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Gamma-ray spectroscopy determination of radioactive elements in late-Hercynian plutonic rocks of Val Biandino and Val Trompia (Lombardy, Italy)

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Abstract. — The results from natural gamma radiation measurements in main plutonic rocks outcropping in Val Biandino (VB) and Val Trompia (VT), pertaining to the central sector of the South Alpine domain, are presented and compared with data on Valle del Cervo pluton. The measurements were performed with the aid of a high-resolution gamma-ray spectroscopic system using HPGe detector. The aim is to contribute to the establishing of a baseline map of environmental radioactivity levels. In the VB samples the granite activities of ^{235}U and ^{238}U are only slightly higher than ^{232}Th specific activity, while the opposite occurs in more basic rocks; moreover, U and Th contents are in agreement with the levels of rocks of calc-alkaline affinity and Hercynian age. In VT rock types the activities of ^{238}U are in the range 48-74 Bq kg^{-1} and the granite shows the lowest value of activity. The ^{232}Th activities are quite similar for granite and granodiorite. Samples coming from Torgola fluorite mine, hosted in the granitic-granodioritic rocks, show U and Th activities that do not exceed 80 and 70 Bq kg^{-1} respectively. The U and Th specific activities of VT rocks are not completely explained by the magmatic character of the pluton; in fact, in the granite the U activity is lower than the Th one. This opposite trend could be due to the effects of a large-scale hydrothermal system coeval with upper Palaeozoic plutono-volcanic activity and tectonism.

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Riassunto. — Vengono riportati i risultati delle misure della radiazione gamma, ottenuti per la prima volta, sui principali litotipi costituenti i plutoni tardo-ercinici affioranti in Val Biandino e in Val Trompia (Val Torgola e Val Navazze). Le misure sono confrontate con quelle ottenute con lo stesso metodo sulle rocce della Valle del Cervo. La tecnica usata per l'analisi è la spettrometria gamma ad alta risoluzione, con rivelatore a semiconduttore HPGe, che risulta particolarmente valida, sia perché non richiede specifiche procedure per la preparazione dei campioni, sia per l'elevata risoluzione energetica. Lo scopo del lavoro è quello di contribuire alla costruzione di una mappa della radioattività, relativamente a rocce ignee che, in diversa misura, vengono a contatto con l'uomo e le sue attività (materiale per edilizia o ornamentale, rocce incassanti mineralizzazioni all'interno di miniere). Tra i campioni della Val Biandino, le rocce acide (graniti e apliti) mostrano attività specifiche di ^{235}U e ^{238}U solo debolmente più basse rispetto a quella di ^{232}Th, mentre opposta tendenza si osserva nei litotipi basici (quarzodioriti e gabbrodioriti); inoltre, le concentrazioni di U e Th sono in accordo con quelle di rocce a tendenza calcalcalina e di età ercinica.

Nelle rocce della Val Trompia (graniti e granodioriti), le attività di ^{238}U rientrano nell'intervallo compreso tra 48-74 Bq kg^{-1} , ma il granito presenta il più basso valore dell'attività contrariamente alla norma; per le attività di ^{232}Th non si osservano differenze tra le due litologie. In particolare, nei campioni che provengono dalla miniera di fluorite di Torgola, si sono misurate attività comprese tra 70 e 80 Bq kg^{-1}. Le attività specifiche di U e Th nelle rocce della Val Trompia non vengono spiegate completamente dalla composizione del magma, in particolare, la minore attività di U rispetto a quella di Th nel granito. Si può ipotizzare che il comportamento dei due elementi possa essere il risultato degli effetti dell'azione di fluidi, legati a un sistema idrotermale a grande scala, che ha agito durante le fasi finali dell'attività magmatico-tettonica permiana, producendo anche la diffusa tormalinizzazione osservata in quest'area.

Key words: *Uranium; Thorium; Gamma Spectroscopy; Late- Hercynian plutonic rocks; Lombardy.*

Introduction

The study of naturally occurring radioactive materials (NORM) is of great interest to many fields of Earth sciences, most of them involving the determination of the U, Th and K content of rocks.

The natural environmental radiation mainly depends on the outcropping rock types: higher radiation levels are associated with igneous rocks, granites in particular, due to the geochemical behaviour of these elements which, during the magmatic processes of partial melting and/or fractional crystallisation, are concentrated in the liquid phase and become incorporated into related products of solidification.

Radioactivity is mostly dependent on the three well-known radioactive series: the uranium series originating with ^{238}U, the thorium series originating with ^{232}Th and the actinium series originating with ^{235}U. As the ratio ^{235}U to ^{238}U is less than 1%, the contribution of ^{235}U to environmental radioactivity is very small. There are also several singly occurring radionuclides, the most important one being ^{40}K that contributes significantly to natural gamma emission.

Concerning the content of these elements in the rocks, K is considered a major element (crustal abundance or Clarke value = 18,400 ppm; Fortescue, 1992), while the two radioactive elements U and Th occur as trace elements (Clarke values of 2.30 and 8.10 ppm , respectively). Values of 2.2 to 17 ppm for Th and of 0.6 to 4.8 ppm for U are the abundances for the two main types of crustal rocks as basalt and granite in Levinson (1980). The Th/U ratio is about 2.5 in the most basic MORBs but tends to be much more variable in sialic (andesitic) rocks with a large range between 1.5 to 10.

The objective of the present study is to evaluate the concentrations of ^{238}U, ^{232}Th and ^{40}K in rock samples collected from Val Biandino and Val Trompia plutons, outcropping in the central part of Northern Italy, and to compare them with Valle del Cervo plutonic rocks occurring in the three main complexes, with the aim of contributing to, and establishing a baseline map of environmental radioactivity levels.

There are no systematic data on this subject available except for the Valle del Cervo Pluton, a magmatic composite body well known for its radioactivity (Fiorentini Potenza, 1959 a, b; Cesana *et al.*, 1976 a, b) and recently measured on a high-resolution gamma-ray spectroscopic system (Sesana *et al.*, 2006).

Most of the rocks forming the Val Biandino and Val Trompia plutonic masses are mainly subalkaline (biotite only or biotite- and amphibole-bearing), so called high-K calc-alkaline granitoids, sometimes with secondary muscovite, developed during late- to post-magmatic hydrothermal alteration, potentially an environment for possible U and Th mineralisation (De Capitani and Liborio, 1988; Thoeni *et al.*, 1992; De Capitani *et al.*, 1994).

Moreover, there is some evidence that radioactivity in granites is often linked to fluorite occurrences (Salem *et al.*, 2001). Well known are the fluorite deposits of the Val Trompia, in particular those of the Torgola mine, hosted in the granitic-granodioritic rocks. The mineralisation consists mainly of fluorite and quartz veins with Pb - Zn sulphides cross-cutting the plutonic masses. In the rocks of Val Biandino there is no evidence of fluorite occurrence; on the other hand, granites and aplitic granites form a considerable portion over the entire outcrop together with more basic rock facies.

Monitoring of radioactivity in the environment is very important for environmental protection and the application of rapid and accurate methods for the assay of radioactivity are essential. In this paper, natural gamma radiation measurements were performed with the aid of a high-resolution gamma-ray spectroscopic system, calibrated to determine the natural radioactivity also in geological materials coming from mines and quarries. In the mines, particularly significant is the presence of ^{222}Rn associated with Radium and its ultimate precursor Uranium. The inhalation of its short-lived daughter products is a major contributor to the total radiation dose in exposed subjects (UNSCEAR, 1993).

Geological and petrological outlines

The areas of Val Biandino and Val Trompia are located in Lombardy and belong to the central sector of the South Alpine domain (fig.1).

The Val Biandino composite pluton (indicated in short as VB), is located at the eastern side of Lake Como, and is one of the numerous 'late Hercynian' intrusives that indicate wide spread magmatic activity along the Periadriatic Lineament in the South Alpine basement.

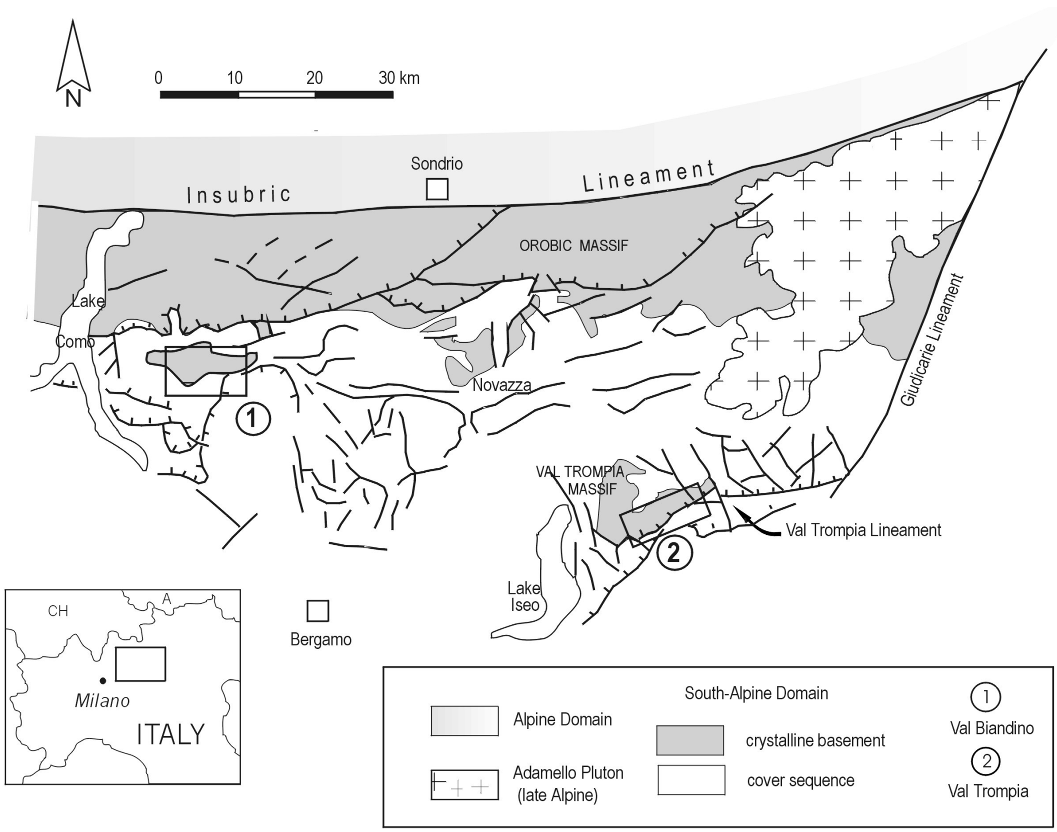

Fig. 1 – Simplified geological sketch map of the central sector of South Alpine domain showing the main tectonic lineaments and distribution of pre-Hercynian basement and post-Paleozoic cover and the location of the intrusive complexes considered in this study, Val Biandino (1) and Val Trompia (2) .

It is a small composite pluton (5 km^2) consisting of four individual bodies and numerous crosscutting dikes, entirely encased in the schists of the pre-Carboniferous basement of the Orobic Alps into which they produced a contact metamorphic aureole. Along the north side of the main intrusion, a tectonic line trending E-W puts the igneous rocks in direct contact with the Permian sedimentary cover units. Other faults affect various portions of the pluton and dissect the bodies into several blocks.

From the petrochemical point of view, the available data suggest the presence of two main groups: a more acidic showing granitic composition and a more basic one grading from quartzdioritic to gabbrodioritic nature. The two groups appear to belong to a single evolutionary trend, calc-alkaline but slightly potassic and typically orogenic in character. Trace element geochemistry seems to support the derivation of the entire pluton from melts originating from a deep crustal level that evolved by fractional crystallisation within the crust. Rb-Sr data on whole-rock samples and biotites define an age of 286±20Ma (De Capitani and Liborio, 1988; Thoeni *et al.*, 1992).

As well as the Val Biandino igneous rocks, the Val Trompia intrusions too, belong to the widespread "late Hercynian" magmatism of the Southern Alps in the proximity of the Periadriatic Lineament. They consist of three small bodies named Val Navazze, Val Torgola (here considered and called Val Trompia, indicated in short as VT) and Valle di Rango (not considered in the present work). These intrusions crop out along the valleys of three minor rivers which flow into Val Trompia near Bovegno village (north of Brescia). The igneous bodies occur discontinuously and all together cover an area of about 2 km^2. At the surface, the outcrops of Val Navazze and Val Torgola lay about 1 km apart, being separated by the water divide between the two valleys. At depth, they merge into one and the same body, as it was shown by the mining works carried out for the Torgola fluorite mine (Martina, 1966). On the basis of their geochemical, mineralogical and petrographical characteristics the Val Trompia intrusive rocks range from granitic to granodioritic composition and show a subalkaline character and volcanic arc granite affinity. Crystallisation occurred at a shallow level (ca. 3-5 km) in P- T conditions of ca. 1.5 kbar and of ca. 550 °C. The cooling age of the Val Trompia intrusives was determined at 271±4 Ma by Rb-Sr isochron (De Capitani *et al.*, 1994). The Navazze-Torgola intrusive complex may represent a portion of the magmatic chamber that produced the Collio volcanics which, in this area, are represented by ignimbrites and pyroclastites. These volcanic rocks show, on the whole, an alkali-rhyolitic composition (Origoni Giobbi *et al.*, 1981), coherent with the chemical character of the intrusives and representing a potential Uranium source. The Collio volcanics appears to be broadly coeval with VT intrusives (280 Ma for Collio ignimbrites in the Orobic Alps and Val Trompia; in Philippe *et al.*, 1987). The Navazze-Torgola intrusive complex was eroded and covered by the upper Permian Verrucano sandstones.

It is worth remembering that the central-eastern part of the Orobic chain, NW from Val Trompia massif, hosts the Novazza-Val Vedello district, the largest hydrothermal uranium field in Italy, which consists of Permian fault-controlled uranium orebodies hosted in volcanic rocks of the Collio formation. In this area, the Collio volcanic rocks consist of ignimbrites and lavas, erupted in several stages from a regional caldera-collapse structure. They are roughly coherent with the chemical composition of the Collio ignimbrites of Val Trompia. Nevertheless, the Novazza U-mine ignimbrites appear different from U-mineralization free ones which are quite similar to VT ignimbrites. The chemical differences are attributed to the presence of post-magmatic phenomena, responsible for a Na strong depletion and relative Si and K enrichments (Origoni Giobbi *et al.*,1981; Cadel, 1986; Cadel *et al.*, 1987; Fuchs and Maury, 1995). Although a Permian genesis of U mineralization is supported by various pieces of evidence, the U enrichment appear younger than the ignimbrite deposition, cogenetic with the Na leaching, but not necessarily contemporaneous. No granitic intrusions coeval with the volcanic units are exposed in Novazza-Val Vedello area.

In the mine of Torgola, the mineralisation consists mainly of fluorite and quartz veins with Pb-Zn sulphides crosscutting the plutonic masses. These veins represent fillings of open, large and minute fissures developed mainly along fault planes. The fluorite veins are regular but vary in thickness from 0.5 to 5.0 m and in length from 20 to more

TABLE 1

Main lithological and mineralogical features of the Val Biandino and Val Trompia rock types. Volume per cent abundance of single phases from modal analysis are reported in brackets. The abbreviations for rock-forming minerals as in Kretz (1983)

Sample	Lithology	Mineralogical association
Val Biandino		
A4/82	granite	Qtz(35%)+Pl(34%)+Kfs(21%)+Chl(6%)+Wm(1%)+ Zrn(1.5%)+Crd(0.5%)+Ep(0.6%)+Op
Dat 15F	granite	Qtz(35)+Pl(28)+Kfs(29)+Bt(4)+Chl(2)+Crd(2)+ Ep(1)+Wm
A9/82	quartzdiorite	Pl(46)+Qtz(20)+Bt(19)+Cam(11)+Chl(3.5)+Px(0.5)+Ap+Zrn
A4/85	quartzdiorite	Pl(52)+Qtz(24)+Chl(11)+Ep(9)+Kfs(2)+ Cam(1.5)+Bt(0.5)+ Op
Dat 15	quartzdiorite	Pl(43)+Qtz(26)+Bt(14)+Cam(6)+Chl(6)+Kfs(4)+ Ep(1.2)
Dat 18	gabbrodiorite	Pl(47)+Bt(21)+Cum(16)+Qtz(14)+Ep(1)+Chl(0.5)+ Zrn(0.3)+Op+Ap
Val Trompia		
VT3	granite	Pl(35)+Kfs(35)+Qtz(25)+Bt(5)+Chl+Ep+Zrn+Ap
VNE2	granodiorite	Qtz(35)+Kfs(20)+Pl(20)+Bt(15)+Cam(5)+Zrn
VNE4	granodiorite	Qtz(35)+Kfs(30)+Pl(20)+Bt(10)+Cam(5)+Chl+Ep+Ap

than 1000 m. Nevertheless some authors (Cassinis *et al.*, 1997; Frizzo, 1997) are inclined to exclude a link between fluorite deposits and the magmatic event because the fluorite veins crosscut not only the Torgola-Navazze rocks but also the younger Permian volcano-sedimentary country rocks. The evidence of post- Permian hydrothermal activity is testified to both by swarms of siderite-quartz-base metal sulphide veins and associated greisen type wolframite-scheeelite breccias occurring along the margin of the crystalline massif. They may suggest the presence of VT granitoids at shallow depths (Moroni, 1994). Quartz-tourmaline breccia bodies, located close to the main tectonic lineaments in the central Val Trompia area, represent an additional product of hydrothermal activity in the area (De Capitani *et al.*, 1999).

EXPERIMENTAL METHOD

SAMPLING CRITERIA

The rock samples analysed were collected from the outcrops of the different locations and could be considered to be representative for each plutonic mass on the basis of previous personal research experiences for Val Biandino (De Capitani and Liborio, 1988; De Capitani *et al.*, 1988) and for Val Trompia (De Capitani *et al.*, 1994) respectively (see appendix 1 for the chemical composition of the examined rocks).

Six samples were considered as representative of the outcropping rocks from the four bodies of VB; in particular, they consist of granites and quartz-diorites as typical rock types of the main body, and of a gabbrodiorite as representative rock of the peripheral body outcropping as a lens on the south of the main mass .

Three samples were selected as characteristic of the VT outcrops. A granite specimen was sampled on the surface and represents the typical outcropping rocks of the Val Torgola mass, while two granodiorite samples come from the Ester level of the Torgola mine and represent the main rock types of the Val Navazze intrusion.

Some features of the examined specimens are summarised in table 1.

EXPERIMENTAL SET-UP AND GAMMA-RAY MEASUREMENTS

Each sample of about 200 g weight was crushed and afterwards pulverised to obtain a homogeneous grain size between 30 and 40 μm.

The peculiarity of the experimental method is the use of polypropilene containers (200 cm^3) with a polyethylene cover, filled at 100 cm^3. The geometry used in analyses has been conditioned by the available amount of the rock powder.

Gamma spectroscopy at high resolution, with HPGe, is the most common technique for quantitative analysis of gamma emitting radionuclides (Carrera *et al.*, 1997; Walley El-Dine *et al.*, 2001; Tzortzis *et al.*, 2003). Some details on the methodology used for this research are briefly discussed hereafter.

A multi peak source was used for the calibration of the apparatus. Radionuclides were dissolved in a homogeneous solution with density 1 g/cm^3 to which a ^{226}Ra source (185.99 keV) and a ^{40}K (1460.75 keV) source, made with KCl-water solution, were also added. The counting efficiency at different energies is given in table 2 and represented in figure 2.

The linear equation between the logarithm of efficiency ln(ε) and the logarithm of energy ln(E) is assured for energies of gamma from 186 keV to 1460 keV.

The analyses of the gamma spectrum due to rock samples were carried out by using well defined lines for the different radioactive series employed.

The gamma ray lines selected for the measurements of ^{238}U and ^{235}U series are the following:

Table 2
Efficiency of the different calibration lines

Isotopes	Energy (keV)	e%
^{241}Am	59.54	1.42
^{109}Cd	88.04	3.80
^{57}Co	122.07	5.25
^{57}Co	136.43	5.31
^{139}Ce	165.85	4.85
^{51}Cr	320.07	3.16
^{113}Sn	391.71	2.84
^{85}Sr	514.00	2.13
^{137}Cs	661.62	1.79
^{226}Ra	185.99	4.90
^{40}K	1460.75	0.95

a. ^{234m}Pa line at 1000.90 keV shows a low emission probability (Iγ = 0.85 %). Its presence points out the activity of ^{238}U.

b. Gamma ray lines at 185.72 and 185.99 keV. They include two different sources : ^{235}U (Iγ = 56.06%), ^{226}Ra (Iγ = 3.51%) respectively. These lines can be used assuming the hypothesis that the ^{226}Ra is in secular equilibrium with ^{238}U and the isotopic ratio between ^{235}U and ^{238}U is 0.72 %.

c. Gamma ray lines at 143.76 and 144.24 keV. They include two different sources : ^{235}U (Iγ= 10.93%) and ^{223}Ra (Iγ = 3.13%) respectively; both are included into ^{235}U series. Assuming equilibrium, these lines can be used for a further evaluation of ^{235}U activity.

d. Gamma ray line due to ^{222}Rn products: ^{214}Pb (295.22 keV), ^{214}Pb (351.99 keV) and ^{214}Bi (1764.51 keV). For these peaks it is very important that radon exhalation from the sample must be negligible. It has been determined less than 1% .

The gamma ray lines selected for the measurements of ^{232}Th series are: ^{228}Ac (911.07 keV) and ^{212}Pb (238.63 keV).

The counting efficiencies reported in table 3 refer to density equal to 1 g/cm^3; nevertheless, the different rock samples show a range of density from 1.1 to 1.7 g/cm^3. The evaluation of the dependence of efficiency on different densities is very important, therefore four sources were prepared with a mixture of zirconium silicate ($ZrSiO_4$) and calcium sulfate ($CaSO_4$), to obtain densities from 1.10 g/cm^3 up to 1.98 g/cm^3. Note that zirconium silicate has 4000 Bq kg^{-1} of ^{238}U, and calcium sulfate is practically without radionuclides. Efficiency patterns related to density are shown in figure 3 for the different lines of ^{238}U, ^{235}U; similar results were obtained for ^{232}Th and ^{40}K.

Results and discussion

The activities of different radionuclides are calculated for the examined samples which are representative of the rock types occurring in Val Biandino and Val Trompia (see appendix 2). The good agreement between the activities from the lines of the Radon decay products and ^{226}Ra can exclude a significant loss of Radon from the rocks. Moreover, the results give a true ratio between ^{235}U and ^{238}U and both lines of ^{232}Th are in agreement.

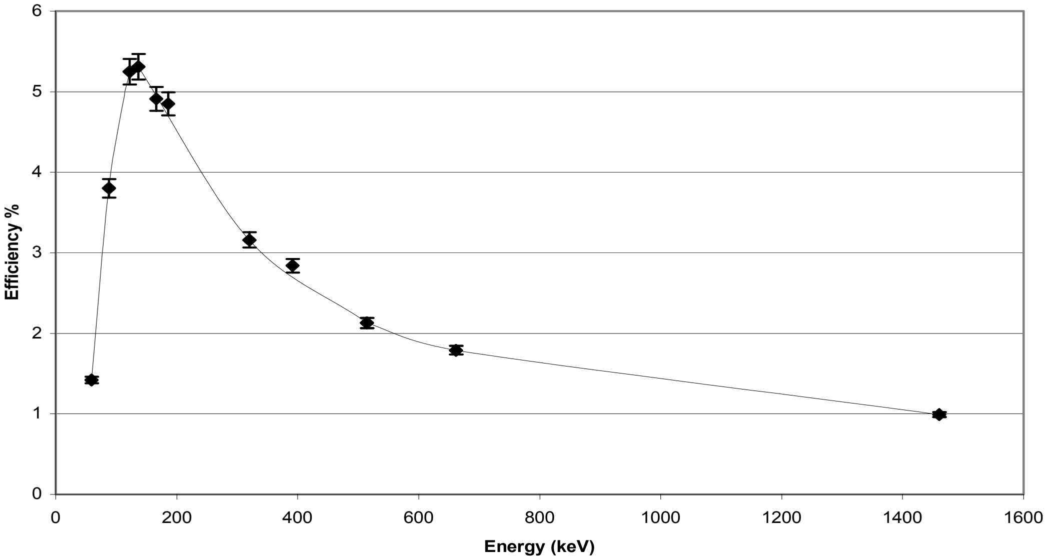

Fig. 2 – Plot of the efficiency calibration of the different calibration lines.

In some cases, because of the low content of the two U isotopes, in particular, for some Val Biandino rocks, the ^{238}U determination obtained by the activities of radon daughters (^{214}Pb and ^{214}Bi) was not comparable, within a safety margin, with ^{234M}Pa activity due to the low counts of this peak at 1000.9 keV.

The averaged values of activities (Bq kg^{-1}) for ^{238}U, ^{235}U, ^{232}Th , ^{40}K and the related concentrations (ppm) are shown in table 4. For all measured rocks the specific activity of ^{40}K is higher than that of ^{238}U and ^{232}Th.

In the VB samples the range of activities of ^{238}U varies from 18 Bq kg^{-1} for the gabbrodiorite (Dat 18) to a maximum value of 86 Bq kg^{-1} for the granite (Dat 15F) and the ratio of the ^{235}U to ^{238}U activities is correct. The ^{232}Th activities are similar to Uranium activities and range from 30 to 80 Bq kg^{-1}. In particular, granites exhibit activities of ^{238}U only slightly higher than the ^{232}Th specific activity; the opposite occurs in more basic rocks. In terms of the elemental contents of Th and U, values are lower for U than for Th and somewhat uniform in the set of analysed rocks (figure 4).

In VT rock types the activities of ^{238}U are in the range 48-74 Bq kg^{-1} and the granite VT3 shows the lower value of activity. ^{232}Th activities are quite similar for the three samples. The two samples coming from Torgola fluorite mine (VNE2, VNE4) have shown that, in the host rocks of the mineralisation, the U and Th activities did not exceed 80 and 70 Bq kg^{-1} respectively.

Figure 5 illustrates correlations between U and Th concentrations for the VB and VT rock types analysed and a comparison with Valle del Cervo (in short VdC) data (Sesana *et al.*, 2006). A direct relationship between U and Th with an overlap for VB more acidic types and VT rocks is evident. Moreover a well separated group corresponding to VdC more enriched rocks can be seen (fig. 5a). The plots of Th and U against Th/U ratio (fig. 5b and 5c) indicate that the negative trends seem to be controlled rather by U variation content than by Th variation. VB rocks have Th/U ratios ranging from 2.7 to 5.9 with the lower values for granites. On the contrary, the VT granite-granodiorite series (Th/U 2.7÷4.1) shows the higher value for the granite facies. Small differences are shown

Table 3

Efficiency related to each gamma line of natural radioactive series. a) efficiency related to 1764.51 keV line extrapolated by means of the linear relation between lnε and lnE

Radionuclide	Energy (keV)	γ%	ε% (ρ=1)
^{235}U+ ^{223}Ra	143.76+144.24	10.93+3.13	5.20
^{235}U/^{226}Ra	185.72/185.99	56.06/3.51	4.90
^{234m}Pa	1000.90	0.85	1.28
^{214}Pb	295.22	17.90	3.39
^{214}Pb	351.99	34.70	2.95
^{214}Bi	1764.51	14.90	0.81[a)]
^{212}Pb	238.63	43.50	4.01
^{228}Ac	911.07	26.60	1.38
^{40}K	1460.75	10.70	0.95

between the granite types of these two groups in contrast with the VdC granites which show lower ratios (< 2). These evidences are in agreement with data from Levinson (1980) previously reported for the different magma types, thereby confirming the calc-alkaline affinity for VB rock suite and the shoshonitic affinity for VdC rock types (De Capitani and Liborio, 1988; Bigioggero *et al.*, 1994). Magma of subalkaline composition and VAG (volcanic arc granite) affinity characterising the Val Trompia granitoids (De Capitani *et al.*, 1994) may suggest higher U and Th contents than those measured.

In granitoid rocks, U and Th can be concentrated either in accessory minerals such as zircon, monazite, apatite or can be hosted in the main phases. The binary relations of Zr/U, Zr/Th vs either U or Th, as shown in figure 6, exhibit significant

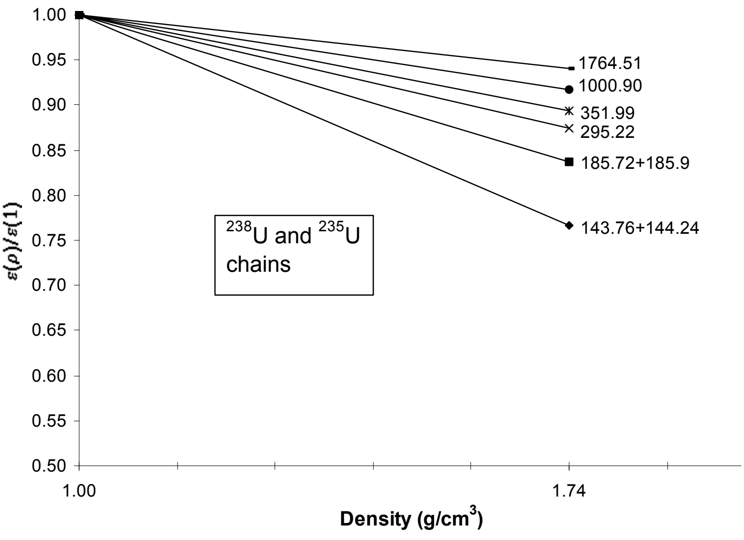

Fig. 3 – Ratio plot between efficiency at density of 1.74 g/cm³ and 1 g/cm³ concerning the lines of ^{238}U and ^{235}U series.

Table 4

Specific activities and standard deviation (Bq kg^{-1}), concentrations (ppm), ratio Th/U of the examined samples

Sample	Lithology	^{235}U (Bq kg^{-1})	^{238}U (Bq kg^{-1})	^{232}Th (Bq kg^{-1})	^{40}K (Bq kg^{-1})	^{235}U (ppm)	^{238}U (ppm)	^{232}Th (ppm)	Th/U
Val Biandino									
A4/82	granite	2.6 ± 0.1	58.4±1.2	59.2±0.9	1243±28	0.2	4.7	14.5	2.96
Dat 15F	granite	4.1 ±0.2	86.3±2.0	80.8±2.3	1230±20	0.3	6.9	19.8	2.73
A9/82	quartz-diorite	1.3 ±0.1	26.2±0.7	44.9±0.8	714±12	0.0	2.1	11.0	4.97
A4/85	quartz-diorite	2.9 ±0.2	62.2±1.6	73.2±2.1	669±12	0.1	5.0	18.0	3.43
Dat 15	quartz-diorite	1.6 ±0.1	34.3±0.9	68.9±2.0	891±15	0.0	2.8	16.9	5.87
Dat 18	gabbrodiorite	1.1±0.1	18.1±0.6	25.9±0.8	431±8	0.0	1.5	6.3	4.12
Val Trompia									
VT3	granite	2.2±0.1	48.3±1.1	67.2±1.9	1295±21	0.2	3.9	16.5	4.07
VNE2	granodiorite	2.4±0.1	54.7±1.3	61.6±1.8	1416±23	0.2	4.4	15.1	3.29
VNE4	granodiorite	3.7±0.2	74.7±1.8	68.9±2.0	1479±24	0.3	6.0	16.9	2.69

negative correlation indicating that both elements may not be preferentially hosted in the accessory mineral phases, such as zircon (see table 1 for the mineralogical assemblages), but they could be associated with major forming minerals (biotite, muscovite, plagioclase) as also observed by Abd El-Naby and Saleh (2003) in the granitoid rocks of Gabal El Fereyid area. The same behaviour

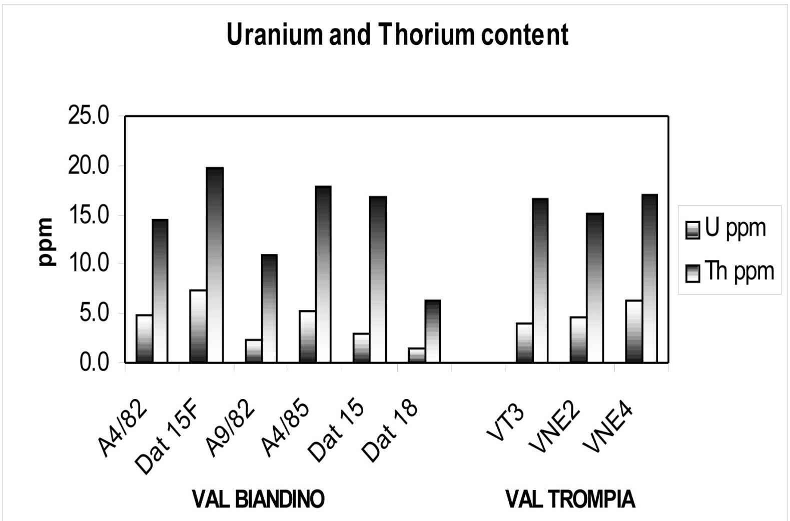

Fig. 4 – Concentrations of U and Th in Val Biandino and Val Trompia rock types.

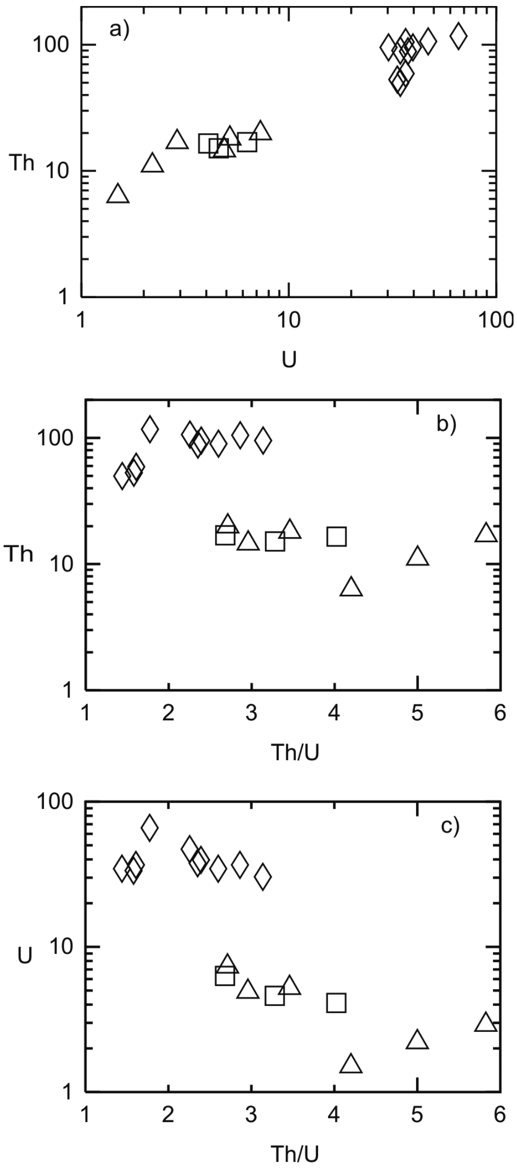

Fig. 5 – Variation diagrams: a) Th vs U; b) Th vs Th/U; c) U vs Th/U. Symbols - Triangle: Val Biandino; Squares: Val Trompia; Diamonds: Valle del Cervo.

shows the Phosphorous in relation either U or Th, excluding also apatite as host mineral.

The geochemical characteristics of VB,VT and some selected VdC rock types are illustrated in figure 7, where the variation patterns of decreasing incompatible elements are shown in a chondrite-normalized diagram. An overall enrichment is evident for incompatible elements for the VdC rocks, particularly strong for Ba, U, Th, Nb and more moderate for Sr, P, Zr; however, these

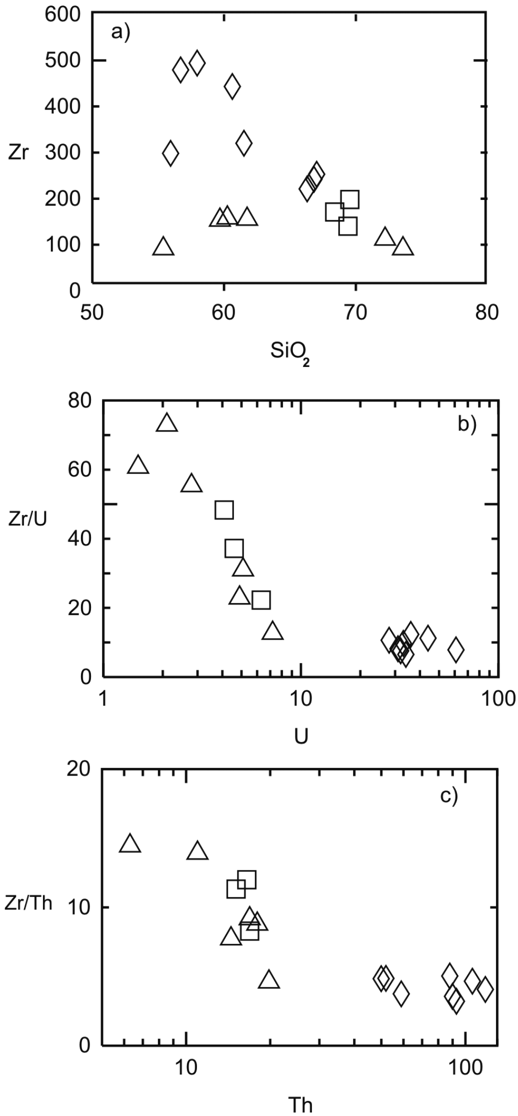

Fig. 6 – Variation diagrams: a) Zr vs SiO_2; b) Zr/U vs U; c) Zr/Th vs Th. Symbols as in Fig.5.

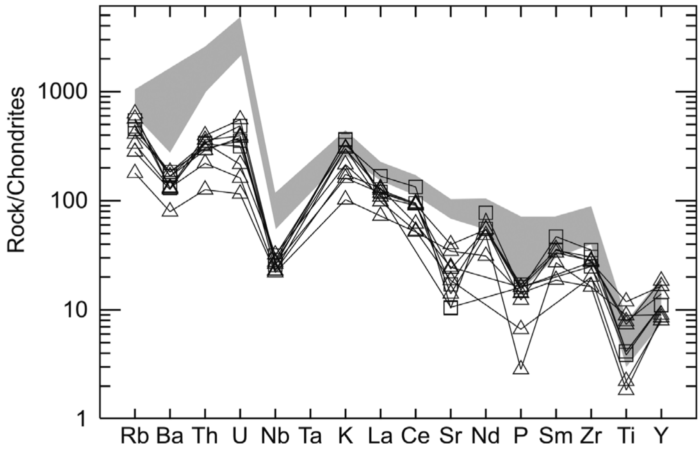

Fig. 7 – Chondrite-normalised spidergram according to Sun (1980). Data for VdC are from Sesana *et al*. (2006) for U and Th and from Bigioggero *et al.* (1994) for other elements. Element concentrations, except for U and Th are from De Capitani *et al.* (1994) for VT; De Capitani and Liborio (1988) for VB. Symbols - Triangle: Val Biandino; Squares: Val Trompia; Grey area: Valle del Cervo.

characters reflect the geochemical signatures of the shoshonitic magmatism active during Oligocene in the western part of the Alps. On the other hand, Val Biandino rocks appear to conform to a calc-alkaline geochemical pattern for a magmatic series from tonalite to granite-aplite and characterised by comparatively lower content of LILE, LREE, P , U and Th. An intermediate position between VdC and VB lithologies is shown by VT rocks produced by the late Hercynian high-K calc-alkaline parental magma, where U and Th show low abundances in spite of the high content of K, Rb, La and Ce. The low contents of U and Th could be due to a large-scale hydrothermal system coeval with upper Palaeozoic plutono-volcanic activity and tectonism. Evidence of hydrothermal alteration on the VT granites-granodiorites are displayed both by primary mineral alteration (sericite replacing plagiocalse and K-feldspar and chlorite±epidote replacing biotite and amphibole) and by disturbed Rb-Sr isotopic system. The data scatter on the Rb-Sr isochron have been interpreted as a possible partial re-opening of the system (De Capitani *et al.*, 1994). The hydrothermal system was characterised by B- rich and F- poor solutions that produced an intense and complex tourmalinisation around the pluton and a system of veins containing Sn-W and base- metal mineralisation (De Capitani *et al.*, 1999). Really, the presence of these minerals associated with Fe^{3+}- bearing tourmalines in the external zone of the plutonic area could be interpreted as a progressive influx of meteoric water to the hydrothermal system. In this complex system, the original U could be removed by the presence of different ligands resulting in the replacements of the primary silicates. Moreover, the oxidation, recorded by the presence of the ferric component of tourmaline and Sn - W oxides, would have produced a favourable environment for the mobilisation and dispersion of Uranium.

Concluding remarks

High resolution gamma-ray spectroscopy tested in this paper provides a sensitive experimental tool in studying natural radioactivity and determining elemental concentrations in crushed rocks even when a small quantity of sample is used. The geometric efficiency of the tested system appears to be better than that obtained using a Marinelli's beaker (1000 ml). The evaluation of efficiency for different densities has allowed for the performance of a calibration suitable for samples of apparent densities ranging from 1 and 3 g/cm^3.

The U and Th contents of VB rock types are in agreement with those measured on rocks of calc-alkaline affinity and Hercynian age in Corsica and in France (Verdoya *et al.*,1998; Ielsch *et al.*, 2001). Moreover, the Val Biandino composite pluton appears to have undergone alteration by deuteric processes like several other members of the 'Late Hercynian' plutonic suite. However, such a weak alteration did not affect the Rb-Sr system and more generally the other trace elements (Thoeni *et al.*, 1992) so also the U and Th contents could be considered as typical of the original magma.

The U and Th specific activities, in particular the low U activity, of VT rocks are not completely explained by the magmatic character of the pluton. This anomalous behaviour seems to be a consequence of the effects of a large-scale hydrothermal system that occurred during the upper-Palaeozoic age and produced several phenomena near to the magmatic bodies as discussed above.

The low values of activities both for U and Th measured in VNE2 and VNE4 samples, representative of the wall rock at the Ester level of the Torgola fluorite mine, can also exclude the presence of high ^{222}Rn activity, that represents a serious problem particularly in indoor environments.

The method also gives the possibility to accurately determine the natural radioactivity in mines and quarries

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Appendix 1

Chemical composition of the Val Biandino and Val Trompia rock types examined (major and minor elements are in wt%, trace elements in ppm). Val Trompia data are all from De Capitani et al. (1994); Val Biandino data are from De Capitani and Liborio (1988) except for REE

	VAL BIANDINO						VAL TROMPIA		
	DAT15F	A4/82	A4-85	DAT15	A9/82	DAT18	VT3	VNE2	VNE4
SiO_2	73.59	72.23	60.26	61.75	59.69	55.39	69.56	68.4	69.41
TiO_2	0.19	0.23	0.81	0.76	1.23	0.92	0.43	0.43	0.40
Al_2O_3	13.98	14.69	16.99	15.78	16.46	17.98	14.48	14.23	13.7
Fe_2O_3	1.52	1.67	6.03	5.91	6.41	8.19	3.68	3.80	3.71
MnO	0.04	0.03	0.10	0.09	0.08	0.13	0.04	0.05	0.06
MgO	0.42	0.53	2.91	3.51	4.36	5.23	0.70	0.85	0.63
CaO	1.46	0.80	4.87	3.58	4.91	7.89	1.82	2.04	1.79
Na_2O	3.03	3.76	2.64	2.40	2.75	1.31	3.31	3.17	3.15
K_2O	4.31	4.34	2.33	3.10	2.52	1.48	4.68	5.19	5.30
P_2O_5	0.03	0.07	0.17	0.13	0.17	0.15	0.16	0.18	0.17
Ba	494	634	482	696	500	302	637	697	494
Rb	220	197	98	143	116	63	167	159	191
Sr	154	205	437	261	271	380	114	188	116
Nb	9.6	8	9.2	11.2	8	7.7	11	10	9
Zr	91	112	158	155	153	91	198	171	140
Y	17	16	28	37	33	18	22	22	22
La	39.5		37.1	34.2		22.8	52.8	37.9	
Ce	76.8		75.1	73.4		42.1	108.7	77.2	
Pr	7.91		8.29	8.21		4.52	12.1	8.69	
Nd	28.9		32.4	32.6		18.6	46.1	33	
Sm	5.2		6.4	6.9		3.6	9.01	6.74	
Eu	0.84		1.33	1.24		1.32	1.27	1.37	
Gd	3.61		5.14	6.24		3.11	7.52	5.42	
Tb	0.54		0.86	1.09		0.52	1.17	0.82	
Dy	2.9		4.87	6.23		2.99	6.97	4.71	
Ho	0.54		0.94	1.24		0.58	1.56	1.03	
Er	1.3		2.6	3.37		1.63	3.94	2.65	
Tm	0.23		0.38	0.55		0.28	0.59	0.38	
Yb	1.18		2.22	3.03		1.61	4.08	2.61	
Lu	0.16		0.34	0.47		0.23	0.61	0.4	

Appendix 2

Specific activities and standard deviation (Bq kg^{-1}) of the different radionuclides measured in each examined sample

	^{238}U Series					^{235}U Series		^{232}Th Series		Potassium
			Radon decay products							
	^{234m}Pa	^{226}Ra	^{214}Pb	^{214}Pb	^{214}Bi	^{235}U	^{235}U	^{228}Ac	^{212}Pb	^{40}K
	1000.90 keV	185.99 keV	295.22 keV	351.99 keV	1764.51 keV	143.76 keV	185.72 keV	911.07 keV	238.63 keV	1460.75 keV
Val Biandino										
A4/82-granite										
Activity (Bq kg^{-1})	59	56	61	60	58	2.9	2.6	59	56	1238
Sigma	15	3	3	3	3	1.0	0.2	2	3	20
Dat 15F-granite										
Activity (Bq kg^{-1})	84	87	85	85	81	3.0	3.9	81	78	1221
Sigma	18	4	4	4	4	0.8	0.2	3	5	20
A9/82-quartz-diorite										
Activity (Bq kg^{-1})	17	28	24	25	26	1.9	1.3	43	43	712
Sigma	20	1	2	2	2	0.6	0.1	2	1	12
A4/85-quartz-diorite										
Activity (Bq kg^{-1})	48	62	61	60	58	3.1	2.8	71	71	664
Sigma	21	4	3	3	3	0.5	0.2	3	5	12
Dat 15-quartz-diorite										
Activity (Bq kg^{-1})	31	34	33	34	34	1.4	1.6	68	68	888
Sigma	23	2	2	2	2	0.4	0.1	3	4	15
Dat 18-gabbro-diorite										
Activity (Bq kg^{-1})	17	23	16	18	18	1.2	1.0	25	25	429
Sigma	15	2	1	1	2	0.5	0.1	1	2	8
Val Trompia										
VT3-granite										
Activity (Bq kg^{-1})	44	48	47	48	46	2.0	2.2	67	67	1291
Sigma	19	2	2	2	3	0.5	0.1	3	4	21
VNE2-granodiorite										
Activity (Bq kg^{-1})	53	57	51	54	53	2.4	2.6	62	58	1411
Sigma	17	3	2	2	3	0.5	0.1	3	4	23
VNE4-granodiorite										
Activity (Bq kg^{-1})	70	78	71	73	73	3.0	3.6	69	68	1475
Sigma	25	4	3	3	4	0.6	0.2	3	4	24