

## Evaluation of GSJ intrusive rocks JG1, JG2, JG3, JG1a, and JGb1 by an objective outlier rejection statistical procedure

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### ABSTRACT

*An objective procedure involving fourteen statistical tests (a total of thirty-four variants) for detection and rejection of outliers in a univariate sample was applied to five geochemical Reference Material (RM) databases of intrusive rocks from the Geological Survey of Japan (GSJ). All available concentration data for JG1, JG1a, and JG3 granodiorites, JG2 granite, and JGb1 gabbro were first grouped in eight general analytical methods. These groups were tested for systematic differences using analysis of variance (ANOVA). After this process, the databases were evaluated by means of statistical tests for detection of possible outliers at a strict confidence level of 99%, minimizing the danger of rejecting a valid observation as an outlier. New concentration mean values and other statistical parameters were computed from final normal distributions. Although 23% of mean concentration values were practically identical to those reported in earlier literature, 67% differ by about 1% to 20%. The present statistical scheme provides a better perspective to evaluate existing geochemical databases than probably erroneous two-standard deviation method involving prior subjective judgments used by the U.S. and Japanese scientists. The present mean values with generally lower %RSD may contribute to a better estimation of precision, accuracy, and sensitivity of routine analysis for intrusive rock samples.*

*Keywords: outlier, reference material, statistical tests, univariate sample, analytical geochemistry.*

### RESUMEN

*Una metodología objetiva que involucra catorce pruebas estadísticas (un total de treinta y cuatro variantes) para la detección y eliminación de valores discordantes en muestras univariadas, se aplicó a cinco bases de datos de Materiales de Referencia (MR) de rocas intrusivas de la Comisión Geológica de Japón (GSJ). Todos los valores de concentración disponibles para las granodioritas JG1, JG1a y JG3, el granito JG2, y el gabro JGb1 fueron primero divididos en 8 grupos generales de métodos analíticos. Los grupos se examinaron para detectar diferencias sistemáticas utilizando el análisis de varianza (ANOVA). Después de este análisis, las bases de datos fueron procesadas aplicando pruebas estadísticas a un estricto nivel de confianza de 99%, minimizando el riesgo de identificar una observación válida como un valor discordante. Se calcularon nuevos valores de concentración promedio y otros parámetros estadísticos a partir de las distribuciones normales finales. No obstante que 23% de los nuevos valores de concentraciones promedio fueron prácticamente idénticos a los reportados en la literatura, 67% difirió entre 1% y 20%. El esquema estadístico aplicado proporciona una mejor perspectiva para evaluar las bases de datos geoquímicos existentes, en comparación con el método estadísticamente erróneo que emplea el criterio de dos desviaciones estándar usado por los científicos de Estados Unidos y Japón. Los valores de concentración promedio obtenidos presentan en general un %DER (porcentaje de desviación estándar relativa) más bajo y pueden contribuir a una mejor estimación de la precisión, exactitud y sensibilidad del análisis de rutina para rocas intrusivas.*

*Palabras clave: valor desviado, material de referencia, pruebas estadísticas, muestra univariada, geoquímica analítica.*

## INTRODUCTION

Geochemical reference materials (RM) have become important in analytical geochemistry not only for calibration procedures but also to estimate accuracy of a measuring method (Kane, 1992). Regardless of the improvements in analytical methods, modern geochemists are concerned about the size of the uncertainties that can often be more important to geochemical interpretation than the concentration value itself (De Bièvre, 1997; Ramsey, 1997). The analytical databases from collaborative programs involving many laboratories are updated periodically on the assumption that quality improves as the size of the database increases (Abbey, 1991). However, lack of a statistically significant difference between original and updated concentrations has been demonstrated (Kane, 1991).

In spite of recent developments in analytical methods with higher accuracy and precision, quality control and role of statistics have not been completely assessed (Bastenaire, 1979). However, rigorous statistical procedures are of little value in resolving disparate data when interlaboratory factors are involved. Thus, if a series of results is not checked for normality or at least for symmetry, the mean is not a good choice of estimate (Lister, 1982; Flanagan, 1986). If the data distribution is not symmetrical, the presence of outliers may be the cause and they should be identified and rejected. Several statistical tests have been used for the identification of discordant observations such as skewness and kurtosis (Dybczynski, 1980; Lister, 1982; Velasco and Verma, 1998), Dixon's criteria (Dixon, 1950; Dybczynski, 1980), Grubb's test (Dybczynski, 1980; Grubbs, 1950, 1969) and many others cited by Barnett and Lewis (1994).

However, the evaluation schemes usually applied to obtain the most probable "true value" of components in a RM (*e.g.*, Abbey, 1981; Gladney and Roelandts, 1990) involve an erroneous application of statistical parameters as pointed out by Verma (1997, 1998). On the other hand, considering the technical guides of the International Organization for Standardization (ISO), the producers of actual RM are encouraged to accept the guidelines to improve credibility of reference materials (ISO, 1989; Kane and Potts, 1997). However, even recognized certification bodies do not comply with all details of these recommendations. The RM produced in the past, amounting to several hundreds, can not be modified to follow ISO criteria, whose practical application is still open to interpretation (Kane and Potts, 1997). It is expected from collaborative programs that quality control data and rejection of outliers be supported on identified technical grounds rather than on strictly statistical procedures. Unfortunately, the databases for existing materials cannot be checked out objectively for technically explainable outliers before the application of a statistical procedure. Therefore, Verma *et al.* (1998) carried out a

detailed analysis of the distribution of outliers as a function of laboratory, country, and analytical method, suggesting an inadequate quality assurance/quality control (QA/QC) practices as the probable cause of the multiple outliers identified.

The existing compilations for the GSJ RM "igneous rock series" were so far processed by eliminating aberrant data as a function of analytical procedures, followed by rejection of all data outside two times the standard deviation from the mean (Terashima *et al.*, 1994; Imai *et al.*, 1995a). This method has been shown to be erroneous by Verma (1997, 1998). The approach of the present work is to apply a totally objective statistical procedure in order to obtain a normal univariate sample before computation of mean concentration and other statistical parameters. The process involves testing for method systematic differences using analysis of variance (ANOVA) before rejection of outliers and then application of fourteen statistical tests (a total of thirty-four single or multiple outlier versions; (Verma, 1997) at a high confidence level of 99% (significance level  $\alpha=0.01$ ). The procedure was applied to latest GSJ compilations (Terashima *et al.*, 1994; Imai *et al.*, 1995a), but also included all new data reported up to 1997.

## REFERENCE MATERIAL DATABASES

A set of five intrusive rocks from GSJ was selected for this work: granodiorites JG1, JG1a and JG3, granite JG2, and gabbro JGb1. The corresponding databases were downloaded from the Internet address <http://www.aist.go.jp/RIODB/geostand/> as recommended by Imai *et al.* (1996). Available information until December 1997 included analytical values, analytical methods, and literature (year, title, volume, page, and analyst) or affiliation and country for personal communications. All data from personal communications were also captured. However, semi-quantitative data (reported as less than a certain value) were not considered in this work. Similarly, elements with less than five individual observations were excluded from the database. These elements comprise: In, Ir, Os, Pd, Pt, Re, Ru, and Te in all five materials; and in addition, W in JG1; Cd, F, Hg, and Se in JG2; Cd, F, Ge, Hg, and Se in JG3; Se in JG1a, and Se and Tl in JGb1.

The raw data were captured in a standard spreadsheet with ninety-five variables arranged in a pre-established sequence, as presented in Verma *et al.* (1998). This particular format was required to process the GSJ databases with SIPVADE, a computer program in TURBOC developed for the study of existing geochemical databases, enabling one to apply seventeen statistical tests for outlier detection in normal univariate sample at a strict confidence level of 99%. Details of the procedure are described in the methodology section.

The individual concentration values in the spread-

Table 1. Group code assigned to analytical methods in GSJ database.

Groups	General description	Methods
A	Classical methods	CHEM, GRAV, TITR, VOLU
B	Atomic absorption methods	AA, AF, CEA, FAA, FE, HAA
C	X-ray fluorescence methods	EPMA, EXRF, XRF
D	Emission spectrometry	ICPES, OES
E	Nuclear methods	ALPHA, DNAA, GAMMA, INAA, NAA, NM, NT, PAA, RNAA
F	Mass spectrometry	ICPMS, IDMS, MS, SSMS
G	Chromatography	CHROM, IC
H	Miscellaneous	ASV, CALC, COLOR, CONV, FA, FLUOR, ISE, POL, SIMS, UU

Method codes are after Imai *et al.* (1995a).

sheets were checked at least three times to correct for typographical errors. Additionally to the variables included in the Internet databases, a group code (A to H) from Table 1 was assigned to each element concentration value depending on the corresponding analytical method. The analytical methods were grouped on the basis of similarity of their physical principles in groups "A" to "G", and in the final group "H" which included all remaining and less commonly used analytical methods with no actual affinity among them. Although it would have been desirable to handle results from individual analytical methods separately, the paucity of such individual concentration data requires that some kind of method grouping be done before applying ANOVA tests.

## METHODOLOGY

### Method applied by US and Japanese scientists

The procedure involving rejection of observations lying outside two standard deviations from the mean (Ando *et al.*, 1987, 1989; Gladney *et al.*, 1991; Imai *et al.*, 1995a; among others), first uses subjective criteria to discard data on either end of the reported concentration spectrum. Following this elimination, all data outside two standard deviations from the mean are dropped and a new mean value is computed. The procedure is repeated until no more outlying values are found. The method does not take into account the strong dependence of the critical value curves on the number of observations (Taylor, 1990). This approach is in fact incorrect (Barnett and Lewis, 1994) and may eliminate data that are not really outliers or may include values that are otherwise erroneous from many statistical criteria. Verma (1997, 1998) discussed in detail that in contrast to the method applied by US and Japanese scientists, the present outlier detection and elimination scheme at a strict 99% confidence level will identify an outlier as a func-

tion of the total number of observations, thus avoiding an artificial decrease of the final standard deviation.

### Present method for outlier detection and rejection

Because contributing laboratories do not provide information that could lead to an identification of technically explainable outliers, it was not possible to check the initial data set for "technical" outliers as recommended by ISO guidelines (ISO, 1989; section 8.3.2). However, frequency distribution for all elements in each RM was observed graphically as recommended (ISO, 1989; section 8.3.4.). All elements showed a single cluster, although most patterns differed significantly from a normal distribution due to the presence of outlying observations. From this unimodal distribution, it was assumed that a consensus value does exist (ISO, 1989; section 8.3.4.2).

The databases were tested for differences between element mean concentration data for groups of analytical methods. ANOVA was chosen because it is relatively robust to deviations from normality of the data tested (Jensen *et al.*, 1997). If a group of data for an element differed significantly at 99% confidence level from two other remaining groups, that particular group was excluded from the data set for that element. Application of ANOVA at 99% confidence level identified a few cases where method groups showed elements with mean values significantly different from other groups (Table 2).

After the elimination of significantly different observations identified by ANOVA, the GSJ databases were processed to detect possible outlying observations using the SIPVADE program. The statistical test labels and nomenclature (summarized in Table 3) are the same as in Barnett and Lewis (1994), Verma (1997) and Verma *et al.* (1998), and include (a) Deviation/spread statistics (N1-N3), (b) Grubbs-type tests (N4 and N16 (k=1)), (c) Dixon-type tests (N7-N13), and (d) High or-

Table 2. Elements identified by ANOVA (at 99% confidence level) with mean values significantly different from other groups.

Group	JG1	JG2	JG3	JG1a	JGb1
A	---	---	MnO, P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	---
B	---	---	---	---	---
C	La, Nd	Gd, Pr	Sb	Fe <sub>2</sub> O <sub>3</sub> , Sm	Bi, Cd, Ce, Cs, Gd, Ge, Pr, Sb, Sm, Sn, Th, U, Yb
D	Cr, Sr	Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	CaO, Ce, Tm	---	---
E	SiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub>	CaO, K <sub>2</sub> O, Ba, Hf	SiO <sub>2</sub> , CaO, Na <sub>2</sub> O, Ga, Pr, V	TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Zr	SiO <sub>2</sub> , TiO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Pr
F	Zr	---	Sc, Tl	---	---
G	---	---	Ce, La, Lu	Lu	Sm
H	---	---	Ni	Cs, Zr	Cu, Zr

For group code see Table 1.

Dashes indicate that differences from other groups were not detected by ANOVA.

der statistics (N14 and N15).

The present application of fourteen tests with thirty-four variants was restricted to a maximum of four observations ( $k=4$ ) simultaneously tested and N16 was used in its simplest form of  $k=1$ . Although some of these tests are applicable to as few as three data (Verma, 1997), a minimum number of five observations was arbitrarily chosen to apply the statistical tests. The maximum number of observations to be evaluated by a given test variant depended on the availability of 1% critical values (99% confidence level).

Tests N5, N6 (Grubbs-type), and N17 were not used in this work because the N5 and N6 tests may detect a genuine lowest observation as an outlier, if an extremely high discordant observation is present in the database (generally by a different analytical method), and test N17 in its various versions, in fact, is a multiple-outlier version of single-valued (number of observations tested at a time,  $k=1$ ) tests N1 and N15 respectively. Furthermore, N17 is a direction-independent test as N5 and N6. Results of processing of all RM databases with the SIPVADE package were obtained in printer output form. The outliers detected were then rejected manually from the initial observations and this process was repeated until no outlying observations were present. Finally, the remaining data considered a "normal" sample from thirty-four variants of fourteen statistical tests were used to compute the mean value and other statistical parameters.

## RESULTS OF DATABASE PROCESSING USING SIPVADE

### Relative efficiency of statistical tests

The results of the SIPVADE program are exemplified in Table 4, showing relative efficiency of the statistical tests for detecting outliers, based on their applica-

tion to major and trace element data. The statistical tests were successful in detecting discordant observations in forty out of sixty-two elements in JG1; in forty-two out of fifty-five elements in JG2; in thirty-nine out of fifty-five elements in JG3; in thirteen out of fifty-six elements in JG1a, and in forty-eight out of fifty-seven elements in JGb1. It is important to note that an observation was detected as outlier by generally more than one test and in general, the Grubbs-type statistics (N4 and N16) seemed to be the most efficient tests in the detection of one or two extreme outliers. An empirical comparison of the performance of statistical tests applied in this work was carried out by Velasco *et al.* (2000). The results indicate that sensitivity of the statistical tests has a strong dependence on sample size, and that block procedures (N3 ( $k=2-4$ ), N4 ( $k=2-4$ ), N11, N12, N13) are more sensitive to detect outliers compared to consecutive statistical tests (N1, N2, N4( $k=1$ ), N7, N8, N9, N10, N14, N15, N16).

The elements with no outlying observations are identified with dash marks in Table 4. For JG1 (Table 4) no discordant data was observed for Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, LOI, H<sub>2</sub>O<sup>+</sup>, B, Be, Cd, Ge, Hg, La, Nb, Pb, Sc, Sn, and U. In JG2, the tests failed to detect outliers for P<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>-</sup>, Au, Be, Co, Ga, Ho, Li, Sm, Ta, Th, and Y in the database. The tests applied to JG3 did not detect discordant observations for Fe<sub>2</sub>O<sub>3</sub><sup>T</sup>, H<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>-</sup>, Fe<sub>2</sub>O<sub>3</sub>, Ag, Au, Ba, Co, Gd, Li, Mo, Sn, Tb, Y, Yb, and Zn. For JG1a there were no outliers for H<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>-</sup>, Au, Be, Er, Ho, Li, Pr, Sb, Sc, Sn, Tl, and W. Finally, for JGb1 the SIPVADE program did not identify erroneous data for Au, F, Hg, Ho, Li, Nd, Tm, W, and Zn.

### Final statistical parameters

The final mean values and other statistical parameters obtained by the present objective statistical procedure are given in Tables 5 to 9. The mean ( $\bar{x}_{in}$  and  $\bar{x}$ )

Table 3. Discordancy tests for normal univariate samples for the evaluation of RM (modified after Barnett and Lewis, 1994; Verma, 1998).

Statistics type <sup>a</sup>	Test label <sup>b</sup>	Description of test <sup>c</sup>	Test statistic <sup>d</sup>	Significance of test <sup>e</sup>	Value(s) tested <sup>f</sup>	Test applied <sup>g</sup>	
						$n_{\min}$	$n_{\max}$
Deviation / Spread Statistics	N1	Upper	$(x_n - \bar{x}) / s$	Greater	$x_n$	3	147
		Lower	$(\bar{x} - x_1)/s$		$x_1$	3	147
	N2	Extreme	$\text{Max} [(x_n - \bar{x})/s, (\bar{x} - x_1) /s]$	Greater	$x_n$ or $x_1$	3	20
	N3	k = 2 Upper	$(x_n + x_{n-1} - 2\bar{x})/s$	Greater	$x_n, x_{n-1}$	5	100
		k = 3 Upper	$(x_n + x_{n-1} + x_{n-2} - 3\bar{x})/s$		$x_n, x_{n-1}, x_{n-2}$	7	100
	N3	k = 4 Upper	$(x_n + x_{n-1} + x_{n-2} + x_{n-3} - 4\bar{x})/s$		$x_n, x_{n-1}, x_{n-2}, x_{n-3}$	9	100
		k = 2 Lower	$(2\bar{x} - x_1 - x_2)$		$x_1, x_2$	5	100
		k = 3 Lower	$(3\bar{x} - x_1 - x_2 - x_3)$		$x_1, x_2, x_3$	7	100
		k = 4 Lower	$(4\bar{x} - x_1 - x_2 - x_3 - x_4)$		$x_1, x_2, x_3, x_4$	9	100
Grubbs Type	N4	k = 1 Upper	$S_n^2/S^2$	Smaller	$x_n$	4	50
		k = 2 Upper	$S_{n,n-1}^2/S^2$		$x_n, x_{n-1}$	4	149
		k = 3 Upper	$S_{n,n-1,n-2}^2/S^2$		$x_n, x_{n-1}, x_{n-2}$	6	50
		k = 4 Upper	$S_{n,n-1,n-2,n-3}^2/S^2$		$x_n, x_{n-1}, x_{n-2}, x_{n-3}$	8	50
	N4	k = 1 Lower	$S_1^2/S^2$	Smaller	$x_1$	4	50
		k = 2 Lower	$S_{1,2}^2/S^2$		$x_1, x_2$	4	149
		k = 3 Lower	$S_{1,2,3}^2/S^2$		$x_1, x_2, x_3$	6	50
		k = 4 Lower	$S_{1,2,3,4}^2/S^2$		$x_1, x_2, x_3, x_4$	8	50
N16	Upper-Lower	Tietjen and Moore's Statistic	Smaller	$x_n$ or $x_1$	4	50	
N7	Upper	$(x_n - x_{n-1})/(x_n - x_1)$	Greater	$x_n$	3	30	
N8	Extreme	$\text{Max} [(x_n - x_{n-1}) / (x_n - x_1), (x_2 - x_1) / (x_n - x_1)]$	Greater	$x_n$ or $x_1$	6	30	
N9	Upper	$(x_n - x_{n-1})/(x_n - x_2)$	Greater	$x_n$	4	30	
	Lower	$(x_2 - x_1)/(x_{n-1} - x_1)$		$x_1$	4	30	
N10	Upper	$(x_n - x_{n-1})/(x_n - x_3)$	Greater	$x_n$	5	30	
	Lower	$(x_2 - x_1)/(x_{n-2} - x_1)$		$x_1$	5	30	
N11	Upper pair	$(x_n - x_{n-2})/(x_n - x_1)$	Greater	$x_n, x_{n-1}$	4	30	
	Lower pair	$(x_3 - x_1)/(x_n - x_1)$		$x_1, x_2$	4	30	
N12	Upper pair	$(x_n - x_{n-2})/(x_n - x_2)$	Greater	$x_n, x_{n-1}$	5	30	
	Lower pair	$(x_3 - x_1)/(x_{n-1} - x_1)$		$x_1, x_2$	5	30	
N13	Upper pair	$(x_n - x_{n-2})/(x_n - x_3)$	Greater	$x_n, x_{n-1}$	6	30	
	Lower pair	$(x_3 - x_1)/(x_{n-2} - x_1)$		$x_1, x_2$	6	30	
High-order moment	N14	Extreme	$[S(x_j - \bar{x})^3/ns^3]$ ; for j=1 to n	Greater	$x_n$ or $x_1$	5	500
	N15	Extreme	$[S(x_j - \bar{x})^4/ns^4] - 3$ ; for j=1 to n	Greater	$x_n$ or $x_1$	5	500

<sup>a</sup>Classification suggested by Tietjen and Moore (1972).

<sup>b</sup>The test labels are after Barnett and Lewis (1994).

<sup>c</sup>Type of observation(s) being tested; k = number of data to be tested at a time (1 to 4).

<sup>d</sup>Parameter to be computed for a given test.

<sup>e</sup>This column indicates whether the test statistic should be greater or smaller than the 1% critical value for a successful detection of an outlier.

<sup>f</sup>Type of value(s) being tested by a given statistic.

<sup>g</sup>Range of observations that can be tested by a given statistic.

Table 4. Relative efficiency of the statistical tests for detecting outliers, based on their application to major and trace element data in GSJ granodiorite JG1.

Element	$n_{in}$	Test applied	Tests successful in detecting outlier(s)
SiO <sub>2</sub>	64	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2), N4(k=2), N15
TiO <sub>2</sub>	67	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N14, N15
Al <sub>2</sub> O <sub>3</sub>	66	N1, N3(k=2-4), N4(k=2), N14, N15	---
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	69	N1, N3(k=3-4), N4(k=2), N14, N15	N3(k=3-4)
MnO	69	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N15
MgO	69	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N14, N15
CaO	67	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N14, N15
Na <sub>2</sub> O	67	N1, N3(k=2-4), N4(k=2), N14, N15	---
K <sub>2</sub> O	73	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N14, N15,
P <sub>2</sub> O <sub>5</sub>	56	N1, N3(k=2-4), N4(k=2), N14, N15	---
LOI	5	N1, N2, N3(k=2), N4(k=1-4), N7, N8, N9, N10, N11, N12, N14, N15, N16(k=1)	---
H <sub>2</sub> O <sub>PL</sub>	31	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	---
H <sub>2</sub> O <sub>MI</sub>	30	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)
Fe <sub>2</sub> O <sub>3</sub>	36	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)
FeO	39	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=2-4), N4(k=2-4), N14
B	14	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Ba	49	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N4(k=1-3), N15, N16(k=1)
Be	6	N1, N2, N3(k=2), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Bi	12	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7, N8, N9, N11, N12, N13, N14, N15, N16(k=1)
Cd	14	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Ce	43	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)
Cl	12	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)
Co	52	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N14, N15
Cr	62	N1, N3(k=2-4), N4(k=2), N14, N15	N1
Cs	26	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N4(k=1-2), N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)
Cu	43	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)
Dy	20	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N2, N3(k=2), N4(k=2-4), N11, N12, N14, N16(k=1)
Er	19	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N2, N3(k=2), N4(k=1-4), N7, N8, N9, N11, N12, N13, N14, N15, N16(k=1)
Eu	37	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=4)
F	15	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)
Ga	18	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N2, N4(k=1), N9, N10, N12, N13, N15, N16(k=1)
Gd	22	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N3(k=2-3), N4(k=2-4), N14, N15, N16(k=1)
Ge	8	N1, N2, N3(k=2-3), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Hf	23	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N3(k=3-4), N4(k=3-4)
Hg	10	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Ho	16	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)
La	39	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)
Li	21	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---

Table 4. (Continued).

Element	$n_{in}$	Test applied	Tests successful in detecting outlier(s)
Lu	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)
Nb	21	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Nd	31	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)
Ni	50	N1, N2, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N2, N3(k=2-4), N4(k=2-4), N14, N15, N16(k=1)
Pb	50	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	---
Pr	14	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-2), N11, N12, N13, N16(k=1)
Rb	73	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N15
S	9	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N3(k=2), N4(k=2-4),
Sc	26	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Se	5	N1, N2, N3(k=2), N4(k=1-2), N7, N8, N9, N10, N11, N12, N14, N15, N16(k=1)	N3(k=2), N4(k=2), N11, N12
Sm	43	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N4(k=1-3), N14, N15, N16(k=1)
Sn	10	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	---
Sr	76	N1, N3(k=2-4), N4(k=2), N14, N15	N1, N3(k=2-4), N4(k=2), N14, N15
Ta	15	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N3(k=2), N4(k=2), N13
Tb	22	N1, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N3(k=2), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)
Th	42	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)
Tl	14	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N3(k=2), N4(k=1-4), N11, N12, N13, N14
Tm	14	N1, N2, N3(k=2-4), N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)	N1, N2, N4(k=1-4), N7, N8, N9, N10, N11, N12, N13, N14, N15, N16(k=1)
U	41	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	---
V	42	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)
Y	32	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N1, N4(k=1), N16(k=1)
Yb	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, N15, N16(k=1)
Zn	55	N1, N3(k=2-4), N4(k=2), N14, N15	N3(k=2-3), N4(k=2)
Zr	43	N1, N3(k=2-4), N4(k=1-4), N14, N15, N16(k=1)	N3(k=4)

The major source of information on these tests is Verma (1997). "Test Labels" are after Barnett and Lewis (1994); k = number of outliers to be tested at a time (k varies from 1 to 4); Ni = Test applied (see Table 3). Dashes indicate no success in detecting outliers.

and standard deviation ( $s_{in}$  and  $s$ ) values are rounded to make them mutually compatible (e.g., Taylor, 1982), but an extra digit is retained when the  $s$  value was lower than "1/2" (Verma, 1998; Verma *et al.*, 1998).

The fourteen statistical tests applied to five GSI databases were successful in detecting discordant observations with %O<sub>i</sub> (percentage of outliers or discordant observations) varying from about 9% to 16% for major elements and from 14% to 19% for trace elements. The present mean values are characterized by smaller standard deviations (Tables 5 to 9) than those obtained by Terashima *et al.* (1994) and Imai *et al.* (1995a, b) for

major and trace elements respectively.

## DATA EVALUATION

A comparison of mean values obtained by the present multiple-test approach with those by the two-standard deviation method is shown in Figure 1. The percentage-normalized difference between present mean values and the literature data (Figure 1) shows that for sixteen elements in JG1 (26%), seven in JG2 (13%), sixteen in JG3 (29%), eleven in JG1a (20%), and fifteen in

Table 5. Initial and final (after outlier detection and elimination) statistical data on major and trace elements in GSJ granodiorite JG-1.

Element	n <sub>in</sub>	$\bar{X}_{in}$	s <sub>in</sub>	O <sub>t</sub>	n <sub>out</sub>	%Otd	Min	Max	$\bar{X}$	s	95% Confidence limits		%RSD
SiO <sub>2</sub>	64	72.33	0.40	5	59	8	71.78	73.06	72.35	0.29	72.27	72.42	0.4
TiO <sub>2</sub>	67	0.258	0.033	4	63	6	0.230	0.310	0.264	0.019	0.259	0.269	7.3
Al <sub>2</sub> O <sub>3</sub>	66	14.24	0.24	1	65	2	13.70	14.73	14.23	0.22	14.17	14.28	1.5
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	69	2.18	0.13	4	65	6	1.86	2.41	2.15	0.11	2.13	2.18	5.0
MnO	69	0.06	0.01	5	64	7	0.050	0.080	0.062	0.007	0.061	0.064	11
MgO	70	0.76	0.22	12	58	17	0.670	0.820	0.736	0.036	0.727	0.746	4.9
CaO	67	2.2	0.1	10	57	15	2.090	2.270	2.175	0.038	2.165	2.185	1.8
Na <sub>2</sub> O	67	3.4	0.1	0	67	0	3.1	3.70	3.40	0.10	3.36	3.41	2.9
K <sub>2</sub> O	73	3.95	0.25	8	65	11	3.86	4.10	3.98	0.06	3.96	3.99	1.4
P <sub>2</sub> O <sub>5</sub>	56	0.100	0.022	4	52	7	0.060	0.120	0.095	0.015	0.091	0.100	15
LOI	5	0.50	0.09	0	5	0	0.410	0.620	0.450	0.09	0.385	0.607	18
H <sub>2</sub> O <sub>PL</sub>	31	0.54	0.13	0	31	0	0.31	0.81	0.54	0.13	0.50	0.59	23
H <sub>2</sub> O <sub>MI</sub>	30	0.10	0.07	6	24	20	0.030	0.110	0.069	0.021	0.060	0.078	30
Fe <sub>2</sub> O <sub>3</sub>	36	0.42	0.31	8	28	22	0.24	0.50	0.38	0.06	0.35	0.40	16
FeO	39	1.61	0.15	4	35	10	1.45	1.83	1.64	0.09	1.61	1.68	5.7
B	14	6.7	2.4	0	14	0	1.4	12.0	6.7	2.4	5.3	8.0	35
Ba	49	465	38	4	45	8	429	525	465	25	457	472	5.3
Be	6	3.2	0.5	0	6	0	2.400	4.0	3.2	0.5	2.6	3.7	17
Bi	12	0.63	0.44	4	8	33	0.41	0.52	0.47	0.05	0.42	0.50	10
Cd	14	0.040	0.014	0	14	0	0.020	0.060	0.040	0.014	0.032	0.048	35
Ce	43	45	6	4	39	9	40.00	57.00	46.6	4.3	45.2	48.0	9.2
Cl	12	69	42	4	8	33	51.00	57.00	54.6	2.4	52.6	56.7	4.5
Co	52	5.0	4.0	8	44	15	2.0	6.0	4.0	0.7	3.8	4.2	18
Cr	62	53.5	8.4	9	53	15	41.2	65.0	54	7	52	56	12
Cs	26	10.1	1.1	2	24	8	9.0	12.3	10.3	0.8	9.9	10.6	7.9
Cu	43	3.7	3.8	8	35	19	0.1	4.2	2.0	1.0	1.9	2.6	45
Dy	20	4.1	1.2	4	16	20	3.0	4.7	3.7	0.6	3.3	4.0	17
Er	19	2.5	1.2	4	15	21	1.5	3.0	2.0	0.6	1.7	2.3	28
Eu	37	0.70	0.10	6	31	16	0.62	0.88	0.72	0.06	0.70	0.74	8.0
F	15	518	80	4	11	27	470	513	493	14	483	502	2.8
Ga	18	17.3	3.7	4	14	22	15.0	20.0	17.8	1.4	16.2	17.9	8.4
Gd	22	4.3	0.7	4	18	18	3.50	4.56	4.04	0.34	3.87	4.20	8.4
Ge	8	1.44	0.28	0	8	0	0.97	1.70	1.44	0.28	1.21	1.67	19
Hf	23	3.4	1.2	8	15	35	3.00	3.93	3.51	0.32	3.38	3.69	9.2
Hg	10	17.0	5.0	0	10	0	10.00	26.80	16.92	5.02	13.32	20.51	30
Ho	16	0.90	0.41	4	12	25	0.48	0.95	0.74	0.18	0.62	0.85	24
La	39	22.1	3.4	3	36	8	16.6	28.4	22.6	2.6	21.7	23.5	11
Li	21	87	9	0	21	0	68	106	87	9	83	91	10
Lu	31	0.43	0.26	4	27	13	0.18	0.52	0.40	0.10	0.33	0.41	28
Nb	21	12.4	1.2	0	21	0	9.8	15.0	12.4	1.2	11.8	13.0	10
Nd	31	19.3	2.5	6	25	19	18.1	24.1	20.3	1.4	19.7	20.9	7
Ni	50	8.2	3.7	4	46	8	2.5	14.0	7.3	2.3	6.7	8.0	32
Pb	50	25.4	3.1	0	50	0	19.7	33.0	25.4	3.1	24.5	26.3	12
Pr	14	4.8	0.9	2	12	14	4.5	6.1	5.1	0.5	4.8	5.5	9.6
Rb	73	182	9	15	58	21	175.5	188.0	182.0	2.9	181.3	182.8	1.6
S	9	13	5	4	5	44	9.3	11.0	10.2	0.8	9.3	11.1	7.4
Sc	26	6.5	0.8	0	26	0	4.7	8.6	6.5	0.8	6.2	6.8	12
Sm	43	4.7	0.7	4	39	9	3.61	5.50	4.62	0.44	4.48	4.76	9.6
Sn	10	3.8	0.8	0	10	0	2.8	5.5	3.8	0.8	3.2	4.4	22
Sr	76	185	17	21	55	28	173	199	186	5	184	187	3
Ta	15	1.8	0.5	6	9	40	1.58	1.80	1.66	0.07	1.61	1.72	4.2
Tb	22	0.9	0.5	6	16	27	0.54	1.04	0.73	0.14	0.66	0.81	19
Th	42	13.2	1.6	4	38	10	11.0	16.0	13.6	0.9	13.2	13.9	7.0
Tl	14	1.2	0.5	4	10	29	0.950	1.040	1.009	0.031	0.986	1.031	3.1
Tm	14	0.50	0.29	4	10	29	0.22	0.51	0.36	0.11	0.28	0.44	31
U	41	3.5	0.7	0	41	0	1.8	5.0	3.5	0.7	3.2	3.7	21
V	42	28	12	4	38	10	20.0	32.0	25.2	3.5	24.0	26.3	14
Y	32	29	7	11	21	34	28.0	35.0	31.4	1.6	30.6	32.1	5.1
Yb	39	3.0	1.8	4	35	10	1.4	3.5	2.4	0.7	2.2	2.7	27
Zn	55	41	6	3	52	5	26	49	40	5	39	42	11
Zr	43	103	38	9	34	21	74	152	114	16	109	120	14

n<sub>in</sub> = initial number of observations;  $\bar{X}_{in}$  = arithmetic mean of the initial set of observations before outlier rejection; s<sub>in</sub> = initial standard deviation; O<sub>t</sub> = number of outlier data detected by seventeen statistical tests outlined in this paper; n<sub>out</sub> = final number of observations remaining after outlier rejection; %Otd = percentage of outlier data eliminated from the initial observations; Min = minimum value of the final set of observations; Max = maximum 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 relative standard deviation. Major element concentration in % m/m; trace element concentration in  $\mu\text{g g}^{-1}$ .



Table 6. Initial and final (after outlier detection and elimination) statistical data on major and trace elements in GSJ granite JG-2.

Element	$n_{in}$	$\bar{X}_{in}$	$s_{in}$	$O_t$	$n_{out}$	%Otd	Min	Max	$\bar{X}$	s	95% Confidence limits		%RSD
SiO <sub>2</sub>	43	76.61	1.03	8	35	19	76.20	77.77	76.93	0.32	76.82	77.04	0.4
TiO <sub>2</sub>	40	0.045	0.009	1	39	2	0.030	0.060	0.046	0.008	0.044	0.049	17
Al <sub>2</sub> O <sub>3</sub>	46	12.5	0.5	16	30	35	12.28	12.58	12.41	0.07	12.38	12.44	0.6
Fe <sub>2</sub> O <sub>3T</sub>	46	0.96	0.08	7	39	15	0.88	1.1	0.99	0.05	0.96	1.0	5.4
MnO	44	0.0162	0.0042	1	43	2	0.009	0.020	0.0158	0.0037	0.0147	0.017	23
MgO	35	0.045	0.023	4	31	11	0.010	0.070	0.039	0.016	0.033	0.045	40
CaO	46	0.75	0.22	3	43	7	0.62	0.8	0.70	0.05	0.69	0.72	6.6
Na <sub>2</sub> O	46	3.56	0.12	12	34	26	3.42	3.60	3.52	0.05	3.51	3.54	1.3
K <sub>2</sub> O	50	4.9	1.2	12	38	24	4.6	4.8	4.71	0.06	4.69	4.73	1.2
P <sub>2</sub> O <sub>5</sub>	19	0.012	0.009	0	19	0	0.002	0.030	0.012	0.009	0.008	0.017	71
LOI	18	0.6	0.6	4	14	22	0.3	0.5	0.37	0.05	0.34	0.40	13
H <sub>2</sub> O <sub>PL</sub>	10	0.32	0.14	0	10	0	0.020	0.52	0.32	0.14	0.21	0.42	46
H <sub>2</sub> O <sub>MI</sub>	14	0.12	0.05	0	14	0	0.030	0.22	0.12	0.05	0.10	0.15	37
Fe <sub>2</sub> O <sub>3</sub>	15	0.43	0.27	8	7	53	0.300	0.420	0.367	0.039	0.331	0.403	11
FeO	14	0.57	0.07	4	10	29	0.490	0.560	0.532	0.024	0.515	0.549	4.4
As	9	1.0	0.5	2	7	22	0.40	1.00	0.76	0.18	0.59	0.93	24
Au	5	0.05	0.03	0	5	0	0.013	0.080	0.049	0.030	0.012	0.086	60
Ba	40	85	34	11	29	28	44	100	69	13	65	74	18
Be	6	3.4	0.6	0	6	0	2.5	4.04	3.4	0.6	2.8	4.0	17
Ce	36	48	5	4	32	11	42.7	54.4	48.6	2.7	47.6	49.6	5.6
Co	30	3.6	0.7	0	30	0	2.0	5.0	3.5	0.7	3.3	3.8	21
Cr	29	36	160	4	25	14	2.2	9.15	6.2	2.1	5.3	7.1	34
Cs	20	6.8	0.9	4	16	20	6.3	8.2	7.2	0.4	7.0	7.4	6.1
Dy	22	10.7	2.9	4	18	18	10.1	13.4	11.8	1.0	11.2	12.3	8.9
Er	16	6.5	1.8	4	12	25	5.99	8.9	7.4	0.9	6.9	8.0	12
Eu	27	0.12	0.08	4	23	15	0.01	0.14	0.090	0.030	0.077	0.103	33
Ga	17	18.0	1.5	0	17	0	14.95	20.8	18.0	1.5	17.2	18.7	8.4
Gd	16	8.7	1.7	1	15	6	6.7	10.7	9.1	1.2	8.4	9.7	13
Ho	16	2.1	0.7	0	16	0	1.1	3.745	2.1	0.7	1.7	2.5	35
La	35	19.7	2.3	4	31	11	17	22	19.6	1.1	19.2	20.0	5.7
Li	9	40.7	4.2	0	9	0	32	44.8	40.7	4.2	37.5	43.9	10
Lu	23	1.19	0.23	7	16	30	1.07	1.32	1.21	0.07	1.18	1.25	5.7
Mo	11	0.6	0.6	4	7	36	0.22	0.46	0.29	0.09	0.21	0.37	31
Nb	32	15.1	2.3	4	28	12	12	16.2	14.5	1.2	14.0	15.0	8.5
Nd	28	26	5	6	22	21	22	29.6	25.5	2.1	24.6	26.4	8.1
Ni	18	16	50	7	11	39	0.5	3.7	2.2	1.1	1.5	2.9	47
Pb	26	37	24	10	16	38	30	33.2	31.7	0.9	31.2	32.2	3.0
Pr	17	6.1	1.2	5	12	29	5.8	7.0	6.5	0.5	6.2	6.8	7.2
Rb	51	300	12	6	45	12	288	313.7	300.6	6	298.7	302.6	2.1
Sc	22	2.3	0.6	4	18	18	2.16	3.1	2.52	0.31	2.37	2.67	12
Sm	31	7.8	1.0	0	31	0	5.9	10	7.8	1.0	7.4	8.2	13
Sn	16	2.1	1.5	8	8	50	2.2	3.1	2.60	0.30	2.40	2.90	11
Sr	47	17.3	3.5	6	41	13	12	22	17.1	2.1	16.5	17.8	12
Ta	19	2.7	0.6	0	19	0	1.9	3.63	2.7	0.6	2.4	3.0	23
Tb	18	1.70	0.30	4	14	22	1.51	2.08	1.79	0.18	1.69	1.90	9.8
Th	33	31.8	3.4	0	33	0	25.36	39.7	31.8	3.4	30.6	33.0	10
Tm	10	1.2	0.5	4	6	40	1.02	1.19	1.12	0.06	1.06	1.19	5.8
U	27	10.9	1.7	2	25	7	9.48	14	11.2	1.3	10.7	11.8	11.3
V	15	9	17	4	11	27	1.6	6.5	3.7	1.4	2.8	4.7	37
W	9	25	6	2	7	22	25	31	27.8	2.4	25.6	30.0	8.7
Y	37	85	8	0	37	0	72	100	85	8	82	88	9.4
Yb	27	7	2.1	6	21	22	6.93	9.8	8.1	0.8	7.7	8.4	9.6
Zn	40	13.0	3.2	1	39	2	8	20	13.2	2.8	12.4	14.1	21
Zr	42	94	23	8	34	19	80	112	96	8	93	99	8.6

For abbreviations see footnote of Table 5. Major element concentrations are expressed in % m/m and trace element concentrations in  $\mu\text{g g}^{-1}$ .

Table 7. Initial and final (after outlier detection and elimination) statistical data on major and trace elements in GSJ granodiorite JG-3.

Element	n <sub>in</sub>	$\bar{X}_n$	s <sub>in</sub>	O <sub>t</sub>	n <sub>out</sub>	%O <sub>td</sub>	Min	Max	$\bar{X}$	s	95% Confidence limits		%RSD
SiO <sub>2</sub>	33	68.25	3.85	2	31	6	66.36	68.93	67.3	0.6	67.1	67.5	0.9
TiO <sub>2</sub>	36	0.481	0.026	0	36	0	0.41	0.54	0.481	0.026	0.472	0.490	5.3
Al <sub>2</sub> O <sub>3</sub>	35	15.40	0.40	4	31	11	15	15.9	15.47	0.19	15.40	15.54	1.2
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	32	3.70	0.13	0	32	0	3.42	3.95	3.70	0.13	3.65	3.75	3.5
MnO	36	0.073	0.014	2	34	6	0.050	0.080	0.070	0.006	0.069	0.072	8.1
MgO	34	1.86	0.26	4	30	12	1.68	1.88	1.79	0.05	1.77	1.81	2.8
CaO	37	3.77	0.16	5	32	14	3.50	3.86	3.72	0.09	3.69	3.76	2.5
Na <sub>2</sub> O	39	4.03	0.22	6	33	15	3.61	4.61	3.98	0.18	3.92	4.05	4.6
K <sub>2</sub> O	42	2.64	0.06	4	38	10	2.57	2.7	2.631	0.034	2.620	2.642	1.3
P <sub>2</sub> O <sub>5</sub>	27	0.14	0.06	1	26	4	0.100	0.320	0.130	0.040	0.116	0.148	30
LOI	11	0.76	0.17	4	7	36	0.58	0.7	0.661	0.041	0.623	0.700	6.3
H <sub>2</sub> O <sub>PL</sub>	8	0.67	0.12	0	8	0	0.5	0.87	0.67	0.13	0.56	0.77	19
H <sub>2</sub> O <sub>MI</sub>	10	0.17	0.07	0	10	0	0.09	0.33	0.17	0.07	0.12	0.22	41
Fe <sub>2</sub> O <sub>3</sub>	15	2.4	1.0	0	15	0	1.41	3.7	2.4	1.0	1.8	2.9	40
FeO	12	1.77	0.29	4	8	33	1.76	2.05	1.93	0.09	1.85	2.00	4.6
Ag	5	0.036	0.016	0	5	0	0.025	0.064	0.036	0.016	0.015	0.056	46
Au	6	0.17	0.15	0	6	0	0.04	0.4	0.17	0.15	0.02	0.33	85
Ba	31	464	39	0	31	0	369	565	464	39	450	478	8.3
Ce	26	40.6	4.2	8	18	31	34.0	44.0	40.4	2.3	39.3	41.6	5.7
Co	26	11.7	1.1	0	26	0	10	14	11.7	1.1	11.2	12.1	9.5
Cr	28	23.0	4.1	4	24	14	20	27	22.8	1.8	22.1	23.6	7.8
Cs	16	1.85	0.37	3	13	19	1.46	1.94	1.72	0.18	1.61	1.83	11
Cu	20	8.0	4.2	5	15	25	5.6	7.7	6.5	0.7	6.2	6.9	10
Dy	17	2.6	0.5	7	10	41	2.55	2.8	2.65	0.08	2.60	2.70	2.9
Er	14	1.52	0.34	4	10	29	1.57	1.95	1.70	0.13	1.61	1.79	7.6
Eu	22	0.89	0.10	4	18	18	0.77	0.93	0.86	0.05	0.83	0.88	5.3
Ga	9	16.6	1.6	1	8	11	14.0	17.0	16.0	1.0	15.3	17.0	6.1
Gd	13	2.91	0.25	0	13	0	2.4	3.355	2.91	0.25	2.76	3.06	8.5
Hf	15	4.0	1.0	4	11	27	4.1	4.9	4.40	0.30	4.19	4.60	6.9
Ho	12	0.46	0.16	5	7	42	0.51	0.63	0.570	0.042	0.531	0.609	7.4
La	24	20.8	1.9	3	21	13	16.7	23.0	21.2	1.4	20.6	21.9	6.5
Li	6	20.9	1.6	0	6	0	18.2	22.83	20.9	1.6	19.2	22.6	7.8
Lu	20	0.30	0.15	2	18	10	0.16	0.35	0.27	0.05	0.24	0.29	18
Mo	8	0.38	0.17	0	8	0	0.02	0.54	0.38	0.17	0.24	0.52	44
Nb	23	6.3	1.2	4	19	17	4.8	7	5.8	0.6	5.6	6.1	9.6
Nd	22	17.2	1.5	4	18	18	15.3	17.745	16.7	0.6	16.4	17.0	3.7
Ni	19	14.7	2.8	1	18	5	12.0	19.0	14.0	2.0	13.3	15.2	14
Pb	19	12.8	4.1	4	15	21	9.4	12.4	11.2	0.9	10.7	11.7	8.2
Pr	13	4.8	1.2	4	9	31	3.1	5.195	4.3	0.7	3.8	4.8	15
Rb	40	66	12	8	32	20	64.8	72	67.8	1.8	67.1	68.5	2.7
Sb	6	0.4	0.8	1	5	17	0.038	0.09	0.07	0.02	0.04	0.10	29
Sc	16	10	6	1	15	6	2.1	11.0	8.4	1.9	7.4	9.5	23
Sm	24	3.38	0.38	2	22	8	3.05	4.20	3.45	0.29	3.32	3.58	8.3
Sn	7	1.36	0.28	0	7	0	1.0	1.70	1.35	0.28	1.10	1.61	20
Sr	38	376	25	8	30	21	356	390	373	8	370	376	2.2
Ta	11	0.69	0.11	4	7	36	0.59	0.65	0.616	0.022	0.595	0.636	3.6
Tb	15	0.45	0.04	0	15	0	0.39	0.56	0.451	0.044	0.427	0.475	9.8
Th	24	8.1	0.9	4	20	17	7.8	9.37	8.4	0.5	8.2	8.6	5.7
Tm	8	0.21	0.09	1	7	13	0.200	0.270	0.236	0.029	0.209	0.263	12
U	21	2.0	1.0	4	17	19	1	2.6	2.08	0.41	1.87	2.29	20
V	26	67	11	3	23	12	58.0	79.63	70.0	6.0	67.5	72.4	8.2
Y	29	17.3	1.5	0	29	0	13.9	21	17.3	1.5	16.7	17.9	8.6
Yb	22	1.70	0.30	0	22	0	1	2.45	1.70	0.30	1.60	1.87	18
Zn	28	45.4	4.2	0	28	0	38	52.6	45.4	4.2	43.8	47.0	9.2
Zr	31	141	24	6	25	19	127	153	143	7	130	145	4.8

For abbreviations see footnote of Table 5. Major element concentrations are expressed in % m/m and trace element concentrations in  $\mu\text{g g}^{-1}$ .

Table 8. Initial and final (after outlier detection and elimination) statistical data on major and trace elements in GSJ granodiorite JG-1a.

Element	n <sub>in</sub>	$\bar{X}_n$	s <sub>n</sub>	O <sub>t</sub>	n <sub>out</sub>	%O <sub>td</sub>	Min	Max	$\bar{X}$	s	95% Confidence limits		%RSD
SiO <sub>2</sub>	46	72.0	1.0	5	41	11	71.35	73.19	72.29	0.5	72.14	72.44	0.7
TiO <sub>2</sub>	46	0.26	0.08	6	40	13	0.23	0.282	0.250	0.012	0.25	0.25	4.8
Al <sub>2</sub> O <sub>3</sub>	47	4.27	0.42	8	39	17	13.8	14.56	14.18	0.17	14.13	14.24	1.2
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	44	2.00	0.08	2	42	4	1.86	2.11	1.99	0.07	1.97	2.01	3.3
MnO	46	0.057	0.006	4	42	9	0.05	0.07	0.0586	0.0042	0.0573	0.0599	7.2
MgO	45	0.69	0.13	8	37	18	0.63	0.78	0.700	0.039	0.687	0.713	5.6
CaO	49	2.0	0.25	10	39	20	2.08	2.26	2.150	0.042	2.137	2.164	1.9
Na <sub>2</sub> O	46	3.40	0.13	6	40	13	3.25	3.6	3.40	0.07	3.38	3.42	2.2
K <sub>2</sub> O	52	3.9	0.5	10	42	19	3.82	4.13	4.00	0.07	3.98	4.02	1.7
P <sub>2</sub> O <sub>5</sub>	39	0.082	0.014	2	37	5	0.06	0.11	0.083	0.011	0.080	0.087	13
LOI	18	0.69	0.24	2	16	11	0.47	1.05	0.70	0.15	0.62	0.78	21
H <sub>2</sub> O <sub>PL</sub>	12	0.58	0.13	0	12	0	0.3	0.75	0.58	0.13	0.50	0.67	22
H <sub>2</sub> O <sub>MI</sub>	14	0.12	0.05	0	14	0	0.02	0.19	0.12	0.05	0.09	0.15	44
Fe <sub>2</sub> O <sub>3</sub>	21	0.8	0.7	8	13	38	0.72	1.76	1.36	0.22	1.26	1.45	16
FeO	22	1.36	0.22	4	18	18	1.19	1.5	1.37	0.10	1.32	1.42	7.1
Au	7	0.21	0.10	0	7	0	0.12	0.4	0.20	0.10	0.19	0.31	48
Ba	49	460	70	9	40	18	422	488	458	17	452	463	3.8
Be	7	3.2	0.5	0	7	0	2.6	4	3.2	0.5	2.8	3.7	14
Ce	41	44	6	8	33	20	42.9	51	46.9	1.9	46.2	47.5	4.0
Co	41	8	11	8	33	20	3.8	6.7	5.3	0.7	5.0	5.5	14
Cr	41	19	7	13	28	32	14.1	20.6	17.6	1.7	17.0	18.3	9.9
Cs	22	11.0	2.0	1	21	5	9.1	11.9	10.8	0.6	10.5	11.04	5.9
Cu	25	7	21	8	17	32	0.6	3.1	1.7	0.7	1.4	2.1	38
Dy	23	4.4	0.7	2	21	9	3.41	5	4.3	0.5	4.1	4.5	11
Er	19	2.6	0.6	0	19	0	1.75	3.7	2.6	0.6	2.3	2.8	22
Eu	31	0.71	0.07	5	26	16	0.61	0.75	0.694	0.037	0.679	0.710	5.4
F	8	509	200	3	5	38	364	459	428	39	380	477	9.1
Ga	16	17.2	3.2	4	12	25	15	17	16.3	0.7	15.8	16.8	4.4
Gd	19	7	11	6	13	32	3.8	4.4	4.14	0.22	4.00	4.27	5.3
Hf	21	3.6	0.7	9	12	43	3.6	3.83	3.71	0.07	3.66	3.76	2.0
Ho	20	0.84	0.16	0	20	0	0.61	1.1	0.84	0.16	0.76	0.91	19
La	39	21.5	3.1	8	31	21	18.7	23.14	21.4	1.1	21.0	21.9	5.2
Li	13	79.1	4.3	0	13	0	71	88.2	79.1	4.3	76.5	81.7	5.4
Lu	31	0.43	0.11	2	29	6	0.247	0.63	0.45	0.09	0.42	0.48	19
Mo	11	0.35	0.28	3	8	27	0.04	0.35	0.20	0.10	0.11	0.28	53
Nb	36	11.2	1.8	8	28	22	11	12.5	11.7	0.5	11.5	11.9	4.2
Nd	35	20.0	2.5	8	27	23	18	20.99	19.7	0.8	19.4	20.0	4.1
Ni	37	11.0	17.0	4	33	11	3	11.2	6.8	1.8	6.2	7.4	27
Pb	27	26.8	4.1	9	18	33	25.8	28	26.7	0.7	26.4	27.0	2.5
Pr	21	5.5	1.4	0	21	0	2.5	8.7	5.5	1.4	4.9	6.1	25
Rb	63	175	24	5	58	8	162	189	178	5	177	180	2.7
Sb	8	0.056	0.018	0	8	0	0.022	0.085	0.056	0.018	0.041	0.071	33
Sc	26	6.2	0.5	0	26	0	5	7.4	6.2	0.5	6.0	6.4	8.6
Sm	38	4.6	1.1	10	28	26	4.2	4.8	4.50	0.16	4.43	4.56	3.5
Sn	15	4.4	0.6	0	15	0	3.6	5.5	4.4	0.6	4.1	4.8	14
Sr	63	182	39	14	49	22	175	195	184	5	182	185	2.5
Ta	18	1.92	0.36	4	14	22	1.5	2	1.76	0.16	1.67	1.85	9.0
Tb	24	0.78	0.13	7	17	29	0.66	0.85	0.78	0.05	0.75	0.81	6.7
Th	40	12.6	1.5	4	36	10	10	14.78	12.29	1.05	11.93	12.65	8.6
Tl	9	0.98	0.13	0	9	0	0.8	1.16	0.98	0.13	0.88	1.08	13
Tm	15	0.49	0.43	4	11	27	0.25	0.45	0.36	0.08	0.30	0.41	22
U	39	4.9	1.8	7	32	18	3.5	5.9	4.7	0.6	4.4	4.9	13
V	32	41	110	5	27	16	15	27	21.7	3.4	20.4	23.0	16
W	11	13.0	3.0	0	11	0	9.43	18	13.0	3.0	11.0	15.0	23
Y	47	30.7	5.0	5	42	11	25.7	38	31.5	2.9	30.6	32.4	9.2
Yb	36	2.8	0.8	9	27	25	2.4	3.21	2.90	0.26	2.80	3.00	8.9
Zn	47	38	11	4	43	8	31	39.6	35.9	2.3	35.2	36.6	6.4
Zr	44	114	28	12	32	27	103	124	113	6	112	116	5.2

For abbreviations see footnote of Table 5. Major element concentrations are expressed in % m/m and trace element concentrations in  $\mu\text{g g}^{-1}$ .

Table 9. Initial and final (after outlier detection and elimination) statistical data on major and trace elements in GSJ gabbro JGb-1.

Element	$n_{in}$	$\bar{X}_n$	$s_n$	$O_t$	$n_{out}$	%Otd	Min	Max	$\bar{X}$	s	95% Confidence limits		%RSD
SiO <sub>2</sub>	50	43.8	0.5	8	42	16	42.86	44.18	43.60	0.26	43.52	43.69	0.6
TiO <sub>2</sub>	55	1.6	0.21	9	46	16	1.51	1.74	1.62	0.05	1.60	1.63	3.3
Al <sub>2</sub> O <sub>3</sub>	55	17.5	0.5	5	50	10	16.44	18.57	17.55	0.39	16.50	17.90	2.2
Fe <sub>2</sub> O <sub>3</sub> <sup>T</sup>	49	15.00	0.40	4	45	8	14.4	15.9	15.10	0.30	14.99	15.18	2.0
MnO	52	0.190	0.020	4	48	8	0.155	0.21	0.186	0.013	0.182	0.190	6.8
MgO	51	7.85	0.28	6	45	12	7.58	8.1	7.84	0.12	7.80	7.88	1.5
CaO	55	11.9	0.5	3	52	5	11.39	12.14	11.90	0.20	11.80	11.91	1.7
Na <sub>2</sub> O	55	1.19	0.12	5	50	9	1	1.32	1.21	0.07	1.19	1.23	6.1
K <sub>2</sub> O	55	0.27	0.24	9	46	16	0.2	0.29	0.237	0.021	0.231	0.244	9.0
P <sub>2</sub> O <sub>5</sub>	43	0.062	0.024	4	39	9	0.03	0.09	0.056	0.014	0.051	0.060	24
LOI	16	0.8	0.6	8	8	50	0.5	0.75	0.60	0.07	0.54	0.67	12
H <sub>2</sub> O <sub>PL</sub>	16	1.09	0.38	4	12	25	1.008	1.67	1.28	0.17	1.17	1.39	14
H <sub>2</sub> O <sub>MI</sub>	19	0.15	0.08	2	17	11	0.04	0.2	0.13	0.05	0.10	0.16	41
Fe <sub>2</sub> O <sub>3</sub>	26	6.3	3.8	6	20	23	3.66	5.18	4.67	0.38	4.49	4.85	8.2
FeO	26	9.6	0.6	4	22	15	8.5	10.01	9.35	0.37	9.18	9.51	3.9
Au	8	0.94	0.27	0	8	0	0.38	1.19	0.94	0.27	0.71	1.16	29
Ba	45	69	33	12	33	27	47	77	62	8	59	64	13
Ce	42	8.6	2.5	3	39	7	6.0	10.2	8.1	0.9	7.8	8.4	11
Co	45	60	9	11	34	24	54	66.5	61.1	2.4	60.2	61.9	3.9
Cr	48	59	17	8	40	17	45	78	59	8	57	62	14
Cs	15	0.9	2.5	5	10	33	0.170	0.270	0.218	0.034	0.194	0.242	16
Cu	36	87	8	2	34	6	78.3	96.1	86.3	4.6	84.6	87.9	5.3
Dy	25	1.59	0.31	4	21	16	1.4	1.84	1.61	0.15	1.54	1.67	9.1
Er	24	0.95	0.31	8	16	33	0.91	1.1	1.01	0.06	0.98	1.04	5.6
Eu	36	0.63	0.09	4	32	11	0.51	0.7	0.606	0.041	0.592	0.621	6.8
F	8	120	50	0	8	0	34	200	120	50	79.186	162	41
Gd	21	2	1	3	18	14	1.4	1.7	1.6	0.1	1.5	1.6	6.2
Hf	22	0.85	0.16	8	14	36	0.77	0.9	0.823	0.043	0.798	0.847	5.2
Hg	5	4.1	1.8	0	5	0	2.1	6.8	4.1	1.8	1.8	6.4	45
Ho	21	0.34	0.06	0	21	0	0.22	0.41	0.34	0.06	0.31	0.36	16
La	40	3.6	0.5	8	32	20	3.125	4	3.57	0.23	3.48	3.65	6.4
Li	8	4.6	0.9	0	8	0	3	6	4.6	0.9	3.8	5.4	20
Lu	34	0.15	0.05	7	27	21	0.12	0.18	0.147	0.015	0.142	0.153	10
Mo	10	3.2	7	4	6	40	0.033	0.78	0.46	0.29	0.15	0.77	64
Nb	34	3.2	1.6	6	28	18	1.7	4	2.6	0.6	2.5	2.9	23
Nd	30	5.3	0.7	0	30	0	3.99	7.1	5.3	0.7	5.1	5.6	14
Ni	44	25	7	4	40	9	10	33	24	5	22	25	21
Pb	25	6	10	12	13	48	1	2	1.62	0.34	1.42	1.82	21
Pr	21	1.2	0.5	8	13	38	1.090	1.200	1.128	0.041	1.104	1.153	3.6
Rb	47	7.3	3.8	15	32	32	3.5	7	5.5	0.8	5.2	5.8	14
S	10	1700	600	5	5	50	1950	2000	1980	21	1954	2006	1.1
Sb	8	0.2	0.3	1	7	12	0.04	0.22	0.10	0.06	0.04	0.16	64
Sc	30	35	5	8	22	27	32.7	38	35.9	1.4	35.2	36.5	4.0
Sm	37	1.6	0.5	5	32	14	1.29	1.74	1.49	0.12	1.45	1.54	7.7
Sn	10	3	5	5	5	50	0.36	0.58	0.44	0.08	0.33	0.54	19
Sr	59	328	36	13	46	22	305	348	327	10	324	330	3.0
Ta	16	0.25	0.27	6	10	38	0.1	0.17	0.133	0.024	0.116	0.150	18
Tb	25	1.1	4.1	6	19	24	0.2	0.34	0.268	0.036	0.251	0.285	13
Th	29	0.7	0.6	9	20	31	0.31	0.50	0.43	0.05	0.40	0.45	11
Tm	15	0.155	0.028	0	15	0	0.12	0.22	0.155	0.028	0.140	0.171	18
U	32	0.6	1.7	7	25	22	0.046	0.200	0.115	0.034	0.101	0.129	29
V	41	620	80	6	35	15	578	728	650	33	638	661	5.1
W	8	3.4	1.9	0	8	0	0.81	6.23	3.4	1.9	1.8	5.0	56
Y	46	10.6	3.6	7	39	15	8	13	10.1	1.3	9.7	10.5	12
Yb	38	1.1	0.4	11	27	29	0.80	1.03	0.93	0.06	0.91	0.95	6.1
Zn	45	109	9	0	45	0	87	130	109	9	106	112	8.3
Zr	47	33	8	3	44	6	21.0	46.0	32	6	30	34	20

For abbreviations see footnote of Table 5. Major element concentrations are expressed in % m/m and trace element concentrations in  $\mu\text{g g}^{-1}$ .

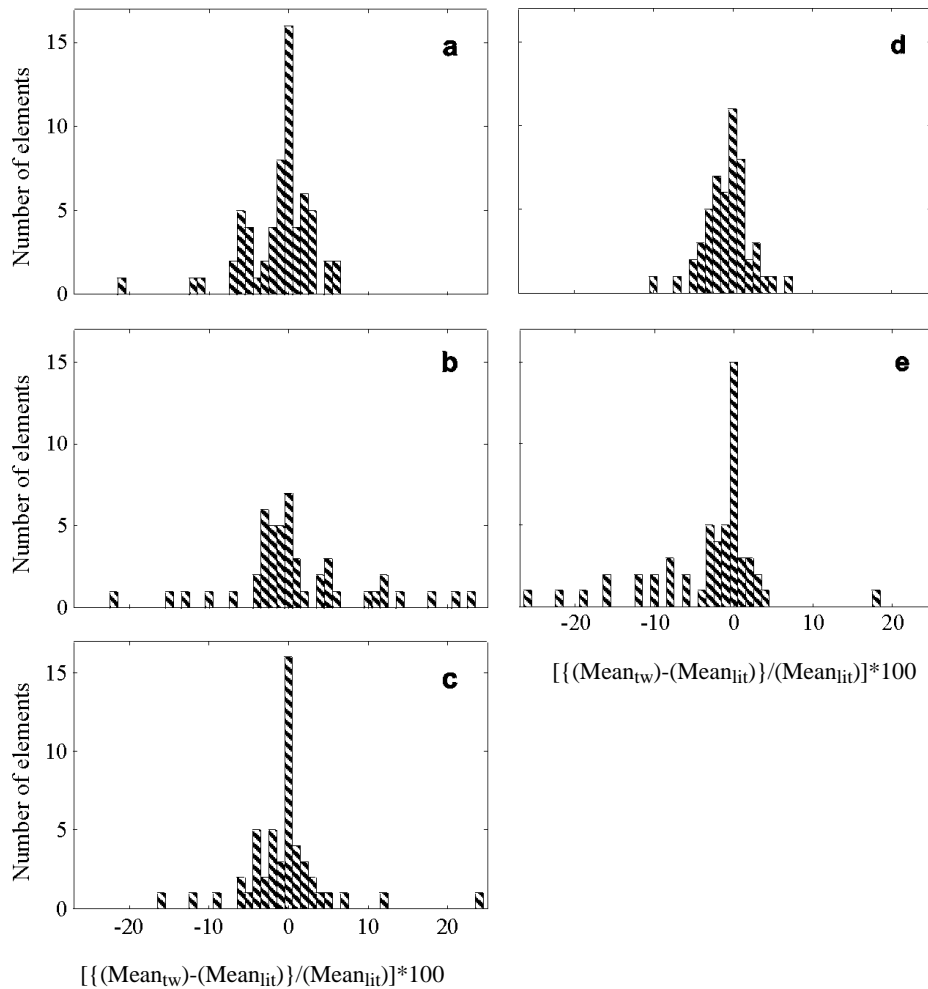


Figure 1. Histogram plot of the % normalized difference of mean concentration obtained in this work for GSJ RM ( $Mean_{tw}$ ) with respect to the literature mean value ( $Mean_{lit}$ ) reported by Terashima *et al.* (1994) for major elements and Imai *et al.* (1995a) for trace elements: (a) JG1; (b) JG2; (c) JG3; (d) JG1a; (e) JGb1.

JGb1 (26%) both sets are practically identical. The remaining data show disagreement ranging from about 1% to 20% (Figure 1). Thirty-five elements exceed 10% difference: three elements (Cu, Dy, and Tm) for JG1; thirteen ( $Fe_2O_3$ , Au, Ba, Dy, Er, Gd, Ho, Mo, Ni, Sn, Tb, W, and Yb) for JG2; six ( $Fe_2O_3$ , Ag, Er, Ho, Mo, and Ta) for JG3; three (Co, Mo, and Sb) for JG1a; ten (Cs, Mo, Nb, Pb, Rb, Sb, Ta, Th, U, and Yb) for JGb1.

F and t-tests (ANOVA) were applied to the data of the five GSJ RM to establish whether the differences between mean values obtained in this work and the earlier literature were statistically significant (Jensen *et al.*, 1997). For all samples with final number of observations remaining after outlier rejection  $n_{out} > 5$ , the final standard deviation values were lower than those reported by Terashima *et al.* (1994) and Imai *et al.* (1995 a, b) for major and trace elements respectively at a confidence level of 99% ( $\alpha=0.01$  significance level). The applica-

tion of t-test showed that the two sets of mean values differed, at 95% confidence level, for some trace elements (Cu and Pr in JG1; Ba, Er, Ni, and Yb in JG2; Ho in JG3; Sb in JG1a; Rb and Yb in JGb1) and a few major elements such as CaO in JG1,  $Fe_2O_3$  in JG3 and JG1a, and  $P_2O_5$  for JG2. Even for those cases for which these differences are not statistically significant or are significant at a lower confidence level, the use of different sets of mean values will affect strongly the instrumental calibrations because such calibrations are generally based only on the mean values without a reference to the respective standard deviations (Verma, 1998). The use of the present mean values may therefore result in a better estimation of traceability, precision, accuracy, and sensitivity of routine analysis of intrusive rock samples.

The two-standard deviation method used by Terashima *et al.* (1994) and Imai *et al.* (1995a, b) for the GSJ RM data processing show higher values of percent-

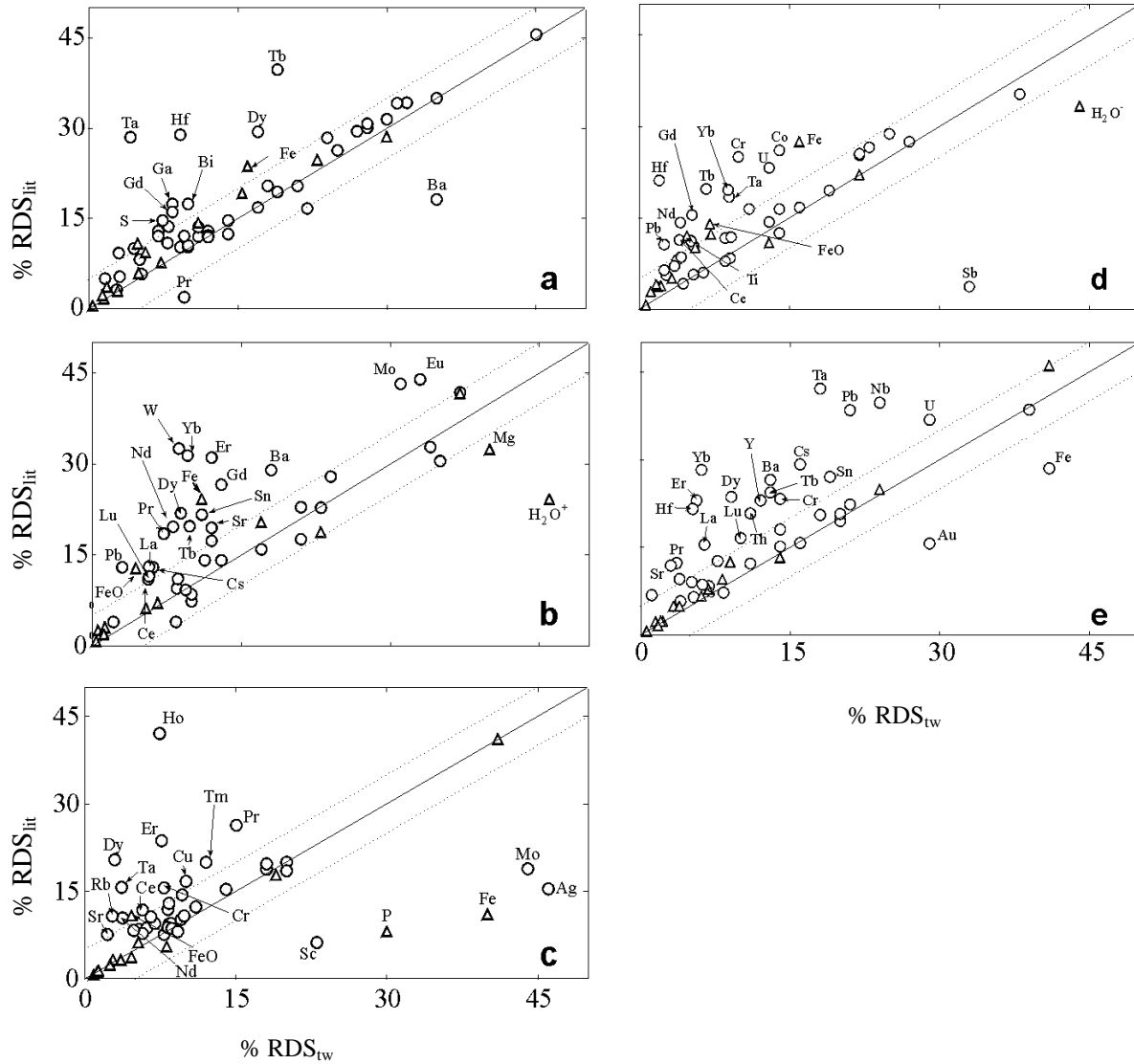


Figure 2. Comparison of  $\%RSD_{tw}$  for mean concentration data obtained in this work (Tables 5 to 9) with  $\%RSD_{lit}$  reported by Terashima *et al.* (1994) for major elements and Imai *et al.* (1995a) for trace elements. The dashed lines represent 5% difference between the two sets of  $\%RSD$ : (a) JG1; (b) JG2; (c) JG3; (d) JG1a; (e) JGb1; △: major element oxides (some of them indicated by their element symbols); ○: trace elements.

age of Relative Standard Deviation ( $\%RSD$ ) for most major and trace elements in all five RM (Figure 2). This is true for all major elements, except  $MgO$  and  $H_2O^+$  in JG2,  $Fe_2O_3$  and  $P_2O_5$  in JG3;  $H_2O^-$  in JG1a; and  $Fe_2O_3$  in JGb1. Similarly, exceptions for trace elements include: Ba in JG1; Ag, Mo, and Sc in JG3; Sb in JG1a; and Au in JGb1. These exceptions may be due to the fact that the two-standard deviation method may detect a genuine observation as an outlier, whereas the present method is applied at a strict confidence level of 99% (Verma, 1997, 1998).

On the other hand, the mean values obtained in this work (with lower  $\%RSD$ ) may be closer to the “true value” according to geochemical criteria based on bulk

partition coefficients (Rollinson, 1993) as shown by mean values of BIR-1 (Verma, 1998) and WS-E (Verma *et al.*, 1998).

## CONCLUSIONS

The present evaluation scheme for five GSJ updated databases by means of appropriate statistical tests is beneficial in better refining mean values and other statistical parameters, and is free from subjective criteria of the existing two-standard deviation method. Outlier detection at a strict 99% confidence level avoids an artificial decrease of the final standard deviation values. The

present mean values compared with earlier compilations give lower %RSD and their use may result in a better estimation of traceability, precision, accuracy, and sensitivity of routine analysis for intrusive rock samples.

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