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QUALITY CONTROL OF ANALYTICAL ROUTINES FOR WHOLE-ROCK GEOCHEMISTRY: I: PARTICIPATION OF THE CHEMISTRY AND ICP-OES LABORATORY, INSTITUTE OF GEOSCIENCES, UNIVERSITY OF SÃO PAULO, IN THE INTERNATIONAL PROFICIENCY ROUNDS GEOPT 2, 3 AND 4

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ABSTRACT

This paper discusses the results obtained during participation of the Chemistry and ICP-OES Laboratory, Institute of Geosciences, University of São Paulo, in the International Proficiency Test program for Analytical Geochemistry Laboratories (GeoPT, rounds 2, 3 and 4), from 1996 to 1998. Previously prepared and homogenized rock samples were distributed to participating laboratories, for analysis by their routine methods. The organisers of the tests evaluate statistically all contributed data and the resultant robust mean is taken as the assigned value X(a) (best available estimate of true value), from which a target precision is calculated. The comparison of this value for each analyte with each laboratories' individual result produces a z-score. This score can be used by each laboratory to judge the accuracy of its routine determinations; "satisfactory" results should be within ±2z. Our laboratory participated in the three cited rounds, analysing major, minor and the trace elements Ba, Be, Ce, Co, Cr, Cu, La, Li, Nb, Nd, Ni, Sc, Sr, V, Y, Zn and Zr by ICP-OES.

RESUMO

O trabalho discute os resultados obtidos durante participação do Laboratório de Química e ICP-OES, Instituto de Geociências, Universidade de São Paulo, no "Proficiency Test program for Analytical Geochemistry Laboratories" (GeoPT, rodadas 2, 3 e 4), de 1996 a 1998. Amostras de rochas previamente preparadas e homogeneizadas foram distribuídas para os laboratórios participantes, a fim de efetuar as análises pelos métodos rotineiros de cada laboratório. Os organizadores dos testes avaliam estatisticamente todos os dados enviados e a média robusta resultante é tomada como o valor atribuído para cada analito (melhor estimativa do valor real), para a qual é calculada uma precisão estimada. A comparação do valor estimado de cada analito com o valor individual fornecido pelo laboratório participante gera um número z. Este número permite a cada laboratório julgar a exatidão de suas técnicas analíticas rotineiras; resultados "satisfatórios" devem estar no intervalo ±2z. Nosso laboratório participou nas três rodadas mencionadas, analisando os elementos maiores, menores e os traços Ba, Be, Ce, Co, Cr, Cu, La, Li, Nb, Nd, Ni, Sc, Sr, V, Y, Zn e Zr por ICP-OES.

INTRODUCTION

The GeoPT proficiency tests (now GeoPT™; Thompson, 2002), an international program of analytical determinations of selected geologic materials, is organized by the International Association of Geoanalysts (Thompson *et al.*, 1996). It started in 1995 with the GeoPT1 program and continued with GeoPT2, 3 and 4, from 1996 to 1998. The aim is to provide a regular, independent, external check of accuracy and allow participants to detect and subsequently correct any unexpected source of error (Analytical Methods Committee, 1995). The organizers distributed a ground and homogenized sample to each participating laboratory in the 4 cited GeoPT programs, and the results were evaluated statistically. The participating laboratories were asked to perform their analytical determinations following their normal routine techniques. Details about the number of analysed elements, methods and statistical results presented by all participating laboratories in GeoPT rounds 2, 3 and 4 are summarized in Table 1.

The laboratories have the choice to express the results in terms of quality 1 or 2, according to accuracy and precision normally developed for the particular analyte. For quality 1 data, the relative standard deviation, RSD, should be ±1% to ±2% for major elements (concentrations from 100% m/m to around 1% m/m), from ±2% to ±2.8% for minor elements (concentrations between 1% m/m and 0.1% m/m), and from ±2.8% to ±16% for trace elements (concentrations varying between 1000 μg/g to 0.01 μg/g), and twice the cited values for quality 2 data (Thompson *et al.*, 1998; Thompson, 2002).

The Chemistry and ICP-OES Laboratory of the Department of Mineralogy and Geotectonics of the Geosciences Institute, University of São Paulo, established an ICP-OES routine procedure in 1995 for the analysis of major and minor elements, and some selected trace elements (Ba, Be, Co, Cr, Cu, La, Ni, Sc, Sr, V, Y, Zn, Zr; later, also Ce, Li, Nb and Nd), together with a LOI procedure and the determination of FeO by a titrimetric method. Two routines were prepared in our laboratory for sample dissolution, the alkaline fusion with Li-borates and an acid attack method in microwave oven, with a dilution factor of 1:1000 and 1:400, respectively.

The Laboratory began its participation in the GeoPT2 program in 1996, and also participated in the GeoPT3 and 4 rounds. The results obtained in these three programs by our laboratory are discussed, with special emphasis on methodology and accuracy and precision of results.

This contribution is presented in order to stimulate discussion on geochemical techniques and the convenience of preparing local in-house geologic reference materials, and to encourage laboratories to particípe in interlaboratory analytical tests.

ANALYTICAL METHODS

In GeoPT2, the entire analysis was performed with the alkaline fusion method. A thoroughly mixed powder of 0.2500 g rock sample and 0.7500 g of a Li tetra- and metaborate mixture were melted in a furnace at 1000°C in a graphite crucible, followed by quenching of the bead and dissolution of the glass in an acid solution with a magnetic agitator, then filtering and dilution to 250 ml in a volumetric flask. The analytical determinations were performed with a Meinhard nebulizer in an ARL 3410 ICP-OES equipment. The method is a slightly modified version of the one used at the Imperial College, London (kindly communicated by Dr. Peter Watkins; Janasi *et al.*, 1995). The calibration lines were constructed using solutions of similarly prepared international reference materials. LOI was obtained by heating the sample powder to 1000°C in a porcelain crucible, and the FeO determination was performed with a modified version of the Wilson titrimetric method (Andrade *et al.*, 2002).

For the next rounds, the major and minor elements were analysed from solutions prepared as in GeoPT2. Ba, Sr and Zr were also analysed from these solutions, for the following reasons: 1) the borate fusion method dissolves all refractory Zr-bearing phases better than other dissolution techniques; 2) Ba and Sr show high sensitivities and are usually present in significant amounts in rocks, and so can be successfully determined in solutions obtained by fusion, where the dilution factor is larger (1:1000 vs. 1:400 in the acid attack), therefore causing no overflow in the counting detector.

The other trace elements were analysed from solutions obtained by an acid attack method. Rock powder (0.2500 g) was dissolved in 100 ml PFA bombs (liners) in a microwave oven in two steps, at 70 and 100 psi (temperatures about 180 and 220°C, respectively), using a mixture of 5 ml of deionized H_2O, 5 ml of concentrated

Table 1 – Participating laboratories in rounds GeoPT 2, 3 and 4: number of analysed elements, techniques, statistics of acceptable results.

Round GeoPT 2: Number of elements analysed by laboratories (total of 60 participating laboratories)

	≤ 20 elements	21-30 elements	31-40 elements	41-46 elements
	14 labs	22 labs	9 labs	15 labs
Methods:	5: F; 2: F,I or F,A; 3: NA; 2: I; 2: A or A,T,G,	7: F; 3: F,I; 3: F,A or F,A,D; 2: F,Ch or F,T; 1: NA; 3: I or I,T; 1: I,A; 2: M.	1: F; 2: F,NA; 1: F,M; 2: I or I,A; 1: I,M; 1: I,A,Ch; 1: M	6: F,M; 4: F,I.M; 1: F,A,M; 1: F,NA,I,M; 3: I,M.
"Satisfactory" results				
≥70%	10(7)	12(6)	5(2)	11(6)
≥80%	4(3)	8(5)	3(2)	8(5)
≥90%	1(1)	2(1)	1(1)	2(1)

Round GeoPT 3: Number of elements analysed by laboratories (total of 72 participating laboratories)

	≤ 20 elements	21-30 elements	31-40 elements	41-54 elements
	15 labs	29 labs	9 labs	19 labs
Methods:	6: F; 2: F,I or F,A; 1: F,A,T; 2: A or A,Ch; 3: I; 1: Ch	11: F; 2: F,G or F,G,T; 3: F,A or F,A,C; 1: F,D; 2: F,I or F,I,A; 1: F,M; 2: NA; 2: I; 2: I,A; 3: M	2: F; 2: F,A or F,M; 2: I or I,A; 2: I,M; 1: I,M,A	5: F,M; 4: F,I,M; 2: F,I,A or F,A,D; 1: F,I,T; 1: F,A,M; 2: A,I or A,I,M; 2: I,M
"Satisfactory" results				
≥70%	8(6)	16(10)	4(4)	16(12)
≥80%	4(2)	12(8)	3(3)	11(9)
≥90%	0(0)	2(2)	2(2)	5(5)

Round GeoPT 4: Number of elements analysed by laboratories (total of 75 participating laboratories)*

	≤ 20 elements	21-30 elements	31-40 elements	41-49 elements
	17 labs	31 labs	13 labs	13 labs
Methods	8: F; 1: F,A,T; 2: A,Co, C or A,Co,T; 2: A,G or I,G; 2: I or I,A; 1: Ch; 1: NA.	11: F; 3: F,T; 3: F,A or F,A,I or F,A,C; 2: F,M; 3: NA; 3: I; 2: I,A; 1: I,T; 3: M.	2: F; 2: F,M; 2: F,A or F,I; 2: F,I,A or F,IR; 1: F,I,M,NA; 2: I or I,M; 1: M; 1: A,I,Ch.	3: F,M; 3: F,I,M; 2: F,M,IR or F,M,A; 1: F,I,M,A; 3: I,M; 1: I,M,A.
"Satisfactory" results				
≥70%	12(10)	25(14)	10(8)	13(8)
≥80%	8(7)	19(11)	8(7)	11(8)
≥90%	4(4)	9(5)	3(3)	7(6)

"Satisfactory" results are within the ±2**z** statistics (cf. text). The numbers: " ≥90% 4(4) " indicate that 4 labs had better than (or equal to) 90% of "satisfactory" results; in *parenthesis*, the number of labs that presented their results as Quality "2" or "1,2" data. *: in GeoPT4, laboratory 73 is not cited, since it presented only results for Ag, Pt, Pd, Rh and Au, not included in the final list of statistically evaluated elements.

Methods: A: atomic absorption; Ch: classical methods; C: combustion; Co: colorimetry; D: DC arc spectrometry; F: XRF; G: gravimetry; I: ICP-OES; IR: infrared methods; ISE: ion selective electrode; M: ICP-MS; NA: INAA; T: titrimetric determination. *Abbreviations in methods* should be read as follows: "6: F; 2: F,I,A" → 6 labs used XRF, 2 used combined XRF, ICP-OES and atomic absorption; etc.

HNO_3 and 15 ml of 40% HF. The obtained solution was evaporated in a PFA becker to dryness on a hot plate, followed by dissolution of the residue in 10 ml of HNO_3 8 M and then dilution to 100 ml in a volumetric flask (Sulcek & Povondra, 1989; CEM Corporation, 1994). The analytical determinations were performed with an ultrasonic CETAC U5000AT nebulizer by ICP-OES. In a first attempt, the calibration lines were constructed with similarly treated solutions of reference materials (GeoPT3), later substituted by solutions prepared from ultrapure salts (GeoPT4), in order to achieve a better spread of trace element values in the calibration lines. In most cases, the correlation factor in these lines, obtained by regression, is around 0.999n (n= 7, 8, or 9). A significant increase in sensitivity is achieved in the acid attack: the background counts are lowered as SiO_2 is completely taken out of the solution, and the spray efficiency is greatly improved with the use of the ultrasonic nebulizer, in most cases by at least an order of magnitude.

The analytical conditions established for the routine ICP-OES determination of the several elements in our laboratory are listed in Table 2, together with other indications, for both fusion and acid attack methods. Our established detection (DL) and quantitation limits (QL) are listed in Table 3. DL and QL decrease significantly with the use of the acid attack method, but experience indicates that the "effective analytical limits" have to be placed at higher concentrations (e.g., at 1 ppm for Ba, instead of 0.09 ppm cited as the QL of the element; Thompson & Walsh, 1989).

Analytical results obtained in routine analysis in our laboratory. Several hundred specimens of geologic materials were analyzed with a routine technique (Janasi *et al*. 1995) during the period 1995-1998, with special emphasis on determinations of igneous rocks, covering the spectrum from basalts to differentiated granites, also including several alkaline and ultrabasic rocks as well as soils and metamorphic rocks. As a routine, one or two intercalated reference materials were always included and analysed as unknown samples and the results compared with the published certified or recommended values. The data obtained for the reference materials during this period can now be used to evaluate our results in terms of accuracy.

Most of our *major element* results are within 1-1.5% of the certified or recommended values, including results for SiO_2, Al_2O_3, Na_2O and K_2O, which are usually considered difficult elements to analyse with ICP-OES (cf. sensitivity and peak profiles in Table 2). The results for SiO_2 are particularly critical, since the oxide values range from about 40-45% for basalts to about 70-76% for differentiated granites, so that an error of ±1% is equivalent to ±0.40-0.76%. Results obtained for CaO, Fe_2O_3(total) and MgO also show RSD ranges within ±1-1.5%. Larger errors may arise in the case of low values of some oxides (typically, less than 1.0-0.5%), in particular with Na_2O and K_2O in basalts and ultrabasic rocks and with MgO and CaO in granites and some alkaline rocks, which can lie close to the QL or even the DL (Table 3).

The *minor elements* Ti, Mn and P show low abundances in most rocks, frequently close to the QL (Table 3); in these cases, our errors may be as high as 10-20%.

The ICP-OES technique is very sensitive for the determination of the *trace elements* Ba, Sr and Be, and also shows good results for the other trace elements usually analysed with the method, such as Co, Cr, Cu, La, Ni, Sc, V, Y, Zn and Zr (fusion and acid attack). The acid attack technique (Table 3) also allows analyses of the elements Ce, Li, Nb and Nd in routine determinations. Many important trace elements, however, are present in very low concentrations in rocks, controlled by petrogenetic factors, so that in these cases the analytical errors can be high, posing problems for the ICP-OES method. Examples are the compatible elements Cr, Co and Ni, present in small amounts in granitoids, and Be, usually a rare element in most rocks.

GEOPT SAMPLES

The GeoPT2 sample, distributed in December of 1996, is the tuff OU-1, from the Bardon quarry, near Leicester, UK. This tuff is a fine-grained greenish-grey rock, partially recrystallized by a weak metamorphism. Predominant minerals are plagioclase and K-feldspar, with some epidote, chlorite and minor amounts of quartz. It is part of a 600-Ma old Leicestershire Charnian volcanic center. The grain size distribution of the powder is as follows: 86.9% below 63 microns, 12.8% between 63-125 microns, and 0.3% below 125 microns. Homogeneity tests vere performed by means of XRF analysis of random samples (Thompson *et al*., 1998).

Table 2 – Analytical conditions registered for routine analysis by ICP-OES

Elem.	Peak (nm)	FWHM (nm)	BG1 (nm)	BG2 (nm)	Sensitivity (kc/ppm)	Comments
Si	288.149	0.010	—	—	1.105	Sharp peak, VLS
Al	308.230	0.011	—	—	3.355	Sharp, LS
Fe	259.934	0.010	—	—	8.292	Sharp, LS
Ca	317.963	0.010	—	—	6.600	Sharp, LS
Mg	279.088	0.010	—	0.037	8.461	Sharp, LS
Na	588.997	0.012	—	—	7.999	Asymmetric, broad, LS
K	766.493	0.012	—	—	1.662	Asymmetric, broad, VLS
P	213.654	0.010	—	0.020	8.622	Sharp, LS
Ti	337.282	0.010	—	—	18.50	Sharp
Mn	257.614	0.010	—	—	104.6	Sharp
Ba	455.394	0.010	—	—	60.54(f) 99.54(a)	Sharp
Be	313.046	0.010	-0.038(f) 0.022(a)	— —	1247.2(f) 9146.7(a)	Sharp, VHS
Ce	418.641	0.014	-0.028(a)	—	607.9(a)	Broad
Co	228.650	0.012	-0.025(f) 0.032(a)	— —	5.400(f) 14707(a)	Sharp,VHS(a)
Cr	267.725	0.012	—	0.032(b)	23.00(f) 29658(a)	Sharp,VHS(a)
Cu	324.768	0.012	—	0.028(f) 0.028(a)	23.80(f) 20687(a)	Sharp,VHS(a)
La	398.829	0.017	—	0.035(f) 0.041(a)	106.0(f) 330.0(a)	Broad
Li	670.766	0.023	-0.041(a)	—	666.7(a)	Broad, asymmetric, shoulder at 670.795
Nb	309.431	0.016	-0.016(a)	0.013(a)	511.3(a)	Broad
Nd	430.339	0.011	-0.029(a)	0.024(a)	333.6(a)	Sharp
Ni	231.632	0.012	—	0.037(b)	7.080(f) 14652(a)	Sharp, VHS(a)
Sc	361.379	0.010	—	0.024(f) 0.040(a)	211.4(f) 191.5(a)	Sharp
Sr	407.749	0.009	—	—	202.8(f) 62.93(a)	Sharp
V	290.889	0.011	-0.024(b)	—	48.51(f) 135.4(a)	Sharp
Y	371.027	0.010	—	0.020(f) 0.034(a)	605.2(f) 221.8(a)	Sharp
Zn	213.894	0.012	—	0.026(f) 0.035(a)	32.60(f) 8094(a)	Sharp
Zr	339.207	0.017	-0.029(b)	—	42.77(f) 135.6(a)	Broad

Major and minor elements expressed as weight %, trace elements as ppm; Fe is Fe_2O_3(t). Kc: kilocounts. BG1 and BG2: background before and after the peak; when not nil, reading for background correction is done at the indicated nm. (f) valid for fusion, (a) acid attack, (b) both methods. FWHM: "full width at half maximum". VLS, LS, VHS: very low, low, very high sensitivity.

Table 3 – Detection (DL) and quantitation (QL) limits for major, minor and trace elements.

Elem.	DL(1)	QL(1)	DL(2)	QL(2)*	Elem.	DL(1)	QL(1)	DL(2)	QL(2)*
SiO_2	0.02	0.07(%)			Co(ppm)	15	50	0.25	0.82 (2)
TiO_2	0.006	0.02			Cr	15	50	0.16	0.53 (~2)
Al_2O_3	0.01	0.033			Cu	15	50	0.20	0.67 (2)
Fe_2O_3	0.006	0.02			La	15	50	0.54	1.79 (~5)
MnO	0.006	0.02			Li			0.25	0.79 (2)
MgO	0.01	0.033			Nb			0.29	0.98 (10)
CaO	0.006	0.02			Nd			0.90	2.99 (~1)
Na_2O	0.01	0.033			Ni	15	50	0.47	1.47 (5)
K_2O	0.03	0.10			Sc	10	33	0.02	0.05 (1)
P_2O_5	0.01	0.033			Sr	5	17	0.02	0.08 (1)
LOI	0.01	0.033			V	15	50	0.52	1.74 (2)
H_2O-	0.01	0.033			Y	10	33	0.09	0.29 (1)
Ba	10	33(ppm)	0.03	0.09 (1)	Zn	10	33	0.02	0.08 (5)
Be	1	3.3	0.02	0.08 (0.5)	Zr	25	83	0.17	0.55 (~2)
Ce			1.25	4.18 (10)					

DL and QL, 3s and 10s background, respectively. Trace elements in ppm, rest as %. (1), (2), respectively Li-borate fusion and acid attack with loss of SiO_2. * QL(2) column: in parenthesis, effective limits for quantitative analysis, in ppm.

In the GeoPT3 round, the distributed sample was the YG-1 Yewrangara granite, a part of the Yewrangara pluton of the Wyangala batholith, in the Lachlan plutonic province of eastern Australia. It is an inequigranular medium-grained felsic granite, showing some K-feldspar megacrysts with over 20 mm. The sample, collected in January of 1997, was prepared in the Gannet Holding Laboratory, Perth, Australia, and tested for homogeneity at the Open University by WD-XRF analysis (Thompson *et al.*, 1999a).

The dolerite OU-2 was distributed in September of 1998 for the GeoPT4 round. The rock comes from the Craghil quarry, Belford, Northumberland, UK. A fine-grained dark grey rock, it presents plagioclase (size of about 0.5 mm), K-feldspar, both ortho- and clinopyroxene (the last one as clusters of up to 1.2 mm), and opaque oxides. The rock was ground and homogenized at the Open University, and tested for homogeneity by WD-XRF (Thompson *et al.*, 1999b).

RESULTS

Sixty laboratories participated in the GeoPT2 round (quality 1 and 2 results; cf. list in Thompson *et al.*, 1998), seventy-two in GeoPT3 (Thompson *et al.*, 1999a) and seventy-five in GeoPT4 (Thompson *et al.*, 1999b). The analytical mean **X**(a) for each element was calculated with a "robust statistics", a modern approach for data-treatment containing outliers (Analytical Methods Committee, 1989a, 1989b; Thompson *et al.*, 1993). The target precision **h**(a) was determined with a modified version of the Horwitz function (Equation 1) and the **z**-scores were calculated with Equation 2 (Thompson *et al.*, 1996; Thompson, 2002):

$$\mathbf{h}(a) = k\,[X(a)]^{0.8495} \qquad [1]$$

$$\mathbf{z} = [X - X(a)]\,/\,\mathbf{h}(a) \qquad [2]$$

where the concentration X(a) is the *assigned value*, taken as the "best available estimate of true value" (weight fraction in eq. 1; for nomenclature, see Thompson, 2002) and X is the result obtained by the laboratory for that analyte. The constant k is 0.01 for quality 1 data and 0.02 for quality 2.

The **z**-scores obtained by the laboratories for each element were considered "satisfactory" if enclosed in the interval $-2 \leq \mathbf{z} \leq +2$ (e.g., Thompson, 2002). Common experience indicates that only results that lie well outside $-3<\mathbf{z}<+3$ should be considered with concern, pointing to significant errors either in the procedures and/or the state and calibration of the equipment (Thompson, 2002). In these cases, remedial action should be taken. Large uncertainties also arise when the concentration of the determined element is close to the DL or even the QL. Errors close to the DL can tend to infinite values, and the ones around the QL should show ideally, at least, 10% RSD (Potts, 1992). This agrees with the increase in the RSD as concentration decreases (Horwitz, 1982).

The results obtained by our laboratory are reproduced in Tables 4, 5 and 6 for GeoPT 2, 3 and 4, respectively. In GeoPT2, the stated results for the analysed 23 elements (Cr and La below DL) were obtained with sample treatment by alkaline fusion. Most of our trace element results were reported as of quality 2.

Our results of GeoPT3 were obtained for 27 elements (Co below QL), adding Ce, Li, Nb and Nd to the list of analysed elements; the FeO value was not reported. Similar techniques were used for the GeoPT4 round, for 29 elements (including FeO), but with calibration lines for trace elements constructed from solutions prepared with ultrapure reagents.

DISCUSSION

For the GeoPT2 round, most of the 60 participants analysed between 20 to 35 elements,

Table 4 – Analytical means and z values obtained by the organizers for the OU-1 tuff (GeoPT2) compared to the ones obtained by the Chemistry-ICP OES laboratory.

Analysed elements	Assigned value (Xa)*	Horwitz precision (ha)*	Chemistry-ICP AES values	Analytical quality	Z value of laboratory
SiO_2	58.247	0.632	58.50	1	0.40
TiO_2	0.440	0.010	0.45	1	1.00
Al_2O_3	15.136	0.201	15.16	1	0.12
Fe_2O_3 (t)	8.987	0.129	9.33	1	2.66
FeO	4.995	0.078	5.16	1	2.10
MnO	0.129	0.004	0.137	1	2.28
MgO	4.727	0.075	4.81	1	1.12
CaO	6.488	0.098	6.69	1	2.06
Na_2O	2.463	0.043	2.49	1	0.63
K_2O	0.215	0.005	0.21	1	-0.88
P_2O_5	0.050	0.002	0.03	1	-12.74
LOI	3.058	0.052	3.05	1	-0.15
Ba	131.40	5.044	126	1	-1.07
Be	0.43	0.039	3	2	32.91
Co	24.41	1.207	18	2	-2.66
Cr	27.65	1.342	(1)		
Cu	61.55	2.648	28	2	-6.33
La	5.60	0.346	(1)		
Ni	13.00	0.707	17	2	2.83
Sc	32.69	1.547	32	2	-0.22
Sr	104.76	4.161	109	1	1.02
V	222.23	7.881	253	2	1.95
Y	21.63	1.089	18	2	-1.67
Zn	74.40	3.111	51	2	-3.76
Zr	55.00	2.407	32	2	-4.78

*: values indicated in the original Committee report (Thompson et al., 1998). From SiO_2 to LOI, values in weight %; from Ba to Zr, in ppm. (1) Values below, or close to, detection limits (Cr<15 ppm; La< 15 ppm). Sample treatment by borate fusion; see text.

but 10 analysed only up to 15 elements, while 18 laboratories presented results for 35 or more elements; a few laboratories (codes 49, 47, 51 and 59) analyzed 46 elements. Twent-three participants showed at least 80% of "satisfactory" results in the interval ±2**z**, 6 of them with 90% or over (Table 1). Most participants presented acceptable results for 60 to 80% of the analysed elements. The ICP-OES method was used by 20 participants for major and trace element determination; of these, 11 laboratories show "satisfactory" results for 80% or more elements. Our laboratory (code number 53) analysed 23 elements (Cr and La are below DL) and obtained 52.2% "satisfactory" results; elevan elements show "unsatisfactory" values, 6 of which with **z** values between ±2**z** and ±3**z** (Table 4). The largest errors are found for the elements Be

Table 5 – Analytical means and z values obtained by the organizers for the YG-1 granite (GeoPT3) compared to the ones obtained by the Chemistry-ICP OES laboratory.

Analysed elements	Assigned value (Xa)*	Horwitz precision (ha)*	Chemistry-ICP AES values	Analytical quality	Z value of laboratory
SiO_2	73.363	0.7686	73.79	1	0.56
TiO_2	0.2012	0.0051	0.22	1	3.67
Al_2O_3	13.056	0.1774	13.12	1	0.36
Fe_2O_3 (t)	2.8064	0.0481	2.88	1	1.53
MnO	0.0498	0.0016	0.05	1	0.15
MgO	0.1264	0.0035	0.10	1	-7.64
CaO	1.0961	0.0216	1.15	1	2.49
Na_2O	3.6028	0.0594	3.73	1	2.14
K_2O	5.0599	0.0793	5.20	1	1.77
P_2O_5	0.0325	0.0011	0.03	1	-2.31
LOI	0.2633	0.0064	0.24	1	-3.62
Ba	534.91	16.62	527	1	-0.48
Be	4.5292	0.2886	5	2	0.82
Ce	129.5	4.9815	127	2	-0.25
Co	2.0000	0.1441	(1)	2	
Cr	9.2217	0.5280	13	2	3.58
Cu	5.0000	0.3139	5	2	0.00
La	63.40	2.7155	65	2	0.30
Li	32.33	1.5327	32	2	-0.11
Nb	48.78	2.1735	48	2	-0.18
Nd	56.66	2.4684	51	2	-1.15
Ni	6.8620	0.4107	8	2	1.39
Sc	4.4816	0.2860	4	2	-0.84
Sr	88.53	3.6061	94	1	1.52
V	6.0000	0.3665	7	2	1.36
Y	54.44	2.3860	58	2	0.75
Zn	68.42	2.8974	78	2	1.65
Zr	271.38	9.3396	244	1	-2.93

*: values as in Thompson et al. (1999a). See also footnotes, Table 4. (1): Value below QL (Co<2 ppm). FeO was not determined. Major and minor elements, and Ba, Sr and Zr, were analysed from solutions obtained by borate fusion, the other trace elements from solutions by acid attack (see text).

(**z**=32.91, QL= 3.3 ppm), P_2O_5 (-12.74, 0.03%), Cu (-6.33, 50 ppm), Zn (-3.76, 33 ppm) and Zr (-4.78, 83 ppm; Table 4). The assigned value for Be is below our QL for the fusion method, and is therefore affected by large errors; as a comparison, 5 of the 12 laboratories reporting Be values show deviations over ±2**z**. The assigned values for P_2O_5, Co, Cu and Ni are, respectively, 0.05%, 24.4, 61.55 and 13 ppm (Table 4), below, or close to, our QL (fusion method, Table 3). Many laboratories also had difficulties in the determinations of these elements (56.3%, 26.7%, 47.7%, and 65% presented "unsatisfactory" results for P_2O_5, Co, Cu and Ni, respectively). The Zn result of GeoPT 2, lower than the assigned value, is faulty on account of some unknown factor (interferences in the fusion method?; in the next round, the Zn values were satisfactorily determined, with dissolution by acid attack). Our low Zr value is probably due to loss by precipitation, even though an effort was made to keep the element in solution, with the addition of 1700 mg/g HF to form a fluoride complex; no loss of Zr occurred during sample preparation, since the borate fusion technique is very efficient in dis-

Table 6 – Analytical means and z values obtained by the organizers for the OU-2 dolerite (GeoPT4) compared to the ones obtained by the Chemistry-ICP OES laboratory.

Analysed elements	Assigned value (Xa)*	Horwitz precision (ha)*	Chemistry-ICP AES values	Analytical quality	Z value of laboratory
SiO_2 (1)	51.095	0.565	51.50	1	0.72
TiO_2	2.425	0.042	2.43	1	0.12
Al_2O_3	13.801	0.186	13.53	1	-1.46
$Fe_2O_{3\,(t)}$	13.253	0.180	13.44	1	1.04
FeO	8.404	0.122	8.56	1	1.28
MnO	0.170	0.004	0.18	1	2.25
MgO	5.585	0.086	5.57	1	-0.17
CaO	8.994	0.129	9.04	1	0.35
Na_2O	2.480	0.043	2.49	1	0.22
K_2O	0.990	0.020	1.05	1	3.03
P_2O_5	0.300	0.007	0.29	1	-1.32
LOI			0.91	1	
Ba	341.1	11.3	343	1	0.16
Be	1.11	0.09	0.8	2	-1.77
Ce	60.2	2.6	55	2	-1.00
Co	44.8	2.0	56	2	2.77
Cr	97	3.9	87	2	-1.28
Cu	63	2.7	61	2	-0.37
La	27.71	1.34	28	2	0.11
Li	12.79	0.70	13	2	0.15
Nb	17.25	0.90	30	2	7.09
Nd	33.35	1.57	31	2	-0.75
Ni	51.77	2.29	46	2	-1.26
Sc	28.21	1.36	25	2	-1.18
Sr	403.7	13.1	415	1	0.86
V	339.3	11.3	321	2	-0.81
Y	30.93	1.48	29	2	-0.65
Zn	113.0	4.4	107	2	-0.68
Zr	200.5	7.2	219	1	2.57

*: values as in Thompson et al. (1999b). See footnotes, Tables 4 and 5. See text.

solving Zr-bearing minerals, including the most refractory phases such as zircon. Our **z** scores for most major elements, including Si, Al, Na and K, are low (Table 4).

In the GeoPT3 round, 30 of the 72 participants obtained "satisfactory" scores for over 80% of the analysed elements, 2 laboratories with a maximum score of up to 95%. Eight laboratories determined less than 15 elements, while 18 analysed over 45 elements (up to a maximum of 53 and 54 elements), most participants however analysing between 20 and 35 elements (Table 1). Our laboratory (code number 67) analysed 27 elements (Co below QL) and obtained "satisfactory" scores for 19 elements (70.4%; Table 5). Twenty-seven participants used the ICP-OES technique for the determination of at least 20 to 35 elements. Of these, 13 ICP-OES users showed acceptable results of over 80%. Our laboratory obtained "unsatisfactory" results for TiO_2 (**z**=3.67), MgO (-7.64), CaO (+2.49), Na_2O (+2.14), LOI (-3.62), Cr (+3.58), P_2O_5 (-2.31) and again Zr (-2.93) (Table 5), several below the ±3**z** score. They should not affect significantly the entire analytical results or the evaluation of data (e.g., during geochemical or petrological considerations), since the absolute differences are rather slight: TiO_2, 0.20% (assigned value) vs. 0.22 (our value); MgO, 0.13% vs. 0.10; CaO, ~1.10% vs. 1.15; LOI, 0.26% vs. 0.24; Cr, 9.221 vs. 13; P_2O_5, 0.0325 vs. 0.03. The possible exception is Na_2O, 3.60% (assigned) vs. 3.73 (our value, Table 5), which may affect disproportionately some geochemical indicators, such as the CIPW norm values. Our experience shows that MgO values lower than 0.50 % are difficult to analyse with our ICP-OES and the fusion method. The recommended Cr value (9.22 ppm) is rather low, but still above the effective QL (~2 ppm) for the acid attack technique, and the negative error in Zr (271 vs. 244 ppm, our value) again shows that the probable cause may still be Zr loss by precipitation in the analytical solution. Most participating laboratories presented data that do not pass the ±2**z** test for MgO, P_2O_5 and Cr: respectively, 60.3%, 63.3% and 73.9%. Slight absolute deviations in the values of major and minor elements from the assigned values are sufficient to create larger **z** scores than is the case with trace elements (cf. our results for Ti, Mg, Ca, P and LOI, Table 6). This is evident from equation 2 that calculates the **z** value, which is dependent on the Horwitz precision. The values h(a) for major and minor elements are all below 0.200, with the exception of the value for SiO_2 (> 0.500), whereas those for trace elements are mostly well over 1.0, with some exceptions (Tables 4, 5 and 6).

In the GeoPT4 round, 14 laboratories, out of a total of 75 participants, analysed over 40 elements (up to 48-49 by 4 participants), while 8 presented results for only 15 elements (or less). A general improvement in all laboratories is clearly seen in the **z** scores: 33 laboratories show "satisfactory" values for at least 85% of the analysed elements (95% "satisfactory" scores, or higher, for 10 participants; Table 1). Our laboratory (code number 71) analysed 29 elements with 82.7% "satisfactory" results, and "unsatisfactory" values for 5 elements, again an improvement over GeoPT3 (Table 6). Twenty-four laboratories used ICP-OES as the main or only analytical methodology, a decrease since GeoPT2 and 3, indicating that the technique is being gradually replaced by newer ones, especially by ICP-MS or a combination (XRF, ICP-OES and ICP-MS; Table 1). Of these 24 laboratories, 14 show a score of over 80% of "satisfactory" results (including our own), with the added remark that 10 of them reported their data as of quality 2, 8 also using ICP-MS for auxiliary determinations (Table 1). Our results are "unsatisfactory" for 5 elements, 3 of which with **z** < ±3 (Mn, **z**=2.25, Co 2.77, Nb 7.09, Zr 2.57 and, for the first time, also K_2O, 3.03; Table 6). Our determined Mn content of 0.18% is close to the assigned value of 0.17%. The value of K_2O for the dolerite (0.990 vs. our 1.05%) is relatively low and the intensity readout affected by large errors. Our Zr result is too high (assigned 200.5 ppm, vs. our 219 value), indicating that, this time, the unsatisfactory analysis was unrelated to Zr loss or precipitation in the solution. Our obtained Nb value is far too high (30 ppm vs. the assigned 17.25 ppm, Table 6), in contrast with the value obtained in the GeoPT3 test (assigned value of 48.78 vs. our value of 48 ppm, Table 5), on account of a previously undetected V interference on Nb. The V content of 6 ppm in the GeoPT3 granite is not enough to increase the readout of the Nb peak, in contrast to the Nb value in the GeoPT4 dolerite (339.3 ppm). Vanadium shows an atomic spectral line at 290.880 nm, with additional atomic emission lines at 309.311 and 310.25 nm, all interfering with the atomic spectral line of Nb at 309.419 nm. A quantitative correction factor is now systematically applied to our Nb determinations.

CONCLUSIONS

Our laboratory applied routine techniques for the quantitative analysis of geochemical samples to participate in the GeoPT rounds 2, 3 and 4, using mainly the ICP-OES technique with Li borate fusion for major and minor elements (as well as for Zr, Sr and Ba) and acid attack in a microwave oven for other 14 trace elements. The results obtained by the participating laboratories were tested by the members of the Organizing Committee against **z** scores, showing that our "satisfactory" results increased steadily from GeoPT2 (52.2% of "satisfactory" results) to GeoPT3 and 4 (70.4% and 82.7%; "unsatisfactory" results, with comments, are summarized in Table 7). This improvement was obtained with a better control of preparation techniques, calibration lines and equipment conditions, and the adoption of the acid attack method for the determination of most trace elements.

The largest deviations in our results, with **z** values well over ±3, occur haphazardly in the several rounds, in assorted elements such as P, Mg, Be, Cr, Cu, Zn and Zr (GeoPT2, 3 and 4; Table 7), many of which occur in the tested rocks close to our QL or even DL. Most of the faulty results were obtained for "quality 1" data, subjected to more stringent statistical tests than the "quality 2" ones, and present, in any case, **z** values of less than ±3, therefore close enough to the "satisfactory" range. Systematic and repeated errors did occur mainly for Zr, in part due to precipitation of the element in the analytical solution, related to still unidentified causes, which we tried to remedy by addition of HF and the corresponding complex formation.

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Table 7 – "Unsatisfactory" results in rounds GeoPT2, 3 and 4

Elem.	**z**-scores 2	**z**-scores 3	**z**-scores 4	Comments
Fe(t)	***2.66*** (8.9-9.33)			Low Horwitz precision*
Fe2	***2.10*** (5.0-5.16)	n.d.		Low h(a)
Mg		***-7.64*** (0.12-0.10)		Low Mg value, close to QL.
Ca	***2.06*** (6.49-6.69)	***2.49*** (1.096-1.15)		Low h(a)
Na		***2.14*** (3.60-3.73)		Low h(a)
K			***3.03*** (0.99-1.05)	Broad peak; low h(a)
Ti		***3.67*** (0.20-0.22)		Low h(a)
Mn	***2.28*** (0.13-0.137)		***2.25*** (0.17-0.18)	Low h(a)
P	***-12.74*** (+0.05-0.03)	***-2.31*** (0.032-0.03)		2, 3: close to QL; also, low h(a).
LOI		***-3.62*** (0.26-0.24)	no z-score	Low h(a)
Be	***32.91*** (0.43-0.30)			Below DL (fusion)
Co	***-2.66*** (24.42-18)		***2.77*** (44.8-56)	2: below QL (fusion)
Cr	n.d.	***3.58*** (9.2-13)		Faulty calibration line
Cu	***-6.33*** (61.5-28)			Close to QL (fusion)
Nb	n.d.		***7.09*** (17.2-30)	V interference, see text
Ni	***2.83*** (74.4-51)			Close to QL (fusion)
Zn	***-3.76*** (74.4-51)			Undetected interference? (fusion)
Zr	***-4.78*** (55-32)	***-2.93*** (271.4-244)	***2.19*** (200.5-219)	2: below QL (fusion), see text

Major and minor elements expressed as %, other elements as ppm; Fe(t) and Fe2 are Fe_2O_3(total) and FeO. **z**-scores 2, 3 and 4 refer to GeoPT2, 3 and 4, respectively. **z**-scores in italics. In parenthesis, assigned value vs. value obtained by our laboratory. See also text and Tables 2, 4, 5 and 6. * "Low Horwitz precision" is responsible for more stringent conditions in the **z** scores (eq. 2, see text).

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