	7.55		INAA	5
0.130		NAA	5	0.047		SSMS	6	9	◆ ○	XRF	3	7.7		INAA	5
0.131	◆ ○	RNAA	5	0.072		IC	7			Pr (ppm)					
0.131	◆ ○	NAA	5	0.072		IC	7							Sm (ppm)	
3.6	◆ ○	XRF	3	0.073		ICPMS	6					0.006		INAA	5
5	◆ ○	EXRF	3	0.27	◆ ○	INAA	5	0.012		MS	6	0.0076		INAA	5
6.1	◆ ○	INAA	5	0.3	◆ ○	XRF	3	0.014		SSMS	6	0.0095		INAA	5
6.1	◆ ○	NAA	5	1	◆ ○	XRF	3	0.014		ICPMS	6	0.014		IC	7
6.1	◆ ○	INAA	5					0.019		IC	7	0.019		MS	6
26	◆ ○	RNAA	5			Ni (ppm)		0.020		IC	7	0.020		NAA	5
								0.1	◆ ●	XRF	3	0.020		RNAA	5
										Rb (ppm)		0.020		NAA	5
				1890	◆ ○	XRF	3					0.020		SSMS	6
				2170	◆ ○	XRF	3					0.021		IC	7
0.0044		INAA	5	2300	◆ ○	ICPES	4					0.026		IC	7
0.005		INAA	5	2306		XRF	3	0.2		XRF	3	0.035	◆ ○	NAA	5
0.005		MS	6	2377		XRF	3	0.3		XRF	3				

Table 3 (Contd.-5)

Application of statistical tests on the sample population of analytical data for GSJ JP-1

DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR	DATA	OUTLIER	METH	GR
A	B			A	B			A	B			A	B		
<u>Zr (ppm) Cont.</u>				<u>Zr (ppm) Cont.</u>				<u>Zr (ppm) Cont.</u>				<u>Zr (ppm) Cont.</u>			
12.2	◆ ○	XRF	3	16	◆ ○	XRF	3	21	◆ ○	XRF	3	25	◆ ○	XRF	3

METH (Codes for analytical methods) are same as in Table 2, except for some additional or different abbreviations: DNA=Delayed neutron activation analysis; GAMMA=Gamma-ray counting; IC=Ion chromatography; INAA=Instrumental neutron activation analysis; MS=Mass spectrometry (general); NAA=Neutron activation analysis (general or unspecified); NM=Nuclear method; NT=Nuclear technique; RNAA=Radiochemical neutron activation analysis; SIMS=Secondary ion mass spectrometry. For method grouping see footnotes of Table 2.

Table 4

Relative efficiency of statistical tests for detecting outliers, based on their application to major and trace element data in USGS basalt BIR-1 using Option (A).

Elem.	n _m	Tests applied to database	Tests successful to detect outlier(s)
Major elements (%)			
Si	30	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N4(k=1-3), N7, N9-N13, N15, N16(k=1)
Ti	42	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=2-4), N4(k=2-4), N14, N15
Al	40	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N4(k=1), N16(k=1)
Fe ^t	42	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=4)
Mn	40	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	---
Mg	35	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=3), N4(k=2)
Ca	37	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2,3), N4(k=1-4), N14, N15, N16(k=1)
Na	42	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N14, N15, N16(k=1)
K	28	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N7-N13, N14, N15, N16(k=1)
P	22	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=4), N4(k=1-4), N7-N9, N11, N14, N16(k=1)
H ₂ O ⁺	11	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-3), N7-N12, N14, N16(k=1)
H ₂ O ⁻	7	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
FeO	11	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N10, N13
Trace elements (ppm or ppb)			
Ba	19	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N7-N9, N11- N13, N14, N15, N16(k=1)
Ce	19	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7-N9, N11-N13, N14, N15, N16(k=1)
Co	40	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=2,3), N4(k=2-4), N15
Cr	38	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N4(k=1,4), N16(k=1)

Table 4 (Contd.)

Relative efficiency of statistical tests for detecting outliers, based on their application to major and trace element data in USGS basalt BIR-1 using Option (A).

Elem.	n_{in}	Tests applied to database	Tests successful to detect outlier(s)
Cu	29	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N3(k=2-4), N4(k=2-4), N14, N15
Dy	14	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N3(k=2), N4(k=2-4), N11-N13, N14
Er	6	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
Eu	29	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N11-N13, N14, N15, N16(k=1)
Ga	11	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Gd	15	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N7-N9, N11-N13, N14, N15, N16(k=1)
Hf	15	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N3(k=2)
Ho	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N11-N13
La	25	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Li	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1), N7, N8, N11, N14, N16(k=1)
Lu	18	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2,3), N4(k=2-4), N11-N13, N14, N15
Nb	12	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Nd	13	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N3(k=2,3), N4(k=2-4)
Ni	31	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=2-4), N4(k=2-4), N14, N15
Rb	11	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N4(k=2-4), N14, N16(k=1)
Sb	13	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Sc	24	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N3(k=3)
Sm	28	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Sr	31	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N14, N15, N16(k=1)
Ta	6	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
Tb	12	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-3), N7-N13, N14, N15, N16(k=1)
Th	10	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Tm	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
V	28	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N11-N13, N14, N15, N16(k=1)
Y	25	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Yb	27	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2,3), N4(k=1-4), N11-N13, N14, N15, N16(k=1)
Zn	24	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N4(k=1-4)
Zr	15	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=2-4), N7-N13, N14, N15, N16(k=1)

n_{in} =initial number of observations of element concentration data; N1 to N16 refer to the individual tests of Table 1.

Table 5

Relative efficiency of statistical tests for detecting outliers, based on their application to major and trace element data in GSJ peridotite JP-1 using Option (A).

Elem.	n_n	Tests applied to database	Tests successful to detect outlier(s)
<u>Major elements (%)</u>			
SiO ₂	36	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=2-4), N4(k=1-4), N14, N15
TiO ₂	19	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Al ₂ O ₃	37	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N14, N15, N16(k=1)
Fe ₂ O ₃ ⁴	35	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)
MnO	41	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=2-4), N4(k=2-4), N14, N15, N16(k=1)
MgO	35	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N15
CaO	36	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N14, N15, N16(k=1)
Na ₂ O	31	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2,3), N4(k=1-4), N14, N15, N16(k=1)
K ₂ O	25	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N16(k=1)
P ₂ O ₅	18	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N11-N13, N14, N15, N16(k=1)
LOI	17	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
H ₂ O ⁺	6	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
H ₂ O ⁻	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
Fe ₂ O ₃	11	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
FeO	14	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
<u>Trace elements (ppm or ppb)</u>			
As	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1,2), N7-N13, N14, N15, N16(k=1)
Ba	25	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N7-N9, N11-N13, N14, N15, N16(k=1)
Ce	13	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Co	31	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2,3), N4(k=1-4), N14, N15
Cr	36	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)
Cs	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N3(k=2), N4(k=2), N11-N13
Cu	22	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Dy	7	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---

Table 5 (Contd.)

Relative efficiency of statistical tests for detecting outliers, based on their application to major and trace element data in GSJ peridotite JP-1 using Option (A).

Elem.	n_{in}	Tests applied to database	Tests successful to detect outlier(s)
Eu	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1,2), N7-N13, N14, N15, N16(k=1)
Gd	6	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1,2), N7-N13, N14, N15, N16(k=1)
Hf	14	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Ho	5	---	---
La	20	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N7-N9, N11-N13, N14, N15, N16(k=1)
Lu	9	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1,2), N7-N13, N14, N15, N16(k=1)
Mo	7	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
Nb	13	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Nd	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1,2), N7-N9, N11, N14, N16(k=1)
Ni	32	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-3), N15, N16(k=1)
Pb	7	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N7
Pr	6	N1, N2, N4(k=1), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1), N7-N11, N14, N16(k=1)
Rb	20	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Sc	16	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N8-N13, N14, N15, N16(k=1)
Sm	14	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N11-N13, N14, N15, N16(k=1)
Sr	18	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Tb	8	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1,2), N7-N13, N14, N15, N16(k=1)
Th	11	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N11-N13, N14, N15, N16(k=1)
U	17	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7-N13, N14, N15, N16(k=1)
V	28	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Y	16	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Yb	12	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7-N9, N11-N13, N14, N15, N16(k=1)
Zn	36	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N4(k=1), N16(k=1)
Zr	30	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N11, N14, N15, N16(k=1)

n_{in} =initial number of observations of element concentration data; N1 to N16 refer to the individual tests of Table 1.

Table 6

Relative efficiency of statistical tests for detecting outliers, based on their application to major and trace element data in USGS basalt BIR-1 using Option (A).

Elem.	n_n	Tests applied to database	Tests successful to detect outlier(s)
<u>Major elements (%)</u>			
Ti	40	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)
Mn	39	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N14, N16(k=1)
<u>Trace elements (ppm or ppb)</u>			
Co	38	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=2-4), N4(k=2-4), N14
Cr	36	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1,4), N14, N16(k=1)
Cu	26	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N3(k=2-4), N4(k=2-4), N14, N15
Ga	9	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
Gd	14	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N16(k=1)
Li	7	N1, N2, N4(k=1), N7-N13, N14, N15, N16(k=1)	---
Lu	17	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Nb	11	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N13
Nd	11	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	N1, N2, N4(k=1), N7, N9, N11, N12, N14, N16(k=1)
Ni	29	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N4(k=1-4), N8-N13, N14, N15, N16(k=1)
Zn	13	N1, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---

The results of the application of Option (B) to the other elements in BIR-1 were same as in Option (A) (see Tables 2 and 4 for more details).

For JP-1 different variants of the tests were applied to fifteen major and twenty-two trace elements (Table 3). Using Option (A), the major elements TiO_2 , LOI (loss on ignition), H_2O^+ , H_2O^- , Fe_2O_3 , and FeO and trace elements Dy, Ho, Mo, Nb, Sr, Tb, and Y showed no outliers in JP-1 (Table 5). For other elements, outliers were generally detected by several tests and their variants. In Option (B), two major elements (SiO_2 and CaO) and six trace elements (As, Gd, Pr, U, Yb, and Zn) showed significant method-related differences. Neutron activation analysis (NAA) gave significantly greater concentrations than the other more conventional methods used for major element analysis. XRF did so for As, Gd, Pr, U, and Yb. Chemical methods gave biased results for CaO and Zn in JP-1 (Table 3). Later application of statistical tests by SIPVADE to the remaining data for these eight elements

(Table 7) detected outliers for only three elements (SiO_2 , CaO, and U).

For both RM (BIR-1 and JP-1), the outlying observations were generally obtained by similar analytical methods as those used for the valid observations. The outliers may correspond to observations with greater analytical errors involved during sample preparation, instrumental calibrations, and sample measurements.

DATA PRESENTATION

Statistical information

The final mean concentrations and other statistical parameters are given in Tables 8 and 9 for Option (A) and

Table 7

Relative efficiency of statistical tests for detecting outliers, based on their application to major and trace element data in GSJ peridotite JP-1 using Option (B).

Elem.	n_{in}	Tests applied to database	Tests successful to detect outlier(s)
<u>Major elements (%)</u>			
SiO ₂	33	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)
CaO	34	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=2-4), N14, N15
<u>Trace elements (ppm or ppb)</u>			
As	7	N1, N2, N3(k=2), N4(k=1,2), N7-N13, N14, N15, N16(k=1)	---
Gd	5	---	---
Pr	5	---	---
U	16	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N7-N13, N14, N15, N16(k=1)
Yb	11	N1, N2, N3(k=2-4), N4(k=1-4), N7-N13, N14, N15, N16(k=1)	---
Zn	35	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	---

The results of the application of Option (B) to the other elements in BIR-1 were same as in Option (A) (see Tables 3 and 5 for more details).

Tables 10 and 11 for Option (B) respectively. The new mean values are categorised, following the criteria proposed by Potts and Kane (1992) and modifications by Verma (1997) for downgrading the provisional values. In this classification, the criteria, %RSD (relative standard deviation in percent) as a function of the concentration band of analyte and the number of observations remaining (n_{out}) after outlier rejection as well as the number of independent methods to obtain these data, are used to define the quality of the resulting data as: high-quality *cv*e (certified value equivalent), intermediate-quality *rv* (recommended value), and low-quality *pv* (provisional value) downgraded to pv_1 and pv_2 . The presentation of all individual data along with the respective analytical methods in Tables 2 and 3 enables the reader to check this category assignment, particularly for elements with small number of total valid observations.

Using Option (A), the proportion of outliers for major elements varied from 0% to 36% in BIR-1 (Table 8) and 0% to 25% in JP-1 (Table 9). For trace elements, the %Otd were from 0% to about 40% in BIR-1 and from 0% to about 46%

in JP-1. The proportions of outliers were slightly smaller for Option (B) (Tables 10 and 11).

For USGS basalt BIR-1 using Option (A), four major elements (Ti, Fe^t, Ca, and FeO) are characterized as *cv*e and five (Si, Al, Mn, Mg, and Na) as *rv*, with the remaining four elements still as *pv* or pv_1 (Table 8). For this RM four trace elements (Cu, Eu, Sc, and Sr) are *cv*e, eighteen *rv*, and the remaining ten are only provisional (eight *pv*, one pv_1 , and one pv_2). Three major elements (SiO₂, Fe₂O₃^t, and CaO) in GSJ peridotite JP-1 are of *cv*e quality, three (MnO, MgO, and FeO) are *rv*, and three *pv*, and the remaining six pv_1 or pv_2 (Table 9). In this RM only three trace elements (Co, Ni, and Sc) are at present *cv*e, nine *rv*, six *pv*, and the remaining four downgraded provisional values. The application of Option (B) resulted in *cv*e quality for two elements (Ti and Cu) and *rv* for all the other eleven elements for BIR-1 included in Table 10. For JP-1 two major elements (SiO₂ and CaO) are *cv*e quality and three trace elements (As, Yb, and Zn) *rv*, whereas two trace elements (Gd and Pr) are still of *pv* quality due to small number of observations (Table 11).

Table 8

Initial and final statistical data (after outlier detection and rejection) on major and trace elements in USGS basalt BIR-1, using Option (A).

Elem.	n_m	\bar{x}_{in}	s_{in}	O_t	n_{out}	%Otd	Min.	Max.	\bar{x}	s	95% Confidence limits		%RSD	Qv
Major elements (%)														
Si	30	22.3	0.5	4	26	13	21.8	22.77	22.31	0.24	22.22	22.41	1.1	rv
Ti	42	0.55	0.08	9	33	27	0.533	0.605	0.57	0.02	0.565	0.577	2.9	cve
Al	40	8.1	0.5	1	39	2.5	7.14	8.89	8.07	0.39	7.94	8.19	4.8	rv
Fe ^t	42	7.83	0.25	4	38	9.5	7.48	8.26	7.89	0.18	7.83	7.95	2.3	cve
Mn	41	0.13	0.01	0	41	0	0.099	0.172	0.132	0.014	0.128	0.137	10	rv
Mg	35	5.83	0.43	2	33	5.7	4.64	6.33	5.76	0.33	5.64	5.88	5.7	rv
Ca	37	9.4	0.5	4	33	11	9.01	9.84	9.48	0.19	9.41	9.55	2.0	cve
Na	42	1.32	0.17	4	38	11	1.05	1.41	1.29	0.09	1.25	1.32	7.3	rv
K	28	0.03	0.03	5	24	14	0.007	0.031	0.020	0.007	0.017	0.024	36	pv
P	22	0.023	0.017	8	14	36	0.009	0.019	0.013	0.004	0.010	0.015	30	pv
H ₂ O ⁺	11	0.11	0.07	3	8	27	0.04	0.11	0.080	0.025	0.059	0.100	31	pv
H ₂ O ⁻	7	0.07	0.04	0	7	0	0.013	0.14	0.07	0.04	0.033	0.107	57	pv_i
FeO	11	8.36	0.22	2	9	18	8.30	8.72	8.43	0.15	8.31	8.54	1.8	cve
Trace elements (ppm)														
Ba	19	26	48	4	15	21	5	19	9.5	4.4	7.1	12.0	46	pv
Ce	19	10	29	4	15	21	1.2	5	2.5	1.1	1.9	3.1	45	pv
Co	40	51	11	8	32	20	43.5	62.0	51.8	3.8	50.4	53.2	7.4	rv
Cr	38	387	56	4	34	11	286	450	374	39	360	387	11	rv
Cu	29	116	27	9	20	31	117	131	125	4	124	127	3.0	cve
Dy	14	3.0	1.2	4	10	29	2.0	3.0	2.41	0.33	2.18	2.64	14	rv
Er	6	1.85	0.26	0	6	0	1.58	2.30	1.85	0.26	1.57	2.12	14	rv
Eu	29	0.57	0.09	4	25	14	0.48	0.61	0.54	0.04	0.53	0.56	7.0	cve
Ga	11	15	5	0	11	0	7	23	15	5	12.1	18.4	31	pv
Gd	15	2.1	0.9	4	11	27	1.41	2.00	1.76	0.24	1.59	1.92	14	rv
Hf	15	0.61	0.10	2	13	13	0.48	0.67	0.57	0.06	0.54	0.61	10	rv
Ho	8	0.9	0.7	2	6	25	0.40	0.62	0.50	0.07	0.42	0.58	15	rv
La	24	5	15	8	16	33	0.51	1.0	0.77	0.17	0.68	0.86	22	rv
Li	8	3.7	0.9	3	5	38	3	3.4	3.21	0.19	2.97	3.45	5.9	pv
Lu	18	0.31	0.14	4	14	22	0.2	0.302	0.25	0.03	0.23	0.27	12	rv
Nb	12	12	34	4	8	33	0.78	2.30	1.9	0.5	1.5	2.3	26	rv
Nd	13	2.7	0.8	4	9	31	1.83	2.40	2.20	0.20	2.04	2.35	9.2	rv
Ni	31	160	52	8	23	26	139	198	166	13	161	172	7.8	rv
Rb	11	1.8	2.1	4	7	36	0.28	1.10	0.69	0.31	0.40	0.98	45	pv
Sb	13	0.52	0.22	0	13	0	0.15	0.83	0.52	0.22	0.38	0.65	43	pv

Table 8 (Contd.)

Initial and final statistical data (after outlier detection and rejection) on major and trace elements in USGS basalt BIR-1, using Option (A).

Elem.	n_{in}	\bar{x}_{in}	s_{in}	O_t	n_{out}	%Otd	Min.	Max.	\bar{x}	s	95% Confidence limits		%RSD	Qv
Sc	24	42	9	9	15	38	41	45.1	43.5	1.2	42.8	44.2	2.9	<i>cve</i>
Sm	28	1.12	0.20	4	24	14	0.92	1.20	1.06	0.08	1.03	1.10	7.5	rv
Sr	31	147	220	10	21	32	100	122	110	5	107	112	4.7	<i>cve</i>
Ta	6	0.08	0.06	0	6	0	0.03	0.18	<i>0.08</i>	0.06	0.02	0.14	71	<i>pv₁</i>
Tb	12	0.43	0.13	3	9	25	0.26	0.42	0.37	0.05	0.34	0.41	13	rv
Th	10	0.8	0.7	0	10	0	0.14	2.0	<i>0.8</i>	0.7	0.36	1.3	80	<i>pv₂</i>
Tm	8	0.27	0.07	0	8	0	0.195	0.40	0.27	0.07	0.22	0.33	25	rv
V	28	317	60	8	20	29	290	350	313	16	306	321	5.1	rv
Y	25	16.7	4.3	0	25	0	7.2	27.2	<i>16.7</i>	4.3	14.9	18.5	26	<i>pv</i>
Yb	27	1.8	0.5	4	23	15	1.14	1.97	1.67	0.21	1.58	1.76	13	rv
Zn	24	72	10	4	20	17	57.5	80	69	6	66	72	9.3	rv
Zr	15	28	24	4	11	27	12.0	25.8	<i>19.2</i>	4.0	16.5	21.9	21	<i>pv</i>

The abbreviations are: n_{in} =initial number of observations for concentration of an element; \bar{x}_{in} =arithmetic mean of the initial set of observations before outlier detection and rejection; s_{in} =initial standard deviation; O_t =number of outlier data detected by the statistical tests outlined in this paper; n_{out} =final number of observations remaining after outlier rejection; %Otd=percentage of outlier data eliminated from the initial observations; Min.=minimum concentration value of the final set of observations; Max.=maximum concentration value of the final set of observations; \bar{x} =arithmetic mean of the final set of observations remaining after outlier rejection; s=final standard deviation; 95% Confidence limits=probability limits of the final mean at 95% confidence level; %RSD=percentage of final relative standard deviation with respect to the final mean concentration; Qv=quality value according to Potts and Kane (1992) and modifications for downgrading of provisional values proposed by Verma (1997).

Reasons for dispersion of inter-laboratory data

The standard deviations for many trace elements were still high resulting in a poor characterization of these RM. This may be due to several reasons: (i) the presence of systematic differences between the concentration data obtained by different analytical methods; (ii) use of all available data irrespective of whether or not they included explicitly their precision; or (iii) real dispersion in the data from different laboratories. The first possibility was statistically tested using ANOVA and when a bias was detected, these differences were taken into account and the data were processed adequately using Option (B) as explained above. The second possible cause is now examined for BIR-1, because only for this RM (and not for JP-1) some individual data are presented explicitly with the information on their precision (Gladney and Roelandts, 1988). Results for two

elements, Ba and Ce, that are critically important from geochemical point of view, are presented here as typical examples. The individual data with reported precision for Ba and Ce were compiled and processed for outliers using the SIPVADE program. Then the initial and final statistics was computed and the results were compared in Table 12 with those obtained earlier (Table 8) using all available individual data. The initial dispersion of the data with precision is comparable to that shown by all available data (compare %RSD_{in} in Table 12). Both sets of data showed the presence of outliers that were eliminated. The final dispersion is in fact greater for the data with reported precision (compare %RSD_{out} in Table 12). The lack of improvement in the final statistics from the data with precision vs. all data is most likely due to the fact that the reported precision of individual data does not correspond to the reproducibility of the entire experiment but only a part of it. For example, it is customary

Table 9

Initial and final statistical data (after outlier detection and rejection) on major and trace elements in GSJ peridotite JP-1, using Option (A).

Elem.	n_{in}	\bar{x}_{in}	s_{in}	O_t	n_{out}	%Otd	Min.	Max.	\bar{x}	s	95% Confidence limits		%RSD	Qv
Major elements (%)														
SiO ₂	36	43	2	9	27	25	41.73	42.8	42.25	0.33	42.12	42.38	0.8	<i>cve</i>
TiO ₂	19	0.016	0.007	0	17	0	0.012	0.019	<i>0.016</i>	0.007	0.003	0.03	47	<i>pv₁</i>
Al ₂ O ₃	37	0.66	0.16	4	33	11	0.56	0.99	<i>0.69</i>	0.11	0.65	0.73	16	<i>pv</i>
Fe ₂ O ₃ [†]	35	8.5	0.5	6	29	17	7.78	8.83	8.36	0.20	8.28	8.44	2.4	<i>cve</i>
MnO	41	0.12	0.01	5	36	12	0.11	0.13	0.122	0.006	0.120	0.124	5.1	<i>rv</i>
MgO	35	44.7	1.2	2	33	5.7	44.96	47.26	44.7	0.8	44.4	45.0	1.9	<i>rv</i>
CaO	36	0.6	0.3	8	28	22	0.53	0.60	0.555	0.019	0.55	0.56	3.4	<i>cve</i>
Na ₂ O	31	0.05	0.05	6	25	19	0.01	0.06	<i>0.028</i>	0.013	0.023	0.034	46	<i>pv₁</i>
K ₂ O	25	0.014	0.010	1	24	4.0	0.003	0.03	<i>0.013</i>	0.009	0.009	0.016	69	<i>pv₂</i>
P ₂ O ₅	18	0.017	0.017	4	14	22	0.001	0.02	<i>0.011</i>	0.007	0.006	0.015	66	<i>pv₂</i>
LOI	17	2.9	0.7	0	17	0	2.01	4.44	<i>2.9</i>	0.7	2.54	3.25	24	<i>pv₁</i>
H ₂ O ⁺	6	2.39	0.15	0	6	0	2.23	2.68	<i>2.39</i>	0.15	2.23	2.55	6.3	<i>pv</i>
H ₂ O ⁻	8	0.46	0.09	0	8	0	0.34	0.60	<i>0.46</i>	0.09	0.39	0.54	20	<i>pv</i>
Fe ₂ O ₃	11	2.0	0.6	0	11	0	1.05	3.09	<i>2.0</i>	0.6	1.58	2.37	30	<i>pv₂</i>
FeO	14	5.9	0.6	0	14	0	4.58	6.75	5.9	0.6	5.57	6.20	9.3	<i>rv</i>
Trace elements (ppm)														
As	8	0.8	1.1	2	6	25	0.26	0.40	0.34	0.05	0.29	0.39	13	<i>rv</i>
Ba	25	22	15	4	21	25	7.3	29	<i>17</i>	6	13.9	19.4	37	<i>pv</i>
Ce	13	8	17	6	7	46	0.056	0.8	<i>0.35</i>	0.29	0.08	0.62	83	<i>pv₂</i>
Co	31	112	21	4	27	13	107	130	117	5	115	120	4.6	<i>cve</i>
Cr	36	2650	670	4	32	11	2468	3272	2850	200	2779	2926	7.1	<i>rv</i>
Cs	8	0.1	0.1	2	6	25	0.02	0.06	0.045	0.015	0.028	0.061	34	<i>rv</i>
Cu	22	8	5	4	18	18	3	10.4	<i>6.2</i>	2.1	5.1	7.2	34	<i>pv</i>
Dy	7	0.02	0.05	0	7	0	0.019	0.032	0.024	0.005	0.020	0.029	19	<i>rv</i>
Eu	8	0.02	0.06	2	6	25	0.003	0.037	<i>0.019</i>	0.015	0.038	0.035	76	<i>pv₁</i>
Gd	8	0.4	1.0	2	4	33	---							
Hf	14	0.20	0.13	4	10	40	0.08	0.20	0.135	0.030	0.11	0.16	22	<i>rv</i>
Ho	5	0.013	0.007	0	5	0	0.005	0.018	<i>0.013</i>	0.007	0.004	0.022	56	<i>pv</i>
La	20	3	6	8	12	40	0.026	0.130	<i>0.019</i>	0.015	0.004	0.035	76	<i>pv₁</i>
Lu	9	0.5	1.4	2	7	22	0.0044	0.038	<i>0.018</i>	0.017	0.003	0.033	91	<i>pv₁</i>
Mo	7	0.6	0.6	0	7	0	0.01	1.6	<i>0.6</i>	0.6	0.2	0.9	99	<i>pv₂</i>
Nd	8	0.2	0.3	3	5	38	0.039	0.073	0.061	0.016	0.040	0.081	27	<i>rv</i>
Nb	13	1.2	1.0	0	13	0	0.058	3	<i>1.2</i>	1.0	0.6	1.8	80	<i>pv₂</i>

Table 9 (Contd.)

Initial and final statistical data (after outlier detection and rejection) on major and trace elements in GSJ peridotite JP-1, using Option (A).

Elem.	n_{in}	\bar{x}_{in}	s_{in}	O_t	n_{out}	%Otd	Min.	Max.	\bar{x}	s	95% Confidence limits		%RSD	Qv
Ni	32	2460	170	6	26	19	2306	2600	2460	72	2440	2490	2.9	<i>cve</i>
Pb	7	2	3	1	6	14	0.114	3	1.1	1.5	-0.46	2.64	135	<i>pv₂</i>
Pr	6	0.03	0.03	1	5	17	0.012	0.020	0.016	0.003	0.011	0.020	22	<i>pv</i>
Rb	20	1.6	1.6	4	16	20	0.2	2.1	1.0	0.7	0.65	1.41	70	<i>pv₁</i>
Sc	16	7.0	0.6	4	12	25	7	7.7	7.29	0.25	7.1	7.5	3.4	<i>cve</i>
Sm	14	0.9	2.2	4	10	29	0.006	0.026	0.016	0.007	0.012	0.021	40	<i>pv</i>
Sr	18	3	2	0	18	0	0.2	8	3	2	2.1	4.4	70	<i>pv₁</i>
Tb	8	0.008	0.007	2	6	25	0.002	0.012	0.006	0.005	0.001	0.011	78	<i>pv₁</i>
Th	11	0.6	1.0	4	7	36	0.014	0.2	0.1	0.7	0.04	0.18	69	<i>pv₁</i>
U	17	0.2	0.5	4	13	24	0.0078	0.055	0.026	0.016	0.016	0.037	63	<i>pv₁</i>
V	28	27	7	8	20	29	23	32	26.9	2.7	25.6	28.1	10	rv
Y	16	0.14	0.12	0	16	0	0.064	4	1.4	1.2	0.82	2.05	81	<i>pv₂</i>
Yb	12	5	17	4	8	33	0.017	0.024	0.020	0.003	0.018	0.023	14	rv
Zn	36	44	9	1	35	2.8	27	54	43	7	40	45	17	rv
Zr	30	8	5	4	26	13	3.0	12	6.8	2.6	5.8	7.9	38	<i>pv</i>

For abbreviations, see explanation of Table 8.

to report as precision the errors related to the counting statistics in nuclear methods, without taking into account the possible errors related to irradiation conditions and to calibrations. Thus, the second possibility was also unsuccessful to explain the dispersion observed in the final element concentration data in BIR-1. I conclude that there is a real dispersion in the analytical data obtained by different laboratories.

COMPARISON WITH EARLIER COMPILATIONS

The results obtained by the present objective statistical approach are compared in Table 13, with the two standard deviation method used for basalt BIR-1 by Gladney and Roelandts (1988) and peridotite JP-1 by Imai *et al.* (1995). This method has recently been criticized by Verma (1997).

For BIR-1, the present statistical method gives mean values that are generally characterized by smaller standard deviations (Table 13 and Figure 2) than those obtained by

Gladney and Roelandts (1988). Smaller standard deviations were obtained for P, Rb, Sc, Sr, Zr, and some of the REE (La, Nd, and Gd). The elements Ba, Ga, Sb, and Y, on the other hand, show higher standard deviations for the present results. This may be due to the fact that in the two standard deviation method, valid observations lying in the field B and the extreme left-part of field A in Figure 1 were erroneously identified as outliers, resulting in smaller standard deviations of the corresponding final mean values. Some mean concentration values are also different than in the earlier literature (Figure 3). Those with more than 10% difference are P, H₂O⁺, Ba, La, Nd, Rb, Sb, Tb, Zn, and Zr (Figure 3). Similar conclusions are reached for peridotite JP-1 (Table 13; Figures 4 and 5). The %RSD for major elements in JP-1 could not be compared with earlier literature, as no standard deviations were available for these elements (Ando *et al.*, 1987; internet address <http://www.aist.go.jp/RIODB/geostand/welcome.html>). For trace elements Ba, Hf, V, and Sm, the present method gave mean values characterized by a smaller standard deviation than the earlier literature (Imai *et al.*, 1995). The opposite is true for

Table 10

Initial and final statistical data (after outlier detection and rejection) on major and trace elements in USGS basalt BIR-1, using Option (B).

Elem.	n_{in}	\bar{x}_{in}	s_{in}	O_t	n_{out}	%Otd	Min.	Max.	\bar{x}	s	95% Confidence limits		%RSD	Qv
Major elements (%)														
Ti	40	0.56	0.06	8	32	20	0.533	0.604	0.570	0.016	0.565	0.576	2.8	<i>cve</i>
Mn	39	0.134	0.011	4	35	10	0.116	0.148	0.131	0.007	0.129	0.133	5.3	rv
Trace elements (ppm)														
Co	38	53	8	4	34	11	35	62	51	5	49	53	9.7	rv
Cr	36	393	52	4	32	11	311	450	379	34	367	391	8.9	rv
Cu	26	122	16	8	18	31	117	131	124.9	3.6	123	127	2.9	<i>cve</i>
Ga	9	17.0	3.0	0	9	0	13.5	23	17.0	3.0	14.7	19.3	18	rv
Gd	14	1.91	0.42	1	13	7.1	1.41	2.3	1.83	0.29	1.66	2.00	16	rv
Li	7	3.39	0.35	0	7	0	3.0	3.9	3.39	0.35	3.07	3.72	10	rv
Lu	17	0.29	0.10	4	13	24	0.200	0.292	0.246	0.029	0.228	0.263	12	rv
Nb	11	2.2	0.8	2	9	18	0.78	2.45	2.0	0.5	1.6	2.4	25	rv
Nd	11	2.35	0.44	2	9	18	1.83	2.40	2.20	0.20	2.04	2.35	9.1	rv
Ni	29	168	41	6	23	21	148	200	169	13	163	175	7.7	rv
Zn	13	79	8	0	13	0	67	92	79	8	74	84	10	rv

The results of the application of Option (B) to the other elements in BIR-1 were same as in Option (A) (see Table 8 for more details).

%RSD of Zr in JP-1. The mean values differ by more than 10% for Ba, Hf, La, Nb, Sm, and Zr in this RM. Imai *et al.* (1995) failed to compute mean values with respective standard deviations for several elements (Cs, Ce, Pr, Nd, Eu, Gd, Tb, Ho, and Lu), for which such information is now computed and reported in Table 13. This makes JP-1 more useful as a RM than was possible earlier.

Statistical F and t-tests were carried out to learn if the differences in the mean values between the present results and the literature data are statistically significant (Davis, 1973; Jensen *et al.*, 1997). The F test showed unequal variance for Al, Mg, Ba, Co, and Y in BIR-1. For the other elements in BIR-1 and all elements in JP-1, no significant difference in variance was observed at the 95% confidence level. From t-tests, the mean values for P and Zn in BIR-1 and Hf and La in JP-1 were found to be significantly different at 95%

confidence level. The mean values of Tb and H_2O^+ in BIR-1 also differed at a smaller significance level of about 90% and 80% respectively. Based on their analytical work on BIR-1, Jochum and Jenner (1994) pointed out method-related systematic differences in concentrations of some trace elements in this RM, although they did not use any population tests.

For many elements the difference in the mean values was not statistically significant. However, the use of different sets of values will affect instrumental calibrations such as those involved in XRF and NAA, because these calibrations are generally based only on the mean values without a reference to their standard deviations. Note that the concentration data with only provisional quality (*pv* but more particularly downgraded *pv₁* or *pv₂*) should not be used in such calibrations.

Table 11

Initial and final statistical data (after outlier detection and rejection) on major and trace elements in GSJ peridotite JP-1, using Option (B).

Elem.	n_{in}	\bar{x}_{in}	s_{in}	O_t	n_{out}	%Otd	Min.	Max.	\bar{x}	s	95% Confidence limits		%RSD	Qv
Major elements (%)														
SiO ₂	33	42.6	1.0	6	27	18	41.73	42.80	42.25	0.33	42.12	42.38	0.8	<i>cve</i>
CaO	34	0.55	0.05	8	26	24	0.53	0.59	0.553	0.017	0.546	0.560	3.1	<i>cve</i>
Trace elements (ppm)														
As	7	0.36	0.07	0	7	0	0.26	0.5	0.36	0.07	0.30	0.43	19	<i>rv</i>
Gd	5	0.015	0.001	0	5	0	0.013	0.016	0.015	0.001	0.013	0.013	6.7	<i>pv</i>
Pr	5	0.016	0.003	0	5	0	0.012	0.020	0.016	0.003	0.011	0.020	19	<i>pv</i>
U	16	0.04	0.05	4	12	25	0.0078	0.050	0.024	0.015	0.015	0.034	62	<i>pv₁</i>
Yb	11	0.022	0.004	0	11	0	0.017	0.028	0.022	0.004	0.020	0.025	18	<i>rv</i>
Zn	35	43	7	0	35	0	27	54	43	7	40	45	16	<i>rv</i>

The results of the application of Option (B) to other elements in JP-1 were same as in Option (A) (see Table 9 for more details).

Table 12

Comparison of the results processed by the present Option (A) for Ba and Ce in USGS BIR-1, using all data vs. only those data with reported precision in Gladney and Roelandts (1988).

Parameter	Ba		Ce	
	All data	Data with precision	All data	Data with precision
n_{in}	19	10	19	12
\bar{x}_{in}	26	41	10	15
s_{in}	48	64	29	36
%RSD _{in}	185	156	290	240
O_t	4	2	4	4
n_{out}	15	8	15	8
x_{min}	5	5.7 ± 0.6	1.2	1.2 ± 0.4
x_{max}	19	33.8 ± 1.3	5	5 ± 3
\bar{x}_{out}	9.5	14.5	2.5	2.4
s_{out}	4.4	9.3	1.1	1.3
%RSD _{out}	46	64	44	54

The abbreviations are same as in Table 8. The subscripts n_{in} and n_{out} refer to the initial and final sets of data respectively. x_{min} = smallest observation in the final set of data; x_{max} = greatest observation in the final set of data.

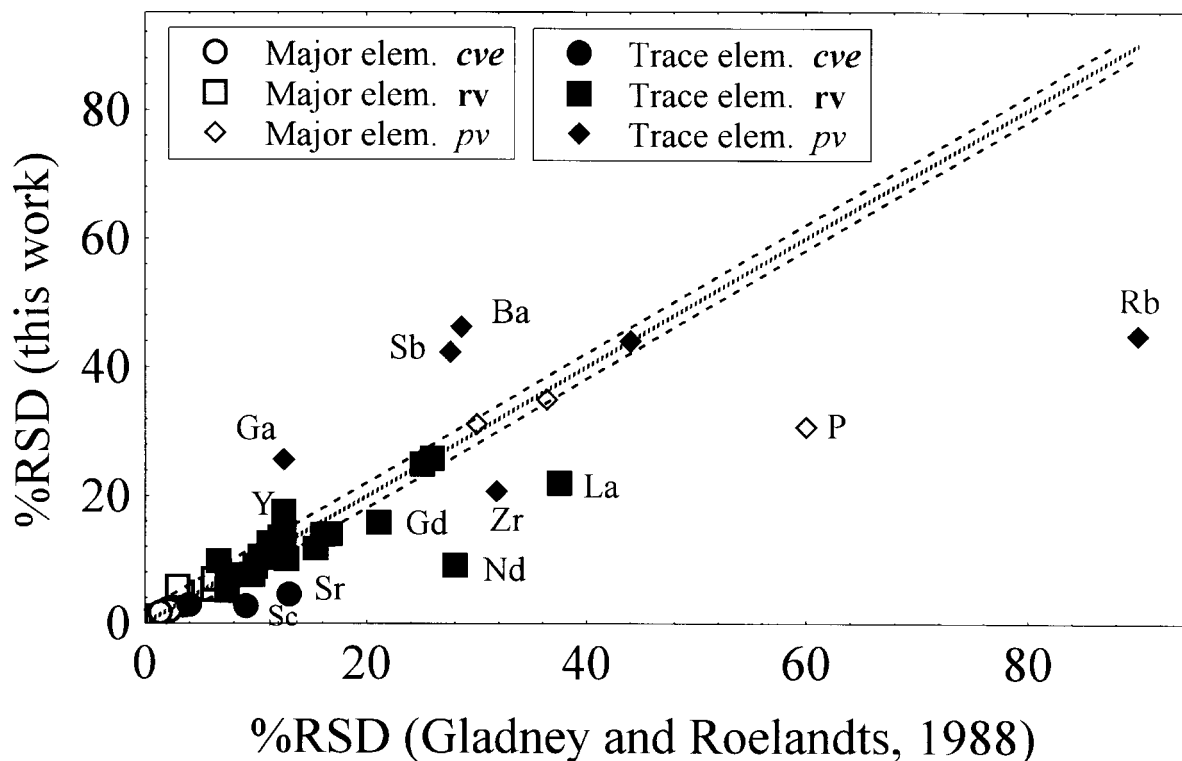


Fig. 2. Comparison of %RSD (relative standard deviation expressed in %) obtained in the present work for several major and trace elements in basalt BIR-1 (Tables 8 and 10) with %RSD reported by Gladney and Roelandts (1988). The diagonal dotted line is the trace of equal %RSD. The dashed lines represent 2% difference between these two %RSD values (present work vs. Gladney and Roelandts, 1988).

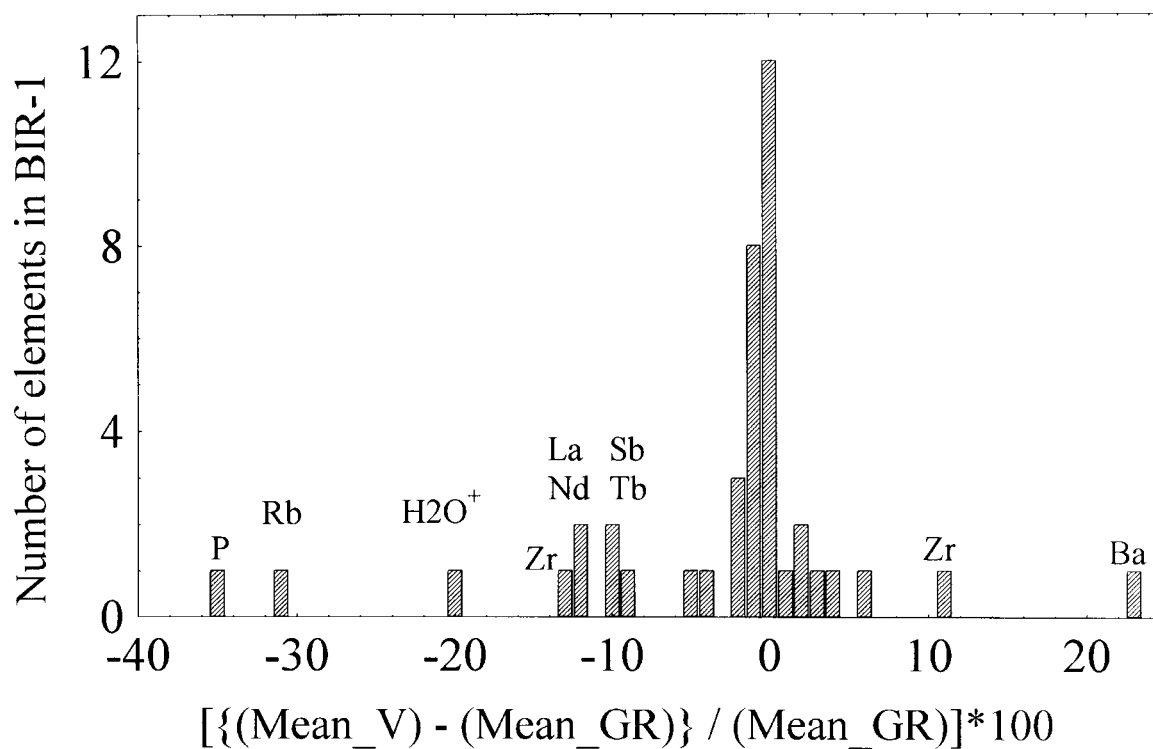


Fig. 3. Histogram plot of the % normalized difference of mean concentration (Mean_V) obtained in this work for forty-two major and trace elements with respect to the mean value (Mean_GR) reported by Gladney and Roelandts (1988) for basalt BIR-1.

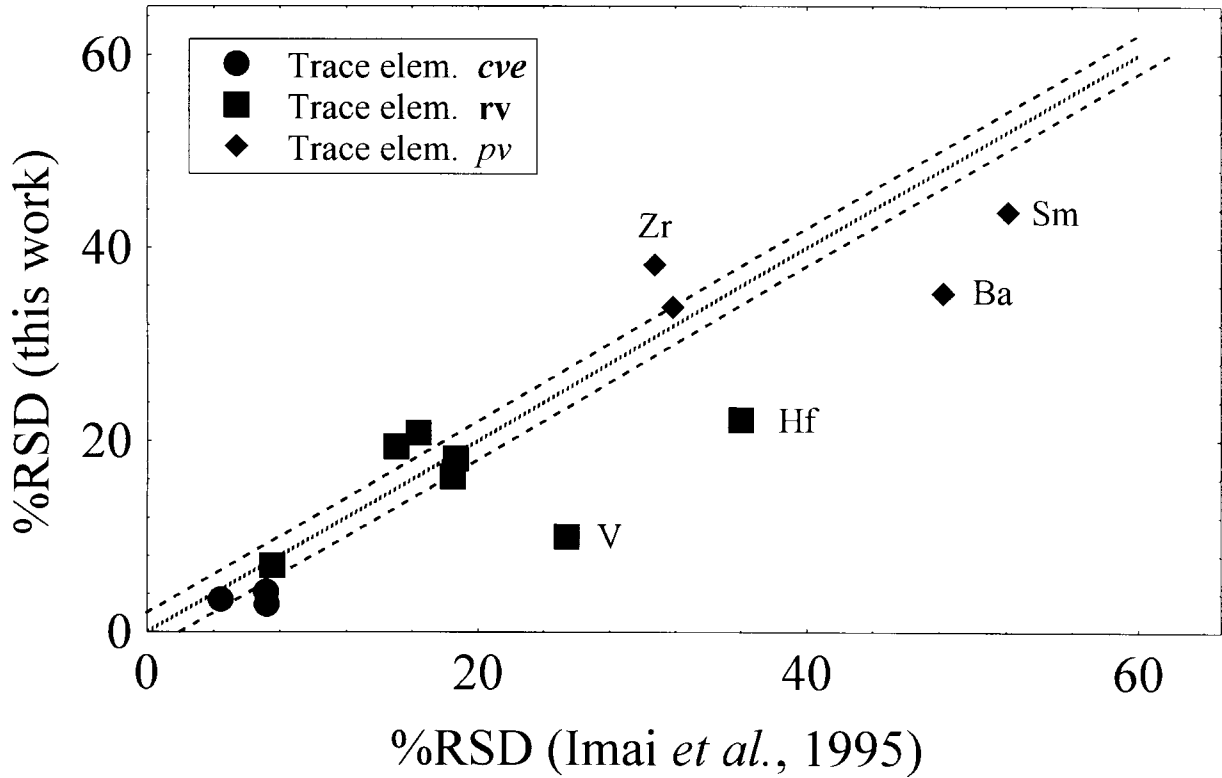


Fig. 4. Comparison of %RSD obtained in the present work for several trace elements in peridotite JP-1 (Tables 9 and 11) with %RSD reported by Imai *et al.* (1995). The diagonal dotted line is the trace of equal %RSD. The dashed lines represent 2% difference between these two sets of %RSD.

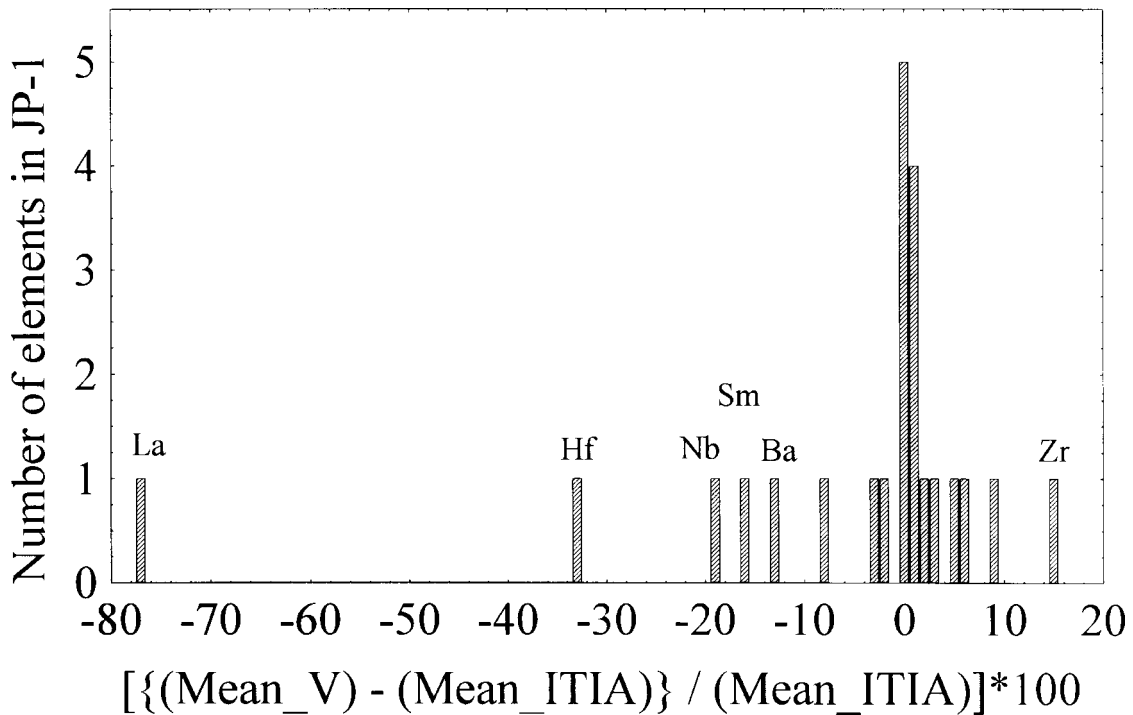


Fig. 5. Histogram plot of the % normalized difference of mean concentration (Mean_V) obtained in this work for twenty-three major and trace elements with respect to the mean value (Mean_ITIA) reported by Imai *et al.* (1995) for peridotite JP-1. The major element mean values for comparison were taken from internet <http://www.aist.go.jp/RIODB/geostand/welcome.html>.

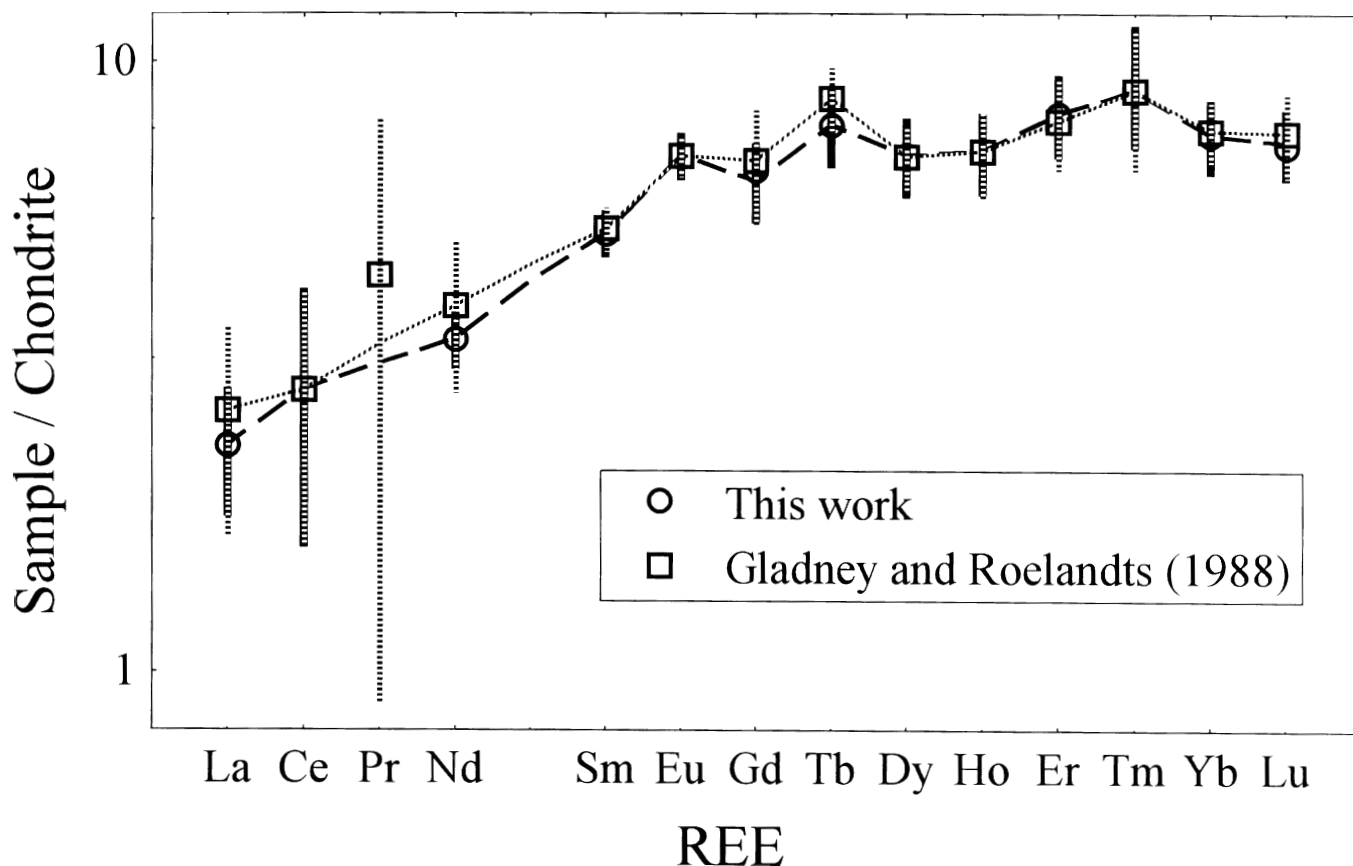


Fig. 6. Masuda-Coryell plot (chondrite-normalized diagram) for the REE mean concentration data from this work and comparison with the most recent literature compilation (Gladney and Roelandts, 1988) for basalt BIR-1 (both sets of data synthesized in Table 13). Vertical error-bars (\pm one standard deviation; Table 13) are also included for reference, using solid lines for this work and dashed lines for Gladney and Roelandts (1988). The chondrite data used for normalization of the REE plots are from Nakamura (1974) by isotope dilution mass spectrometry complemented by Haskin *et al.* (1968) by instrumental neutron activation analysis: La=0.329, Ce=0.865, Pr=0.112, Nd=0.63, Sm=0.203, Eu=0.077, Gd=0.276, Tb=0.047, Dy=0.343, Ho=0.07, Er=0.225, Tm=0.03, Yb=0.22, and Lu=0.0339.

A graphical comparison between the calculated mean REE data for BIR-1 and the published values from the most recent literature compilation (Table 13) is shown in Figure 6. The normalizing values are taken from Nakamura (1974) by isotope dilution mass spectrometry and complemented by data of Haskin *et al.* (1968) by neutron activation analysis, as recommended by Rock (1987). The main value of this normalized diagram lies in the possibility to identify aberrant values of REE concentrations when there are significant departures from the expected coherent and smooth nature of these patterns for most elements except Ce and Eu (e.g., Itoh *et al.*, 1993). The present mean values define, in general, a smoother normalized curve than that based on the average REE data by Gladney and Roelandts (1988). Inclusion of vertical error-bars (\pm one standard deviation) facilitates a comparison of the quality of these REE data, which seems to be generally satisfactory and better for the present method. No Pr mean value was obtained in the present work because sufficient observations (at least six data) were not available

in the database. A poorly characterized value from Gladney and Roelandts (1988) is included in Figure 6.

The present mean values for La, Sm, Dy, and Yb in JP-1 (Table 13) are smaller than those reported by earlier compilers (Ando *et al.*, 1989; Itoh *et al.*, 1993; Imai *et al.*, 1995). In the most recent compilation of JP-1 (Imai *et al.*, 1995), only four REE could be assigned mean values with respective standard deviations (Table 13). At present, three elements (Nd, Dy, and Yb) in JP-1 are classified as recommended values (*rv*) and four (Pr, Sm, Gd, and Ho) as provisional values (*pv*). This poor characterization is due to the paucity of the REE data for JP-1, as at least six valid observations were not available for Er and Tm.

The main reason for inaccuracies in the REE in JP-1 is obviously the great difficulty in measuring these elements at chondritic to sub-chondritic concentration levels. Samples, such as JP-1, with very low REE concentrations, need to be

Table 13

Comparison of final summary of major and trace element data in two reference materials (BIR-1 and JP-1) with published literature data derived by two standard deviation method (an outdated and less strict statistical method).

Elem.	BIR-1						JP-1							
	n_{out}	\bar{x}_V	S_V	Qv	n_{GR}	\bar{x}_{GR}	S_{GR}	n_{ITIA}	\bar{x}_V	S_V	Qv	n_{out}	\bar{x}_{ITIA}	S_{ITIA}
Major elements (%)														
Si SiO ₂	26	22.31	0.24	rv	26	22.31	0.24	27	42.25	0.33	cve	-	42.38	-
Ti TiO ₂	32	0.570	0.016	cve	36	0.572	0.020	17	0.016	0.007	pv ₁	-	0.006	-
Al Al ₂ O ₃	39	8.07	0.39	rv	32	8.12	0.27	33	0.69	0.11	pv	-	0.66	-
Fe ⁺ Fe ₂ O ₃ ⁺	38	7.89	0.18	cve	36	7.87	0.16	29	8.36	0.20	cve	-	8.37	-
Mn MnO	35	0.131	0.007	rv	36	0.132	0.008	36	0.122	0.006	rv	-	0.121	-
Mg MgO	33	5.76	0.33	rv	28	5.84	0.17	33	44.7	0.8	rv	-	44.60	-
Ca CaO	33	9.48	0.19	cve	34	9.47	0.21	28	0.555	0.019	cve	-	0.55	-
Na Na ₂ O	38	1.29	0.09	rv	38	1.30	0.08	25	0.028	0.013	pv ₁	-	0.021	-
K K ₂ O	24	0.020	0.007	pv	25	0.022	0.008	24	0.013	0.009	pv ₂	-	0.003	-
P P ₂ O ₅	14	0.013	0.004	pv	21	0.020	0.012	14	0.011	0.007	pv ₂	-	0.002	-
H ₂ O ⁺	8	0.080	0.025	pv	9	0.10	0.03	17	2.39	0.15	pv	-	2.39	-
FeO	9	8.43	0.15	cve	9	8.38	0.11	14	5.9	0.6	rv	-	5.99	-
Trace elements (ppm)														
As								7	0.36	0.07	rv	5	0.34	0.051
Ba	15	9.5	4.4	pv	12	7.7	2.2	25	17	6	pv	16	19.5	9.4
Co	34	51	5	rv	30	51.4	3.4	27	117	5	cve	24	116	8.3
Cr	32	379	34	rv	32	382	38	32	2850	200	rv	26	2807	211
Cs								6	0.045	0.015	rv	4	NC	
Cu	18	124.9	3.6	cve	23	126	5	18	6.2	2.1	pv	17	6.72	2.14
Ga	9	17.0	3.0	rv	8	16	2							
Hf	13	0.57	0.06	rv	12	0.58	0.06	10	0.135	0.030	rv	8	0.20	0.072
Li	7	3.39	0.35	rv	7	3.4	0.4							
Nb	9	2.0	0.5	rv	10	2.0	0.5	13	1.2	1.0	pv ₂	10	1.48	0.95
Ni	23	169	13	rv	25	166	16	32	2460	72	cve	28	2458	177
Rb	7	0.69	0.31	pv	9	1.0	0.9							
Sb	13	0.52	0.22	pv	11	0.58	0.16							
Sc	15	43.5	1.2	cve	19	44	4	16	7.29	0.25	cve	12	7.24	0.32
Sr	21	110	5	cve	28	108	14							
V	20	313	16	rv	24	313	23	28	26.9	2.7	rv	21	27.6	7.0
Y	25	16.7	4.3	pv	20	16	2							
Zn	13	79	8	rv	23	71	9	35	43	7	rv	29	41.8	7.7
Zr	11	19.2	4.0	pv	14	22	7	30	6.8	2.6	pv	15	5.92	1.82

Table 13 (Contd.)

Comparison of final summary of major and trace element data in two reference materials (BIR-1 and JP-1) with published literature data derived by two standard deviation method (an outdated and less strict statistical method).

Elem.	BIR-1							JP-1						
	n_{out}	\bar{x}_V	s_V	QV	n_{GR}	\bar{x}_{GR}	s_{GR}	n_{ITIA}	\bar{x}_V	s_V	QV	n_{out}	\bar{x}_{ITIA}	s_{ITIA}
La	16	0.77	0.17	rv	18	0.88	0.33	12	0.019	0.015	pv_1	7	0.084	0.047
Ce	15	2.5	1.1	pv	15	2.5	1.1	7	0.35	0.29	pv_2	5	NC	
Pr								6	0.016	0.003	pv	3	NC	
Nd	9	2.20	0.20	rv	12	2.5	0.7	5	0.061	0.016	rv	4	NC	
Sm	24	1.06	0.08	rv	25	1.08	0.09	14	0.016	0.007	pv	7	0.019	0.0099
Eu	25	0.54	0.04	cve	25	0.54	0.04	6	0.019	0.015	pv_1	6	NC	
Gd	13	1.83	0.29	rv	14	1.9	0.4	5	0.015	0.001	pv	3	NC	
Tb	9	0.37	0.05	rv	10	0.41	0.05	8	0.006	0.005	pv_1	4	NC	
Dy	10	2.41	0.33	rv	10	2.4	0.3	7	0.024	0.005	rv	4	0.022	0.0036
Ho	6	0.50	0.07	rv	6	0.50	0.08	5	0.005	0.018	pv	4	NC	
Er	6	1.85	0.26	rv	6	1.8	0.3							
Tm	8	0.27	0.07	rv	8	0.27	0.07							
Yb	23	1.67	0.21	rv	22	1.70	0.19	11	0.022	0.004	rv	6	0.022	0.0041
Lu	13	0.246	0.029	rv	15	0.26	0.04	7	0.018	0.017	pv_1	4	NC	

The abbreviations are: n_{out} , \bar{x}_V , and s_V are the number of final data, mean, and standard deviation in the present work; n_{GR} , \bar{x}_{GR} , and s_{GR} from Gladney and Roelandts (1988); n_{ITIA} , \bar{x}_{ITIA} , and s_{ITIA} from Imai *et al.* (1995); be computed in the present work; **NC**=could not be computed by Imai *et al.* (1995). The major elements refer to BIR-1 whereas major element oxides are for JP-1.

better characterized if they are to be used as RM for the REE. Their main value may lie in evaluating detection limits of the analytical methods for the REE. However, this RM could be useful for major and trace element calibrations in XRF, in order to extend the calibration curves to higher concentrations for well characterized elements (*cve* or *rv*) such as MgO, Cr, and Ni, as well as to provide a better control on the intercept of such calibrations for CaO and V. The new element concentration data in BIR-1 should be similarly useful as a well-characterized RM for trace elements such as Cu, Sc, Sr, and the REE.

All compilations on BIR-1 and JP-1 were previously treated by a combination of subjective and objective criteria. The present approach is objective, based on a large number of statistical tests for outlier detection and rejection, and is, therefore, preferable on these grounds alone. Furthermore,

the resulting mean values are generally characterized by smaller standard deviations than the earlier ones.

CONCLUSIONS

Outlier detection and rejection procedure involving fourteen statistical tests is successfully applied to derive new element concentration values for two difficult samples, a mafic rock (basalt BIR-1) from U.S.A. and an ultramafic rock (peridotite JP-1) from Japan. The method should be useful in evaluation of other univariate databases, such as the compilation of analytical data on RM, including other "difficult" materials.

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