

Evaluation of geochemical sedimentary reference materials of the Geological Survey of Japan (GSJ) by an objective outlier rejection statistical method

Kailasa Pandarinath

*Departamento de Sistemas Energéticos, Centro de Investigación en Energía,
Universidad Nacional Autónoma de México, Priv. Xochicalco s/no., Col Centro,
Apartado Postal 34, Temixco, Mor. 62580, México.
pk@cie.unam.mx*

ABSTRACT

Nine geochemical sedimentary reference materials (RMs), JCh-1, JDo-1, JLS-1, JSI-1, JSI-2, JLk-1, JSd-1, JSd-2 and JSd-3, of the Geological Survey of Japan (GSJ) were evaluated by an objective outlier rejection statistical method. An extensive chemical database for these reference materials, created from the Internet website of the GSJ Geochemical Reference Samples Database (<http://riodb02.ibase.aist.go.jp/geostand/>) and from research articles published up to December 2008, is evaluated by a statistical scheme consisting of: (i) detection and elimination of the discordant outlier values with the application of 33 discordancy test variants (instead of routinely used inaccurate “two-standard deviation” method); (ii) calculation of new central tendency and dispersion parameters; and (iii) comparison of confidence limits (calculated by incorporating the recently available new, precise critical values for Student t-test) and normalized mean difference percentages of the geochemical parameters obtained in the present work with those calculated for the data of the literature. Evaluation of these RMs by application of the more appropriate statistical method resulted in more precise new central tendency and dispersion parameter values, and also facilitated to propose recommended values for the first time for some of the geochemical parameters. The results obtained in this work could be useful for better calibrations models and for evaluation of method precision, accuracy, sensitivity and detection limits.

Key words: geochemical reference material, sediments, sedimentary rocks, outlier statistical tests.

RESUMEN

Nueve materiales sedimentarios de referencia geoquímica, JCh-1, JDo-1, JLS-1, JSI-1, JSI-2, JLk-1, JSd-1, JSd-2 y JSd-3, del Geological Survey of Japan (GSJ) fueron evaluados por una metodología estadística objetiva para la eliminación de valores discordantes. Una extensa base de datos químicos para estos materiales de referencia, creada a partir de la base de datos de Muestras de Referencia Geoquímica de la GSJ (<http://riodb02.ibase.aist.go.jp/geostand/>) y complementada con artículos de investigación publicados hasta diciembre de 2008, se evaluó con un esquema estadístico que consiste en: (i) la detección y eliminación de los valores discordantes por medio de la aplicación de 33 variantes de pruebas de discordancia (en vez del método inexacto rutinariamente utilizado de “dos-desviaciones

estándar”); (ii) el cálculo de nuevos parámetros de tendencia central y de dispersión; y (iii) la comparación de límites de confianza (calculados con nuevos y precisos valores críticos, recientemente disponibles para la *t* de Student) y los porcentajes de diferencia de la media obtenidos en el presente trabajo con respecto a la reportada en la literatura. La evaluación de estos materiales de referencia mediante este método estadísticamente más apropiado resultó en nuevos y más precisos valores de tendencia central y dispersión. Así mismo, permitió, por primera vez, proponer valores recomendados para algunos parámetros geoquímicos. Los resultados obtenidos en este trabajo podrían ser útiles para mejores modelos de calibración y para la evaluación de la precisión exactitud, sensibilidad y límites de detección de método.

Palabras clave: materiales de referencia geoquímica, sedimentos, rocas sedimentarias, pruebas estadísticas para valores discordantes.

INTRODUCTION

Numerous geochemical reference materials (RMs) are available (Roelandts, 1989a, 1989b, 1991, 1992, 1993, 1996a, 1996b) to estimate the precision, accuracy, sensitivity and calibration of routine analytical techniques. Most of the available RMs for use in geoanalytical laboratories are strictly not certified reference materials (CRMs) as they have not been prepared following stringent guidelines and by proper certifying bodies (Velasco-Tapia *et al.*, 2001), as recommended by the International Organization of Standardization (ISO, 1989). Availability of more sophisticated analytical equipment and the explosive growth of analytical methods in recent years for determination of chemical elements in geological materials has obviously stimulated the necessity of reference materials (RMs) with more precise and accurate reference values.

Reliable estimates of both central tendency and dispersion parameters are necessary for all RMs to be used in calibration of analytical equipment. For this purpose, geochemical data traditionally obtained by several laboratories on RMs have been processed. The Geological Survey of Japan (GSJ) has taken up the standard reference material project to improve and check the reliability of analytical data obtained from different methods and different laboratories. For this purpose, GSJ has distributed 42 RMs (23 samples of igneous rocks, seven samples of sedimentary rocks, seven samples of sediments, two samples of coal fly ash and soil, and three samples of ore materials) to analytical laboratories in 43 countries worldwide and the analytical data obtained with cooperative works were compiled by different researchers (Ando *et al.*, 1987, 1989, 1990; Terashima *et al.*, 1992; Imai *et al.*, 1995a, 1995b, 1996) and the database is also available at the internet website <<http://riodb02.ibase.aist.go.jp/geostand/>>. Ando *et al.* (1987, 1989) and Imai *et al.* (1995a, 1995b, 1996) have reported approximate values of major and minor elements for some of the GSJ RMs of “igneous rock series” based on the available analytical data up to one year before the respective published years. Reference values of major and minor elements for sedimentary RMs of the GSJ “sedimentary rock series” were

also reported on the basis of the available analytical data (up to March 1989 for three sedimentary RMs JLk-1, JLs-1 and JDo-1, Ando *et al.*, 1990; and up to December 1996 for nine sedimentary RMs, Imai *et al.*, 1996). In compiling and evaluating the data of all the above referred works of igneous and sedimentary series, the researchers have rejected the data outside two standard deviation from the mean by using the subjective criteria to discard data on either end of the reported concentration spectrum. A new mean value is computed with the remaining data and the procedure is repeated until no more outlying values are found. This method does not take into account the strong dependence of the critical value curves on the number of observations (Taylor, 1990) and the approach is in fact incorrect (Barnett and Lewis, 1994) as it may eliminate the data that are not really outliers or may include values that are otherwise erroneous from many statistical criteria. Verma (1997, 1998), and Guevara *et al.* (2001) have discussed in detail the disadvantages of this method.

To obtain reliable estimates of both central tendency and dispersion parameters, which are necessary for calibration of any analytical equipment, inter-laboratory geochemical data on RMs have been processed traditionally by both robust and outlier-based methods (Dybcznski *et al.*, 1979; Govindaraju and Roelandts, 1989; Verma, 1997, 1998; Velasco and Verma, 1998; Verma *et al.*, 1998; Velasco *et al.*, 2000; Guevara *et al.*, 2001; Velasco-Tapia *et al.*, 2001; Verma, 2004; Villeneuve *et al.*, 2004). More recently, Verma *et al.* (2009) and González-Ramírez *et al.* (2009) have discussed in detail these methods and highlighted the importance of using a better statistical methodology (Verma, 1997, 1998, 2005) for identifying discordant outliers in the data with a totally objective approach. Verma (1997, 1998, 2005) suggested an outlier detection and elimination scheme called multiple-test method, which is to be applied at a strict 99% confidence level in order to identify an outlier as a function of the total number of observations, thus avoiding an artificial decrease of the final standard deviation. In order to facilitate the application of this methodology, Verma and Díaz-González (unpublished) developed a computer program named DODESYS by incorporating the recently

available new, precise and accurate critical values (Verma and Quiroz-Ruiz, 2006a, 2006b, 2008; Verma *et al.*, 2008) to render more reliable statistical inferences. This objective outlier rejection statistical method has been successfully applied to the evaluation of geochemical RMs (Velasco *et al.*, 2000; Guevara *et al.*, 2001; Velasco-Tapia *et al.*, 2001; Marroquín-Guerra *et al.*, 2009) and other studies (Pandarinath, 2009; Verma, 2009a, 2009b; Torres-Alvarado *et al.*, 2009).

The Geological Survey of Japan distributed the geochemical RMs to use as reference materials for free of cost up to 1st April 2001 and for cost thereafter (<http://riodb02.ibase.aist.go.jp/geostand/>). As per the available information in the literature, the last compilation and evaluation of GSJ geochemical RMs is by Imai *et al.* (1996) for sedimentary rock series (with the data available until December 1996) and by Guevara *et al.* (2001) for intrusive rocks (with the data available until December 1997). As several geochemical laboratories started using these RMs, more new geochemical data for these materials has been generated. For example, the literature reveals that several researchers have recently analyzed the GSJ sedimentary reference materials (Kawabe, 1995; Terashima, 2000; Igarashi *et al.*, 2003; Itoh *et al.*, 2004; Inoue *et al.*, 2004; Yamamoto *et al.*, 2005; Watanabe and Nakai, 2006; Mabrouk *et al.*, 2006). The reported data on these GSJ sedimentary reference materials was not included in the earlier studies of compilation and evaluation of GSJ geochemical RMs.

In view of this, I have compiled all the chemical data available on nine GSJ reference sedimentary materials up to December 2008 and evaluated them through the more precise statistical methodology as suggested by Verma (1997, 1998, 2005), using the software DODESYS (Verma and Díaz-González, unpublished). On this basis, a new set of more precise recommended values for these GSJ sedimentary reference materials is proposed. These new values could be advantageously used by geologists and geochemists for instrumental calibrations and method evaluation.

REFERENCE MATERIAL DATABASES

Nine sedimentary material of Geological Survey of Japan (GSJ) were selected for this work: five sedimentary rocks JCh-1 (chert), JDo-1 (dolomite), JLS-1 (limestone), JSI-1 (clay slate), JSI-2 (clay slate) and four sediments Jlk-1 (lake sediment), JSd-1 (stream sediment), JSd-2 (stream sediment), JSd-3 (stream sediment). An extensive chemical database for these reference materials was created by downloading the available data from the GSJ Geochemical Reference Samples Database (<http://riodb02.ibase.aist.go.jp/geostand/>) and also by compiling data from articles published up to December 2008 (other than those already added in the website: Kawabe, 1995; Terashima, 2000; Igarashi *et al.*, 2003; Itoh *et al.*, 2004; Inoue *et al.*, 2004; Yamamoto *et al.*, 2005; Watanabe and Nakai, 2006;

Mabrouk *et al.*, 2006). All the required information like analytical methods used and other reference details (authors, title of the work, year of publication, journal name, volume, page numbers and name of the analyst) were also included in this database. The data were captured in a standard Excel spreadsheet and the individual data were cross checked to correct the typographical errors, if any. Data mentioned as from personal communication were also included in this database. Elements with less than five individual observations were excluded from the final database. An additional reference material (JcP-1, coral), which is included in the sedimentary series of the GSJ, has very low (<5) number of measurements for almost all elements, and hence was eliminated from the final database. The individual observations in each compilation were gathered in eight general analytical groups. A group code (Gr1 to Gr8) was assigned to each element concentration value depending on the corresponding analytical method (analytical method codes are generally after Gladney *et al.*, 1992 and as shown in tab. 1 of Velasco-Tapia *et al.*, 2001).

STATISTICAL APPROACHES FOR DATA PROCESSING AND EVALUATION

The discordant outlier values were detected and eliminated with the application of 33 discordancy test variants following the methodology reported by Verma (1997, 1998, 2005) and using the computer program DODESYS (Verma and Díaz-González, unpublished). As an innovation, this program uses recently simulated, new precise and accurate critical values (Verma and Quiroz-Ruiz, 2006a, 2006b, 2008; Verma *et al.*, 2008). The detection and elimination of the discordant outliers in the database is carried out in two steps: (1) concentrations of elements in each group code (assigned depending on the corresponding analytical method) of the reference material are considered as separate populations and processed by selecting the “Single-outlier tests (all 13 test variants)” option in the program DODESYS; (2) output data of step 1 (concentrations of elements after detecting and eliminating the outliers) were again processed for detection and elimination of outliers by considering all the data as a single combined statistical sample (by combining all eight groups as one group) and by selecting the “Default-outlier tests (all 33 test variants)” option in the program DODESYS.

For comparison of the results obtained by the present multi-test statistical approach with those in the literature for GSJ RMs, I have used the confidence limit $\{CL = (t_{cv} * s) / (n)^{1/2}\}$ (Verma, 2005) instead of routinely used standard deviation (s). As CL involves s , number of measurements (n) and critical values for Student t -test (t_{cv}), it is a much better parameter than only s for comparison of two sets of data. Because the Student t critical values were not available for all degrees of freedom, new best interpolation equations have been recently proposed (Verma, 2009a) for

accurately estimating them. These equations were used in the present work. The final statistical parameters x (mean value), s , (obtained from the output files of the DODESYS analysis) and CL were rounded following the procedure recommended in standard text books on statistics (e.g., Bevington, 1969; Verma, 2005).

DATA EVALUATION

The data of all the nine GSJ RMs were evaluated by comparing the statistical parameters obtained by the present multiple-test approach with those obtained by the two-standard deviation method of Imai *et al.* (1996). The data reported by Imai *et al.* (1996) have been taken as it is (without rounding) for comparison. Subsequently in the text, this work (tw) refers to the results obtained from the updated database of this work and the literature data (lit) refers to that of Imai *et al.* (1996). The final number of parameters (n_{tw}), mean (x_{tw}), standard deviation (s_{tw}), confidence limit (CL_{tw}) and outliers percentage ($Or\%$) obtained using the present statistical approach and those reported in the literature (n_{lit} , x_{lit} , s_{lit}) are shown in Table 1 and in Tables A1-A8 (one table each for each sedimentary RM) in the electronic supplement. Confidence limits for the literature data were also similarly calculated using best interpolated Student t critical values of Verma (2009a) and are included in these tables for comparison. Comparison of CL s is carried out in a binary plot (Figure 1) of CL data of this work (CL_{tw}) with that of the literature (CL_{lit}). Chemical elements and/or element oxides plotting exactly on the diagonal line in these figures (Figures 1a-1i) indicate no difference in CL values of this work and the data reported in the literature. Elements placed above the diagonal line (towards y-axis) represent higher CL values for literature data than those in the present work. Similarly, elements placed below the diagonal line (towards x-axis) represent lower CL values for literature data comparing to the data in the present work. As CL value is proportional to s and inversely proportional to n (as discussed in the above section), data of the elements placed above the diagonal line are characterized by higher s or lower n or both, and *vice versa* for the elements placed below the diagonal line. For the majority of the elements, CL values of literature data are higher for RMs JDo-1, JSI-1, JSI-2, JLk-1, JSd-1 and JSd-2 (Figures 1b, d-h), and lower for RM JLS-1 (Figure 1c). Most of the elements are placed just above the diagonal line or very near to either side of it for RM JSd-3 (Figure 1i) and in almost in equal number of elements located either side of the diagonal line for RM JCh-1 (Figure 1a). The final CL values for 305 of 467 total elements (~65%) in the nine GSJ RMs evaluated using the present statistical approach (CL_{tw}) were characterized by lower CL values than those calculated for the data processed by the “two-standard deviation method” (CL_{lit}) and reported by Imai *et al.* (1996). In comparison to the CL data in the present work (CL_{tw}), the difference percentage of CL data

from the literature (CL_{lit} ; Imai *et al.*, 1996) is between 0-1 % higher for 22 elements, 1-10 % for 30 elements, 10-20 % for 42 elements and >20 % for 209 elements. The opposite is true for some elements, that is, with respect to the CL data of the present work (CL_{tw}), CL data of the literature (CL_{lit} ; Imai *et al.*, 1996) are between 0-1 % lower for 21 elements, 1-10 % for 26 elements, 10-20 % for 28 elements and >20 % for 87 elements.

Mean values of the elements in all the nine GSJ RMs are evaluated by comparing the normalized mean difference percentages of elements calculated for the data processed by present statistical approach ($Mean_{tw}$) with those calculated for the data of the literature ($Mean_{lit}$; Imai *et al.*, 1996). The mean percentage-normalized differences for elements were calculated as follows:

$$\text{Mean percentage-normalized difference} = \frac{\{(Mean_{lit} - Mean_{tw}) / Mean_{tw}\} \times 100}{}$$

A comparison of mean percentage-normalized difference values obtained by the present multiple-test statistical method with those obtained by the two-standard deviation method (as reported by Imai *et al.*, 1996) is shown in Figures 2a-2i. About 36 % of mean values of the total elements (173 out of 477) obtained for the nine RMs were identically comparable to the literature data, with a disagreement of $\leq \pm 1\%$ (Figures 2a-2i). In another ~30 % of mean values of the total number of elements evaluated (140 out of the remaining 304 elements), the literature mean value ($Mean_{lit}$) is higher than the values of $Mean_{tw}$ and *vice versa* ($Mean_{lit}$ values are lower than $Mean_{tw}$ values) for the remaining 34 % of the elements (164 elements). In detail, in comparison to the present mean values ($Mean_{tw}$), the literature mean values ($Mean_{lit}$) are higher between 1-5 % for 89 elements, 5-10 % for 24 elements, 10-20 % for 13 elements and >20 % for 14 elements. For the opposite, $Mean_{lit}$ values are lower than $Mean_{tw}$ values by between 1-5 % for 83 elements, 5-10 % for 38 elements, 10-20 % for 17 elements and >20% for 26 elements (Figures 2a-2i; for individual element details of each group, a STATISTICA file containing the results and the corresponding elements can be obtained by request from the author).

A possible reason for the above discussed higher/lower CL_{lit} and $Mean_{lit}$ values compared to the corresponding CL_{tw} and $Mean_{tw}$ obtained in the present work may be the use of an inappropriate statistical method (“two-standard deviation” method) in evaluating the data reported in the literature and the application of the multiple-test method at the strict 99% confidence level. The two-standard deviation method, used to evaluate the data reported in the literature, does not take into account the strong dependence of the critical value curves on the number of observations and the approach is in fact incorrect (Taylor, 1990; Barnett and Lewis, 1994; Verma, 1998; Verma and Quiroz-Ruiz, 2006b; Verma *et al.*, 2009) because it may eliminate numerous data that are not truly discordant outliers or may include some values

Table 1. Statistical parameters for chemical data from the literature (Imai *et al.*, 1996) and this work for the geochemical sedimentary reference material JCh-1 (chert).

Element	n_{lit}	x_{lit}	s_{lit}	CL_{lit} 95%	n_{tw}	x_{tw}	s_{tw}	CL_{tw} 95%	Or%
<i>Major element oxides (%)</i>									
SiO ₂	12	97.81	0.484	0.308	14	97.949	0.442	0.255	17.7
TiO ₂	13	0.0316	0.0144	0.0087	14	0.0253	0.0063	0.0036	26.3
Al ₂ O ₃	14	0.734	0.0889	0.0513	20	0.748	0.092	0.043	9.09
Fe ₂ O ₃	7	0.272	0.0992	0.0918	10	0.307	0.100	0.071	0
FeO	6	0.0867	0.0615	0.0645	6	0.087	0.062	0.065	0
Fe ₂ O ₃ ^T	12	0.356	0.0413	0.0262	14	0.3534	0.0369	0.0213	17.6
MnO	14	0.0173	0.0035	0.0020	14	0.01844	0.00149	0.00086	12.5
MgO	10	0.0754	0.00786	0.00562	13	0.0834	0.0150	0.0091	23.5
CaO	11	0.0449	0.0128	0.0086	11	0.0447	0.0079	0.0053	31.2
Na ₂ O	10	0.0305	0.0108	0.0077	13	0.0338	0.0075	0.0045	18.8
K ₂ O	14	0.221	0.0264	0.0152	16	0.2214	0.0151	0.0081	20.0
P ₂ O ₅	6	0.0167	0.00516	0.00542	9	0.01592	0.00449	0.00345	25.0
LOI					9	0.450	0.093	0.071	0
H ₂ O ⁺	5	0.356	0.109	0.135	5	0.356	0.109	0.136	0
H ₂ O ⁻	5	0.152	0.0217	0.0269	6	0.133	0.050	0.052	0
<i>Trace elements (ppm)</i>									
La	8	1.52	0.42	0.35	7	1.378	0.303	0.280	36.4
Ce	10	5.21	0.29	0.21	11	5.177	0.306	0.206	21.4
Nd	5	2.05	0.8	1.0	5	1.642	0.249	0.309	16.7
Sm	7	0.359	0.078	0.072	7	0.343	0.077	0.072	12.5
Eu	5	0.0594	0.009	0.011	5	0.0692	0.0173	0.0215	28.6
Tb	4	0.0385	0.0064	0.0102	6	0.0450	0.0135	0.0142	14.3
Dy	4	0.378	0.015	0.024	5	0.3602	0.0418	0.0519	28.6
Yb	6	0.182	0.025	0.026	7	0.1800	0.0230	0.0213	22.2
Lu	5	0.0344	0.0048	0.0060	6	0.0330	0.0055	0.0057	0
Ba	12	302	10.1	6.4	16	297.8	13.1	7.0	15.8
Co	17	15.5	1.57	0.81	20	15.70	1.91	0.89	0
Cr	14	7.04	1.54	0.89	17	7.46	2.24	1.15	0
Cs	7	0.243	0.057	0.053	9	0.251	0.052	0.040	0
Cu	12	15.3	1.14	0.72	12	15.03	1.29	0.82	0
Hf	5	0.195	0.031	0.038	6	0.1872	0.0335	0.0352	14.3
Nb	4	1.7	1.29	2.05	6	1.065	0.324	0.340	25.0
Ni	11	8.76	1.14	0.77	13	8.74	1.07	0.64	18.8
Pb	6	2	0.63	0.66	5	2	0	0	16.7
Rb	13	8.61	0.953	0.576	16	8.64	0.86	0.46	11.1
Sc	7	0.979	0.026	0.024	7	0.9791	0.0261	0.0242	12.5
Sr	8	4.2	0.703	0.588	12	4.57	0.97	0.61	20.0
Th	6	0.735	0.17	0.18	7	0.710	0.169	0.156	12.0
V	11	10.4	2.34	1.57	13	10.22	2.52	1.52	0
Y	9	1.81	0.34	0.26	14	1.97	0.79	0.45	12.5
Zn	12	7.93	1.55	0.98	12	8.94	2.56	1.63	14.3
Zr	9	11.5	3.99	3.07	13	10.82	3.75	2.27	13.3
As	6	0.567	0.242	0.254	7	0.541	0.231	0.214	0

n : number of measurements; x : mean value; s : standard deviation; CL : 95% confidence limit; lit : literature data (Imai *et al.*, 1996); tw : this work (results obtained from the updated database of the present work); $Or\%$ =outliers percentage.

that are otherwise erroneous from other statistical criteria. Velasco-Tapia *et al.* (2001) and Guevara *et al.* (2001) also evaluated igneous RMs of U.S. Geological Survey (BHVO-1, RGM-1, AGV-1, W-1 and W-2) and intrusive rock RMs of Geological Survey of Japan (JG1, JG2, JG1a, JG3 and JGb1), respectively, by presently used objective outlier rejection statistical method (initially suggested by Verma 1997, 1998) and reported significant differences in s and x concentrations for elements compared to those obtained by “two-standard deviation” method reported in the literature. They also attributed the observed significant differences in s and x of the elements in the RMs to the incorrect/inaccurate

statistical method (“two-standard deviation”) followed in the literature.

The present evaluation work of nine GSJ sedimentary RMs resulted in mean values (Tables 1 and A1-A8) that are more precise than those reported in the literature, because the RMs were evaluated by a more appropriate objective outlier rejection statistical method (suggested by Verma 1997, 1998, 2005) and by incorporating the recently available new, precise critical values (Verma and Quiroz-Ruiz, 2006a, 2006b, 2008; Verma *et al.*, 2008). Apart from this, the present evaluation of GSJ sedimentary RMs also allows to propose recommended values for the first time for: (1)

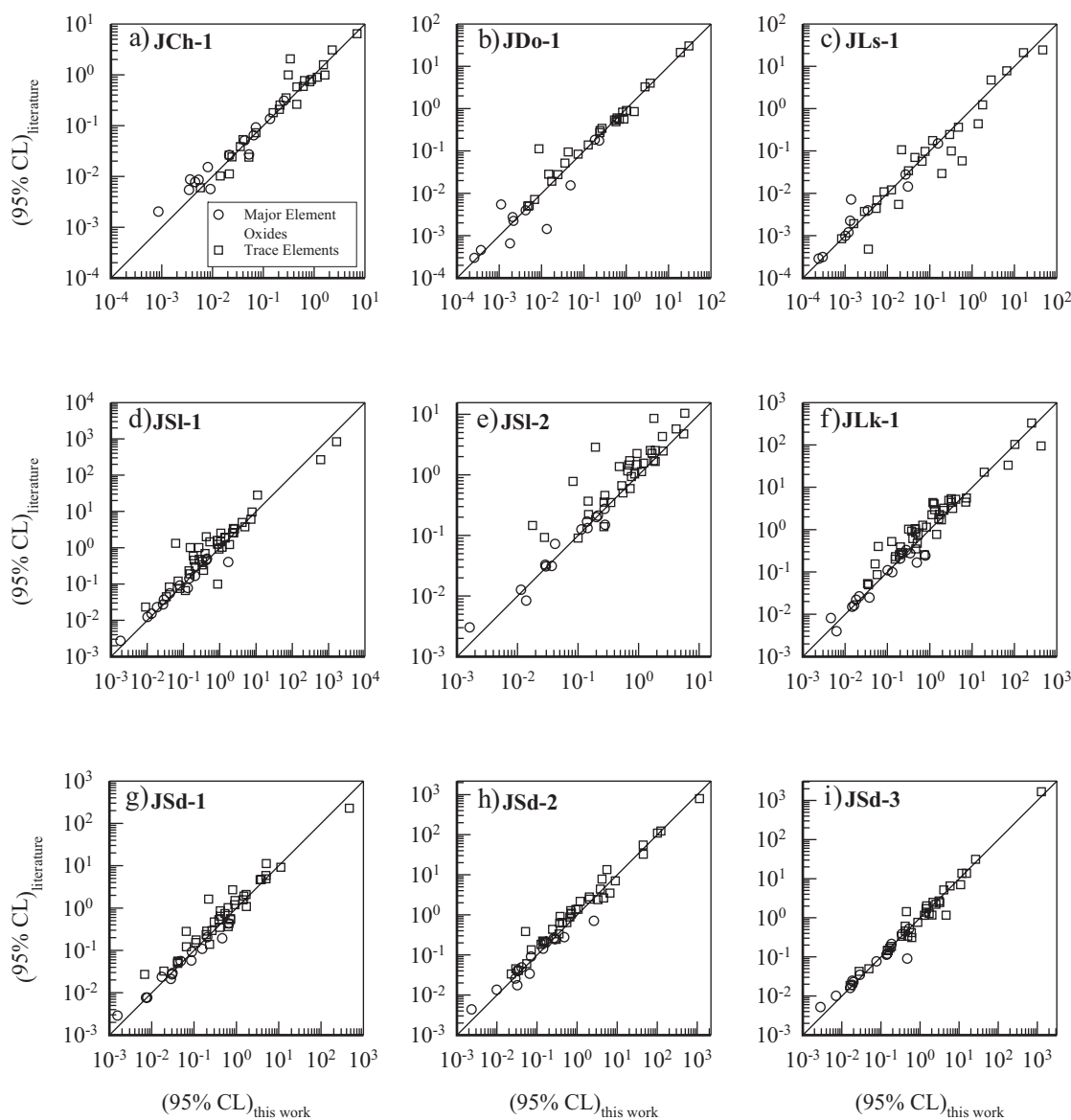


Figure 1. Comparison of confidence limits (CL) obtained for the data of this work with those reported in the literature. See the text for details on the calculation of CL .

LOI for JCh-1; (2) LOI and Pb for JDo-1; (3) LOI, Pr, Gd, Ho, Er, Ga and Rb for JLs-1; (4) LOI, Tm, B and Bi for JSI-1; (5) LOI, Mo and Sn for JSI-2; (6) LOI, B, BI and Sn for JLk-1; (7) CO₂, LOI and B for JSd-1; (8) LOI, Tm, B, Sb and Ag for JSd-2; (9) CO₂, LOI, Sb and Bi for JSd-3 (Table 1 and Tables A1-A8). Imai *et al.* (1996) reported only “mean range” values (no standard deviation) for these parameters because the number of measurements (n) was <4. Compilation of data on the RMs up to December 2008 and application of more appropriate statistical methodology in evaluating these RMs in this work made possible to report recommended values (where $n \geq 5$) for these parameters.

These new central tendency and dispersion parameter values for sedimentary RMs from GSJ would be useful for calibrations based on weighted least-squares linear regres-

sion models as well as for evaluation of method precision, accuracy, sensitivity and detection limits (Baumann, 1997; Zorn *et al.*, 1997; Santoyo and Verma, 2003; Guevara *et al.*, 2005; Santoyo *et al.*, 2006; Tellinghuisen, 2007; Verma and Santoyo, 2007). Consequently, better quality data could be obtained in future for geological materials, which would facilitate proposal and use of new discrimination diagrams widely used in geosciences (*e.g.*, Verma, 2009b, in press). In fact, although statistically correct log-ratio transformed discriminant function diagrams are already available for igneous rocks (*e.g.*, Verma *et al.*, 2006; Agrawal *et al.*, 2008), for sedimentary rocks there is still an urgent need because most existing discrimination diagrams do not work properly (*e.g.*, Armstrong-Altrin and Verma, 2005). Thus, the new statistical data for RMs obtained in this work would help

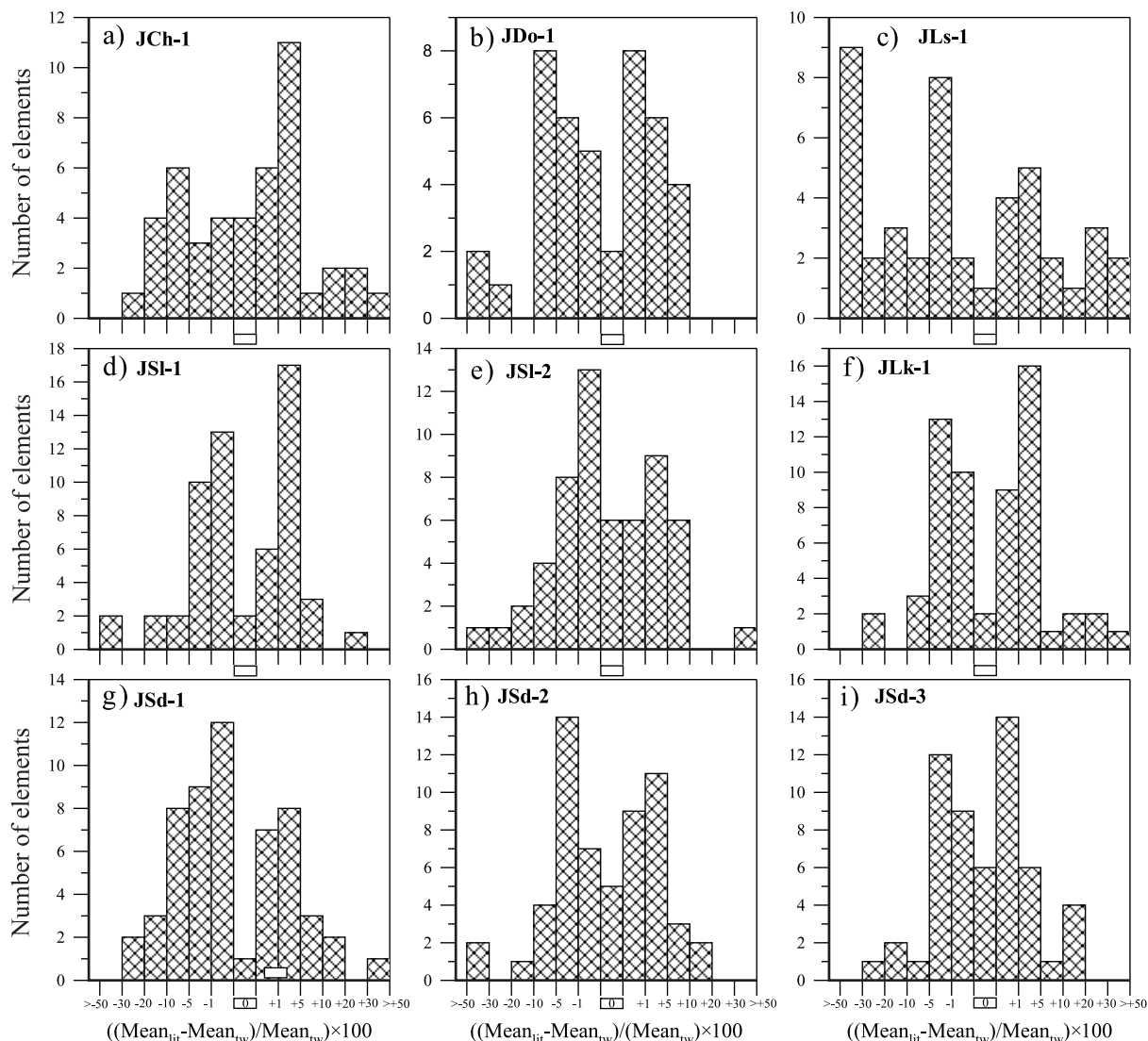


Figure 2. Histogram plot of the percentage-normalized difference of mean concentrations of the literature ($Mean_{lit}$) with respect to the mean concentrations of this work ($Mean_{tw}$).

in future to eventually achieve such goals for sedimentary rocks as well. Similar work should therefore be done for other sedimentary RMs.

CONCLUSIONS

The evaluation of nine GSJ sedimentary RMs based on more appropriate objective outlier rejection statistical method at a strict 99% confidence level and incorporating the recently available new, precise critical values resulted in new central tendency and dispersion parameter which are more precise than those reported in the literature. This evaluation work permitted to propose recommended values for the first time for some of the chemical elements for these RMs. The new mean and standard deviation values may be useful for a better evaluation of method precision, accuracy,

sensitivity and detection limits in routine analysis of sediments and sedimentary rocks.

ACKNOWLEDGEMENTS

I would like to thank two reviewers for their positive evaluation of my work. I am also much grateful to Dr. Surendra P. Verma for his valuable suggestions during the course of this work.

APPENDIX A. SUPPLEMENTARY DATA

Tables A1 to A8 can be found at the journal web site <<http://rmcg.unam.mx/>>, in the table of contents of this issue (electronic supplement 26-3-01).

REFERENCES

- Agrawal S., Guevara M., Verma S.P., 2008, Tectonic discrimination of basic and ultrabasic rocks through log-transformed ratios of immobile trace elements: *International Geology Review*, 50, 1057-1079.
- Ando, A., Kamioka, H., Itoh, S., 1987, 1986 values for fifteen GSJ rock reference samples: *Geostandards Newsletter*, 11, 159-166.
- Ando, A., Kamioka, H., Terashima, S., Itoh, S., 1989, 1988 values for GSJ rock reference samples, "Igneous rock series": *Geochemical Journal*, 23, 143-148.
- Ando, A., Okai, T., Inouchi, Y., Igarashi, T., Sudo, S., Marumo, K., Itoh, S., Terashima, S., 1990, Jlk-1, JLS-1 and JDo-1, GSJ rock reference samples of the "Sedimentary rock series": *Bulletin of the Geological Survey of Japan*, 41(1), 27-48.
- Armstrong-Altrin, J.S., Verma, S.P., 2005, Critical evaluation of six tectonic setting discrimination diagrams using geochemical data of Neogene sediments from known tectonic settings: *Sedimentary Geology*, 177(1-2), 115-129.
- Barnett V., Lewis T., 1994, *Outliers in statistical data*: Chichester, UK, John Wiley & Sons, Third edition, 584 p.
- Baumann, K., 1997, Regression and calibration for analytical separation techniques. Part II: Validation, weighted and robust regression: *Process Control and Quality*, 10, 75-112.
- Bevington, P.R., 1969, *Data reduction and error analysis for the physical sciences*: Mc-Graw Hill book company, New York, 336pp.
- Dybczynski R., Tugsavul A., Suschny O., 1979, Soil-5, a new IAEA certified reference material for trace element determinations: *Geostandards Newsletter*, 3, 61-87.
- Gladney, E.S., Nickell, E.J., Roelandts, I., 1992, 1988 compilation of elemental concentration data for USGS AGV-1, GSP-1 and G-2: *Geostandards Newsletter*, 16, 111-300.
- González-Ramírez, R., Díaz-González, L., Verma, S.P., 2009, Eficiencia relativa de 15 pruebas de discordancia con 33 variantes aplicadas al procesamiento de datos geoquímicos: *Revista Mexicana de Ciencias Geológicas*, 26(2), 501-515.
- Govindaraju K., Roelandts I., 1989, 1988 compilation report on trace elements in six ANRT rock reference samples: Diorite DR-N, serpentinite UB-N, bauxite BX-N, disthene DT-N, granite GS-N and potash feldspar FK-N: *Geostandards Newsletter*, 13, 5-67.
- Guevara, M., Verma, S. P., Velasco-Tapia, F., 2001, Evaluation of GSJ intrusive rocks JG1, JG2, JG3, JG1a, and JGb1: *Revista Mexicana de Ciencias Geológicas*, 18(1), 74-88.
- Guevara, M., Verma, S.P., Velasco-Tapia, F., Lozano-Santa Cruz, R., Girón, P., 2005, Comparison of linear regression models for quantitative geochemical analysis: Example of X-ray fluorescence spectrometry: *Geostandards and Geoanalytical Research*, 29(3), 271-284.
- Imai, N., Terashima, S., Itoh, S., Ando, A., 1995a, 1994 compilation values for GSJ reference samples, "Igneous rock series": *Geochemical Journal*, 29, 91-95.
- Imai, N., Terashima, S., Itoh, S., Ando, A., 1995b, 1994 compilation of analytical data for minor and trace elements in seventeen GSJ geochemical reference samples, "Igneous rock series": *Geostandards Newsletter*, 19, 135-213.
- Imai, N., Terashima, S., Itoh, S., Ando, A., 1996, 1996 compilation of analytical data on nine GSJ geochemical reference samples, "Sedimentary rock series": *Geostandards Newsletter*, 20, 165-216.
- Igarashi, K., Akagi, T., Fu, F-Fu., Yabuki, S., 2003, Determination of Rare-Earth elements in a limestone geological standard reference material by ICP-MS following solvent extraction: *Analytical Sciences*, 19, 441-445.
- Inoue, M., Nohara, M., Okai, T., Suzuki, A., Kawahata, H., 2004, Concentrations of trace elements in carbonate reference materials coral JCp-1 and giant clam JCT-1 by Inductively Coupled Plasma-Mass Spectrometry: *Geostandards and Geoanalytical Research*, 28(3), 411-416.
- ISO, 1989, Guide 35, Certification of reference material – general and statistical principles: Committee on Reference Materials (REMCO), International Organization for Standardization, Geneva, 32 p.
- Itoh, A., Nagasawa, T., Zhu, Y., Lee, K-H., Fujimori, E., Haraguchi, H., 2004, Distributions of major-to-ultratrace elements among the particulate and dissolved fractions in natural water as studied by ICP-AES and ICP-MS after sequential fractionation: *Analytical Sciences*, 20, 29-36.
- Kawabe, I., 1995, Tetrad effects and fine structures of REE abundance patterns of granitic and rhyolitic rocks: ICP-AES determinations of REE and Y in eight GSJ reference rocks: *Geochemical Journal*, 29, 213-230.
- Mabrouk, A., Belayouni, H., Jarvis, I., Moody, T.J., 2006, Strontium, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ as palaeo-indicators of unconformities: Case of the Aleg and Abiod formations (Upper Cretaceous) in the Miskar Field, southeastern Tunisia: *Geochemical Journal*, 40, 405-424.
- Marroquín-Guerra, S.G., Velasco-Tapia, F., Díaz-González, L., 2009, Evaluación estadística de Materiales de Referencia Geoquímica del Centre de Recherches Péetrographiques et Géochimiques (Francia) aplicando un esquema de detección y eliminación de valores desviados: *Revista Mexicana de Ciencias Geológicas*, 26(2), 530-542.
- Pandarinath, K., 2009, Clay minerals in SW Indian continental shelf sediments cores as indicators of provenance and paleomonsoonal conditions: a statistical approach: *International Geology Review*, 51, 145-165.
- Roelandts, I., 1989a, Geological reference materials: *Spectrochimica Acta Part B: Atomic Spectroscopy*, 44(1), 5-29.
- Roelandts, I., 1989b, Environmental reference materials: *Spectrochimica Acta Part B: Atomic Spectroscopy*, 44(9), 925-934.
- Roelandts, I., 1991, News on reference materials: Fourth international symposium on biological and environmental reference materials (BERM-4). Orlando, Florida, 5–8 February 1990: *Spectrochimica Acta Part B: Atomic Spectroscopy*, 46(9), 1299-1303.
- Roelandts, I., 1992, Additional geochemical reference materials: *Spectrochimica Acta Part B: Atomic Spectroscopy*, 47(7), 935-945.
- Roelandts, I., 1993, Fifth international symposium on biological and environmental reference materials (BERM-5), Aachen, F.R.G., 11–14 May 1992: *Spectrochimica Acta Part B: Atomic Spectroscopy*, 48(10), 1291-1295.
- Roelandts, I., 1996a, Sixth international symposium on biological and environmental reference materials (BERM-6), Kona, Hawaii, 17–21 April 1994: *Spectrochimica Acta Part B: Atomic Spectroscopy*, 51(1), 189-196.
- Roelandts, I., 1996b, Geochemical reference materials: update 1996: *Spectrochimica Acta Part B: Atomic Spectroscopy*, 51(12), 1435-1441.
- Santoyo, E., Verma, S.P., 2003, Determination of lanthanides in synthetic standards by reversed-phase high performance liquid chromatography with the aid of a weighted least-squares regression model: estimation of method sensitivities and detection limits: *Journal of Chromatography A*, 997(1-2), 171-182.
- Santoyo, E., Guevara, M., Verma S.P., 2006, Determination of lanthanides in international geochemical reference materials by reversed-phase high performance liquid chromatography: an application of error propagation theory to estimate total analysis uncertainties: *Journal of Chromatography A*, 1118(1), 73-81.
- Taylor, J.K., 1990, *Statistical techniques for data analysis*: Chelsea, Lewis Publishers, 200 p.
- Tellinghuisen, J., 2007, Weighted least-squares in calibration: what difference does it make?: *Analyst*, 132, 536-543.
- Terashima, S., 2000, Determination of indium and tellurium in geological reference materials by solvent extraction and graphite-furnace AAS: *Bunseki Kagaku*, 49(10), 787-790.
- Terashima, S., Itoh, S., Ando, A., 1992, 1991 compilation of analytical data for silver, gold, palladium and platinum in twenty-six GSJ geochemical reference samples: *Bulletin of the Geological Survey of Japan*, 43, 141-152.
- Torres-Alvarado, I.S., Smith, A.D., Castillo-Román, J., 2009, Sr, Nd, and Pb isotopic and geochemical constraints for the origin of magmas in Popocatepetl volcano (Central Mexico) and their relationship with the adjacent volcanic fields: *International Geology Review*

- (in press).
- Velasco, F., Verma S.P., 1998, Importance of skewness and kurtosis statistical tests for outlier detection and elimination in evaluation of geochemical reference materials: *Mathematical Geology*, 30(1), 109-128.
- Velasco, F., Verma, S.P., Guevara, M., 2000, Comparison of the performance of fourteen statistical tests for detection of outlying values in geochemical reference material databases: *Mathematical Geology*, 32(4), 439-464.
- Velasco-Tapia, F., Guevara, M., Verma, S. P., 2001, Evaluation of concentration data in geochemical reference materials: *Chemie der Erde*, 61(1), 69-91.
- Verma M.P., 2004, A revised analytical method for HCO_3^- and CO_3^{2-} determinations in geothermal waters: An assessment of IAGC and IAEA interlaboratory comparisons: *Geostandards and Geoanalytical Research*, 28(3), 391-409.
- Verma, S.P., 1997, Sixteen statistical tests for outlier detection and rejection in evaluation of international geochemical reference material: example of microgabbro PM-S: *Geostandards Newsletter*, 21(1), 59-75.
- Verma, S.P., 1998, Improved concentration data in two international geochemical reference materials (USGS basalt BIR-1 and GSJ peridotite JP-1) by outlier detection and rejection: *Geofísica Internacional*, 37(3), 215-250.
- Verma S.P., 2005, Estadística básica para el manejo de datos experimentales: Aplicación en la geoquímica (geoquimiometría): Universidad Nacional Autónoma de México (Mexico), D.F., 186p.
- Verma, S.P., 2009a, Evaluation of polynomial regression models for the Student t and Fisher F critical values, the best interpolation equations from double and triple natural logarithm transformation of degrees of freedom up to 1000, and their applications to quality control in science and engineering: *Revista Mexicana de Ciencias Geológicas*, 26(1), 79-92.
- Verma, S.P., 2009b, Continental rift setting for the central part of the Mexican Volcanic Belt: A statistical approach: *The Open Geology Journal*, 3, 8-29.
- Verma, S.P., in press, Statistical evaluation of bivariate, ternary and discriminant function tectonomagmatic discrimination diagrams: *Turkish Journal of Earth Sciences*.
- Verma, S.P., Quiroz-Ruiz, A., 2006a, Critical values for six Dixon tests for outliers in normal samples up to sizes 100, and applications in science and engineering: *Revista Mexicana de Ciencias Geológicas*, 23(2), 133-161.
- Verma, S.P., Quiroz-Ruiz, A., 2006b, Critical values for 22 discordancy test variants for outliers in normal samples up to sizes 100, and applications in science and engineering: *Revista Mexicana de Ciencias Geológicas*, 23(3), 302-319.
- Verma, S.P., Quiroz-Ruiz, A., 2008, Critical values for 33 discordancy test variants for outliers in normal samples of very large sizes from 1,000 to 30,000 and evaluation of different regression models for the interpolation and extrapolation of critical values: *Revista Mexicana de Ciencias Geológicas*, 25(3), 369-381.
- Verma, S.P., Santoyo, E., 2007, High-performance liquid or ion chromatography: separation and quantification analytical techniques for rare-earth elements: *Geostandards and Geoanalytical Research*, 31(3), 161-184.
- Verma S.P., Orduña-Galván L.J., Guevara M., 1998, SIPVADE: A new computer programme with seventeen statistical tests for outlier detection in evaluation of international geochemical reference materials and its application to Whin Sill dolerite WS-E from England and Soil-5 from Peru: *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 22, 209-234.
- Verma S.P., Guevara M., Agrawal S., 2006, Discriminating four tectonic settings: five new geochemical diagrams for basic and ultrabasic volcanic rocks based on log-ratio transformation of major-element data: *Journal of Earth System Science*, 115(5), 485-528.
- Verma, S.P., Quiroz-Ruiz, A., Díaz-González, L., 2008, Critical values for 33 discordancy test variants for outliers in normal samples up to sizes 1000, and applications in quality control in Earth Sciences: *Revista Mexicana de Ciencias Geológicas*, 25(1), 82-96.
- Verma, S.P., Díaz-González, L., González-Ramírez, R., 2009, Relative Efficiency of Single-Outlier Discordancy Tests for Processing Geochemical Data on Reference Materials and Application to Instrumental Calibrations by a Weighted Least-Squares Linear Regression Model: *Geostandards and Geoanalytical Research*, 33(1), 29-49.
- Villeneuve J.-P., de Mora S., Cattini C., 2004, Determination of organochlorinated compounds and petroleum in fish-homogenate sample IAEA-406: Results from a worldwide interlaboratory study: *Trends in Analytical Chemistry*, 23(7), 501-510.
- Watanabe, Y., Nakai, S., 2006, U-Th radioactive disequilibrium analyses for JCP-1, coral reference distributed by the Geological Survey of Japan: *Geochemical Journal*, 40, 537-541.
- Yamamoto, K., Yamashita, F., Adachi, M., 2005, Precise determination of REE for sedimentary rocks issued by the Geological Survey of Japan: *Geochemical Journal*, 39, 289-297.
- Zorn, M.E., Gibbons, R.D., Sonzogni, W.C., 1997, Weighted least-squares approach to calculating limits of detection and quantification by modeling variability as a function of concentration: *Analytical Chemistry*, 69, 3069-3075.

Manuscript received: May, 13, 2009

Corrected manuscript received: June 24, 2009

Manuscript accepted: June 25, 2009