

Inductively coupled plasma-mass spectrometric (ICP-MS) analysis of silicate rocks and minerals

Jacqueline VANDER AUWERA, Guy BOLOGNE, Iwan ROELANDTS
& Jean Clair DUCHESNE

(2 figures & 5 tables)

Laboratoires associés de Géologie, Pétrologie, Géochimie, Université de Liège, B-4000 Liège, Belgium.

ABSTRACT. The accurate measurement of low levels of trace elements is now necessary in most petrological studies. In this paper, we present the methods used in our laboratory ("Collectif interinstitutionnel de géochimie instrumentale") to analyse simultaneously, with the ICP-MS instrument, 26 trace elements in silicate rocks and minerals. Whole-rocks are prepared using a lithium metaborate fusion in order to assure dissolution of resistant mineral phases, whereas mineral separates (plagioclases, pyroxenes, apatites) are prepared using an open acid digestion. Calibration of the ICP-MS is made with international reference materials for whole-rocks and with synthetic aqueous solutions for mineral separates. The accuracy of the data as well as limits of quantification (LOQ) vary among elements but are usually very good (accuracy better than 6%, LOQ usually below 1 µg/g in solids). Combination of XRF and ICP-MS capabilities enables us to determine 38 elements (major and trace) on a routine basis.

KEYWORDS: Inductively coupled plasma mass spectrometry, trace elements geochemistry, sample preparation.

RESUME. Analyse des roches silicatées et des minéraux par spectrométrie de masse à plasma couplé inductivement. La mesure exacte de faibles quantités d'éléments en trace est maintenant nécessaire dans toute étude pétrologique. Dans ce papier, nous présentons les méthodes utilisées dans notre laboratoire («Collectif interinstitutionnel de géochimie instrumentale») pour analyser simultanément avec l'ICP-MS, 26 éléments en trace dans des roches silicatées et des minéraux séparés. Les échantillons de roches totales sont préparés à l'aide d'une fusion au métaborate de lithium, de manière à assurer la dissolution complète de phases minérales résistantes, alors que les minéraux séparés (plagioclases, pyroxènes, apatites) sont préparés à l'aide d'une attaque acide en bombes ouvertes. La calibration de l'ICP-MS se fait avec des standards internationaux dans le cas des roches totales et avec des solutions standards synthétiques pour les minéraux séparés. L'exactitude des données ainsi que les limites de quantification (LOQ) varient d'un élément à l'autre mais sont habituellement très bonnes (exactitude meilleure que 6 %, LOQ inférieure à 1 µg/g dans le solide). En combinant les capacités de la Fluorescence-X et de l'ICP-MS, nous avons maintenant la possibilité de déterminer en routine 38 éléments (majeurs et traces).

MOTS-CLES : Spectrométrie de masse à plasma couplé inductivement, géochimie des éléments en traces, préparation des échantillons.

1. Introduction

In most petrogenetic and geochemical studies, quantitative determination of a wide variety of elements is now required. In our laboratory, the "Collectif interinstitu-

tionnel de géochimie instrumentale", major elements as well as selected trace elements (Ba, Ce, Co, Cr, Nb, Ni, Rb, Sr, V, Y, Zn, Zr) have been measured by XRF (Alpha 2020, CGR) for about twenty years (Bologne & Duchesne, 1991). Nevertheless, detection limits for this

technique are relatively high, usually between 10 to 25 $\mu\text{g/g}$. They thus preclude the determination of trace elements occurring at low contents in silicate rocks like REE, U, Th, Ta. In 1992, an ICP-MS VG Plasma Quad PQ2 from Fisons Instruments has thus been acquired to enlarge the analytical capacity of our laboratory. The aim of this paper is to present the analytical procedure followed here as well as some data on accuracy, precision and limits of quantification.

2. Sample preparation

Prior to being analysed by ICP-MS, rocks or mineral samples must be put into solution. Alkali fusion and open acid digestion are used in many geological laboratories and are well-established methods (Jarvis, 1992; Totland *et al.*, 1992). Nevertheless, the precise recipe varies between laboratories and the exact methods used at Liège are described here.

2.1. Alkali fusion

250 mg of powdered rock (sample or reference material) are weighed into a Pt crucible and mixed with 1.25 g of lithium metaborate (Aldrich, USA) (Jarvis, 1992; Totland *et al.*, 1992). The sample is fused over a Meker burner and an average of 15 min is usually required to completely fuse the sample. The hot melt is then poured directly into a beaker containing 150 ml of 0.8M HNO_3 . Solution is mixed continuously on a magnetic stirrer until complete dissolution of all solids and finally diluted to 250 ml in a volumetric flask. Solutions are stored in polypropylene bottles and diluted to 1: 5000 prior to being analysed by ICP-MS. When total dissolved solids (TDS) in samples exceed 2000 $\mu\text{g/ml}$, they cause partial blocking of the sampling cone aperture and important signal drift with time. Dilution of 1: 5000 maintains the TDS below 2000 $\mu\text{g/ml}$.

2.2. Open acid digestion

Until now, in our laboratory, open acid digestion has been performed only on rocks deficient in trace elements and mineral separates (plagioclase, pyroxenes, apatite) as this method of sample preparation is time-consuming and does not assure complete dissolution of the sample when resistant accessory phases, usually rich in incompatible elements, are present. Minerals have been separated from whole rocks using classical separation techniques (Duchesne, 1966). 0.5 g of sample are weighed into clean Pt crucible and moistened with 2ml of distilled H_2O . 10 ml of HF and 2ml of HCl (pyroxenes) or HNO_3 (plagioclase) are added. The samples are allowed to stay in the acid mixture for several hours before the evaporation stage, as this improves the effectiveness of the acid digestion. The crucibles are then heated on a hot plate (170 °C) to incipient dryness. The acid digestion is repeated three times. 10 ml of HNO_3 are then added to the samples and the evaporation cycle is repeated three times in order to

eliminate all traces of HF. When HCl has been used during the digestion (pyroxenes), 10 ml of H_2O are added to the samples after the acid digestion and samples are transferred into pyrex beakers in order to avoid mixing of HNO_3 and HCl in contact with Pt. The beakers are then put on the hotplate for evaporation: 10 ml of HNO_3 are added to the samples and the evaporation cycle is repeated three times in order to eliminate all traces of HCl. The samples are then transferred in 250 ml volumetric flasks and made to volume giving a dilution factor of 500. In the case of apatites, the digestion procedure is simplified as this mineral can be put into solution simply by adding 20% HNO_3 . When the REE content is expected to be low in the sample (below 1 time chondrite levels), REE can be concentrated using the cation exchange technique (Roelandts & Michel, 1986).

Table 1. Instrumental operating conditions for trace element determination of the Liège ICP-MS (VG Plasma Quad PQ2).

Coolant gas-flow (Ar)	11.25 l/min
Auxiliary gas-flow (Ar)	0.65 l/min
Nebuliser gas-flow (Ar)	0.725 l/min
Nebuliser type	de Galan, high dissolved solids nebuliser
Forward power	1.35 kW
Reflected power	< 5 W
Washing time	150 s
Detector type	Galileo
Detector mode	Pulse counting
Acquisition mode	Peak jumping

3. Instrumentation

The ICP-MS instrument is a VG Elemental Plasma Quad PQ2. The operating conditions are given in Table 1. Samples are introduced with a peristaltic pump and a de Galan nebuliser is used. The "peak jumping mode" is preferred as this optimises counting times and the Galileo detector is set in the "pulse counting mode". In the case of whole-rock analyses, calibration is performed with five international reference materials (BE-N, DR-N, GS-N, GH, AC-E: these samples are currently being distributed by the CRPG, BP20, F54501 Vandoeuvres-Nancy Cedex, France) and granite GA is used as a control. For mineral separates, standard solutions are prepared by diluting 1.000g l^{-1} single element AAS standard solutions (Aldrich, USA) and the international reference material FK-N or one of our samples of known composition is used as a control. A blank solution prepared following the same procedure (alkali digest or open acid digestion) as the samples is also used in the calibration. For each sample or standard, data are acquired in 3 runs. $^{115}\text{In} + ^{187}\text{Re} + ^{209}\text{Bi}$ (50 ng/ml) are added to all samples and calibration solutions and are used as internal standards to correct for signal drift with time (see section 4). The isotopes chosen for the determination of each element are given in Table 2. Usually,

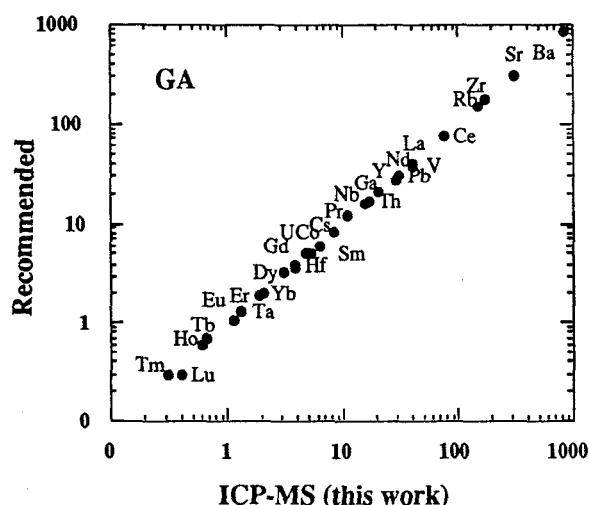


Figure 1. Comparison between recommended values (Govindaraju, 1995) and measured contents by ICP-MS for the international reference material GA.

the most abundant isotope, free of interferences and isobaric overlap, is selected. When several isotopes are determined for the same element, an average value is calculated.

4. Matrix, drift and interference problems

The sensitivity of one given element (counts per second per ng/g) is mainly controlled by its concentration but also by matrix effects like the presence of acids and the amount of TDS. As a perfect matrix match between standards and samples cannot be obtained, these interferences must be corrected with the use of internal standards. Moreover, as matrix effects also depend on the mass of the elements, three distinct internal standards (^{115}In , ^{187}Re , ^{209}Bi) are added to all solutions in order to cover the complete mass range. These spikes are also used to correct for the instrumental drift caused by progressive blocking of the cones apertures.

Interferences may arise from isobaric overlaps, the presence of doubly charged ions, and the formation of oxides and hydroxides (Table 2). The polyatomic forming reactions involve the plasma and atmospheric gases (O_2 , N_2) as well as Cl, S which can be present in some solutions. The oxide level strongly depends on the plasma conditions. Significant molecular ion interferences occur below 80 amu (see for example Sc, V, Co, Cu, Ga in Table 2). Control of the oxide and hydroxide interferences has shown that in the case of geological materials, the severe interferences are the following: $^{135}\text{Ba}^{16}\text{O}$ and $^{134}\text{Ba}^{16}\text{OH}$ on ^{151}Eu ; $^{137}\text{Ba}^{16}\text{O}$ and $^{136}\text{Ba}^{16}\text{OH}$ on ^{153}Eu ; $^{141}\text{Pr}^{16}\text{O}$ on ^{157}Gd ; $^{143}\text{Nd}^{16}\text{O}$ on ^{159}Tb ; $^{150}\text{Nd}^{16}\text{O}$ on ^{166}Er . Correction factors for these interferences are monitored with synthetic standard solutions or calculated with interference equations introduced in the PQ vision software.

Table 2. Compilation of isotopes selected for analysis and quantification as well as potential spectral interferences.

Element	Abundance (%)	m/z	Interferences, remarks
Sc	100	45	$^{12}\text{C}^{16}\text{O}_2\text{H}$, $^{26}\text{Mg}^{16}\text{OH}$, $^{28}\text{Si}^{16}\text{OH}$, $^{29}\text{Si}^{16}\text{O}$, $^{44}\text{CaH}^+$, $^{38}\text{Ar}^{7}\text{Li}$ in fusion digests
V	99.76	51	$^{35}\text{Cl}^{16}\text{O}$, $^{34}\text{S}^{16}\text{OH}$, $^{36}\text{Ar}^{15}\text{N}$, $^{36}\text{Ar}^{14}\text{NH}$, $^{37}\text{Cl}^{14}\text{N}$, $^{36}\text{S}^{15}\text{N}$, $^{33}\text{S}^{18}\text{O}$
Co	100	59	$^{36}\text{Ar}^{23}\text{Na}$, $^{42}\text{CaOH}^+$, $^{43}\text{Ca}^{16}\text{O}$
Cu	69.2	63	$^{40}\text{Ar}^{23}\text{Na}$, $^{31}\text{P}^{16}\text{O}_2$, $^{47}\text{Ti}^{16}\text{O}$
	30.8	65	$^{49}\text{Ti}^{16}\text{O}$, $^{130}\text{Ba}^{++}$, $^{33}\text{S}^{16}\text{O}_2$, S_2
Zn	27.8	66	$^{50}\text{Ti}^{16}\text{O}$, $^{50}\text{V}^{16}\text{O}$, $^{50}\text{Cr}^{16}\text{O}$, $^{132}\text{Ba}^{++}$, SO_2 , S_2
Ga	39.8	71	$^{36}\text{Ar}^{35}\text{Cl}$, $^{142}\text{Ce}^{2+}$, $^{142}\text{Nd}^{2+}$, $^{40}\text{Ar}^{31}\text{P}$, $^{35}\text{Cl}^{18}\text{O}_2$, SO_2 , $^{38}\text{Ar}^{33}\text{S}$
Rb	72.2	85	$^{170}\text{Er}^{++}$, $^{170}\text{Yb}^{++}$
Sr	82.5	88	$^{40}\text{Ar}^{48}\text{Ca}$, $^{176}\text{Lu}^{++}$, $^{176}\text{Yb}^{++}$
Y	100	89	
Zr	51.5	90	
	11.2	91	
Nb	100	93	$^{56}\text{Fe}^{37}\text{Cl}$
In	95.7	115	Internal standard
Cs	100	133	
Ba	6.59	135	
	11.3	137	
La	99.9	139	
Ce	88.5	140	
Pr	100	141	
Nd	12.2	143	
	17.2	146	$^{130}\text{Ba}^{16}\text{O}$
Sm	15.1	147	$^{130}\text{Ba}^{16}\text{OH}$
	14	149	$^{132}\text{Ba}^{16}\text{OH}$
Eu	47.8	151	$^{135}\text{Ba}^{16}\text{O}$, $^{134}\text{Ba}^{16}\text{OH}$
	52.2	153	$^{137}\text{Ba}^{16}\text{O}$, $^{136}\text{Ba}^{16}\text{OH}$
Gd	15.7	157	$^{141}\text{Pr}^{16}\text{O}$, $^{140}\text{Ce}^{16}\text{OH}$
Tb	100	159	$^{143}\text{Nd}^{16}\text{O}$
Dy	18.9	161	$^{145}\text{Nd}^{16}\text{O}$
	25	163	$^{147}\text{Sm}^{16}\text{O}$
Ho	100	165	$^{149}\text{Sm}^{16}\text{O}$
Er	33.4	166	$^{150}\text{Nd}^{16}\text{O}$, $^{150}\text{Sm}^{16}\text{O}$
	22.9	167	$^{151}\text{Eu}^{16}\text{O}$
Tm	100	169	$^{153}\text{Eu}^{16}\text{O}$
Yb	21.8	172	$^{156}\text{Gd}^{16}\text{O}$, $^{156}\text{Dy}^{16}\text{O}$
	16.1	173	$^{157}\text{Gd}^{16}\text{O}$
Lu	97.4	175	$^{159}\text{Tb}^{16}\text{O}$
Hf	18.5	177	$^{161}\text{Dy}^{16}\text{O}$
	27.1	178	$^{162}\text{Dy}^{16}\text{O}$, $^{162}\text{Er}^{16}\text{O}$
Ta	99.9	181	$^{165}\text{Ho}^{16}\text{O}$
Re	62.9	187	Internal standard
Pb	23.6	206	
	22.6	207	
	52.3	208	
Bi	100	209	Internal standard
Th	100	232	
U	99.3	238	

Memory effects can occur during ICP-MS analysis and correspond to an enhancement of the signal produced by erosion of elements deposited along the sample path during the analysis of previous samples. We observed significant memory effects for Cu as well as for Zr, Hf, Nb and Ta. These problems are reduced by using a wash-out solution containing 5% HNO_3 and long washing times (150s).

5. Detection and quantification limits, accuracy, precision

It has been shown that ICP-MS has higher sensitivity and lower instrumental detection limits than other rapid multi-element techniques. Following the recommendations of Jarvis (1992), we have distinguished detection limits and lower limits of quantitative analysis. Instrumental detection limits, usually given as 3s on 11 determinations of the signal produced by a blank solution, give estimates of the technical performance of a specific instrument but do not correspond to realistic detection limits for quantitative analysis, as the errors at the level of detection limits are very high. Consequently, the limits of quantitative determination (LOQ) are based on 11 determinations of the signal produced by a "blank reagent" solution (containing LiBO₂, HNO₃, H₂O) and the lower limits of quantification are determined by using ten sigma standard deviation as proposed by the "American Society Committee on Environmental Improvement" (Jarvis, 1992). These limits of quantitative determinations, based on 12 separate runs, are reported in Table 3 (LOQ) and are expressed as concentrations (µg/g) in the solid. These LOQ are similar to those proposed in the literature (Jarvis, 1990).

The accuracy of the method is controlled by comparing our ICP-MS results obtained on the reference material GA with the recommended values of Govindaraju (1995). Results shown in % in Table 3 and Fig. 1 indicate that the accuracy is usually very good except for Lu (34.3%), whose content in GA is close to the LOQ. Analyses of mineral separates (plagioclase, apatite, orthopyroxene) are shown on Fig. 2. In Table 4, the REE content, measured in the international reference material FK-N are presented. FK-N was prepared with an open acid digestion and REE were preconcentrated with the ion-exchange technique (Roelandts & Michel, 1986).

In order to determine the long term precision of the method, the reference materials GA, GS-N, DR-N and

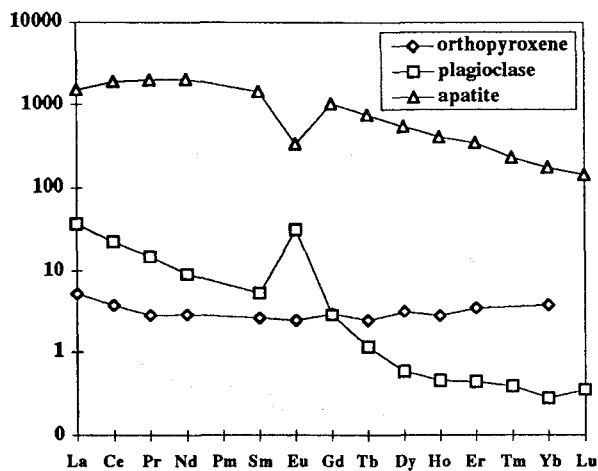


Figure 2. REE patterns normalized to chondrites (Sun & McDonough, 1989) of plagioclase, apatite and orthopyroxene.

Table 3. Accuracy, precision and limits of quantification.

	GA/ICP-MS µg/g n=11 independent analyses (this work)	GA/REC (1) µg/g	+/- CL (2) µg/g	Acc %	LOQ µg/g in solids
Rb	174±3	175	5	0.8	0.32
Sr	308±21	310	12	0.6	1.22
Y	20.2±2.4	21.0	2.0	4.0	0.57
Zr	150±13	150	12	0.2	5.00
Nb	10.7±1.9	12.0	1.6	10.8	1.31
Cs	6.46±0.10	6.00	0.50	7.6	0.15
Ba	846±17	840	22	0.7	3.95
La	40.7±1.2	40.0	3.0	1.7	0.50
Ce	77.4±2.6	76.0	4.0	1.8	0.10
Pr	8.5±0.3	8.30	0.30	2.0	0.07
Nd	28.9±1.3	27.0	3.0	7.1	0.62
Sm	5.37±0.20	5.00	0.50	7.4	0.47
Eu	1.14±0.0	1.08	0.05	5.8	0.09
Gd	3.90±1.0	3.80	0.30	2.7	0.77
Tb	0.62±0.1	0.60	0.10	2.7	0.12
Dy	3.13±0.3	3.30	0.30	5.2	0.18
Ho	0.66±0.1	0.70	0.10	5.7	0.06
Er	1.89±0.1	1.90	0.20	0.7	0.12
Tm	0.31±0.0	0.30	0.04	2.3	0.03
Yb	2.06±0.1	2.00	0.20	3.0	0.12
Lu	0.40±0.2	0.30	0.03	34.3	0.04
Hf	3.82±0.8	4.00	0.30	4.5	0.80
Ta	1.32±0.2	1.30	0.20	1.6	0.15
Pb	31.1±1.7	30.0	3.0	3.6	1.24
Th	17.5±0.8	17.0	1.8	3.2	0.10
U	5.19±0.4	5.00	0.50	3.9	0.22

1. Recommended values from Govindaraju (1995).
2. 95% confidence limits (CL) from Govindaraju (1995).

BE-N have been included in several runs (15). As indicated in Tables 3 & 5, the accuracy and precision obtained on these four distinct compositions are usually very good, especially for the REE. In the case of Sr, Ba and Zr, the precision is not as good as for the other elements. This probably results from a higher background for Sr and Ba and memory effects for Zr.

Table 4. Results obtained for standard FK-N.

	FK-N This work	FK-N (1) Recommended values
La	1.008	1 (0.95 (2))
Ce	1.17	1
Pr	0.099	0.09 (2)
Nd	0.353	0.3
Sm	0.058	0.06 (0.05 (2))
Eu	0.405	0.42 (0.45 (2))
Gd	0.069	0.05 (0.06 (2))
Tb	<0.05	0.01
Dy	0.065	0.06
Ho	<0.05	0.012 (2)
Er	<0.05	0.04
Tm	<0.05	0.006 (2)
Yb	0.052	0.04
Lu	<0.05	0.01 (0.006 (2))

1. Govindaraju & Roelandts (1989).
2. Govindaraju (1995).

Table 5. Results obtained on three international reference materials.

	GS-N		DR-N		BE-N	
	X (1)	REC(2)	X (1)	REC(2)	X (1)	REC(2)
Rb	186±4	185	74±2	73	49±2	47
Sr	576±22	570	397±16	400	1401±72	1370
Y	16.0±1.1	16.0	26±1	26	29±1	30
Zr	218±13	235	132±9	125	262±11	260
Nb	21.9±1.3	21.0	7.2±1.0	7.0	110±7	105
Cs	5.5±0.2	5.4	6.2±0.2	6.3	0.7±0.1	0.8
Ba	1393±22	1400	382±9	385	1037±37	1025
La	71.0±3.1	75.0	21.5±1.0	21.5	82±1	82
Ce	133.5±4.3	135.0	44.8±1.6	46.0	153±3	152
Pr	14.5±0.6	14.5	5.7±0.2	5.7	17.6±0.4	17.5
Nd	48.5±2.2	49.0	23.2±0.6	23.5	67±1	67
Sm	7.3±0.3	7.5	5.2±0.2	5.4	12.1±0.4	12.2
Eu	1.6±0.1	1.7	1.47±0.03	1.45	3.7±0.2	3.6
Gd	4.9±0.3	5.2	4.9±0.2	4.7	9.9±0.5	9.7
Tb	0.60±0.02	0.60	0.8±0.0	0.77	1.28±0.04	1.30
Dy	3.0±0.1	3.1	4.5±0.2	4.6	6.3±0.2	6.4
Ho	0.57±0.03	0.60	0.98±0.04	1.00	1.1±0.1	1.1
Er	1.4±0.1	1.5	2.6±0.1	2.5	2.4±0.1	2.5
Tm	0.22±0.01	0.22	0.38±0.02	0.39	0.33±0.02	0.34
Yb	1.4±0.1	1.4	2.5±0.1	2.5	1.8±0.1	1.8
Lu	0.21±0.03	0.22	0.38±0.02	0.40	0.25±0.03	0.24
Hf	6.2±0.2	6.2	3.4±0.2	3.5	5.8±0.1	5.6
Ta	2.4±0.1	2.6	0.6±0.1	0.6	4.9±1.0	5.7
Pb	56.3±1.2	53.0	54.7±0.9	55.0	4.3±0.4	4
Th	42.1±1.6	41.0	4.7±0.4	5.0	10.9±0.4	10.4
U	7.7±0.4	7.5	1.5±0.1	1.5	2.4±0.2	2.4

1. Average of 15 independent analyses.
2. Govindaraju (1995).

6. Conclusions

A routine method has been developed for simultaneous determination of 26 trace elements by ICP-MS. Application of the method has shown that accuracy is good or excellent for 24 elements. The limits of quantification are much lower (0.03 to 5 µg/g) than those obtained for XRF. A clear advantage of the ICP-MS is that a multi-element data set can be obtained with one single instrument, and ICP-MS also appears as a very good technique for the determination of REE. Moreover, combination of XRF and ICP-MS capabilities enables us to determine 38 elements on a routine basis.

7. Acknowledgements

Acquisition and installation of the ICP-MS was made possible by a FRFC convention (2.4508.91) together with a Lotto grant (9.4808.90).

8. References

- BOLOGNE, G. & DUCHESNE, J. -C., 1991. Analyse des roches silicatées par spectrométrie de fluorescence X: précision et exactitude. *Service Géologique de Belgique, Professional Paper*, 249.
- DUCHESNE, J.-C., 1966. Séparation rapide des minéraux des roches. *Annales de la Société Géologique de Belgique*, 89: 347-356.
- GOVINDARAJU, K. & ROELANDTS, I., 1989. 1988 compilation report on trace elements in six ANRT rock reference samples: diorite DR-N, serpentine UB-N, bauxite BX-N, disthene DT-N, granite GS-N and potash feldspar FK-N. *Geostandards Newsletter*, 13: 5-67.
- GOVINDARAJU, K., 1995. 1995 working values with confidence limits for twenty-six CRPG, ANRT and IWG-GIT geostandards. *Geostandards Newsletter*, 19, Special Issue July: 1-32.
- JARVIS, I., 1992. Sample preparation for ICP-MS. In Jarvis, K., Gray, A. & Houk, R., eds, *Handbook of inductively coupled plasma mass spectrometry*. Blackie, Glasgow, p. 172-224.
- JARVIS, K., 1990. A critical evaluation of two sample preparation techniques for low-level determination of some geologically incompatible elements by inductively coupled plasma-mass spectrometry. *Chemical Geology*, 83: 89-103.
- ROELANDTS, I. & MICHEL, G., 1986. Sequential inductively coupled plasma determination of some rare-earth elements in five French geostandards. *Geostandards Newsletter*, 10: 135-154.
- SUN, S.S. & McDONOUGH, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. In Saunders, A. D., & Norry, M. J., eds, *Magmatism in the ocean basins*. Geological Society Special publication n° 42, Blackwell Scientific Publications, p. 313-345.
- TOTLAND, M., JARVIS, I. & JARVIS, K., 1992. An assessment of dissolution techniques for the analysis of geological samples by plasma spectrometry. *Chemical Geology*, 95: 35-62.

Manuscript received on 05.03.1996 and accepted for publication on 02.02.1997.