Current Research (1994) Newfoundland Department of Mines and Energy, Geological Survey Branch, Report 94-1, pages 117-134

ANALYTICAL ACCURACY: A REVIEW OF ANALYSES OF THE STANDARDS SY-2 AND MRG-1 FROM DEPARTMENTAL RECORDS

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ABSTRACT

Geochemical data collected by the Geological Survey Branch (GSB) vary in analytical accuracy. Some elements show variation within the same analytical system and some differences reflect changes in analytical methods. Generally, variations in accuracy of the major-element analyses are insufficient to affect most types of geological interpretation. The variations in trace-element accuracy, however, are more significant and must be taken into account when the data are interpreted. Some of the problems that arise can be resolved by using the international standards to level the data. An example of how accuracy may affect the interpretation of geochemical data has been prepared from GSB data.

INTRODUCTION

The analysis of geological materials is an important component of many bedrock and surficial geological investigations including those undertaken by the Geological Survey Branch (GSB). Classification of rock types, assessment of metallic and non-metallic mineralized samples, regional geochemical surveys of both bedrock and surficial materials may all use geochemical data. The quality of geochemical data must be assessed prior to use. Data quality is difficult to assess in small datasets because they contain a limited amount of quality control data. Most questions regarding data quality arise when detailed comparisons and compilations of analytical data are made.

In Newfoundland and Labrador, geological studies that make extensive use of geochemical data have only been undertaken since the early 1970s. The growth in geochemical surveys has followed the availability of rapid multi-element geochemical techniques. For example, the systematic sampling and analysis of granitoid rocks in Newfoundland has been an ongoing effort of the Survey since the early 1970s (Strong *et al.*, 1974) and continues into the present. An extensive collection of lithogeochemical and geological data have been acquired for granitoid rocks of insular Newfoundland. This project was initially undertaken to document the accuracy of geochemical analyses in the Integrated Lithogeochemical Database for the Granitoid Rocks of Newfoundland (Kerr *et al.*, 1994) for which all known analyses of standards were compiled and released as an open file (Hayes, 1994). The data collected and organized through that project have general application to lithogeochemical and to surficial geochemistry programs that share the analytical methodology. These data warrant attention from all users of datasets containing Department of Mines and Energy major-element and trace-element analyses from 1982 to 1991. A significant portion of the trace-element data in the database was obtained by XRF (X-ray fluoresecence spectroscopy) at Memorial University of Newfoundland from 1982 to 1986. The analytical results from international standards analyzed by this facility are included here. This paper presents a historical overview of the analytical accuracy of XRF, ICP-ES (inductively coupled plasma-emmision spectrometry) and AAS (atomic absorption spectrometry) for GSB datasets.

REPORTING ANALYTICAL ACCURACY VERSUS REPORTING ANALYTICAL PRECISION

The two components of data quality are precision and accuracy. These are estimated independantly. Analytical quality depends upon the various components of an analytical system. An analytical system encompasses the sample material, the sample preparation (crushing, dissolution, weighing and/or encapsulation) and the analytical device. Analytical precision is the ability of an analytical system to reproduce a result. It is calculated to determine the contribution of variance from analytical sources to the overall variance in the dataset. Analytical accuracy is the ability of an analytical system to return the correct value. It is an indication of the difference between the true-element content of a sample and the value returned by the analytical system.

The precision of an analytical system is dependant upon the nature of the samples within the system. Practically, this means that reporting global estimates of precision for an analytical system are impossible because the definition of the analytical system changes with the sample material. Thus analytical precision is estimated using duplicate samples. These are made by splitting a sample within the analytical batch. Since the sample material and the concentration of the component of interest plays an important role in determining the precision of an analytical system, there can be no typical value for analytical precision. Often the relative standard deviation (RSD) of data obtained by the repeated analysis of a sample (usually a standard) is published as an indication of data quality. This produces an estimate of machine precison because few of the sample preparation procedures are actually repeated. It does not measure the influence of the analytical system on the element of interest within the sample material or the performance of the laboratory at the time the unknowns were analyzed. These estimates do not necessarily measure the contribution of analytical variance to the overall variance within a dataset in the manner of duplicate samples. Users are therefore recommended to devise estimates of analytical precision from their duplicate samples wherever possible. Methods for treating duplicate data are described by Davenport (1990).

Analytical accuracy can be reported globally if all components of the analytical system are fixed. Each time a standard sample is used in the analytical process an attempt to measure a known concentration is made. As the sample material is fixed, changes in the values returned from the laboratory indicate fluctuations in analytical accuracy within the analytical system. If neither the standard, sample preparation or analytical device changes, these data may be examined and summarized over extended time intervals according to the users needs. Within the laboratory they are generally examined batch to batch. In this report, they are examined on a yearly basis to discern long-term trends.

ANALYTICAL ACCURACY AND STANDARDS

A sample included in a sample batch but having a known concentration is generally referred to as a control. Certified reference materials (or standards) are commonly used for this purpose. These are materials that have had their composition established through repeated analyses. By including standards within batches of unknowns, it is possible to observe variation from accepted values and thus monitor the accuracy of all the analyses in the batches. Using the same standards allows reproducibility to be monitored. Reproducibility is the method-to-method variation or variation over longer time intervals (cf. Kane, 1992). It is especially important to consider when geochemical programs are conducted over a number of years. Ideally, a standard should have element concentrations within the range of interest and be of similar composition to the samples being studied. Datasets with large variations in element abundances require a range of standards. Standards are important in maintaining data quality (Thompson, 1983) and methods for their preparation and certification are established (Kane, 1992).

GEOLOGICAL SURVEY BRANCH (GSB) QUALITY CONTROL PRACTICES

The GSB has an established program of laboratory quality control. Each block of twenty samples contains an analytical split and a control sample. The control sample is typically an international reference material. A list of the international standards used by the GSB is presented in Table 1. CCRMP standards are used for major- and trace-element analyses. ANRT, USGS and CCRMP standards are used for major-element analyses. Samples submitted to external laboratories for analysis contain a series of control samples inserted blind by the GSB laboratory.

Table 1. International Standards in use at the Department of Mines and Energy

Name	Organization	Description
BX-N	ANRT	Bauxite
DR-N	ANRT	Diorite
DT-N	ANRT	Disthene
FK-N	ANRT	K-Feldspar
GS-N	ANRT	Granite
UB-N	ANRT	Serpentine
VS-N	ANRT	Glass standard
MRG-1	CCRMP	Gabbro
SY-2	CCRMP	Syenite
AGV-1	USGS	Andesite
BCR-1	USGS	Basalt
BHVO-1	USGS	Basalt
G-2	USGS	Granite
GSP-1	USGS	Granodiorite
MAG-1	USGS	Marine Mud
RGM-1	USGS	Rhyolite
SCO-1	USGS	Cody Shale
SDC-1	USGS	Mica Schist
STM-1	USGS	Syenite

Notes:

ANRT —Association National de la Recherche
CCRMP —Canadian Certified Reference Materials Project
USGS —United States Geological Survey

APPLICABILITY OF SUMMARY DATA

Control samples, including international standards are a part of each geochemical dataset and should either be included when reporting analytical results or reference given as to where the information may be obtained. Accuracy, strictly, can only be estimated using control samples that are from the dataset. Users quoting the statistics in this report, in lieu of control data from within their datasets, implicity make the assumption that this compilation represents the accuracy of the samples in their dataset. This is correct only to the extent that their control data has influenced the summary statistics reported here. Very small datasets (<20 samples) are unlikely to contain more than one control sample hence laboratory summary values are the only indication of analytical accuracy in these cases. Table 2 presents a summary of analytical techniques used by the GSB for granitoid rocks although many of these techniques are used for the analysis of other materials.

LABORATORY VALUES, ACCURACY AND SUMMARY STATISTICS

A standard sample, submitted to a laboratory, will return a result that depends upon its composition and the analytical procedures and equipment used in the analysis. Each

Table 2. Summary of analytical techniques used in the granite file

Suite	Reported Units	Element/Constituent	Analytical Method	Decomp./Digestion	Lab
Major elements pre-1980	wt %	SiO_2 TiO_2 Al_2O_3 Fe_2O_3 MnO Mgo CaO Na_2O K_2O P_2O_5	AAS	HF-HCl-H_3BO_3	GSB
Major elements	wt %	SiO_2 TiO_2 Al_2O_3 Fe_2O_3 MnO Mgo CaO Na_2O K_2O P_2O_5		$LiBO_2$ fusion/ HF-HCl-	GSB
1980-1984 1984-present			AAS ICP-ES	H_3BO_3	
Major elements	wt %	LOI	gravimetric	none	GSB
Major elements	wt %	FeO	Titr.	HF-HCl-H_3BO_3	GSB
Fusion trace	ppm	Ba Cr Zr	AAS ICP-ES	$LiBO_2$ fusion/HF-HCl-H_3BO_3	GSB
XRF trace	ppm	V Cr Ga Rb Sr Y Zr Nb Ba La Ce Th	XRF	pressed pellet	MUN
ICP trace	ppm	Li Be V Cr Ga Sr Y Zr Nb Ba La Ce Th	ICP-ES	HF-$HClO_4$-HCl	GSB
AA trace	ppm	Li Be V Cr Co Ni Cu Zn Rb Sr Mo Ba Pb	AAS	HF-$HClO_4$-HCl	GSB
Fluorine	ppm	F	ISE	Na_2CO_3 / KNO_3 fusion	GSB
Misc.	ppm	U Sn W	INAA	none	various
		Sn, W	AAS	various*	GSB

Notes:
AAS —Atomic Absorption Spectrometry
XRF —X-Ray Fluorescence Spectrometry
ICP-ES —Inductively Coupled Plasma—Emission Spectrometry
ISE —Ion Selective Electrode
INAA —Instrumental Neutron Activation Analyses
Titr. —Wilson method colorimetric
* —see Wagenbauer *et al.*, 1983
GSB —Geological Survey Branch, Newfoundland Department of Mines and Energy
MUN —Memorial University of Newfoundland

The reporting limits for these techniques as reported by the laboratories are as follows:

Major elements incl. LOI, FeO (all methods)	0.01 wt %
ICP-ES/AAS	2 ppm, except Be and Li 0.1 ppm, Mn 5 ppm
Fusion Trace	10 ppm
Fluorine	40 ppm
XRF traces	V–6, Cr–5, Ni–2, Cu–3, Zn–9, Ga–3, Rb–4, Sr–5, Y–5, Zr–2, Nb–3, Ba–35, La–10, Ce–10, Pb–12, Th–8, U–16 ppm
INAA	U–0.1 ppm

laboratory is likely to produce a range of results from the same sample because equipment and procedures vary. In general, all laboratories (by repeated analysis of a standard) are likely to produce a set of results showing a particular range of values. These results will indicate the laboratory value for that standard under the specified analytical conditions. It is important to obtain this dataset so that data between different laboratories or analytical methods can be compared. The laboratory value for an element in a standard can be determined by using summary statistics to examine the results reported by the laboratory. The laboratory value may vary from the recommended concentration.

Recommended values are compilations of analyses of standards (e.g., Govindaraju, 1989). By comparing the laboratory values and recommended values it is possible to estimate accuracy, and a method is given in Equation 1. This method calculates the discrepancy between the laboratory value and the recommended value of the standard. Accuracy estimates were calculated for each element, by year and method, for each international standard (Hayes, 1994).

(Equation 1)

$$\text{ACCURACY \%} = \frac{\text{Laboratory Value} - \text{Recommended Value}}{\text{Recommended Value}} \times 100$$

Table 3 provides estimates of the accuracy of the analytical data. It has been abridged from the computer file SUMMARY.DAT in Hayes (1994). The data are arranged by standard, year and element by different analytical methods.

The most common approach to summarizing values in geological literature is to calculate their mean or average. The mean is influenced strongly by extreme values (either high or low), many of which may be outliers. Robust statistics are less affected by outliers and are, therefore, more reliable. The application of robust statistics to geochemical datasets was investigated by Rock (1988), who found that for many purposes robust statistics provide excellent summaries of geochemical data. A summary statistic should estimate the bulk, or the central tendency, of the data. The trimmed mean is ideal for this purpose and it has been applied here to calculate the yearly laboratory value of each element, wherever possible.

Trimmed means are calculated by removing n percent of values from the head and tail of a sorted dataset and calculating the mean of the remaining values. If $n = 25$ percent, for example, the top and bottom quarters of the data are eliminated. The trimmed mean is described by Efron and Tibshirini (1991) along with a method for selecting trim levels. The ordinary mean tends to give too high a value for the central tendency in positively skewed datasets, and too low in negatively skewed datasets. Trimming removes the skewness, making the mean of the remaining data more representative of the central tendency of the entire population. Rock (1988) recommended 25 percent as a general trim level.

Although the trimmed mean is effective in dealing with outliers, its utility is limited by the size of the dataset. If the dataset is subdivided too much, the number of cases can be insufficient to calculate a trimmed mean. In this report, the ordinary mean is used for groups of less than 5 samples (indicated by asterisks on Table 3).

As a final note, other methods are employed to examine standards or control data in the laboratory. The most popular of these is probably the control chart (e.g., Thompson, 1992). This method plots each determination against its batch number or order of analyses and is particularly useful for monitoring analytical drift. At the GSB laboratory, a batch of samples that contains a control outside of a specified range are entirely reanalysed. The method used in this report is different because the objective is to compare laboratories and analytical methods yearly. By calculating accuracy as a relative measure, it is also possible to compare standards having different compositions on the same diagram. Graphs constructed using year of analysis as the independant variable, show changes in apparent accuracy with time and analytical method. Some such graphs are presented here and readers are referred to Hayes (1994) for a graphs of data accuracy for the most common elements.

VARIATION IN ANALYSES OF STANDARDS

All the laboratory values calculated using the standard data differ from their recommended values (Table 3). Accuracy appears to vary yearly for some trace elements and abrupt differences in accuracy are common for elements that have been analyzed using different analytical techniques. Ce, Ga, La, Nb, V, and Y show variations in accuracy between XRF and ICP-ES methods and indicate that method-to-method reproducibility is poor for these elements. Care should, therefore, be exercised in comparing the data from these techniques. Accuracy appears to be substantially better for Ce (Figure 1) and La (Figure 2) by ICP-ES. Most major-element analyses of standards appear to be close to their recommended values regardless of analytical technique. A notable exception is TiO_2 (Figure 3). The ICP-ES has a greater sensitivity for this element (C. Finch, personal communication, 1993) and, consequently some of the standards having lower concentrations show a less variable response by ICP-ES.

Ga (Figure 4) and Nb (Figure 5) appear to have analytical problems that are due to matrix effects. Matrix effects are suspected when two standards having similar concentrations of a given component behave differently in the same analytical system. This may result from other material in the sample having an effect upon the analysis by producing an interference in the analytical device. The problem is most severe in the ICP-ES data for Nb, which has similar recommended values in both SY-2 and MRG-1, but sharply different accuracies. The matrix effect in Ga has been traced to spectral interference from Fe and Mn in the sample and subsequently post-1992 Ga analyses are corrected for this interference. The Ga data are affected significantly by the interference when the elemental Fe content exceeds 5 wt

Table 3. Summary analytical values for International Standards, MRG-1 and SY-2

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
MRG-1	Ag	1983	AA	2	**	0.25	0.25	0.21	0.11	127.3
MRG-1	Ag	1984	AA	4	**	0.10	0.10	0.00	0.11	-9.09
MRG-1	Ag	1985	AA	11	0.13	0.10	0.16	0.14	0.11	13.64
MRG-1	Ag	1986	AA	5	0.21	0.10	0.16	0.19	0.11	86.36
MRG-1	Ag	1988	AA	1	**	0.05	0.05	0.11	-54.5	
MRG-1	Al_2O_3	1978	MAJ	6	8.31	8.28	8.32	0.14	8.46	-1.79
MRG-1	Al_2O_3	1980	MAJ	6	8.58	8.58	8.56	0.12	8.46	1.46
MRG-1	Al_2O_3	1981	MAJ	6	8.56	8.55	8.55	0.07	8.46	1.16
MRG-1	Al_2O_3	1982	MAJ	6	8.73	8.73	8.72	0.06	8.46	3.13
MRG-1	Al_2O_3	1985	MAJ	9	8.53	8.51	8.49	0.17	8.46	0.79
MRG-1	Al_2O_3	1986	MAJ	6	8.58	8.57	8.58	0.03	8.46	1.42
MRG-1	Al_2O_3	1987	MAJ	2	**	8.48	8.48	0.08	8.46	0.18
MRG-1	Al_2O_3	1989	MAJ	4	**	8.44	8.45	0.03	8.46	-0.12
MRG-1	Al_2O_3	1990	MAJ	2	**	8.39	8.39	0.02	8.46	-0.89
MRG-1	Al_2O_3	1991	MAJ	1	**	8.53	8.53	0.00	8.46	0.83
MRG-1	Ba	1980	AA	3	**	46.00	63.33	45.54	61.00	3.83
MRG-1	Ba	1982	XRF	8	115.8	120.0	113.8	42.48	61.00	89.75
MRG-1	Ba	1983	AA	7	84.14	78.00	88.43	26.49	61.00	37.94
MRG-1	Ba	1983	XRF	17	175.0	176.0	170.7	24.60	61.00	186.9
MRG-1	Ba	1984	XRF	16	75.13	81.00	71.75	52.60	61.00	23.16
MRG-1	Ba	1985	XRF	1	**	146.0	146.0	0.00	61.00	139.3
MRG-1	Ba	1986	AA	5	137.9	131.0	130.2	34.65	61.00	126.1
MRG-1	Ba	1987	ICP	92	45.30	45.00	45.89	3.34	61.00	-25.7
MRG-1	Ba	1988	AA	1	**	102.0	102.0	0.00	61.00	67.21
MRG-1	Ba	1988	ICP	21	46.81	47.00	47.38	2.75	61.00	-23.3
MRG-1	Ba	1989	ICP	80	47.78	48.00	48.11	2.89	61.00	-21.7
MRG-1	Ba	1990	ICP	84	46.86	47.00	46.95	1.50	61.00	-23.2
MRG-1	Ba	1991	ICP	87	47.49	47.00	47.33	1.74	61.00	-22.1
MRG-1	Be	1984	AA	4	**	1.05	1.05	0.06	0.61	72.13
MRG-1	Be	1985	AA	11	1.02	1.00	1.04	0.11	0.61	67.66
MRG-1	Be	1988	AA	1	**	0.80	0.80	0.61	31.15	
MRG-1	Be	1988	ICP	18	0.72	0.70	0.74	0.08	0.61	17.49
MRG-1	Be	1989	ICP	16	0.93	0.80	0.96	0.25	0.61	51.64
MRG-1	Be	1990	ICP	31	1.03	1.00	1.04	0.16	0.61	68.43
MRG-1	Be	1991	ICP	86	0.82	0.80	0.81	0.09	0.61	34.39
MRG-1	CaO	1978	MAJ	6	14.79	14.77	14.76	0.19	14.71	0.56
MRG-1	CaO	1979	MAJ	6	14.70	14.70	14.68	0.26	14.71	-0.07
MRG-1	CaO	1980	MAJ	6	14.64	14.61	14.52	0.43	14.71	-0.48
MRG-1	CaO	1981	MAJ	6	14.53	14.49	14.47	0.39	14.71	-1.25
MRG-1	CaO	1982	MAJ	6	14.83	14.82	14.79	0.17	14.71	0.84
MRG-1	CaO	1985	MAJ	9	14.86	14.84	14.86	0.12	14.71	1.00
MRG-1	CaO	1986	MAJ	6	14.83	14.79	14.82	0.11	14.71	0.79
MRG-1	CaO	1987	MAJ	2	**	14.62	14.62	0.06	14.71	-0.61
MRG-1	CaO	1989	MAJ	4	**	14.83	14.82	0.05	14.71	0.75
MRG-1	CaO	1990	MAJ	2	**	14.63	14.63	0.19	14.71	-0.58
MRG-1	CaO	1991	MAJ	1	**	15.10	15.10	0.00	14.71	2.65
MRG-1	Cd	1988	AA	1	**	0.10	0.10	0.17	-40.5	
MRG-1	Ce	1982	XRF	8	54.75	55.00	59.38	16.47	26.00	110.6
MRG-1	Ce	1983	XRF	17	50.88	51.00	51.00	3.59	26.00	95.70
MRG-1	Ce	1984	XRF	16	85.38	79.50	96.44	55.12	26.00	228.4
MRG-1	Ce	1985	XRF	1	**	14.00	14.00	0.00	26.00	-46.2
MRG-1	Ce	1987	ICP	83	36.73	38.00	35.72	8.81	26.00	41.29
MRG-1	Ce	1988	ICP	44	27.73	27.50	28.57	5.03	26.00	6.64
MRG-1	Ce	1989	ICP	84	37.00	37.00	37.21	3.52	26.00	42.31
MRG-1	Ce	1990	ICP	83	36.72	37.00	35.87	4.57	26.00	41.22
MRG-1	Ce	1991	ICP	87	32.52	33.00	32.98	4.26	26.00	25.07
MRG-1	Co	1985	AA	11	73.05	73.00	72.73	2.05	87.00	-16.0
MRG-1	Co	1988	AA	1	**	59.00	59.00	0.00	87.00	-32.2
MRG-1	Cr	1980	AA	3	**	319.0	324.7	14.36	430.00	-24.5
MRG-1	Cr	1982	XRF	8	349.0	348.0	350.3	11.20	430.00	-18.8
MRG-1	Cr	1983	AA	7	348.4	337.0	351.0	21.10	430.00	-19.0
MRG-1	Cr	1983	XRF	17	353.7	354.0	353.3	4.84	430.00	-17.7
MRG-1	Cr	1984	XRF	16	384.0	383.5	384.5	6.91	430.00	-10.7
MRG-1	Cr	1985	XRF	1	**	102.0	102.0	0.00	430.00	-76.3
MRG-1	Cr	1986	AA	5	350.0	347.0	346.8	32.70	430.00	-18.6
MRG-1	Cr	1986	XRF	3	**	609.0	613.0	11.53	430.00	42.56
MRG-1	Cr	1988	AA	1	**	318.0	318.0	0.00	430.00	-26.0

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
MRG-1	Cr	1988	ICP	34	341.4	343.5	330.9	38.45	430.00	-20.6
MRG-1	Cr	1989	ICP	21	302.7	303.0	303.0	15.89	430.00	-29.6
MRG-1	Cr	1990	ICP	29	276.8	276.0	275.9	13.64	430.00	-35.6
MRG-1	Cr	1991	ICP	32	298.3	299.5	298.1	20.77	430.00	-30.6
MRG-1	Cu	1980	AA	3	**	119.0	119.7	2.08	134.00	-10.7
MRG-1	Cu	1983	AA	7	124.9	125.0	124.9	1.86	134.00	-6.82
MRG-1	Cu	1984	AA	4	**	115.5	113.3	6.29	134.00	-15.5
MRG-1	Cu	1985	AA	11	110.5	108.0	112.3	8.64	134.00	-17.5
MRG-1	Cu	1986	AA	5	106.1	104.0	106.4	5.68	134.00	-20.8
MRG-1	Cu	1988	AA	1	**	119.0	119.0	0.00	134.00	-11.2
MRG-1	Dy	1990	ICP	57	3.36	3.30	3.21	0.85	2.90	15.91
MRG-1	Fe_2O_3	1978	MAJ	6	17.72	17.73	17.70	0.16	17.93	-1.18
MRG-1	Fe_2O_3	1979	MAJ	6	17.91	17.89	17.89	0.22	17.93	-0.09
MRG-1	Fe_2O_3	1980	MAJ	6	18.19	18.17	18.16	0.35	17.93	1.44
MRG-1	Fe_2O_3	1981	MAJ	6	18.07	18.07	17.97	0.55	17.93	0.76
MRG-1	Fe_2O_3	1982	MAJ	6	17.70	17.67	17.71	0.26	17.93	-1.30
MRG-1	Fe_2O_3	1985	MAJ	9	17.87	17.79	17.83	0.41	17.93	-0.36
MRG-1	Fe_2O_3	1986	MAJ	6	17.75	17.71	17.74	0.34	17.93	-0.99
MRG-1	Fe_2O_3	1987	MAJ	2	**	17.75	17.75	0.03	17.93	-1.00
MRG-1	Fe_2O_3	1989	MAJ	4	**	17.61	17.61	0.16	17.93	-1.76
MRG-1	Fe_2O_3	1990	MAJ	2	**	18.02	18.02	0.00	17.93	0.50
MRG-1	Fe_2O_3	1991	MAJ	1	**	18.15	18.15	0.00	17.93	1.23
MRG-1	FeO	1978	MAJ	32	8.63	8.64	8.61	0.11	8.66	-0.37
MRG-1	FeO	1979	MAJ	32	8.61	8.62	8.61	0.09	8.66	-0.53
MRG-1	FeO	1980	MAJ	24	8.48	8.48	8.37	0.60	8.66	-2.05
MRG-1	FeO	1981	MAJ	42	8.61	8.61	8.61	0.10	8.66	-0.60
MRG-1	FeO	1982	MAJ	8.59	8.59	8.60	0.07	8.66	-0.77	
MRG-1	FeO	1983	MAJ	40	8.58	8.58	8.59	0.07	8.66	-0.94
MRG-1	FeO	1984	MAJ	27	8.64	8.65	8.63	0.06	8.66	-0.21
MRG-1	FeO	1985	MAJ	29	8.60	8.59	8.60	0.10	8.66	-0.74
MRG-1	FeO	1986	MAJ	25	8.63	8.63	8.52	0.62	8.66	-0.31
MRG-1	FeO	1987	MAJ	18	8.62	8.62	8.62	0.06	8.66	-0.48
MRG-1	FeO	1988	MAJ	19	8.70	8.69	8.70	0.06	8.66	0.50
MRG-1	FeO	1989	MAJ	25	8.75	8.73	8.73	0.09	8.66	1.05
MRG-1	FeO	1990	MAJ	41	8.69	8.68	8.70	0.06	8.66	0.34
MRG-1	Ga	1982	XRF	8	14.50	14.00	14.63	2.77	17.00	-14.7
MRG-1	Ga	1983	XRF	17	13.41	13.00	13.71	3.41	17.00	-21.1
MRG-1	Ga	1984	XRF	16	18.63	19.00	18.38	2.36	17.00	9.56
MRG-1	Ga	1985	XRF	1	**	24.00	24.00	0.00	17.00	41.18
MRG-1	Ga	1986	XRF	3	**	4.00	4.33	1.53	17.00	-74.5
MRG-1	Ga	1987	ICP	82	30.30	30.00	30.20	2.37	17.00	78.26
MRG-1	Ga	1988	ICP	42	32.83	33.00	32.71	3.77	17.00	93.14
MRG-1	Ga	1989	ICP	86	35.57	35.00	35.14	4.25	17.00	109.2
MRG-1	Ga	1990	ICP	84	35.93	36.00	35.93	2.36	17.00	111.3
MRG-1	Ga	1991	ICP	87	28.94	29.00	29.41	3.65	17.00	70.25
MRG-1	K_2O	1978	MAJ	6	0.17	0.17	0.17	0.00	0.18	-5.56
MRG-1	K_2O	1979	MAJ	6	0.15	0.15	0.15	0.02	0.18	-16.7
MRG-1	K_2O	1980	MAJ	6	0.17	0.17	0.16	0.01	0.18	-8.33
MRG-1	K_2O	1981	MAJ	5	0.16	0.16	0.16	0.01	0.18	-9.44
MRG-1	K_2O	1982	MAJ	6	0.16	0.16	0.16	0.01	0.18	-11.1
MRG-1	K_2O	1985	MAJ	9	0.17	0.17	0.17	0.01	0.18	-5.56
MRG-1	K_2O	1986	MAJ	6	0.16	0.16	0.16	0.01	0.18	-10.2
MRG-1	K_2O	1987	MAJ	2	**	0.17	0.17	0.00	0.18	-5.56
MRG-1	K_2O	1989	MAJ	4	**	0.17	0.17	0.01	0.18	-6.94
MRG-1	K_2O	1990	MAJ	2	**	0.18	0.18	0.02	0.18	-2.78
MRG-1	K_2O	1991	MAJ	1	**	0.18	0.18	0.00	0.18	0.00
MRG-1	LOI	1978	MAJ	41	1.41	1.40	1.41	0.12	1.56	-9.65
MRG-1	LOI	1979	MAJ	18	1.47	1.49	1.46	0.12	1.56	-5.80
MRG-1	LOI	1980	MAJ	4	**	1.24	1.23	0.17	1.56	-21.3
MRG-1	LOI	1989	MAJ	29	1.39	1.39	1.39	0.05	1.56	-10.9
MRG-1	LOI	1990	MAJ	34	1.36	1.41	1.35	0.14	1.56	-12.5
MRG-1	La	1982	XRF	8	25.25	25.00	28.50	9.53	9.80	157.7
MRG-1	La	1983	XRF	17	22.88	23.00	22.53	3.81	9.80	133.5
MRG-1	La	1984	XRF	16	1.25	1.00	2.13	1.89	9.80	-87.2
MRG-1	La	1987	ICP	84	9.74	10.00	9.74	3.14	9.80	-0.63
MRG-1	La	1988	ICP	45	11.13	11.00	11.07	1.57	9.80	13.61
MRG-1	La	1989	ICP	85	10.00	10.00	10.12	0.75	9.80	2.04

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
MRG-1	La	1990	ICP	84	10.45	10.00	10.43	0.70	9.80	6.66
MRG-1	La	1991	ICP	87	10.47	10.00	10.48	0.82	9.80	6.79
MRG-1	Li	1980	AA	4	**	1.00	1.25	0.50	4.20	-70.2
MRG-1	Li	1983	AA	7	7.64	7.00	8.29	3.82	4.20	81.97
MRG-1	Li	1984	AA	4	**	9.50	8.75	1.89	4.20	108.3
MRG-1	Li	1985	AA	11	9.68	10.00	9.91	1.45	4.20	130.5
MRG-1	Li	1986	AA	5	9.90	9.00	9.00	2.92	4.20	135.7
MRG-1	Li	1988	AA	1	**	7.00	7.00	0.00	4.20	66.67
MRG-1	Li	1988	ICP	37	3.63	3.60	3.75	0.58	4.20	-13.5
MRG-1	Li	1989	ICP	93	3.59	3.60	3.57	0.31	4.20	-14.5
MRG-1	Li	1990	ICP	55	3.65	3.70	3.65	0.17	4.20	-13.1
MRG-1	Li	1991	ICP	86	3.60	3.60	3.59	0.41	4.20	-14.4
MRG-1	MgO	1978	MAJ	6	13.54	13.55	13.50	0.18	13.55	-0.05
MRG-1	MgO	1979	MAJ	6	13.56	13.55	13.51	0.23	13.55	0.06
MRG-1	MgO	1980	MAJ	6	13.48	13.44	13.46	0.20	13.55	-0.50
MRG-1	MgO	1981	MAJ	6	13.59	13.57	13.56	0.31	13.55	0.26
MRG-1	MgO	1982	MAJ	6	13.74	13.73	13.73	0.23	13.55	1.37
MRG-1	MgO	1985	MAJ	9	13.77	13.77	13.75	0.12	13.55	1.63
MRG-1	MgO	1986	MAJ	6	14.06	14.07	14.03	0.16	13.55	3.73
MRG-1	MgO	1987	MAJ	2	**	14.04	14.04	0.12	13.55	3.58
MRG-1	MgO	1989	MAJ	4	**	13.93	13.96	0.19	13.55	3.03
MRG-1	MgO	1990	MAJ	2	**	13.74	13.74	0.33	13.55	1.37
MRG-1	MgO	1991	MAJ	1	**	13.67	13.67	0.00	13.55	0.89
MRG-1	MnO	1978	MAJ	6	0.17	0.17	0.17	0.00	0.17	0.00
MRG-1	MnO	1979	MAJ	6	0.17	0.17	0.17	0.01	0.17	0.98
MRG-1	MnO	1980	MAJ	6	0.18	0.18	0.18	0.01	0.17	6.86
MRG-1	MnO	1981	MAJ	6	0.18	0.18	0.18	0.01	0.17	6.86
MRG-1	MnO	1982	MAJ	6	0.18	0.18	0.18	0.00	0.17	5.88
MRG-1	MnO	1985	MAJ	9	0.18	0.18	0.18	0.01	0.17	5.88
MRG-1	MnO	1986	MAJ	6	0.18	0.18	0.18	0.00	0.17	5.88
MRG-1	MnO	1987	MAJ	2	**	0.18	0.18	0.00	0.17	5.88
MRG-1	MnO	1989	MAJ	4	**	0.18	0.18	0.00	0.17	5.88
MRG-1	MnO	1990	MAJ	2	**	0.19	0.19	0.01	0.17	8.82
MRG-1	MnO	1991	MAJ	1	**	0.17	0.17	0.17	0.00	
MRG-1	Mo	1980	AA	17	4.44	4.00	4.59	1.58	0.87	410.5
MRG-1	Mo	1983	AA	7	4.29	4.00	4.14	0.90	0.87	392.6
MRG-1	Mo	1984	AA	4	**	5.00	4.50	1.00	0.87	417.2
MRG-1	Mo	1985	AA	11	5.05	5.00	5.18	0.87	0.87	479.9
MRG-1	Mo	1986	AA	5	5.00	5.00	4.80	0.84	0.87	474.7
MRG-1	Mo	1988	AA	1	**	5.00	5.00	0.00	0.87	474.7
MRG-1	Na_2O	1978	MAJ	6	0.63	0.63	0.63	0.01	0.74	-15.3
MRG-1	Na_2O	1979	MAJ	6	0.67	0.67	0.67	0.02	0.74	-9.46
MRG-1	Na_2O	1980	MAJ	6	0.70	0.70	0.69	0.02	0.74	-5.86
MRG-1	Na_2O	1981	MAJ	6	0.72	0.72	0.72	0.02	0.74	-2.93
MRG-1	Na_2O	1982	MAJ	6	0.71	0.71	0.71	0.01	0.74	-4.28
MRG-1	Na_2O	1985	MAJ	9	0.71	0.71	0.71	0.01	0.74	-4.05
MRG-1	Na_2O	1986	MAJ	6	0.72	0.72	0.72	0.00	0.74	-2.70
MRG-1	Na_2O	1987	MAJ	2	**	0.73	0.73	0.01	0.74	-1.35
MRG-1	Na_2O	1989	MAJ	4	**	0.71	0.71	0.01	0.74	-4.05
MRG-1	Na_2O	1990	MAJ	2	**	0.72	0.72	0.01	0.74	-3.38
MRG-1	Na_2O	1991	MAJ	1	**	0.73	0.73	0.74	-1.35	
MRG-1	Nb	1982	XRF	8	24.50	24.50	24.00	2.62	20.00	22.50
MRG-1	Nb	1983	XRF	17	25.12	25.00	25.24	2.54	20.00	25.59
MRG-1	Nb	1984	XRF	16	25.88	26.00	25.88	1.75	20.00	29.38
MRG-1	Nb	1985	XRF	1	**	10.00	10.00	0.00	20.00	-50.0
MRG-1	Nb	1986	XRF	3	**	30.00	29.00	2.65	20.00	45.00
MRG-1	Nb	1987	ICP	85	13.54	14.00	13.52	2.11	20.00	-32.3
MRG-1	Nb	1988	ICP	45	11.69	12.00	11.91	1.70	20.00	-41.6
MRG-1	Nb	1989	ICP	85	11.06	11.00	11.11	2.36	20.00	-44.7
MRG-1	Nb	1990	ICP	82	12.07	12.00	11.74	2.61	20.00	-39.6
MRG-1	Nb	1991	ICP	87	15.70	16.00	15.60	1.51	20.00	-21.5
MRG-1	Ni	1980	AA	3	**	163.0	163.7	3.06	193.00	-15.2
MRG-1	Ni	1983	AA	7	149.4	150.0	148.4	5.16	193.00	-22.6
MRG-1	Ni	1984	AA	4	**	148.0	148.0	4.97	193.00	-23.3
MRG-1	Ni	1985	AA	11	155.6	155.0	155.7	5.29	193.00	-19.4
MRG-1	Ni	1986	AA	5	160.3	160.0	158.0	7.04	193.00	-16.9
MRG-1	Ni	1988	AA	1	**	156.0	156.0	0.00	193.00	-19.2

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
MRG-1	P_2O_5	1978	MAJ	5	0.06	0.07	0.05	0.03	0.08	-23.8
MRG-1	P_2O_5	1979	MAJ	5	0.07	0.07	0.06	0.02	0.08	-12.5
MRG-1	P_2O_5	1980	MAJ	5	0.08	0.06	0.08	0.04	0.08	5.00
MRG-1	P_2O_5	1981	MAJ	5	0.06	0.06	0.06	0.01	0.08	-21.3
MRG-1	P_2O_5	1982	MAJ	5	0.06	0.06	0.06	0.01	0.08	-21.3
MRG-1	P_2O_5	1985	MAJ	9	0.06	0.06	0.06	0.01	0.08	-22.9
MRG-1	P_2O_5	1986	MAJ	6	0.06	0.06	0.06	0.01	0.08	-22.9
MRG-1	P_2O_5	1987	MAJ	2	**	0.06	0.06	0.01	0.08	-31.3
MRG-1	P_2O_5	1989	MAJ	4	**	0.06	0.06	0.01	0.08	-25.0
MRG-1	P_2O_5	1990	MAJ	2	**	0.06	0.06	0.00	0.08	-25.0
MRG-1	P_2O_5	1991	MAJ	1	**	0.07	0.07	0.08	-12.5	
MRG-1	Pb	1980	AA	3	**	1.00	1.00	0.00	10.00	-90.0
MRG-1	Pb	1983	AA	7	0.50	0.50	0.50	0.00	10.00	-95.0
MRG-1	Pb	1984	AA	4	**	0.50	0.50	0.00	10.00	-95.0
MRG-1	Pb	1985	AA	11	0.50	0.50	0.50	0.00	10.00	-95.0
MRG-1	Pb	1986	AA	5	0.50	0.50	0.50	0.00	10.00	-95.0
MRG-1	Pb	1988	AA	1	**	0.50	0.50	0.00	10.00	-95.0
MRG-1	Rb	1980	AA	3	**	4.00	4.33	0.58	8.50	-49.0
MRG-1	Rb	1982	XRF	8	11.50	11.50	11.38	2.07	8.50	35.29
MRG-1	Rb	1983	AA	7	7.79	8.00	7.71	2.50	8.50	-8.40
MRG-1	Rb	1983	XRF	17	9.09	9.00	8.65	2.71	8.50	6.92
MRG-1	Rb	1984	XRF	16	11.63	12.00	12.06	5.08	8.50	36.76
MRG-1	Rb	1986	AA	5	14.80	13.00	14.60	2.88	8.50	74.12
MRG-1	Rb	1986	XRF	3	**	17.00	17.33	1.53	8.50	103.9
MRG-1	Rb	1988	AA	1	**	7.00	7.00	0.00	8.50	-17.6
MRG-1	Sc	1990	ICP	58	63.09	63.10	57.69	18.06	55.00	14.71
MRG-1	SiO_2	1978	MAJ	6	39.50	39.30	39.57	0.69	39.09	1.05
MRG-1	SiO_2	1979	MAJ	6	38.92	38.75	38.82	0.62	39.09	-0.44
MRG-1	SiO_2	1980	MAJ	6	39.28	39.25	39.18	0.33	39.09	0.49
MRG-1	SiO_2	1981	MAJ	6	39.07	38.95	39.00	0.51	39.09	-0.06
MRG-1	SiO_2	1982	MAJ	6	39.07	39.10	39.00	0.25	39.09	-0.06
MRG-1	SiO_2	1985	MAJ	9	38.92	38.90	38.78	0.55	39.09	-0.42
MRG-1	SiO_2	1986	MAJ	6	39.05	39.03	39.01	0.30	39.09	-0.10
MRG-1	SiO_2	1987	MAJ	2	**	39.10	39.10	0.01	39.09	0.03
MRG-1	SiO_2	1989	MAJ	4	**	39.20	39.13	0.26	39.09	0.09
MRG-1	SiO_2	1990	MAJ	2	**	39.03	39.03	0.38	39.09	-0.15
MRG-1	SiO_2	1991	MAJ	1	**	39.10	39.10	39.09	0.03	
MRG-1	Sr	1980	AA	3	**	255.0	251.3	6.35	266.00	-5.51
MRG-1	Sr	1982	XRF	8	262.3	262.0	262.3	4.89	266.00	-1.41
MRG-1	Sr	1983	AA	7	272.0	273.0	270.9	5.76	266.00	2.26
MRG-1	Sr	1983	XRF	17	264.6	265.0	263.5	4.56	266.00	-0.53
MRG-1	Sr	1984	XRF	16	265.4	265.0	266.9	9.37	266.00	-0.23
MRG-1	Sr	1985	XRF	1	**	204.0	204.0	0.00	266.00	-23.3
MRG-1	Sr	1986	AA	5	276.6	276.0	276.0	3.32	266.00	3.98
MRG-1	Sr	1986	XRF	3	**	251.0	247.7	7.57	266.00	-6.89
MRG-1	Sr	1987	ICP	84	244.4	243.5	243.5	14.84	266.00	-8.11
MRG-1	Sr	1988	AA	1	**	247.0	247.0	0.00	266.00	-7.14
MRG-1	Sr	1988	ICP	47	253.6	254.0	251.5	8.02	266.00	-4.67
MRG-1	Sr	1989	ICP	89	268.3	268.0	268.6	9.86	266.00	0.87
MRG-1	Sr	1990	ICP	82	260.4	259.5	260.7	9.00	266.00	-2.11
MRG-1	Sr	1991	ICP	87	260.3	260.0	259.8	10.65	266.00	-2.14
MRG-1	Th	1982	XRF	8	1.00	1.00	2.25	3.54	0.93	7.53
MRG-1	Th	1983	XRF	17	1.09	1.00	2.06	2.54	0.93	17.01
MRG-1	Th	1984	XRF	16	1.50	1.00	2.94	3.17	0.93	61.29
MRG-1	Th	1990	ICP	93	0.50	0.50	0.65	0.37	0.93	-46.2
MRG-1	Th	1991	ICP	87	0.53	0.50	1.04	1.44	0.93	-43.5
MRG-1	TiO_2	1978	MAJ	6	4.04	4.03	4.04	0.08	3.77	7.16
MRG-1	TiO_2	1979	MAJ	6	4.21	4.21	4.20	0.14	3.77	11.76
MRG-1	TiO_2	1980	MAJ	6	3.67	3.58	3.68	0.28	3.77	-2.79
MRG-1	TiO_2	1981	MAJ	6	3.75	3.74	3.75	0.06	3.77	-0.57
MRG-1	TiO_2	1982	MAJ	6	3.77	3.77	3.76	0.09	3.77	0.09
MRG-1	TiO_2	1985	MAJ	9	3.92	3.94	3.92	0.06	3.77	4.10
MRG-1	TiO_2	1986	MAJ	6	3.86	3.86	3.86	0.03	3.77	2.43
MRG-1	TiO_2	1987	MAJ	2	**	3.86	3.86	0.01	3.77	2.25
MRG-1	TiO_2	1989	MAJ	4	**	3.87	3.87	0.01	3.77	2.65
MRG-1	TiO_2	1990	MAJ	2	**	3.99	3.99	0.14	3.77	5.84
MRG-1	TiO_2	1991	MAJ	1	**	3.79	3.79	0.00	3.77	0.53

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
MRG-1	V	1980	AA	3	**	887.0	886.0	4.58	526.00	68.44
MRG-1	V	1982	XRF	7	528.5	528.0	527.7	8.32	526.00	0.48
MRG-1	V	1983	AA	7	653.6	651.0	656.9	107.1	526.00	24.27
MRG-1	V	1983	XRF	17	526.1	524.0	532.9	21.93	526.00	0.03
MRG-1	V	1984	XRF	16	556.0	560.5	552.9	22.77	526.00	5.70
MRG-1	V	1985	XRF	1	**	241.0	241.0	0.00	526.00	-54.2
MRG-1	V	1986	AA	5	582.3	582.0	578.8	10.71	526.00	10.70
MRG-1	V	1986	XRF	3	**	561.0	559.3	3.79	526.00	6.34
MRG-1	V	1987	ICP	85	503.5	507.0	497.6	32.55	526.00	-4.28
MRG-1	V	1988	AA	1	**	519.0	519.0	0.00	526.00	-1.33
MRG-1	V	1988	ICP	47	511.7	512.0	510.7	12.55	526.00	-2.71
MRG-1	V	1989	ICP	90	509.0	508.0	508.1	23.32	526.00	-3.23
MRG-1	V	1990	ICP	80	520.1	520.5	518.4	16.92	526.00	-1.12
MRG-1	Y	1982	XRF	8	14.75	15.00	15.00	2.20	14.00	5.36
MRG-1	Y	1983	XRF	17	15.32	15.00	15.06	1.89	14.00	9.45
MRG-1	Y	1984	XRF	16	12.13	12.00	12.06	1.84	14.00	-13.4
MRG-1	Y	1985	XRF	1	**	34.00	34.00	0.00	14.00	142.9
MRG-1	Y	1986	XRF	3	**	7.00	7.33	5.51	14.00	-47.6
MRG-1	Y	1987	ICP	85	11.84	12.00	11.59	0.93	14.00	-15.4
MRG-1	Y	1988	ICP	43	11.71	12.00	11.58	0.54	14.00	-16.4
MRG-1	Y	1989	ICP	85	11.54	12.00	11.67	1.02	14.00	-17.6
MRG-1	Y	1990	ICP	83	13.17	13.00	13.11	0.95	14.00	-5.94
MRG-1	Zn	1980	AA	3	**	19.00	19.33	0.58	191.00	-89.9
MRG-1	Zn	1983	AA	7	198.2	196.0	197.6	6.24	191.00	3.78
MRG-1	Zn	1984	AA	4	**	197.5	198.0	5.72	191.00	3.66
MRG-1	Zn	1985	AA	11	180.8	181.0	181.4	9.91	191.00	-5.35
MRG-1	Zn	1986	AA	5	197.1	198.0	196.4	5.13	191.00	3.19
MRG-1	Zn	1988	AA	1	**	196.0	196.0	0.00	191.00	2.62
MRG-1	Zr	1982	XRF	8	107.5	107.0	107.6	1.51	108.00	-0.46
MRG-1	Zr	1983	XRF	17	105.9	105.0	106.2	2.53	108.00	-1.91
MRG-1	Zr	1984	XRF	16	105.1	107.0	103.4	8.99	108.00	-2.66
MRG-1	Zr	1985	XRF	1	**	107.0	107.0	0.00	108.00	-0.93
MRG-1	Zr	1986	XRF	3	**	117.0	117.7	3.06	108.00	8.95
MRG-1	Zr	1987	ICP	84	107.8	107.5	109.1	14.84	108.00	-0.20
MRG-1	Zr	1988	ICP	8	104.5	105.0	104.3	1.67	108.00	-3.24
MRG-1	Zr	1989	ICP	19	106.5	107.0	106.7	2.94	108.00	-1.39
MRG-1	Zr	1990	ICP	31	106.8	108.0	107.5	7.34	108.00	-1.08
MRG-1	Zr	1991	ICP	86	95.27	95.00	95.35	7.06	108.00	-11.8
SY-2	Ag	1980	AA	1	**	0.20	0.20	1.10	-81.8	
SY-2	Ag	1982	AA	2	**	0.05	0.05	0.00	1.10	-95.5
SY-2	Ag	1983	AA	3	**	0.10	0.08	0.03	1.10	-92.4
SY-2	Ag	1984	AA	5	0.05	0.05	0.05	0.00	1.10	-95.5
SY-2	Ag	1985	AA	12	0.07	0.05	0.13	0.15	1.10	-93.9
SY-2	Ag	1986	AA	12	0.22	0.15	0.25	0.20	1.10	-80.3
SY-2	Ag	1987	AA	1	**	0.05	0.05	1.10	-95.5	
SY-2	Ag	1989	AA	25	-0.07	-0.10	-0.02	0.13	1.10	-107
SY-2	Ag	1990	AA	7	0.08	0.05	0.10	0.07	1.10	-93.2
SY-2	Ag	1991	AA	7	-0.09	-0.10	-0.04	0.10	1.10	-108
SY-2	Al_2O_3	1978	MAJ	4	**	12.30	12.30	0.09	12.04	2.16
SY-2	Al_2O_3	1979	MAJ	4	**	12.30	12.31	0.15	12.04	2.26
SY-2	Al_2O_3	1980	MAJ	5	12.18	12.20	12.14	0.31	12.04	1.20
SY-2	Al_2O_3	1981	MAJ	5	11.96	11.90	11.92	0.11	12.04	-0.66
SY-2	Al_2O_3	1982	MAJ	5	12.20	12.15	12.16	0.18	12.04	1.29
SY-2	Al_2O_3	1985	MAJ	17	12.22	12.21	12.23	0.15	12.04	1.52
SY-2	Al_2O_3	1986	MAJ	6	12.25	12.24	12.23	0.10	12.04	1.70
SY-2	Al_2O_3	1987	MAJ	3	**	12.17	12.09	0.20	12.04	0.44
SY-2	Al_2O_3	1989	MAJ	3	**	12.03	12.03	0.15	12.04	-0.06
SY-2	Ba	1980	AA	4	**	436.0	440.5	12.56	460.00	-4.24
SY-2	Ba	1982	AA	4	**	529.0	526.0	40.71	460.00	14.35
SY-2	Ba	1982	XRF	10	445.2	444.0	445.8	6.46	460.00	-3.22
SY-2	Ba	1983	AA	8	484.0	484.5	483.0	24.24	460.00	5.22
SY-2	Ba	1983	XRF	23	432.7	430.0	434.2	13.41	460.00	-5.95
SY-2	Ba	1984	XRF	17	447.1	444.0	448.6	29.09	460.00	-2.81
SY-2	Ba	1985	XRF	8	468.5	469.5	468.0	11.95	460.00	1.85
SY-2	Ba	1986	AA	11	426.2	396.0	466.1	143.6	460.00	-7.34
SY-2	Ba	1987	AA	1	**	443.0	443.0	0.00	460.00	-3.70
SY-2	Ba	1987	ICP	97	445.1	443.0	444.7	22.69	460.00	-3.25

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
SY-2	Ba	1988	ICP	21	462.0	462.0	462.2	8.64	460.00	0.45
SY-2	Ba	1989	AA	2	**	472.5	472.5	40.31	460.00	2.72
SY-2	Ba	1989	ICP	86	464.0	462.0	465.6	15.17	460.00	0.88
SY-2	Ba	1990	AA	1	**	453.0	453.0	0.00	460.00	-1.52
SY-2	Ba	1990	ICP	84	454.6	455.0	454.5	10.15	460.00	-1.16
SY-2	Be	1980	AA	17	0.22	0.22	4.14	8.73	22.00	-99.0
SY-2	Be	1982	AA	2	**	20.50	20.50	0.71	22.00	-6.82
SY-2	Be	1984	AA	5	23.47	23.20	23.46	0.52	22.00	6.68
SY-2	Be	1985	AA	12	22.08	22.00	22.16	0.79	22.00	0.38
SY-2	Be	1986	AA	7	20.38	20.30	18.04	6.60	22.00	-7.37
SY-2	Be	1988	ICP	23	19.59	19.50	20.01	1.26	22.00	-10.9
SY-2	Be	1989	AA	23	24.32	24.50	24.32	1.00	22.00	10.53
SY-2	Be	1989	ICP	20	22.81	22.80	22.80	0.74	22.00	3.68
SY-2	Be	1990	AA	54	24.03	23.95	24.06	0.72	22.00	9.23
SY-2	Be	1990	ICP	33	22.76	22.60	22.91	1.17	22.00	3.46
SY-2	Be	1991	AA	1	**	23.90	23.90	0.00	22.00	8.64
SY-2	CaO	1978	MAJ	4	**	7.98	7.94	0.12	7.96	-0.28
SY-2	CaO	1979	MAJ	4	**	8.02	8.07	0.11	7.96	1.38
SY-2	CaO	1980	MAJ	5	7.91	7.95	7.88	0.13	7.96	-0.69
SY-2	CaO	1981	MAJ	5	8.11	8.06	8.03	0.17	7.96	1.82
SY-2	CaO	1982	MAJ	5	8.19	8.15	8.17	0.07	7.96	2.84
SY-2	CaO	1985	MAJ	17	7.90	7.89	7.91	0.16	7.96	-0.72
SY-2	CaO	1986	MAJ	6	8.13	8.10	8.13	0.10	7.96	2.07
SY-2	CaO	1987	MAJ	3	**	8.11	8.08	0.06	7.96	1.55
SY-2	CaO	1989	MAJ	3	**	8.20	8.17	0.09	7.96	2.60
SY-2	Cd	1982	AA	2	**	0.05	0.05	0.00	0.21	-76.0
SY-2	Cd	1989	AA	38	0.51	0.50	0.63	0.54	0.21	145.4
SY-2	Cd	1990	AA	57	0.20	0.20	0.25	0.21	0.21	-5.32
SY-2	Cd	1991	AA	32	0.09	0.10	0.11	0.18	0.21	-54.9
SY-2	Ce	1982	XRF	10	66.60	63.50	73.10	21.21	175.00	-61.9
SY-2	Ce	1983	XRF	23	57.33	57.00	57.13	5.19	175.00	-67.2
SY-2	Ce	1984	XRF	17	181.4	184.0	180.2	9.69	175.00	3.68
SY-2	Ce	1985	XRF	8	162.0	160.5	163.8	12.65	175.00	-7.43
SY-2	Ce	1987	ICP	88	168.2	169.0	167.4	14.75	175.00	-3.90
SY-2	Ce	1988	ICP	45	177.5	179.0	177.3	11.07	175.00	1.44
SY-2	Ce	1989	ICP	88	166.9	167.0	166.5	8.30	175.00	-4.62
SY-2	Ce	1990	ICP	87	168.2	169.0	168.1	5.14	175.00	-3.87
SY-2	Co	1980	AA	1	**	6.00	6.00	0.00	8.60	-30.2
SY-2	Co	1982	AA	4	**	8.00	8.00	0.82	8.60	-6.98
SY-2	Co	1985	AA	12	7.33	7.00	7.50	0.67	8.60	-14.7
SY-2	Co	1989	AA	37	8.36	8.00	8.27	0.73	8.60	-2.73
SY-2	Co	1990	AA	37	8.04	8.00	7.97	0.76	8.60	-6.51
SY-2	Co	1991	AA	1	**	8.00	8.00	0.00	8.60	-6.98
SY-2	Cr	1980	AA	4	**	8.00	8.25	1.26	9.50	-13.2
SY-2	Cr	1982	AA	4	**	7.00	7.00	1.63	9.50	-26.3
SY-2	Cr	1982	XRF	10	5.00	5.00	9.20	13.28	9.50	-47.4
SY-2	Cr	1983	AA	8	8.75	9.00	8.50	1.20	9.50	-7.89
SY-2	Cr	1983	XRF	23	5.00	5.00	5.00	0.00	9.50	-47.4
SY-2	Cr	1984	XRF	17	3.88	4.00	4.24	2.91	9.50	-59.1
SY-2	Cr	1985	XRF	8	3.50	3.50	3.75	1.49	9.50	-63.2
SY-2	Cr	1986	AA	11	7.41	7.00	7.27	1.10	9.50	-22.0
SY-2	Cr	1987	AA	1	**	2.00	2.00	0.00	9.50	-78.9
SY-2	Cr	1988	ICP	28	35.00	35.00	37.29	11.09	9.50	268.4
SY-2	Cr	1989	AA	14	7.00	7.00	7.14	0.36	9.50	-26.3
SY-2	Cr	1989	ICP	22	11.95	12.50	11.86	2.75	9.50	25.84
SY-2	Cr	1990	AA	57	7.55	8.00	7.65	0.83	9.50	-20.5
SY-2	Cr	1990	ICP	27	6.17	6.00	6.22	0.85	9.50	-35.1
SY-2	Cr	1991	AA	59	7.31	7.00	7.39	1.14	9.50	-23.0
SY-2	Cr	1991	ICP	33	7.18	7.00	7.42	1.62	9.50	-24.4
SY-2	Cu	1980	AA	4	**	5.00	5.00	0.82	5.20	-3.85
SY-2	Cu	1982	AA	4	**	5.00	4.75	0.50	5.20	-8.65
SY-2	Cu	1983	AA	8	5.75	5.50	6.25	1.58	5.20	10.58
SY-2	Cu	1984	AA	5	5.70	6.00	5.60	0.55	5.20	9.62
SY-2	Cu	1985	AA	12	5.00	5.00	5.00	0.60	5.20	-3.85
SY-2	Cu	1986	AA	11	5.77	6.00	8.82	12.06	5.20	11.01
SY-2	Cu	1987	AA	1	**	5.00	5.00	0.00	5.20	-3.85
SY-2	Cu	1989	AA	62	4.60	5.00	4.79	1.42	5.20	-11.6

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
SY-2	Cu	1990	AA	87	4.60	5.00	4.63	0.67	5.20	-11.5
SY-2	Cu	1991	AA	8	5.00	5.00	4.88	0.35	5.20	-3.85
SY-2	Dy	1990	ICP	59	17.59	17.80	14.84	6.34	18.00	-2.27
SY-2	Dy	1991	ICP	57	3.00	3.00	3.00	1.09	18.00	-83.3
SY-2	Fe_2O_3	1978	MAJ	4	**	6.37	6.36	0.06	6.31	0.75
SY-2	Fe_2O_3	1979	MAJ	4	**	6.30	6.28	0.10	6.31	-0.55
SY-2	Fe_2O_3	1980	MAJ	5	6.24	6.22	6.24	0.04	6.31	-1.05
SY-2	Fe_2O_3	1981	MAJ	5	6.23	6.18	6.17	0.16	6.31	-1.35
SY-2	Fe_2O_3	1982	MAJ	5	6.29	6.23	6.28	0.10	6.31	-0.32
SY-2	Fe_2O_3	1985	MAJ	17	6.45	6.44	6.44	0.15	6.31	2.23
SY-2	Fe_2O_3	1986	MAJ	6	6.28	6.26	6.26	0.09	6.31	-0.50
SY-2	Fe_2O_3	1987	MAJ	2	**	6.34	6.34	0.07	6.31	0.48
SY-2	Fe_2O_3	1989	MAJ	3	**	6.36	6.32	0.07	6.31	0.21
SY-2	FeO	1978	MAJ	35	3.64	3.63	3.63	0.07	3.56	2.11
SY-2	FeO	1979	MAJ	38	3.63	3.64	3.63	0.08	3.56	2.07
SY-2	FeO	1980	MAJ	20	3.63	3.64	3.63	0.05	3.56	1.97
SY-2	FeO	1981	MAJ	40	3.62	3.62	3.62	0.08	3.56	1.63
SY-2	FeO	1982	MAJ	3.62	3.62	3.62.	0.05	3.56	1.70	
SY-2	FeO	1983	MAJ	50	3.63	3.63	3.63	0.04	3.56	1.90
SY-2	FeO	1984	MAJ	24	3.59	3.60	3.60	0.05	3.56	0.91
SY-2	FeO	1985	MAJ	29	3.59	3.60	3.59	0.04	3.56	0.92
SY-2	FeO	1986	MAJ	27	3.61	3.61	3.61	0.04	3.56	1.34
SY-2	FeO	1987	MAJ	18	3.62	3.62	3.62	0.03	3.56	1.65
SY-2	FeO	1988	MAJ	17	3.62	3.62	3.62	0.03	3.56	1.65
SY-2	FeO	1989	MAJ	29	3.61	3.61	3.61	0.03	3.56	1.54
SY-2	FeO	1990	MAJ	41	3.60	3.60	3.60	0.02	3.56	1.22
SY-2	Ga	1982	XRF	10	29.10	28.50	30.30	4.24	29.00	0.34
SY-2	Ga	1983	XRF	23	26.91	27.00	27.30	3.05	29.00	-7.20
SY-2	Ga	1984	XRF	17	27.76	28.00	28.12	2.00	29.00	-4.26
SY-2	Ga	1985	XRF	8	32.50	33.00	34.00	7.48	29.00	12.07
SY-2	Ga	1986	XRF	2	**	21.50	21.50	2.12	29.00	-25.9
SY-2	Ga	1987	ICP	88	28.50	29.00	28.22	2.95	29.00	-1.72
SY-2	Ga	1988	ICP	45	31.14	31.00	31.09	3.83	29.00	7.39
SY-2	Ga	1989	ICP	86	31.17	31.00	31.55	2.77	29.00	7.50
SY-2	Ga	1990	ICP	90	31.63	32.00	31.41	2.18	29.00	9.08
SY-2	K_2O	1978	MAJ	4	**	4.68	4.67	0.11	4.44	5.24
SY-2	K_2O	1979	MAJ	4	**	4.62	4.61	0.10	4.44	3.72
SY-2	K_2O	1980	MAJ	5	4.43	4.42	4.42	0.05	4.44	-0.32
SY-2	K_2O	1981	MAJ	5	4.54	4.54	4.49	0.10	4.44	2.18
SY-2	K_2O	1982	MAJ	5	4.62	4.60	4.59	0.08	4.44	4.01
SY-2	K_2O	1985	MAJ	17	4.54	4.54	4.54	0.08	4.44	2.27
SY-2	K_2O	1986	MAJ	6	4.56	4.55	4.56	0.05	4.44	2.67
SY-2	K_2O	1987	MAJ	3	**	4.58	4.58	0.05	4.44	3.08
SY-2	K_2O	1989	MAJ	3	**	4.59	4.61	0.05	4.44	3.75
SY-2	LOI	1978	MAJ	42	1.29	1.28	1.31	0.13	1.08	19.05
SY-2	LOI	1979	MAJ	22	1.30	1.31	1.30	0.06	1.08	19.91
SY-2	LOI	1980	MAJ	3	**	1.02	1.06	0.07	1.08	-1.85
SY-2	LOI	1989	MAJ	29	1.22	1.21	1.23	0.05	1.08	12.68
SY-2	LOI	1990	MAJ	37	1.24	1.27	1.21	0.14	1.08	15.13
SY-2	La	1982	XRF	10	36.70	34.00	42.40	19.21	75.00	-51.1
SY-2	La	1983	XRF	23	28.76	29.00	29.22	4.37	75.00	-61.7
SY-2	La	1984	XRF	17	65.12	65.00	65.82	8.32	75.00	-13.2
SY-2	La	1985	XRF	8	57.00	57.00	56.25	15.26	75.00	-24.0
SY-2	La	1986	XRF	2	**	84.00	84.00	5.66	75.00	12.00
SY-2	La	1987	ICP	88	69.89	70.00	69.19	4.55	75.00	-6.82
SY-2	La	1988	ICP	45	72.48	72.00	72.56	3.03	75.00	-3.36
SY-2	La	1989	ICP	90	76.32	76.00	76.47	2.89	75.00	1.76
SY-2	La	1990	ICP	86	75.55	76.00	75.55	2.54	75.00	0.73
SY-2	Li	1980	AA	17	7.09	7.00	7.24	0.56	95.00	-92.5
SY-2	Li	1982	AA	4	**	80.50	81.00	1.41	95.00	-14.7
SY-2	Li	1983	AA	8	86.50	87.50	85.38	7.33	95.00	-8.95
SY-2	Li	1984	AA	5	85.70	86.00	74.20	26.41	95.00	-9.79
SY-2	Li	1985	AA	12	90.00	90.00	83.00	23.91	95.00	-5.26
SY-2	Li	1986	AA	12	88.00	88.00	88.67	22.78	95.00	-7.37
SY-2	Li	1987	AA	1	**	84.00	84.00	0.00	95.00	-11.6
SY-2	Li	1988	ICP	36	93.20	93.25	92.96	3.91	95.00	-1.89
SY-2	Li	1989	AA	2	**	86.50	86.50	9.19	95.00	-8.95

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
SY-2	Li	1989	ICP	98	93.21	93.15	93.17	3.40	95.00	-1.89
SY-2	Li	1990	AA	3	**	96.00	93.00	5.20	95.00	-2.11
SY-2	Li	1990	ICP	84	91.96	92.20	91.97	3.32	95.00	-3.20
SY-2	MgO	1978	MAJ	4	**	2.64	2.64	0.03	2.69	-1.77
SY-2	MgO	1979	MAJ	4	**	2.71	2.70	0.03	2.69	0.28
SY-2	MgO	1980	MAJ	5	2.65	2.59	2.63	0.10	2.69	-1.38
SY-2	MgO	1981	MAJ	5	2.66	2.67	2.65	0.06	2.69	-0.97
SY-2	MgO	1982	MAJ	5	2.65	2.65	2.65	0.02	2.69	-1.38
SY-2	MgO	1985	MAJ	17	2.70	2.70	2.69	0.06	2.69	0.44
SY-2	MgO	1986	MAJ	6	2.74	2.73	2.74	0.03	2.69	1.80
SY-2	MgO	1987	MAJ	3	**	2.71	2.70	0.04	2.69	0.37
SY-2	MgO	1989	MAJ	3	**	2.76	2.76	0.01	2.69	2.73
SY-2	MnO	1978	MAJ	4	**	0.33	0.32	0.02	0.32	0.78
SY-2	MnO	1979	MAJ	4	**	0.33	0.34	0.02	0.32	4.69
SY-2	MnO	1980	MAJ	5	0.32	0.32	0.32	0.01	0.32	0.00
SY-2	MnO	1981	MAJ	5	0.32	0.32	0.32	0.02	0.32	0.94
SY-2	MnO	1982	MAJ	5	0.33	0.33	0.33	0.01	0.32	3.13
SY-2	MnO	1985	MAJ	17	0.32	0.32	0.32	0.01	0.32	0.37
SY-2	MnO	1986	MAJ	6	0.33	0.33	0.33	0.00	0.32	3.13
SY-2	MnO	1987	MAJ	3	**	0.33	0.33	0.00	0.32	3.13
SY-2	MnO	1989	MAJ	3	**	0.33	0.33	0.01	0.32	2.08
SY-2	Mo	1980	AA	17	3.00	3.00	2.94	0.75	1.80	66.67
SY-2	Mo	1982	AA	4	**	2.50	2.75	0.96	1.80	52.78
SY-2	Mo	1983	AA	8	3.25	3.00	3.38	0.52	1.80	80.56
SY-2	Mo	1984	AA	5	4.00	4.00	3.80	0.84	1.80	122.2
SY-2	Mo	1985	AA	12	3.33	3.00	3.50	0.67	1.80	85.19
SY-2	Mo	1986	AA	12	3.00	3.00	3.08	0.51	1.80	66.67
SY-2	Mo	1987	AA	1	**	3.00	3.00	0.00	1.80	66.67
SY-2	Mo	1989	AA	31	3.66	4.00	3.55	0.68	1.80	103.4
SY-2	Mo	1990	AA	62	3.66	4.00	3.66	0.63	1.80	103.4
SY-2	Mo	1991	AA	53	3.97	4.00	3.98	1.01	1.80	120.6
SY-2	Na_2O	1978	MAJ	4	**	4.37	4.37	0.03	4.31	1.33
SY-2	Na_2O	1979	MAJ	4	**	4.32	4.33	0.05	4.31	0.46
SY-2	Na_2O	1980	MAJ	5	4.30	4.28	4.29	0.04	4.31	-0.28
SY-2	Na_2O	1981	MAJ	5	4.32	4.30	4.28	0.10	4.31	0.19
SY-2	Na_2O	1982	MAJ	5	4.29	4.31	4.28	0.06	4.31	-0.56
SY-2	Na_2O	1985	MAJ	17	4.35	4.36	4.34	0.04	4.31	0.85
SY-2	Na_2O	1986	MAJ	6	4.33	4.34	4.28	0.13	4.31	0.35
SY-2	Na_2O	1987	MAJ	3	**	4.34	4.33	0.05	4.31	0.54
SY-2	Na_2O	1989	MAJ	3	**	4.35	4.34	0.02	4.31	0.70
SY-2	Nb	1982	XRF	10	35.00	35.50	33.70	4.57	29.00	20.69
SY-2	Nb	1983	XRF	23	35.57	35.00	35.70	1.43	29.00	22.64
SY-2	Nb	1984	XRF	17	37.68	38.00	37.41	2.45	29.00	29.92
SY-2	Nb	1985	XRF	8	37.00	37.00	36.75	1.39	29.00	27.59
SY-2	Nb	1986	XRF	2	**	38.00	38.00	0.00	29.00	31.03
SY-2	Nb	1987	ICP	89	27.62	28.00	27.56	1.94	29.00	-4.75
SY-2	Nb	1988	ICP	45	26.91	27.00	26.98	1.53	29.00	-7.20
SY-2	Nb	1989	ICP	88	28.36	28.00	28.28	1.48	29.00	-2.19
SY-2	Nb	1990	ICP	87	28.02	28.00	28.01	1.49	29.00	-3.37
SY-2	Ni	1980	AA	4	**	2.50	2.75	0.96	9.90	-72.2
SY-2	Ni	1982	AA	4	**	7.00	6.50	1.91	9.90	-34.3
SY-2	Ni	1983	AA	8	4.25	4.00	4.38	0.52	9.90	-57.1
SY-2	Ni	1984	AA	5	4.70	5.00	4.60	0.55	9.90	-52.5
SY-2	Ni	1985	AA	12	5.17	5.00	5.33	0.78	9.90	-47.8
SY-2	Ni	1986	AA	12	5.83	6.00	5.50	0.90	9.90	-41.1
SY-2	Ni	1987	AA	1	**	4.00	4.00	0.00	9.90	-59.6
SY-2	Ni	1989	AA	39	5.22	5.00	5.15	0.81	9.90	-47.3
SY-2	Ni	1990	AA	66	5.89	6.00	5.85	0.85	9.90	-40.5
SY-2	Ni	1991	AA	8	5.00	5.00	4.88	0.64	9.90	-49.5
SY-2	P_2O_5	1978	MAJ	4	**	0.41	0.38	0.06	0.43	-11.0
SY-2	P_2O_5	1979	MAJ	3	**	0.46	0.47	0.05	0.43	8.53
SY-2	P_2O_5	1980	MAJ	4	**	0.44	0.44	0.02	0.43	1.74
SY-2	P_2O_5	1981	MAJ	4	**	0.44	0.44	0.01	0.43	1.16
SY-2	P_2O_5	1982	MAJ	4	**	0.43	0.43	0.01	0.43	0.00
SY-2	P_2O_5	1985	MAJ	17	0.44	0.44	0.44	0.02	0.43	2.05
SY-2	P_2O_5	1986	MAJ	6	0.42	0.42	0.42	0.01	0.43	-2.33
SY-2	P_2O_5	1987	MAJ	3	**	0.43	0.43	0.01	0.43	-0.78

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
SY-2	P_2O_5	1989	MAJ	3	**	0.44	0.44	0.01	0.43	3.10
SY-2	Pb	1980	AA	4	**	76.50	75.25	2.87	85.00	-11.5
SY-2	Pb	1982	AA	4	**	76.50	76.25	1.71	85.00	-10.3
SY-2	Pb	1983	AA	8	76.00	76.00	76.00	2.51	85.00	-10.6
SY-2	Pb	1984	AA	5	76.90	76.00	76.60	2.88	85.00	-9.53
SY-2	Pb	1985	AA	12	79.83	80.00	79.50	3.37	85.00	-6.08
SY-2	Pb	1986	AA	12	73.17	72.50	65.25	22.94	85.00	-13.9
SY-2	Pb	1987	AA	1	**	76.00	76.00	0.00	85.00	-10.6
SY-2	Pb	1989	AA	41	84.28	84.00	84.37	2.01	85.00	-0.85
SY-2	Pb	1990	AA	68	82.88	83.00	83.19	3.58	85.00	-2.49
SY-2	Pb	1991	AA	8	81.25	81.00	81.50	3.21	85.00	-4.41
SY-2	Rb	1980	AA	4	**	175.5	176.5	6.56	217.00	-18.7
SY-2	Rb	1982	AA	4	**	179.5	180.8	4.50	217.00	-16.7
SY-2	Rb	1982	XRF	10	225.4	225.0	226.1	5.20	217.00	3.87
SY-2	Rb	1983	AA	8	214.5	216.0	210.8	20.87	217.00	-1.15
SY-2	Rb	1983	XRF	23	224.8	225.0	224.4	3.81	217.00	3.58
SY-2	Rb	1984	XRF	17	223.5	223.0	222.5	5.39	217.00	3.00
SY-2	Rb	1985	XRF	8	221.3	220.5	222.9	5.74	217.00	1.96
SY-2	Rb	1986	AA	11	198.4	193.0	193.5	27.49	217.00	-8.57
SY-2	Rb	1986	XRF	2	**	237.0	237.0	2.83	217.00	9.22
SY-2	Rb	1987	AA	1	**	221.0	221.0	0.00	217.00	1.84
SY-2	Rb	1989	AA	35	213.4	214.0	213.1	8.93	217.00	-1.65
SY-2	Rb	1990	AA	64	216.3	217.0	215.9	9.42	217.00	-0.35
SY-2	Rb	1991	AA	60	205.3	205.0	204.8	6.24	217.00	-5.39
SY-2	Sc	1990	ICP	61	7.92	7.90	7.16	2.33	7.00	13.13
SY-2	Sc	1991	ICP	90	7.03	7.00	7.23	0.58	7.00	0.38
SY-2	SiO_2	1978	MAJ	4	**	60.15	60.17	0.53	60.05	0.21
SY-2	SiO_2	1979	MAJ	4	**	59.80	59.88	0.34	60.05	-0.29
SY-2	SiO_2	1980	MAJ	5	60.58	60.40	60.54	0.40	60.05	0.88
SY-2	SiO_2	1981	MAJ	5	59.87	59.60	59.78	0.63	60.05	-0.30
SY-2	SiO_2	1982	MAJ	5	59.74	59.50	59.56	0.56	60.05	-0.52
SY-2	SiO_2	1985	MAJ	17	59.92	59.90	59.85	0.47	60.05	-0.22
SY-2	SiO_2	1986	MAJ	6	60.10	59.95	60.11	0.47	60.05	0.08
SY-2	SiO_2	1987	MAJ	3	**	60.00	60.07	0.12	60.05	0.03
SY-2	SiO_2	1989	MAJ	3	**	60.15	60.14	0.09	60.05	0.15
SY-2	Sr	1980	AA	4	**	258.5	259.0	13.34	271.00	-4.43
SY-2	Sr	1982	AA	4	**	264.0	267.8	7.50	271.00	-1.20
SY-2	Sr	1982	XRF	10	265.6	265.5	262.5	13.53	271.00	-1.99
SY-2	Sr	1983	AA	8	276.8	276.5	274.6	11.17	271.00	2.12
SY-2	Sr	1983	XRF	23	261.5	261.0	262.0	3.70	271.00	-3.51
SY-2	Sr	1984	XRF	17	262.1	262.0	261.5	8.28	271.00	-3.28
SY-2	Sr	1985	XRF	8	270.5	270.5	271.4	4.53	271.00	-0.18
SY-2	Sr	1986	AA	11	261.6	246.0	277.0	60.97	271.00	-3.47
SY-2	Sr	1986	XRF	2	**	261.5	261.5	12.02	271.00	-3.51
SY-2	Sr	1987	AA	1	**	279.0	279.0	0.00	271.00	2.95
SY-2	Sr	1987	ICP	90	258.3	259.0	257.0	14.19	271.00	-4.70
SY-2	Sr	1988	ICP	42	267.8	267.5	267.4	7.46	271.00	-1.19
SY-2	Sr	1989	AA	2	**	258.5	258.5	2.12	271.00	-4.61
SY-2	Sr	1989	ICP	93	280.3	280.0	281.8	8.81	271.00	3.42
SY-2	Sr	1990	AA	1	**	249.0	249.0	0.00	271.00	-8.12
SY-2	Sr	1990	ICP	89	272.7	273.0	273.4	8.88	271.00	0.62
SY-2	Th	1982	XRF	10	399.5	402.0	396.8	18.77	379.00	5.41
SY-2	Th	1983	XRF	23	402.2	403.0	402.3	6.22	379.00	6.12
SY-2	Th	1984	XRF	17	390.8	390.0	385.9	17.60	379.00	3.12
SY-2	Th	1985	XRF	8	369.5	369.5	369.0	12.54	379.00	-2.51
SY-2	Th	1986	XRF	2	**	361.5	361.5	19.09	379.00	-4.62
SY-2	Th	1987	ICP	77	373.0	375.0	367.0	35.01	379.00	-1.58
SY-2	Th	1988	ICP	41	387.4	389.0	387.0	15.53	379.00	2.22
SY-2	Th	1989	ICP	68	367.1	368.0	366.6	35.88	379.00	-3.15
SY-2	Th	1990	ICP	91	394.6	395.0	382.7	48.84	379.00	4.11
SY-2	TiO_2	1978	MAJ	4	**	0.16	0.16	0.01	0.14	16.07
SY-2	TiO_2	1979	MAJ	4	**	0.14	0.15	0.02	0.14	5.36
SY-2	TiO_2	1980	MAJ	5	0.16	0.15	0.15	0.02	0.14	11.43
SY-2	TiO_2	1981	MAJ	5	0.20	0.19	0.20	0.03	0.14	44.29
SY-2	TiO_2	1982	MAJ	5	0.17	0.17	0.17	0.01	0.14	21.43
SY-2	TiO_2	1985	MAJ	17	0.13	0.13	0.14	0.01	0.14	-4.83
SY-2	TiO_2	1986	MAJ	6	0.14	0.14	0.14	0.02	0.14	-2.38

Table 3. *Continued*

Standard	Element	Year	Method	Number of Analyses	25% Trimmed Mean	Median	Mean	Standard Deviation	Recommended Value	Accuracy %
SY-2	TiO_2	1987	MAJ	3	**	0.14	0.14	0.01	0.14	2.38
SY-2	TiO_2	1989	MAJ	3	**	0.14	0.14	0.02	0.14	2.38
SY-2	U	1985	XRF	8	299.0	299.0	296.0	11.08	284.00	5.28
SY-2	V	1980	AA	4	**	92.50	93.00	11.22	50.00	86.00
SY-2	V	1982	AA	4	**	66.50	68.00	5.23	50.00	36.00
SY-2	V	1982	XRF	10	49.60	49.50	49.40	2.99	50.00	-0.80
SY-2	V	1983	AA	8	62.50	63.00	61.88	4.82	50.00	25.00
SY-2	V	1983	XRF	23	44.30	44.00	44.91	3.44	50.00	-11.4
SY-2	V	1984	XRF	17	44.35	44.00	44.47	2.55	50.00	-11.3
SY-2	V	1985	XRF	8	44.00	44.00	44.00	2.56	50.00	-12.0
SY-2	V	1986	AA	11	66.73	67.00	66.27	10.77	50.00	33.45
SY-2	V	1986	XRF	2	**	45.50	45.50	2.12	50.00	**
SY-2	V	1987	AA	1	**	61.00	61.00	0.00	50.00	22.00
SY-2	V	1987	ICP	90	46.64	46.00	46.80	4.65	50.00	-6.71
SY-2	V	1988	ICP	47	47.93	48.00	48.09	2.29	50.00	-4.15
SY-2	V	1989	AA	2	**	47.00	47.00	11.31	50.00	-6.00
SY-2	V	1989	ICP	94	48.00	48.00	47.46	3.40	50.00	-4.00
SY-2	V	1990	AA	1	**	53.00	53.00	0.00	50.00	6.00
SY-2	V	1990	ICP	87	49.14	49.00	49.16	2.11	50.00	-1.71
SY-2	V	1991	ICP	90	51.70	52.00	51.62	2.25	50.00	3.40
SY-2	Y	1982	XRF	10	162.6	161.5	162.8	6.84	128.00	27.03
SY-2	Y	1983	XRF	23	165.6	165.0	165.5	3.29	128.00	29.38
SY-2	Y	1984	XRF	17	129.4	125.0	137.4	24.59	128.00	1.10
SY-2	Y	1985	XRF	8	178.0	178.0	178.0	4.54	128.00	39.06
SY-2	Y	1986	XRF	2	**	125.5	125.5	3.54	128.00	-1.95
SY-2	Y	1987	ICP	89	123.3	124.0	123.0	8.76	128.00	-3.67
SY-2	Y	1988	ICP	45	123.7	124.0	123.4	3.48	128.00	-3.36
SY-2	Y	1989	ICP	88	117.0	116.5	117.1	8.20	128.00	-8.59
SY-2	Y	1990	ICP	88	124.8	125.0	124.7	4.96	128.00	-2.49
SY-2	Zn	1980	AA	4	**	24.00	24.00	0.00	248.00	-90.3
SY-2	Zn	1982	AA	4	**	235.5	235.3	6.65	248.00	-5.14
SY-2	Zn	1983	AA	8	256.8	256.5	255.1	7.49	248.00	3.53
SY-2	Zn	1984	AA	5	259.4	254.0	259.8	8.32	248.00	4.60
SY-2	Zn	1985	AA	12	243.7	243.0	245.6	12.65	248.00	-1.75
SY-2	Zn	1986	AA	11	249.1	248.0	231.8	58.69	248.00	0.44
SY-2	Zn	1987	AA	1	**	255.0	255.0	0.00	248.00	2.82
SY-2	Zn	1989	AA	61	255.6	255.0	257.2	10.26	248.00	3.05
SY-2	Zn	1990	AA	82	262.0	262.5	261.4	7.89	248.00	5.63
SY-2	Zn	1991	AA	8	252.3	252.0	251.1	3.98	248.00	1.71
SY-2	Zr	1982	XRF	10	287.6	287.5	288.1	5.61	280.00	2.71
SY-2	Zr	1983	XRF	23	285.1	284.0	285.6	4.80	280.00	1.82
SY-2	Zr	1984	XRF	17	273.4	273.0	273.4	3.91	280.00	-2.36
SY-2	Zr	1985	XRF	8	270.0	269.5	271.4	4.21	280.00	-3.57
SY-2	Zr	1986	XRF	2	**	275.0	275.0	7.07	280.00	-1.79
SY-2	Zr	1987	ICP	88	284.6	284.0	285.9	35.27	280.00	1.64
SY-2	Zr	1988	ICP	9	271.2	272.0	270.0	5.07	280.00	-3.13
SY-2	Zr	1989	ICP	20	284.0	282.5	286.5	11.77	280.00	1.43
SY-2	Zr	1990	ICP	31	283.7	288.0	282.5	19.52	280.00	1.31

percent (reported with the trace-element data, C. Finch, personal communication, 1993).

Other elements show variable reproducibility of results produced by the same technique. This is especially true of elements analyzed by AAS over the 11 year period for which the data is available. AAS data for Cu (Figure 6), Pb, Zn, Co, Be, Li and Rb, show deviations from the recommended value, which fluctuate yearly. LOI and FeO also vary but the results are difficult to assess due to insufficient data (in-house controls were used in some years). Sc and Dy appear to have low accuracy but data are limited to discern any trend. Accuracy of Ag, Cd and Mo is difficult to estimate from the standards because concentrations of these elements in the standards are at or below the reporting limit for the techniques used. The standards, therefore, provide little information on the accuracy of the elements at detectable levels.

DATA LEVELLING

In geochemical studies, it is not uncommon for the data to be acquired over more than a single year. The accuracy of the data between years may therefore differ. This study also indicates that there are significant differences in accuracy according to the analytical method used by the GSB. Both of these factors have the potential to hinder interpretation of

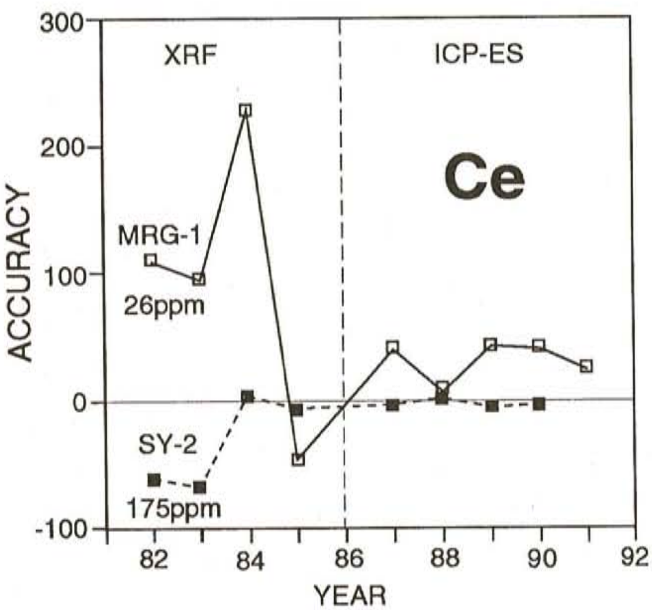

Figure 1. *Accuracy of Ce from analyses of SY-2 and MRG-1 showing improvement in accuracy by ICP-ES.*

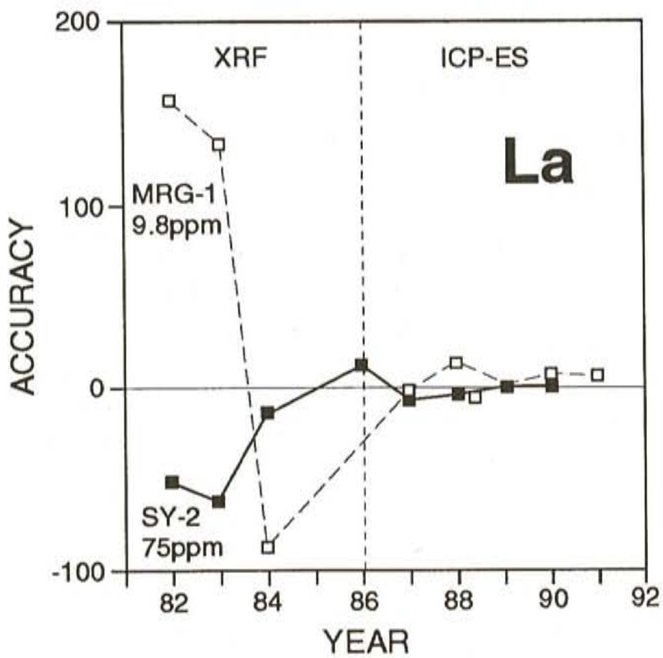

Figure 2. *Accuracy of La from analyses of SY-2 and MRG-1 showing improvement in accuracy by ICP-ES.*

data. Despite these factors, major-element data maintains consistency regardless of analytical device and for most applications the minor variations seen will have little or no effect on interpretation.

The greatest difference between the laboratory values and the recommended values are present in the trace-element data.

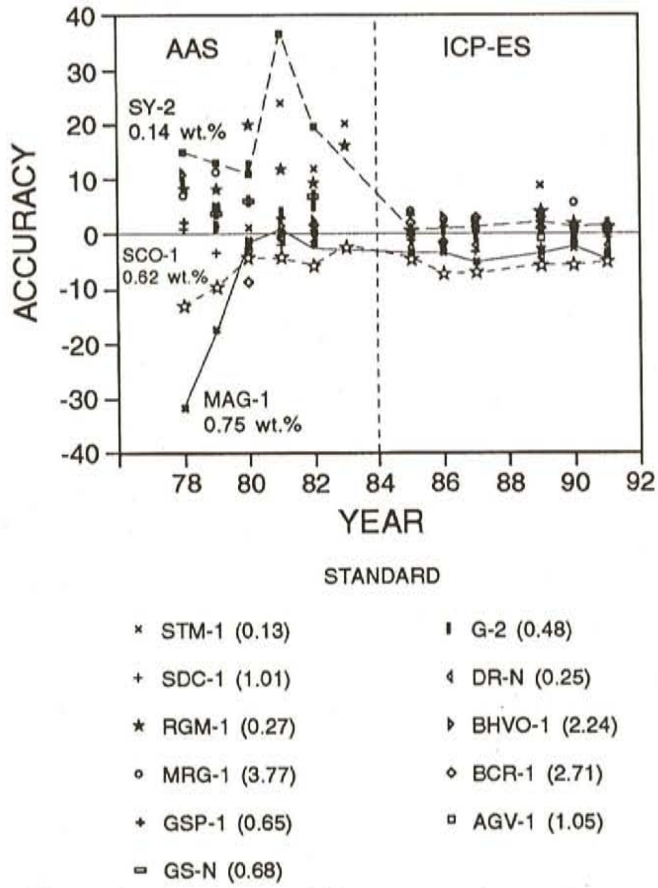

Figure 3. *Accuracy of TiO_2 from analyses of various international standards showing improvement in accuracy by ICP-ES.*

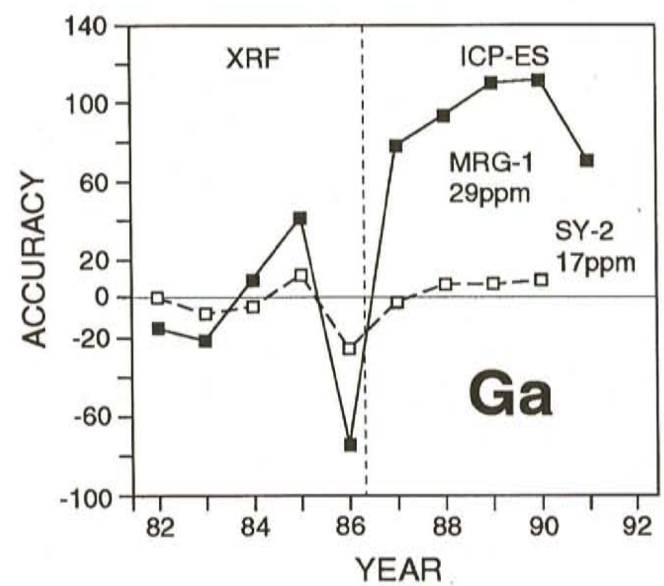

Figure 4. *Accuracy of Ga from analyses of SY-2 and MRG-1 showing accuracy problem by ICP-ES.*

The method-to-method variation is generally greater than the year-to-year variation of the standards.

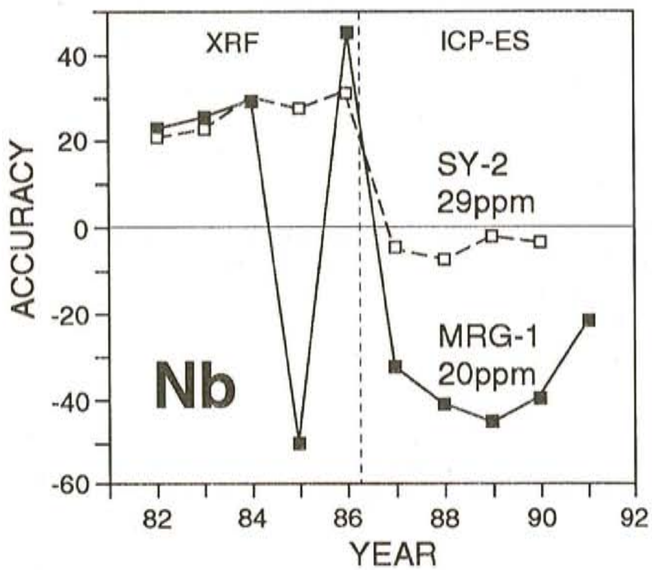

Figure 5. *Accuracy of Nb from analyses of SY-2 and MRG-1 showing accuracy problem by ICP-ES.*

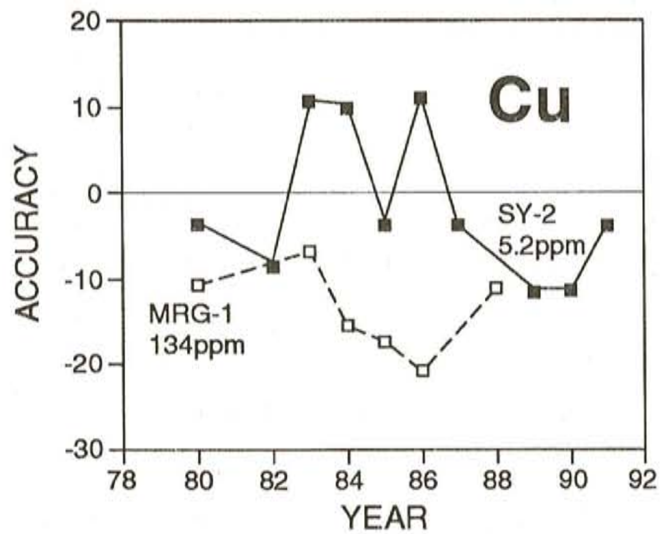

Figure 6. *Accuracy of Cu from analyses of SY-2 and MRG-1 showing changes in analytical accuracy within AAS method.*

The greater accuracy of major-element analysis and the relatively poorer accuracy of trace elements reflect the degree to which the composition of international reference materials are known. Values for major elements are well established and can be characterized by gravimetric analyses as well as instrumental techniques. The trace-element composition of standards is less well established and wider ranges in concentration are reported (Kane, 1992).

Inconsistencies revealed by the analysis of trace elements in the standards are serious and must be evaluated before interpretation of geochemical data, especially large, multiyear datasets. One way to avoid some of these problems is to re-analyse all samples using a single analytical method. In large multi-element datasets, this may not be feasible because of time, cost or the availability of archived sample material. Whereas it may make the data internally consistent, there remains the problem of comparison with data from other laboratories. Re-analysis does not eliminate the requirement for documentation of data accuracy.

Inconsistencies may also be removed by levelling the data to a common standard. In essence, this differs little from the calibration process for the analytical device. Because the standards in this report were analyzed with the data and distributed uniformly with the unknowns, it is possible to apply a factor to each analysis to level the data and remove these inconsistencies. This factor is derived from the ratio between the laboratory values and recommended values for the standards. Options for levelling the trace-element data are limited because only two standards were used. The approach will be slightly different depending upon the cause of the variation seen in the trace-element data. It is important to assess the source of the variation before attempting a correction.

Matrix effects occur within the same year of analysis and are marked by different variations in accuracy for each standard. If variation is attributed to matrix effects, levelling is probably best done by selecting the standard that most closely approximates the bulk composition of the sample data. Since the problem is caused by other elements in the sample and not the analyte itself, the interfering elements must be identified. This underlines the importance of having standards in the dataset, which approximate the bulk composition of the unknowns. There may be other interference in some data that is not detected due to the restricted composition of the standards.

The most widespread problem is to have two standards having different accuracies and also different concentrations of the component of interest. This problem occurs year to year and also method to method. Assuming that both standards are above detection limit for a particular element and have different accuracies (it is possible that the analyte in a standard may be below detection limit in one or more of the analytical systems and thus it cannot be used to level the data), two approaches are possible. The first is the same as that for matrix effects. The standard closest in bulk composition to the dataset is selected and the data is adjusted using that standard. The second option is to average the accuracy of both standards and use the result to level the data. This option attempts to accommodate intermediate values in the dataset. With an extra standard, the intermediate compositions could be more closely adjusted. The error introduced by averaging the accuracy of the standards is likely to be far less than the differences in accuracy introduced by changes in analytical method for most elements.

Once a standard has been selected or the values from both averaged, levelling of the data may be accomplished by using Equation 2 and examples are provided to demonstrate how to correct the geochemical data using the laboratory and recommended values.

Whereas levelling the data provides greater internal consistency, standards are rarely published with geochemical data in the serial literature. It is unfortunate that quantitative comparisons between GSB datasets and many important compilations are therefore often impossible.

Equation 2 New value = Old value x Correction Factor

New value is the corrected value for sample

Old value is the value of sample in original dataset

Correction Factor is derived from laboratory and recommended values (as calculated below)

Example 1: Correction of data using a single standard for Ga in mafic rocks in 1989 (GSB ICP-ES)

$$\text{Correction Factor} = \frac{\text{Recommended Value}}{\text{Laboratory Value}} = \frac{17.00}{35.57} = 0.4779$$

Sample of basalt 5641281 analysed in 1984 (ICP-ES) at 31 ppm (Fe>5%)

New value = 31 ppm x 0.4779 = 14.81
= 15 ppm

Example 2: Correction of data using two standards.

Nb in 1983 XRF data

$$\text{Correction (MRG-1)} = \frac{\text{Recommended Value}}{\text{Laboratory Value}} = \frac{20.0}{25.12} = 0.796178$$

$$\text{Correction (SY-2)} = \frac{\text{Recommended Value}}{\text{Laboratory Value}} = \frac{29.0}{35.7} = 0.812325$$

$$\text{Correction Factor} = \frac{0.796178 + 0.812325}{2} = .804251$$

Sample 2241357 Nb in granite analyzed in 1983 (XRF) = 29 ppm

New Value = = 29 x 0.804251
= 23.32
= 23 ppm

CASE HISTORY–TECTONIC DISCRIMINATION OF THE FRANÇOIS GRANITE

The François intrusion is a posttectonic, composite, high-level biotite granite. It shares these characteristics with the the Ackley batholith, Harbour Breton Granite, Chetwynd Granite, Isle aux Morts Granite and some smaller intrusions that collectively define a zone of high-silica plutonic rocks along the south coast of Newfoundland (Dickson *et al.*, 1989). The François and the Chetwynd granites are considered to be 'syn-collisional granites' on the basis of their age and geological setting, yet attempts at classifying the granites using the Rb versus Y+Nb plot of Pearce *et al.* (1984) indicate that they share geochemical charateristics with 'within plate granites' (Dickson *et al.*, 1989).

Data from the François Granite were re-examined. Figures 7 and 8 are plots produced from the geochemical data of Dickson *et al.* (1989, Figure 5, p. 90). Figure 8 is the original data and it shows that 33 percent of the data lie in the 'within plate granite' field, 48 percent into the 'syn-collisional granite' field and 17 percent into the 'volcanic-arc granite' field. Most of the analyses fall close to the triple point on the diagram precluding unambiguous tectonic classification. For Figure 9, the data were adjusted using the methods outlined above. Most of the data (72 percent) now clearly fall within the syn-collisional granite field, with the bulk of the data having migrated from the within-plate granite field. The apparent conflict between the geochemical data and geological inference has been resolved.

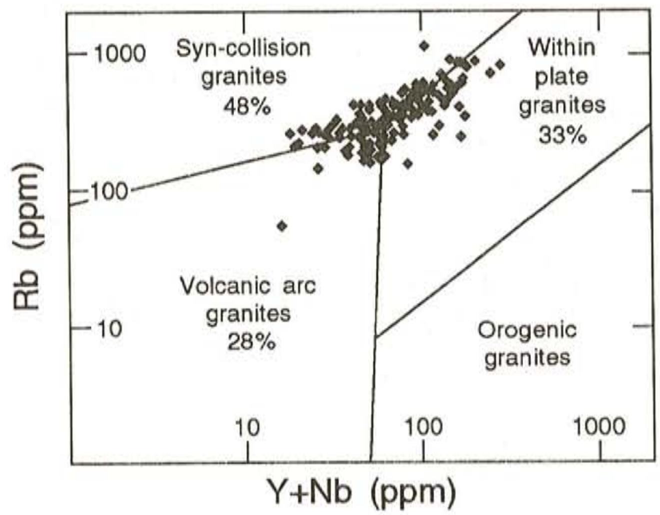

Figure 7. *Rb versus Y+Nb for the François Granite (after Dickson* et al., *1989). Fields from Pearce* et al., *1984; percentage of data in each field also given.*

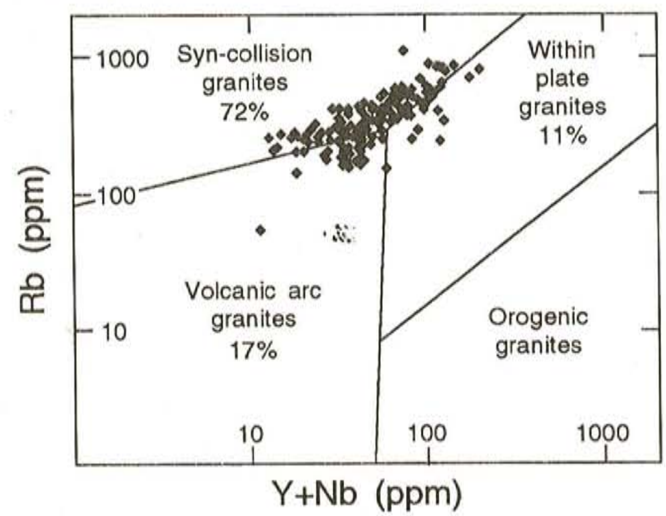

Figure 8. *Rb versus Y+Nb for the François Granite with correction for deviation in analyses of international standards; percentage of data in each field also given.*

ACKNOWLEDGMENTS

I would like to thank Chris Finch of the Geochemical Laboratory for supplying many of the raw datafiles and providing information on GSB laboratory methods. Peter Davenport and Lawson Dickson provided much useful information on the past practices of the laboratory. Peter Davenport and Charles Gower provided critical review of an earlier version of this report. Any remaining discrepancies are the responsibility of the author. The computer unit (of the GSB) is recognized for its role in providing computing services to this project. Joanne Matthews prepared the manuscript and helped compile XRF data.

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