

## **Trace element measurements on selected reference materials using HR-ICP-MS after microwave digestion: an application to archaeometric studies**

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**ABSTRACT.** — In order to enhance a fast and reliable routine method of analysis which could be useful in Earth Sciences and Archaeometry purposes, a number of certified international geo-standards available for laboratory measurements of trace element concentrations were investigated by HR-ICP-MS.

In particular, the study has been focused on Rare Earth Elements and other trace elements as Sc, V, Cr, Co, Cu, Th, U, Rb, Sr, Y, Zr, Nb, Ba, Hf, Ta, Pb. The reference materials used on the basis of different rock matrices was andesite (AGV-1), basalt (BHVO-1), basalt (BCR-1), marine mud (MAG-1) and diorite gneiss (SY-4). Elements have been determined at  $\text{ng} \cdot \text{g}^{-1}$  levels by High Resolution Inductively-Coupled Plasma Mass Spectrometry (HR-ICP-MS) after acid decomposition at controlled pressures and temperatures with a microwave device ( $P_{\text{max}}=400\text{psi}$ ;  $T_{\text{max}}=230^\circ\text{C}$ ). The proposal method of sample preparation and multi-elemental measurements revealed its usefulness because: i) it is applicable to different geological matrices; ii) it requires small quantities of powder and iii) provides the reproducibility of measurements which are fast and precise in a wide range of elements by combining a single internal standard (e.g. rhodium) and an external calibration.

Moreover, the high dilution factors applied on the

samples ( $\geq 20000$ ) and an accurate instrumental optimization permitted to overcome several problems due to the occurrence of both spectroscopic and not-spectroscopic interferences which negatively affect the quality of measurements.

The proposed methodology finds noteworthy applications when the samples to be analysed are archaeological artefacts. For this reason, we tested its applicability in the geochemical characterization and determination of provenance of some granitoid rocks from the Roman Theatre in Catania (Italy).

**RIASSUNTO.** — Allo scopo di mettere a punto un metodo di preparazione e determinazione degli elementi in traccia di matrici geologiche che possa essere al contempo rapido ed affidabile per applicazioni nel campo delle Scienze Geologiche ed Archeometriche, sono stati investigati alcuni standard internazionali mediante HR-ICP-MS (High Resolution-Inductively Coupled Plasma – Mass Spectrometry). I materiali di riferimento certificati utilizzati per le indagini sono: AGV-1 (andesite), BHVO-1 e BCR-1 (basalti), MAG-1 (pelagite) e SY-4 (gneiss dioritico). In particolare, lo studio è stato focalizzato sulle Terre Rare (REE) e su altri elementi in traccia quali Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Hf, Ta, determinati in concentrazioni di  $\text{ng} \cdot \text{g}^{-1}$ , dopo avere sottoposto i campioni a mineralizzazione acida in forno a microonde a pressioni e temperature controllate ( $P_{\text{max}}=400\text{psi}$ ;  $T_{\text{max}}=230^\circ\text{C}$ ).

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Il metodo di dissoluzione e di analisi multi-elementale proposto nel presente lavoro è risultato efficace per i seguenti motivi; i) è applicabile in modo flessibile a diverse matrici geologiche; ii) richiede piccole quantità di campione; iii) garantisce la *riproducibilità* di misure veloci ed al contempo precise di un ampio range di elementi permettendo di combinare un singolo standard interno (rodio) ed una calibrazione esterna (utilizzando materiali di riferimento certificati).

Gli elevati fattori di diluizione dei campioni ( $\geq 20000$ ), insieme ad un'accurata ottimizzazione dei parametri strumentali hanno inoltre permesso di superare i problemi dovuti alle interferenze – spettroscopiche e non spettroscopiche – che possono compromettere la qualità delle misure effettuate sugli isotopi di interesse.

Il metodo proposto trova immediata applicazione in campo archeometrico: nel presente lavoro se ne riporta, come esempio, lo studio di un gruppo di rocce granitoidi provenienti dal Teatro Romano di Catania, la cui caratterizzazione geochemica dettagliata ha fornito indicazioni utili per la determinazione della provenienza.

**KEY WORDS:** *HR-ICP-MS, geological matrices, geochemical characterisation, Archaeometric purposes.*

## INTRODUCTION

As it is well known, elemental chemical investigation is key-tool for the study of the geological materials used in Archaeometry. Over the last years, various approaches have been developed in order to minimize the disturbance on the monument investigated, such as non destructive trace elements characterization of ancient artefacts which employs either XRF spectrometry (Sciuti, 1988; Longoni *et al.*, 1998) or PIXE analysis (Peisach *et al.*, 1991; Jacobson *et al.*, 1991). Even though they are useful and extremely important for Archaeological applications, limitations concerning the above methods are due to the restricted mass range to be investigated.

For this reason, by taking into account the difficulty to recover large amounts of samples from the monument, several instrumental

methods of analysis used for geological purposes have been developed in order to characterize and eventually determinate the provenance of the lithoid materials used for the historical buildings.

In our study, we pointed out the use of HR-ICP-MS for the trace element characterisation, because very small amounts of sample are required and therefore this methodology avoids severe disturbance on the monument. Moreover, the wide mass range of analytes investigable (5-260 a.m.u.) and the detection limits which are about three orders of magnitude lower than PIXE or XRF, make it appropriate for the elemental determination in studies concerning the characterisation and the provenance of archaeological artefacts (Pillay, 2001). For this reason, we employed HR-ICP-MS for performing a fast and reliable routine multi-elemental method of analyses useful for Archaeometrical purposes and Earth Sciences. We paid attention on: 1) reproducibility of measurements in a wide mass range of elements which are of interest in geological and archaeometrical sciences; 2) performing a somehow flexible method in the sample preparation; 3) the possibility of combining a single Internal standard (e.g. Rhodium) and an external calibration (using certified reference materials) for relatively fast and precise measurements of the elements of interest. For this purpose, four U.S.G.S. (United States Geological Survey) reference materials with various trace elements compositions (see Govindaraju, 1994) and one C.C.R.M.P. (Canadian Certified Reference Materials Projects) reference material (Bowman, 1995; [Http://w.w.w.nrcan.gc.ca:80/mms/canmet-mtb/ccrmp.htm](http://w.w.w.nrcan.gc.ca:80/mms/canmet-mtb/ccrmp.htm)) were used.

Moreover, in order to test the applicability of the method here proposed, we also investigated some specimens of granitoid rocks from the Roman Theatre in Catania (Italy), which were previously characterised with different procedures (Corsaro *et al.*, 2000), and compared the geochemical results obtained.

## EXPERIMENTAL

*Sample preparation*

As it is known, an important factor when dissolving geological samples is the nature of the material (Yu *et al.*, 2000; Eggins *et al.*, 1997). In order to achieve complete dissolution, a number of acids and salts was chosen for sample decomposition. All the reactants are by Merck® «Suprapure» quality: Sulphuric acid (86% v/v), Hydrochloric acid (37% v/v), Nitric acid (65% v/v), Phosphoric Acid (85% v/v) and ammonium fluoride. For a detailed discussion of the properties of the reactants used see also Jarvis, 1992.

Water was prepared after bidistilled water with a Millipore® MilliQ apparatus (18.2 Mohm cm<sup>-1</sup>). The wash solution was prepared at 2% (v/v) HNO<sub>3</sub>; the blank as well as the rock samples were prepared at 5% (v/v) HNO<sub>3</sub>.

The high pressure digestion device is a Mars5 microwave oven apparatus (CEM Technologies). Twelve samples can be digested per run. The instrument is provided with pressure (P<sub>max</sub>=800psi) and temperature (T<sub>max</sub>=240°C) controller. The microwave digestion procedure offers the advantages of relatively quick digestion and complete dissolution of refractory minerals.

The procedure steps were:

- Powdered sample (50 mg) was weighed with a 0.01mg analytical balance and put into a tetrafluormethaxyl (TFM) digestion container.

- NH<sub>4</sub>F (500 mg) was added; afterwards, the above mentioned acids were added to the proportions HCl:HNO<sub>3</sub>:H<sub>2</sub>SO<sub>4</sub>:H<sub>3</sub>PO<sub>4</sub> = 2:2:1:1 (total volume = 12 ml).

- The containers were accurately sealed, put into the carousel and heated with 100% power (1200 watt), with a P ramp of 30°, and then maintained at stable P and T conditions (T = 230°C; P = 400psi) for two hours with 50% power.

- After this period, vials were opened and evaporated to incipient dryness. Acid fumes were aspirated by a vacuum pump and neutralised with a strong alkaline solution.

- The solutions were left to warm down for about two hours.

- The sample solutions were diluted to 100 ml with Millipore® water («mother solution») and transferred into clean 100ml polycarbonate bottles.

- Prior to HR-ICP-MS analyses, we prepared for each sample several solutions at various dilution rates by adding 0.1, 0.2, 0.5, 1 ml of «mother solution» to 0.1ml Rhodium solution (obtained from a 10mg g<sup>-1</sup> Merck single element grade solution to a final concentration of 1ng g<sup>-1</sup>). The solutions obtained were diluted to 10 ml total volume at 5% (v/v) HNO<sub>3</sub>. These final solutions were used for both the external calibration curves and for investigation as «unknown» samples.

- In order to minimise any contamination during sample preparation, TFM digestion containers after each run were accurately rinsed with 2% (v/v) HNO<sub>3</sub> water solution for at least 24 hours and subsequently rinsed with Millipore water. Plastic containers, pipette tips, inlet tubes were rinsed with 5% (v/v) HNO<sub>3</sub> solution at room temperature for at least 24h.

The operations concerning both drying of the tools and dilutions of the solutions were carried out under clean air conditions thanks to a flow laminar bench.

The time duration of the acid attack was chosen by carrying out more digestions on each geo-standard and measuring the solutions obtained in 5 replicates.

Firstly, we applied 1 hour dissolution time at P<sub>max</sub>=400psi and T<sub>max</sub>=230°C operational conditions after a ramp of 30°. Results showed that all the analytes were satisfactory recovered in the geo-standards studied with the exception of diorite gneiss SY-4, (see SY-4\*; Table 1). This incomplete dissolution may be explained with the fact that it may contain some mineral phases which are acid resistant. For this reason, we prepared two other mother solutions SY-4\*\* and SY-4\*\*\*, by increasing the acid attack duration by 30' and 60' respectively. These latter showed that a complete sample dissolution occur only in the SY-4\*\*\* mother solution.

TABLE 1

Trace element concentrations in geo-standard SY-4 (diorite gneiss). Values expressed in mg g<sup>-1</sup>.

Stars \*, \*\*, \*\*\* mean measurements on three different «mother solutions»

after 1<sup>h</sup>30', 2<sup>h</sup> and 2<sup>h</sup>30' time of acid attack respectively. Nd = not detected.

$\Delta\% = (\text{observed-reference}) * 100 / \text{reference}$ . Reference values after Bowman (1995).

For further explanations see the text.

	SY-4 *	$\Delta\%*$	SY-4 **	$\Delta\%**$	SY-4 ***	$\Delta\%***$	Sy-4 ref
Rb	47.68	13.31	52.55	4.45	54.25	1.36	55.00
Sr	1198	0.59	1204.20	1.11	1203.8	1.07	1191
Y	108.08	9.18	117.08	1.61	117.10	1.60	119.00
Nb	8.36	35.70	8.61	33.79	12.51	3.78	13.00
Ba	67.99	80.00	341.50	0.44	362.37	6.58	340.00
Th	1.22	13.20	1.39	0.95	1.49	6.20	1.40
U	0.61	23.16	0.80	0.07	0.81	1.86	0.80
V	3.40	57.56	5.29	33.86	7.38	7.79	8.00
Cr	5.39	55.08	8.59	28.44	13.51	12.58	12.00
Co	1.29	53.91	1.76	37.24	2.37	15.25	2.80
Zr	451	12.77	470.3	9.03	516.74	0.05	517
Sc	0.83	24.62	1.06	3.83	0.94	14.22	1.10
Ta	nd		nd		0.92	2.22	0.9
Hf	8.28	21.89	8.82	16.79	10.17	4.06	10.6
La	54.14	6.66	55.88	3.65	57.23	1.33	58.00
Ce	108.85	10.78	116.13	4.81	119.03	2.44	122.00
Pr	8.37	44.21	14.75	1.64	14.75	1.64	15.00
Nd	52.69	7.55	54.68	4.07	57.17	0.30	57.00
Sm	8.07	36.45	8.78	30.90	13.15	3.56	12.70
Eu	1.10	44.90	1.34	32.99	1.99	0.64	2.00
Gd	8.14	41.85	14.44	3.13	13.41	4.22	14.00
Tb	1.52	41.58	1.78	31.65	2.34	9.83	2.60
Dy	15.57	14.46	18.28	0.46	18.03	0.95	18.20
Ho	2.48	42.28	3.01	30.04	4.16	3.25	4.30
Er	7.08	50.15	9.65	32.04	13.61	4.16	14.20
Tm	1.76	23.60	1.62	29.64	2.30	0.07	2.30
Yb	8.93	39.70	14.57	1.57	14.10	4.76	14.80
Lu	1.16	44.69	1.43	31.92	1.99	5.37	2.10
Pb	8.38	16.21	15.43	54.25	7.52	24.80	10.00

As far as REE, they show to be all completely recovered when the longest time of acid dissolution was applied. As it is known, only a part of the REE content of gneiss-type rocks is present in the major mineral phases (Andeltorn *et al.*, 1980), whereas the remains part is accommodated into the accessory minerals such as monazite, sphene, zircon and apatite. In particular, monazite is LREE enriched, zircon contain HREE and apatite is

enriched in MREE (Jain *et al.*, 2001; Middelburg *et al.*, 1988).

As the latter digestion procedure permitted the most satisfactory recovery of the analytes of interest, all of the «mother solutions» were prepared by applying a 2<sup>h</sup> 30' total time of acid attack.

In addition, in order to enhance the quality and the repeatability of the method, more digestions were carried out on each geo-

standard and measurements on each sample solution were variously replicated.

#### *HR-ICP-MS instrumentation and analysis*

The instrument here used is a magnetic sector HR-ICP mass spectrometer (ThermoFinniganMAT «Element 2», Germany), which employs a double focusing mass analyser with reverse Nier-Johnson geometry. The mass range is between 5 and 260 *atomic mass units* a.m.u. These instruments present characteristics such as high sensitivity and low background signals (Cf. Moens *et al.*, 1995) which find worthy applications in the determination of trace and ultra-trace elements, since they provide reliable analytical results at relatively low concentration levels (about  $\text{ng g}^{-1}$ : Cf. Axelsson *et al.*, 2002 and therein references).

It is possible to set three different resolutions  $R$  ( $R = m/\Delta m$  at 10% valley definition of the peak): low ( $R=300$ ); medium ( $R=4000$ ) and high ( $R=10000$ ) respectively.

The instrument signal intensity (in *counts per second*, cps) drops by a factor ten when changing from low to medium resolution, and by a further factor of ten to high resolution.

One of the compromising factors respect to the high quality analyses to be carried out, is the variation in instrument sensitivity meanwhile an analytical sequence is run and the introduction of different sample matrices. Accurate data can be obtained only if these effects can be monitored, minimised and eventually corrected.

The operational parameters such as lens voltages, argon flow rate, forward and reflected power of the generator have been accurately optimised since they affect the ion intensity and therefore the quality of measurements. The instrument settings used in this study are outlined in Table 2. The daily tuning and mass calibration check of the instrument permitted to optimise the performance; a  $1\text{ ng g}^{-1}$  tuning solution was home-made with Merck single element grade solutions by following the

TABLE 2  
*Operational parameters used for ICP-MS routine measurements.*

Parameter	Value
Resolutions ( $m/\Delta m$ )	Low= 300; Medium=4000;High=10000
RF Power	1090 W
Reflected Power	< 3W
Cool argon flow rate	14.55 L/min
Auxiliary argon flow rate	1.06 L/min
Sample argon flow rate	1.076 L/min (daily optimized)
Extraction lens	-2000 V
Focus lens	-860 V (daily optimized)
Spray chamber	Scott -type (double pass)
Cones	Ni sampler (1mm orifice) and skimmer (0.8 mm orifice)
Sample uptake	Pumping via a peristaltic pump
Sample introduction	Automated via a Cetac Technologies Autosampler
Detector	S.E.M. operating in analog and counting mode
Instrument tuning	Performed daily using a $1\text{ ng/mg}$ multi-element solution
Sensitivity	$1.4 \times 10^6$ with $^{115}\text{In}$ and $2.3 \times 10^6$ with $^{238}\text{U}$
Scan type	Magnet jumping with electric scan over a small mass range
Ion lens setting	Optimized in order to obtain maximum signal sensitivity and resolution of peaks

element set suggested by the constructor factory. For further details concerning the instrument see also Robinson *et al.*, 1999 and therein references. In performing the measurements the plasma operated at relatively low power (1000-1090 watts), as optimised working conditions: this enhanced the suppression of polyatomic species which would give rise to not negligible interferences whose amount is positively related to the forward power and which are one of the most severe problems concerning ICP-MS (Tanner, 1995; Houck and Praphairaksit, 1995). In addition, the «Mass Offset» option offered by the constructor factory was applied.

Prior to sample analyses, the instrument was purged with a 2% (v/v) HNO<sub>3</sub> wash solution for about two hours. During each run, sufficient wash time was given in order to achieve adequate blank levels; moreover, the mass calibration, as well as the sensitivity, were monitored and maintained as stable as possible. The total time of each analysis is around eight minutes.

As a rule, we tried to take great accuracy in cleaning the sampler and skimmer cones, torch, injector, spray chamber, nebulizer and sample introduction tubes (including auto-sampler tubing), the latter being periodically replaced. We also monitored any sample contamination by measuring in each sequence the blank solution as unknown.

Detection Limits were calculated as  $3\sigma$  ( $\sigma$  = standard deviation) of ten blank samples measured as unknown and periodically (every two-three months) checked. The reported limits (Table 3) were calculated as three times the standard deviation of 10 blank measurements.

#### ISOTOPES, INTERFERENCES AND RESOLUTION

Prior to analyses of the international geo-standards, several measurements have been carried out with Merck standard solutions. This in order to test the best resolution for each isotope by considering the occurring significant interferences. This was an important step before measurements on rock samples since we

TABLE 3  
*Isotope analysed, Detection Limits (DL) and resolutions. Detection Limits calculated as three times the standard deviation of 10 blanks measured.*

Element	Mass number	DL (ng g <sup>-1</sup> )	Resolution
Y	89	1.09	Low
Nb	93	0.15	Low
La	139	1.2	Low
Ce	140	0.73	Low
Pr	141	0.39	Low
Nd	146	8.12	Low
Sm	147	0.075	Low
Th	232	0.11	Low
U	238	0.74	Low
Sc	45	0.68	Medium
V	51	0.62	Medium
Co	59	0.68	Medium
Rb	85	0.17	Medium
Zr	90	4.57	Medium
Cr	52	2.12	High
Sr	88	22.64	High
Ba	137	2.29	High
Eu	151	0.13	High
Gd	157	0.75	High
Tb	159	0.02	High
Dy	163	0.04	High
Ho	165	0.1	High
Er	166	0.1	High
Tm	169	0.16	High
Yb	172	0.03	High
Lu	175	0.04	High
Hf	178	0.38	High
Ta	181	0.72	High

took into account the occurrence of spectroscopic interferences (e.g. isobaric overlap, polyatomic species). In general, since the most serious interferences are due to the formation of polyatomic species between the most abundant isotopes of H, C, N, O, S, Cl and Ar, we considered the most probable interfering peaks (Jarvis, 1992) and optimised the instrument setting in order to reduce their effects. This led in most cases to a good separation of peaks. As far as REE are concerned, we considered that Ba and LREE

oxides and hydroxides interfere on HREE (Dulski, 1994; Balaram, 1996) and separated, for example,  $^{151}\text{Eu}$  from  $^{135}\text{Ba}^{16}\text{O}$ ,  $^{157}\text{Gd}$  from  $^{141}\text{Pr}^{16}\text{O}$ ,  $^{163}\text{Dy}$  from  $^{147}\text{Sm}^{16}\text{O}$  and  $^{159}\text{Tb}$  from  $^{143}\text{Nd}^{16}\text{O}$  by choosing for these elements the highest resolution ( $R=10000$ ).  $^{52}\text{Cr}$  was also separated from  $^{40}\text{Ar}^{12}\text{C}$  at high resolution, since chromium is severely disturbed in aqueous solutions (Field *et al.*, 1999; Barbante *et al.*, 1999; Riondato *et al.*, 2000), whereas for the other first series transition metals we chose the medium resolution setting ( $R=4000$ ; Tab. 3).

As far as non-spectroscopic interferences are concerned, we focused our interest in order to minimise the so-called «matrix effect» which is due to the high concentrations of Al, Fe, Ca and Mg within the rock solution: these elements cause a decrease in response for trace elements and sometimes make the ICP-MS orifice plugged. Several methods have been developed in order to measure and quantify the matrix effects which causes poorer precision and memory effects (Makishima and Nakamura, 1997; Jarvis, 1992).

We weighed for the acid attack very small quantities of powder (50mg), and therefore applied an average dilution factor of 20,000, since after prepared the «mother solution» we prepared the solutions to be put into the device for measurements by diluting at least by a further factor ten. The dilution of the matrix together with the optimisation of the operational parameters permitted to detect in a satisfactory way the analytes of interest, even at the highest resolution setting.

#### *Internal standard*

As previously noted, we used  $^{103}\text{Rh}$  as internal standard, by adding it to blank, standards for external calibration and «unknown» solutions at  $1\text{ng g}^{-1}$  concentration. This element was preferred to others because of it is mono-isotopic, occurs at very low concentrations in our sample types, is almost 100% ionised ( $\sim 93.8\%$ ), it is not affected by isobaric overlap and its ionisation energy is very similar to the ionisation energy of our

analytes. Moreover, since  $^{103}\text{Rh}$  lies in the central part of the mass range measured, it was allowed to use just one internal standard despite more ones ranging from low to high masses. In this way, the intensities of the elements measured at low, medium and high resolution are corrected for sensitivity.

Finally, the use of rhodium as internal standard permitted us to monitor and eventually to correct the sensitivity variations occurring during the course of an analytical run («instrumental drift») and eventual matrix effects.

#### *External calibration*

Starting from the mother solution obtained for each international geo-standard, the calibration curve was performed by using solutions (prepared with 5% v/v  $\text{HNO}_3$ ) at different dilution rates. In addition, each sequence prepared for this aim included one or two analyses of international geo-standards were analysed as unknown. In performing the calibration curve, we imposed a linear regression through the origin following blank subtraction. The linearity of response resulted to be fairly good as it may be observed from some calibration curves (see Fig. 1).

## RESULTS AND DISCUSSION

Results concerning standards AGV-1, BHVO-1, BCR-1, MAG-1 AND SY-4 are set out on Table 4.

On Fig. 2, the ratios of measured/literature values (Govindaraju, 1994; Bowman, 1995) for the elements of interest are reported. It may be noted, for the different matrices, a fairly good reliability and ratio values next to one, which are indicative of a satisfactory recovery of the analytes of interest. Some analytes exhibit different values from literature: it is evident just for Sr and Tm in standard AGV-1. The over-estimation of Tm with respect to literature data, may be due to: 1) published data are affected by incomplete acid attack in MAG-1; 2) incomparable

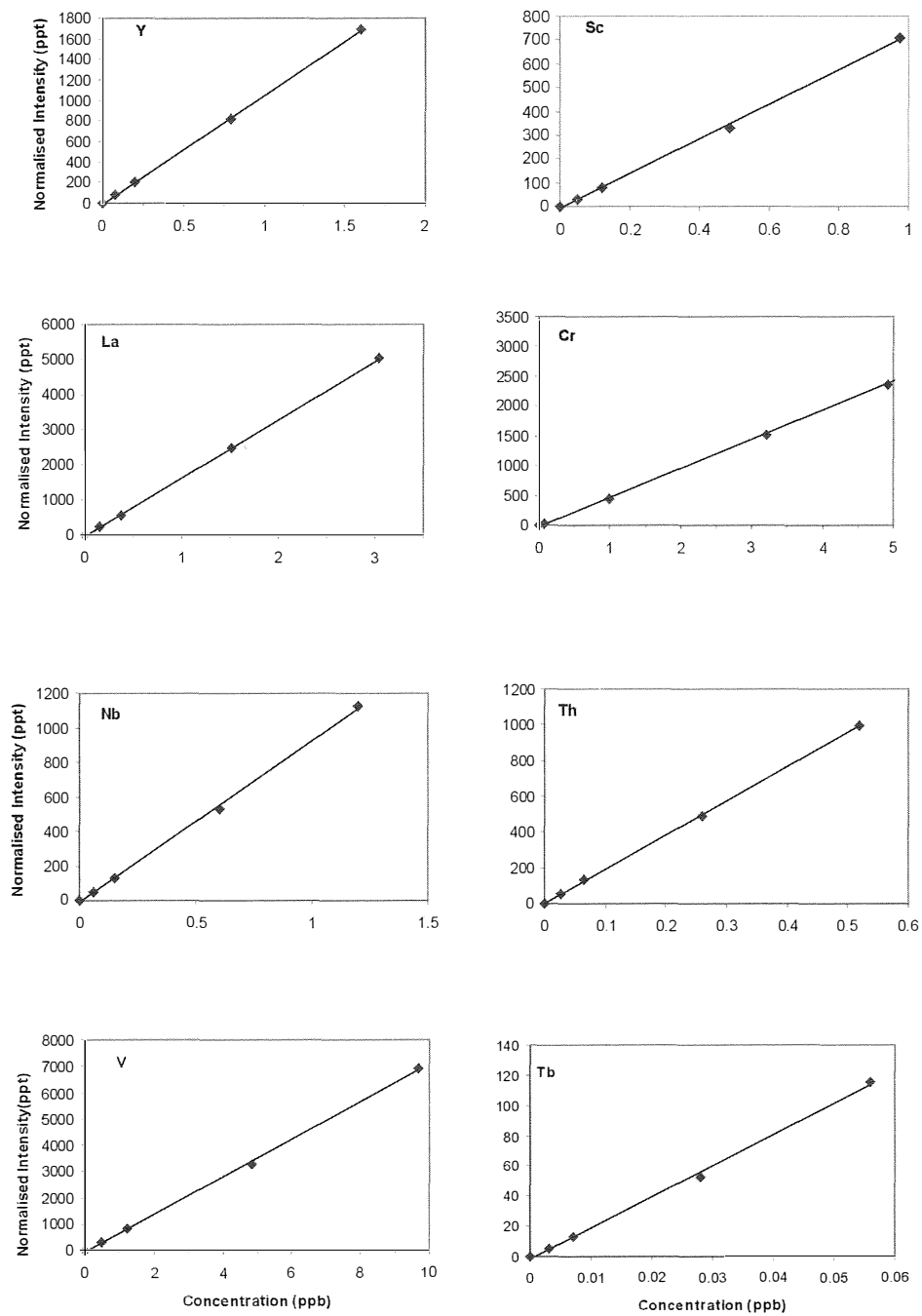


Fig. 1 – Calibration curves of some analytes measured.



TABLE 4

Trace elements concentrations in AGV-1, BCR-1, BHVO-1, MAG-1, SY-4 («Mean»: this work) and comparison with literature data. Govindaraju (1994): «REF(a)»; Bowman (1995): «REF(b). Values expressed in mg g<sup>-1</sup>. n=number of measurements; na= number of independent acid attacks.

AGV-1	Mean	STD	RSD%	REF(a)	BHVO-1	Mean	STD	RSD%	REF(a)
	n=20	na=2				n=15	na=2		
Rb	66.7	4.08	6.0	67.3	Rb	10.96	0.98	8.0	11
Sr	446.04	34.01	7.6	662	Sr	376.44	29.83	7.9	403
Y	20.06	0.32	1.5	20	Y	25.85	1.71	6.6	27.6
Nb	14.95	0.50	3.3	15	Nb	17.12	1.47	8.6	19
Ba	1129	56	4.4	1226	Ba	130.33	10.74	8.2	139
Th	6.89	0.35	4.4	6.5	Th	1.07	0.06	6.0	1.08
U	2.22	0.09	4.1	1.92	U	0.42	0.08	19.0	0.42
V	120.69	4.28	3.6	121	V	306	20.02	6.5	317
Cr	10.87	3.31	30.4	10.1	Cr	264.76	34.74	13.1	289
Co	15.75	0.53	3.2	15.3	Co	43.69	1.60	3.8	45
Cu	60.75	3.87	6.6	60	Cu	139	18	12.0	136
Zr	185.05	9.05	4.9	227	Zr	181.43	24.20	13.3	179
Sc	11.85	0.81	6.7	12.2	Sc	30.75	2.01	6.5	31.8
La	38.33	1.83	4.7	38	La	16.31	0.80	4.9	15.8
Ce	66.05	3.19	4.8	67	Ce	37.62	2.49	6.8	39
Pr	7.92	0.18	2.5	7.6	Pr	5.52	0.62	11.1	5.7
Nd	32.74	2.51	7.6	33	Nd	24.43	1.06	4.3	25.2
Sm	6.2	0.23	3.2	5.9	Sm	6.20	0.31	4.8	6.2
Eu	1.67	0.23	6.0	1.64	Eu	2.01	0.07	3.5	2.06
Gd	5.06	0.14	2.4	5	Gd	6.46	0.39	6.1	6.4
Tb	0.68	0.12	14.7	0.7	Tb	0.98	0.13	13.2	0.96
Dy	3.64	0.09	2.7	3.6	Dy	5.18	0.30	6.4	5.2
Ho	0.69	0.11	14.6	0.67	Ho	1.03	0.09	8.7	0.99
Er	1.82	0.09	5.0	1.7	Er	2.49	0.20	9.3	2.4
Tm	0.51	0.01	2.2	0.34	Tm	0.36	0.04	11.4	0.33
Yb	1.81	0.06	3.3	1.72	Yb	1.97	0.10	5.0	2.02
Lu	0.31	0.01	3.9	0.27	Lu	0.28	0.00	1.6	0.291
Pb	44.93	17.04	37.8	36					

TABLE 4: *Continued*

BCR-1	Mean	STD	RSD%	REF(a)	MAG_1	Mean	STD	RSD%	REF(a)
	n=14	na=3				n=14	na=2		
Rb	47.12	4.87	10.4	47.20	Rb	160.1	27.7	17.3	149
Sr	334.81	33.01	10.4	330.00	Sr	164.8	39.2	23.7	146
Y	39.37	0.88	2.2	38.00	Y	30.4	2.5	8.2	28
Nb	13.31	1.50	11.3	14.00	Nb	12.5	0.8	6.4	12
Ba	671.09	14.78	2.2	681.00	Ba	492.19	89.21	18.1	479
Th	5.59	0.61	11.0	5.98	Th	12.3	1.89	15.4	11.9
U	1.75	0.21	12.0	1.75	U	2.69	0.24	8.9	2.7
V	402	15.76	3.9	407.00	V	143	13.3	9.2	140
Cr	14.65	1.57	10.7	16.00	Cr	95.13	3.39	3.6	97
Co	35.27	1.49	4.2	37.00	Co	21.56	2.49	11.5	20.4
Cu	13.92	4.30	30.8	19.00	Cu	30.22	4.90	16.2	30
Zr	207.1	51.0	24.6	190.00	Zr	113.2	6.1	5.4	126
Sc	30.2	2.6	8.6	32.60	Sc	15.5	3.0	2.5	17.2
La	26.3	1.3	4.9	24.90	La	45.69	2.68	5.9	43
Ce	55.06	2.93	5.3	53.70	Ce	89.48	8.54	9.5	88
Pr	6.10	0.68	11.4	6.80	Pr	9.16	0.87	9.5	9.3
Nd	27.8	3.2	10.7	28.80	Nd	38.7	1.1	2.9	38
Sm	6.41	0.30	4.6	6.59	Sm	7.35	0.58	7.9	7.5
Eu	1.60	0.11	6.0	1.95	Eu	1.71	0.13	7.6	1.55
Gd	6.36	0.42	6.3	6.68	Gd	6.06	0.77	12.7	5.8
Tb	1.14	0.12	1.9	1.05	Tb	1.03	0.11	10.6	0.96
Dy	6.19	0.40	6.5	6.34	Dy	5.31	0.56	10.5	5.2
Ho	1.28	0.09	6.9	1.26	Ho	1.09	0.07	6.4	1.02
Er	3.54	0.25	7.2	3.63	Er	2.81	0.29	10.3	3
Tm	0.58	0.05	7.9	0.56	Tm	0.49	0.05	10.2	0.43
Yb	3.39	0.17	5.3	3.38	Yb	2.48	0.12	4.8	2.6
Lu	0.49	0.02	4.4	0.51	Lu	0.37	0.05	13.5	0.4
Pb	15.49	1.91	12.3	13.6	Pb	25.13	4.08	16.2	24

TABLE 4: *Continued*

SY-4	Mean	STD	RSD%	REF(b)
	n=18	na=2		
Rb	52.85	3.4	6.4	55
Sr	1203.8	6.8	0.56	1191
Y	116.97	3.4	2.9	119
Nb	13.05	0.92	7	13
Ba	336.18	8.9	2.6	340
Th	1.37	0.08	5.8	1.4
U	0.74	0.1	13.5	0.8
V	8.26	1.17	14.1	8
Cr	10.48	1.8	17	12
Co	2.57	0.4	15.5	2.8
Zr	557.21	76.6	13.7	517
Sc	1.099	0.11	10	1.1
Ta	0.93	0.07	7.5	0.9
Hf	10.2	0.4	3.9	10.6
La	56.76	1.6	2.8	58
Ce	119.1	5.05	4.2	122
Pr	14.68	0.6	4.1	15
Nd	56.99	2.16	3.7	57
Sm	12.70	0.6	4.7	12.7
Eu	1.94	0.12	6.2	2
Gd	14.06	0.6	4.3	14
Tb	2.60	0.28	10.7	2.6
Dy	18.58	0.9	4.8	18.2
Ho	4.46	0.12	2.7	4.3
Er	14.5	0.8	5.5	14.2
Tm	2.18	0.6	27.5	2.3
Yb	14.12	3.8	26.9	14.8
Lu	2.14	0.07	3.2	2.1
Pb	10.6	3.2	30.1	10

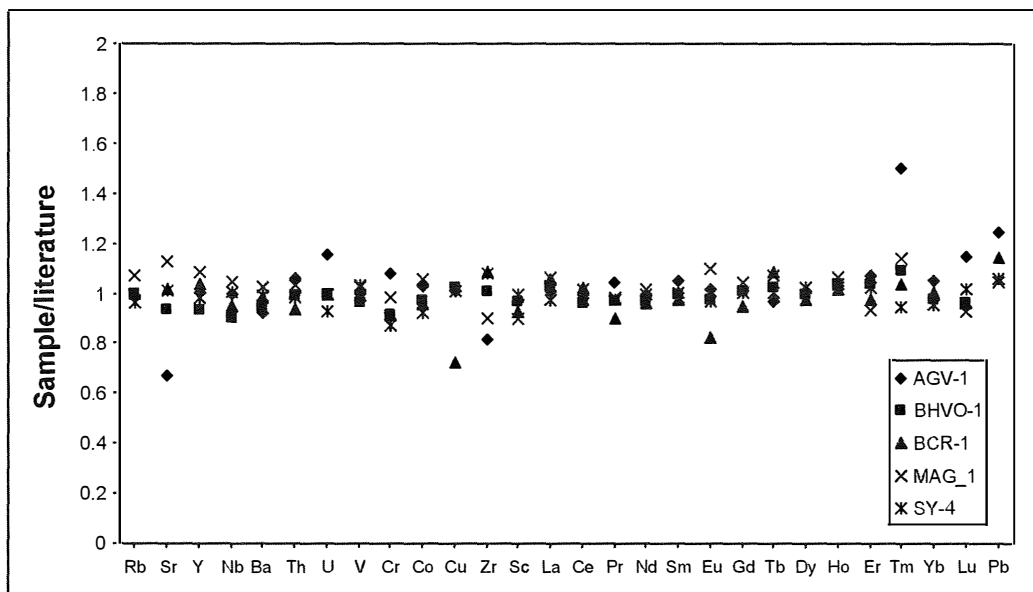


Fig. 2 – Sample/compiled value ratios of the geo-standards investigated. AGV-1, BCR-1, BHVO-1, MAG-1 reference values after Govindaraju (1994). SY-4 reference values after Bowman (1995).

calibration curves; or 3) unknown causes. Points 2) and 3) may be applied to Sr underestimation as well.

As far as Pb is concerned, some unsatisfactory values detected occurring are explained with the use of tools which are resistant to acid attack, responsible of poor reliability in such measurements (MCGinnis *et al.*, 1997).

#### APPLICABILITY OF THE METHOD

In order to show the applicability and to validate the proposed method, we analysed some granitoid rock samples used as building stones for the Roman Theatre in Catania (Italy). The specimens (TR1, TR3, TR8, TR9, TR12, TR13), come from the pavement of the «orchestra» and were previously characterised under a petrographic and geochemical point of view (Corsaro *et al.*, 2000). They are medium-to fine-grained, with mafic enclaves and, according to the normative diagram after

Streckeisen and Le Maitre (1979), they plot within the field of granodiorites. The texture is hypidiomorphic and equigranular. The main minerals occurring are plagioclase, K-feldspar, quartz, amphibole and biotite. Sphene, zircon, apatite and opaque minerals are the main accessory minerals.

Moreover, the geochemical features (major and minor element contents) of such rocks make them to be ascribed to the so-called «Mysian Marble», one of the most important granitoids to be employed in antiquity, extracted in a small quarry near Kozak, western Turkey (Corsaro *et al.*, cit op.)

We digested and analysed the same rock powders which were previously prepared with different procedures and investigated by ICP-MS at the ACTlabs laboratory (Canada): part of such data are unpublished (Prof. Pezzino, *personal communication*; 2002).

The comparison between data from ACTlabs and data from our laboratory is fairly good (Table 5). Exception is given by some U,

TABLE 5

Trace element concentrations of the granitoid rocks from the Roman Theatre in Catania (Italy). (A) = this work; (B) = values after published (*Italic font*) and unpublished data on the same specimens. For further explanations see the text.

(A)								(B)							
	TR1	TR 2	TR 3	TR 8	TR 9	TR 12	TR 13		TR1	TR 2	TR 3	TR 8	TR 9	TR 12	TR 13
V	64.55	72.86	68.62	75.03	81.21	84.33	77.63	V	78	84	86	88	90	100	90
Sr	618	617	682	612	714	626	676	Sr	<i>626</i>	<i>617</i>	<i>664</i>	<i>608</i>	<i>641</i>	<i>569</i>	<i>625</i>
Y	24.73	20.05	22.16	25.69	29.03	29.15	26.74	Y	<i>19.4</i>	<i>21.1</i>	<i>19.5</i>	<i>20.9</i>	<i>22.1</i>	<i>24.8</i>	<i>22.7</i>
Nb	8.69	9.47	10.12	11.44	13.01	14.68	12.01	Nb	9.4	10.5	9.4	9.3	10.1	11.3	10.5
Th	23.45	13.43	17.85	20.6	19.7	26.66	36.32	Th	22	15	20.9	26.8	18.6	24	29.4
U	4.69	3.34	5.09	3.2	6.27	5.11	6.16	U	4.12	2.57	3.27	4.3	4.37	3.93	3.82
Co	10.2	11.19	13.02	12.68	16.15	13.13	12.57	Co	7	9	9	8	9	9	10
Sc	10.53	10.62	10.81	12.46	13.52	12.95	12.1	Sc	10	11	11	11	11	11	11
Cr	11.51	25.41	16.52	18.74	25.48	18.91	9.64	Cr	-20	21	28	-20	21	30	22
Rb	125	116	122	118	115	114	120	Rb	<i>125</i>	<i>116</i>	<i>123</i>	<i>117</i>	<i>116</i>	<i>116</i>	<i>117</i>
Ba	1305	1234	1288	1252	1277	1190	1265	Ba	<i>1350</i>	<i>1240</i>	<i>1430</i>	<i>1240</i>	<i>1380</i>	<i>1170</i>	<i>1330</i>
Zr	160	228	144	171	197	181	219	Zr	<i>159</i>	<i>234</i>	<i>147</i>	<i>170</i>	<i>193</i>	<i>179</i>	<i>213</i>
Pb	10.46	4.02	14.2	18.1	18.45	38.37	13.64	Pb	30	19	19	64	29	111	35
Hf	3.16	3.13	3.91	3.02	2.76	4.25	3.46	Hf	4.3	6.1	3.9	4.8	5.1	4.7	5.4
Ta	0.82	0.96	0.92	1.23	1.31	1.75	1.38	Ta	0.9	1.1	0.9	1	1	1.3	1
La	57.11	26.54	44.49	49.08	51.97	57.4	62.32	La	48.4	49	50	53.9	43.4	55.6	56.7
Ce	87.69	58.03	99.55	89.68	95.69	109.69	110.13	Ce	86.8	90.5	88.5	97.2	81	103	101
Pr	8.51	4.99	7.8	10.01	11.16	12.17	12.12	Pr	9.48	9.71	9.53	10.5	9.38	11.4	11
Nd	30.16	19.89	26.87	36.38	40.79	42.91	42.14	Nd	35.7	36	35.5	38.9	35.9	40.6	41.5
Sm	5.44	4.31	4.9	6.57	7.71	7.65	7.17	Sm	6.03	6.25	5.87	6.73	6.32	6.83	6.95
Eu	1.24	0.98	1.23	1.35	1.66	1.44	1.43	Eu	1.37	1.39	1.32	1.47	1.37	1.38	1.46
Gd	4.18	3.84	4.25	5.47	6.9	6.68	6.18	Gd	5	5.03	5.12	5.32	5.36	5.9	5.84
Tb	0.55	0.55	0.52	0.71	0.86	0.89	0.76	Tb	0.69	0.7	0.67	0.73	0.74	0.79	0.78
Dy	3	2.99	2.95	3.84	4.95	4.52	4.17	Dy	3.54	3.72	3.33	3.87	3.96	4.12	4.09
Ho	0.58	0.58	0.56	0.71	0.97	0.87	0.78	Ho	0.66	0.71	0.62	0.7	0.73	0.82	0.74
Er	1.69	1.57	1.66	2.01	2.77	2.64	2.17	Er	2.05	2.09	1.9	2.07	2.21	2.38	2.25
Tm	0.22	0.23	0.25	0.31	0.37	0.39	0.31	Tm	0.294	0.291	0.263	0.289	0.305	0.331	0.337
Yb	1.38	1.52	1.44	1.74	2.36	2.17	1.92	Yb	1.76	1.94	1.65	1.84	1.86	2.07	2.07
Lu	0.21	0.22	0.21	0.24	0.35	0.31	0.27	Lu	0.253	0.291	0.245	0.298	0.283	0.307	0.286

Co and Cr values, which differ, being somewhat under-estimated in data from the external laboratory. As far as U and Co are concerned, this fact may be due a complete acid attack in our laboratory. As far as Cr is concerned (sometimes below the detection limits for the external laboratory) it must be noted that its determination is affected by: a) the low concentration levels in the granitoid rocks and b) the necessity to analyse this element at the highest resolution mode, determining therefore a dramatic decrease in sensitivity. With our proposal method, these two causes which negatively affect Cr measurements are overcome; this is due to the high sensitivity achieved.

Finally, in order to obtain further details about the provenance of the rocks from the Roman Theatre, data obtained have been also compared with the geochemical features of the granitoid rocks from both the whole Mount Kozak magmatic complex (Altuntayanak and Yilmaz, 1998) and from the extraction site (De Vecchi *et al.*, 2000). Literature data are set out on Table 6.

The Kozak granites belong to the so-called «Mount Kozak magmatic Complex» in western Anatolia, which is a high-K, calc-alkaline suite

of predominately SiO<sub>2</sub> intermediate to acid composition. The geochemical characteristics exhibit affinities to subduction-related magmatic association even though the tectonic regime of the region where the above rocks are located is post-collisional (Altunkaynak & Yilmaz, *cit.op.*).

The trace elements discrimination diagrams applied to the specimens from the Roman Theatre and to the literature granitoids showed that all the samples fit the field of the Volcanic Arc Granites (Fig. 3; Pearce, 1982). Moreover, in the Middle Ocean Ridge Basalt normalised trace elements variation diagram (Fig. 4A), the rocks show LILE enrichment (K, Rb, Ba, Th, Sr), and depletion in HFSE (Zr, Nb, Ti, P); the same pattern is exhibited in the Rock/ Ocean Ridge Granite diagram, which put into evidence the orogenic character of the granitoid rocks investigated (Fig. 4B; Pearce, 1982) and the coherent behaviour of the groups of rocks (Roman Theatre, Kozak magmatic complex and ancient quarry, respectively).

Information obtained allowed to confirm published data concerning the attribution of the granitoids from the Roman Theatre to the Mysian Marble and, at the same time, to complete their petrological features.

TABLE 6

*Selected trace element values of the granitoid rocks from the Kozak Magmatic Complex in western Anatolia, Turkey (samples «S»; Altunkayanak and Yilmaz, 1998) and from the extraction site of the Mysian Marble (samples «tk»; De Vecchi et al., 2000).*

	S 138	S 3	S 119	tk3	tk5	tk6	tk8	tk11	tk14
ppm									
K	28639	20504	29553	29540	29457	29789	28628	29043	30619
Rb	102	95	115	123	133	114	112	105	124
Ba	1206	1163	1373	1081	1127	1179	1194	1477	949
Th	23	25	23	22	31	16	24	14	17
Nb	13	10	13	9	26	9	10	7	11
Zr	161	177	175	148	385	168	15	139	146
Y	23	21	23	21	43	19	18	9	20

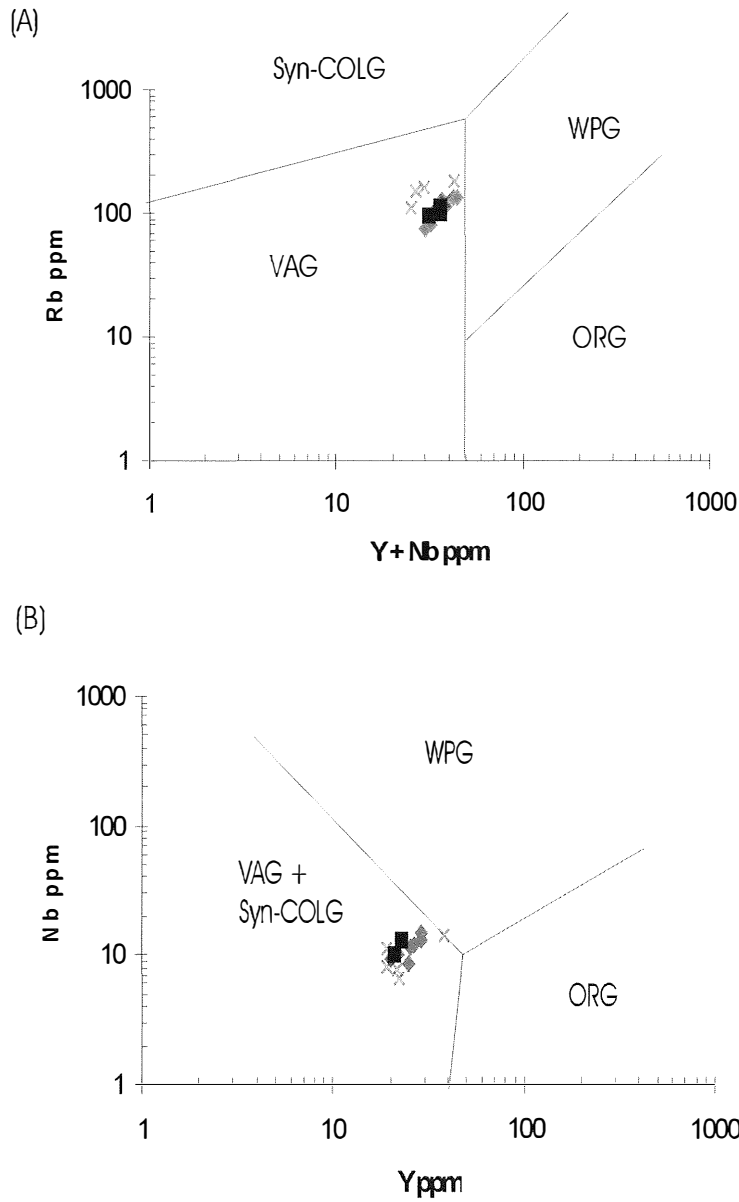


Fig. 3 – Trace elements discrimination diagrams for the granitoid rocks studied. Diamonds: rocks from the Roman Theatre (this work). Squares: rocks from the Kozak complex (Altunkayanak and Yilmaz, 1998). Crosses: rocks from the ancient quarry (De Vecchi *et al.*, 2000). Syn-COLG: Syn-Collisional Granites; WPG: Within Plate Granites; ORG: Ocean Ridge Granites; VAG: Volcanic Arc Granites. Discrimination fields after Pearce *et al.*, (1984).

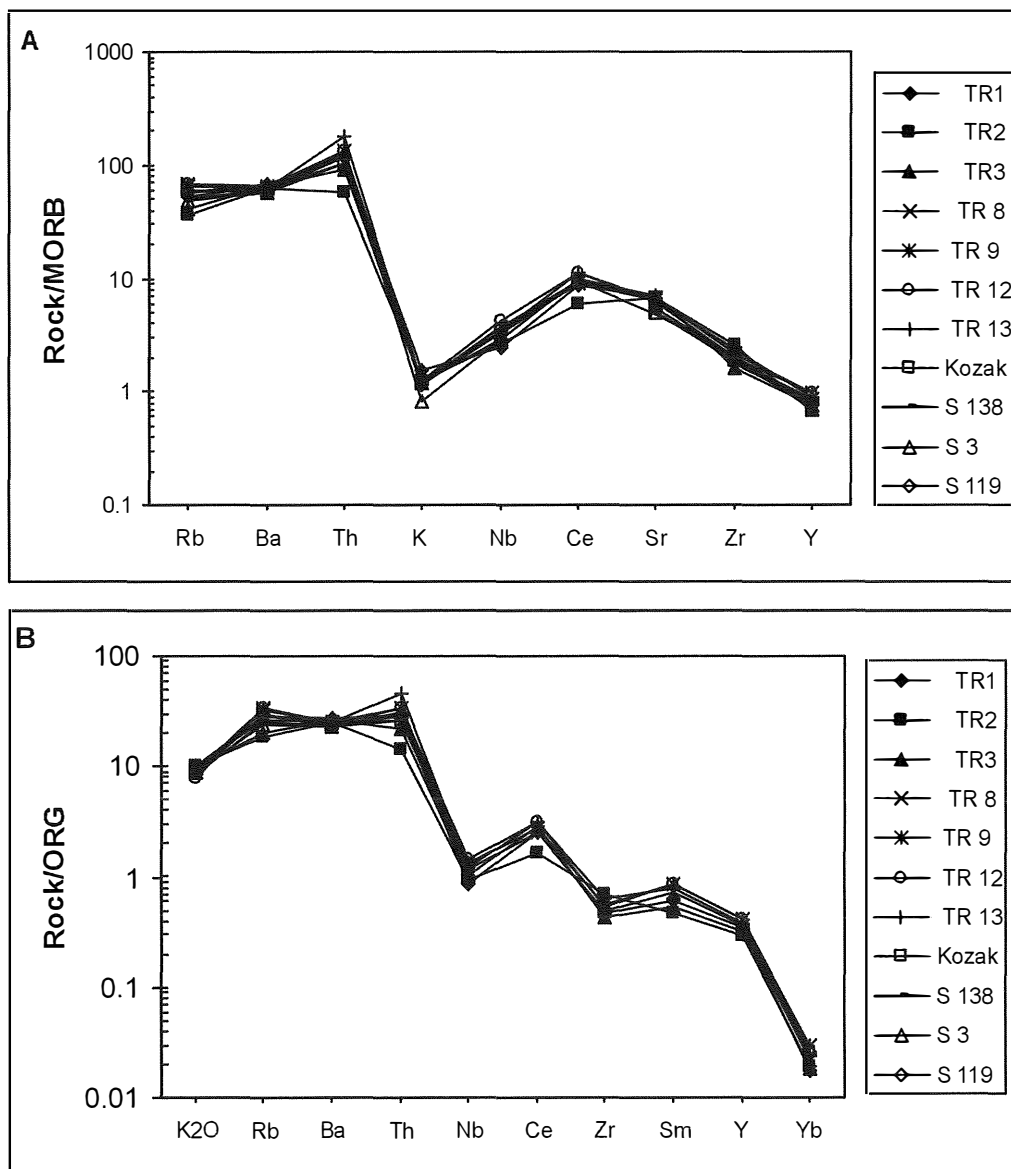


Fig. 4 – Normalisation diagrams for the rocks from the Roman Theatre in Catania and comparison with literature data. A) Rock/MORB spider diagrams. MORB normalisation values after Pearce (1983); Sc and Cr after Pearce (1982). B) ORG normalised spider diagrams. ORG normalisation values after Pearce *et al.* (1984).

«TR» = Roman Theatre in Catania (this work); «S» = Kozak Magmatic Complex (Altunkayanak and Yilmaz, 1998); «Kozak» = ancient quarry (average values; De Vecchi *et al.*, 2000).

Potassium and phosphorus were determined as  $K_2O$  and  $P_2O_5$  by XRF spectrometry.



## CONCLUSIONS

The results presented for the different rock matrices show that HR-ICP-MS is a powerful implement for multi-elements analyses of geological matrices, and may be successfully applied to lithoid materials used in the historical buildings. However, satisfactory measurements require accurate work which involves both sample preparation and operational parameters. The suppression of both spectral and not spectral interferences is very important when working at low concentration levels. DL are strongly dependent on sensitivity and stability of the blank. On the other hand, since sensitivity dramatically decreases by a factor hundred when passing from low to high resolution, we considered it for elements which are too low concentrated in our aqueous solutions; for this reason, the choice of the most suitable resolution for the studied elements it was not a waste of time since at the end, in the method we made for measurements, we tried to achieve for each analyte the most convenient choice (compromise) among expected interferences, count rates (sensitivity) and resolution. The accurate optimisation of the instruments and in particular the relatively low forward power used (the highest values is 1090 watt) if compared to similar HR-ICP mass spectrometers (Makishima and Nakamura, 1997; Yu *et al.*, 2001) permitted to overcome the most important spectral interferences as it may be seen by measurements on of interest. On the other hand, the relatively high dilution factor applied (minimum 20000) played a key-role in the suppression of the matrix effects. This latter was also pointed out by the monitoring of the internal standard, and permitted to avoid some more complex and elaborated methods which consists in the separation of the analytes from matrices by using ion exchange separation or co-precipitation (Carignan *et al.*, 2001) reducing therefore the treatments of the samples and further contamination. The use of the same geo-

standard mother solutions for external calibration and measurements as unknown samples permitted to work in the same matrix conditions during the different steps of the analyses.  $^{103}\text{Rh}$  demonstrated to work as a good internal standard and this fact allows to simplify the procedure without using more complicated «cocktails» of internal standards. Problems related to determination of Sr and Ba were expected because some «memory effects» due to their «sticky» behaviour (McGinnis *et al.*, 1997; Muenker, 1998; Makishima *et al.*, 1999; Yu *et al.*, 2001). We also experienced some problems related to the determination of some transition metals. In particular, determination of Cr was difficult because it is severely disturbed in aqueous solutions, even without matrix (Feldmann *et al.*, 1994); nevertheless the highest resolution setting for Cr determination permitted to overcome the occurring interferences. As far as REE determination is concerned, we tried to overcome the most important spectral interferences by choosing for Eu and elements over 157  $m/z$  the highest resolution setting.

It is noteworthy that use of small amounts of powder sample finds useful applications in the field of Cultural Heritage, where, by taking into account the representative specimens, very often only small fragments are available for investigations.

Finally, the study carried out on the granitoid rocks from the Roman Theatre in Catania (Italy), showed that HR-ICP-MS permits to determinate in a reliable way the trace element contents of the geological materials used for archaeometrical purposes, and, at the same time, gave further information concerning their provenance.

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