

NATURAL RADIOACTIVITY OF GRANITES USED AS BUILDING MATERIALS IN GREECE

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ABSTRACT

The granites used in Greece as building materials and imported from foreign countries, mainly from Spain and Brazil, are rock types similar with the stony building materials world-wide used. Sixteen kinds of different granites, considered as the most popular, were sampled and their natural radioactivity was measured by gamma spectrometry. The, ²²⁶Ra, ²³²Th and ⁴⁰K contents of granites were compared to corresponding ones of other building materials as well as other granite types used all over the world. For the reasons of radiological impact from use of granites as building materials, the absorbed dose and the effective dose as well were determined. Although the annual effective dose is higher than the limit of 1 mSv a⁻¹ for some granites examined, they could be used safely as building materials, considering that their contribution in most of the house constructions is very low. An attempt to correlate the relatively high level of natural radioactivity of different kinds of granites with the presence of radioactive minerals and their chemical composition was also made.

1 INTRODUCTION

It is very well known that the term 'granite' is world-wide used to describe not only granitic rocks considered and studied in igneous petrology, but also many other igneous rock-types used as building materials in the dimension stone market. The last few years, the use of granites as building material is very popular and the global amount of granite production is comparable to that of marble (Tsirambides 1996).

All types of building materials, including granites, have to be tested regarding their radioactivity. Radiation exposure of the population can be increased appreciably by the use of building materials containing above-normal levels of natural radionuclides, and is comparative or even greater than the exposure from the medical use of ionizing radiations (Stranden 1976). This paper is dealing with the natural radioactivity and the mineralogical and chemical study of granite building materials in order to understand and correlate the relationship of natural radioactivity with the radioactive mineral content and estimate possible implication from radiation exposure.

2 MATERIALS AND METHODS

The sixteen kinds of granite used in this study are the most popular types, according to the Hellenic Granites Corporation, that provided the samples. These were polished granite tiles ready for use and were collected at a granite factory unit.

Thin sections of the samples were studied under the polarized-light microscope in order to determine their mineralogical composition and investigate their texture. Polished thin sections were also prepared for the mineral chemistry. The LINK-AN 10000 Energy Dispersive System (EDS), attached on a JEOL JSM 840 Scanning Electron Microscope (SEM), were used to define the chemical composition of the minerals. Atomic absorption spectrometry was used to obtain the chemical

A short description of each sample is given below, as it arises from a macroscopic and microscopic investigation, which are presented elsewhere (Pavlidou 2002). The colour of each sample is the colour of the polished tile, while the nomenclature is based on the Q'-ANOR chemical classification (Streckeisen & Le Maitre 1979).

Salvatierra is a light gray, coarse-grained, porphyritic alkaligranite originating from Spain. It contains quartz, plagioclase, microcline, biotite, titanite, zircon, allanite and chlorite. The feldspars are kaolinized and sericitized.

Rosa porrino is a pinkish coarse-grained alkaligranite, with porphyritic structure, also from Spain. It contains quartz, plagioclase, microcline, biotite, zircon, allanite and a few chlorite. Its minerals are generally unaltered.

Blanco real is a white sample of medium- to coarse-grained alkaligranite originating from Spain. It is composed of quartz, plagioclase, microcline, biotite, muscovite, zircon, apatite and chlorite. The feldspars are kaolinized and sericitized.

Topazio is a yellow to light brown granite originating from Brazil. It contains quartz, plagioclase, orthoclase, biotite, garnet, actinolite, zircon and opaque minerals. This granite is slightly altered.

Yellow cecilia is a yellow-coloured coarse-grained granite with porphyritic structure. It comes from Brazil and its mineralogical composition is quartz, plagioclase, orthoclase, biotite, garnet, zircon and sillimanite. It is an almost unaltered sample.

Blanco crystal is a white, medium- to coarse-grained granite, coming from Spain. It contains quartz, plagioclase, orthoclase, biotite, titanite, zircon and chlorite. The feldspars are kaolinized and sericitized.

Napoleon is yellow-colored coarse-grained granite that originates from Brazil. It contains quartz, plagioclase, microcline, biotite, garnet, muscovite and zircon. The feldspars are kaolinized and sericitized.

Balmoral is a light-red coarse-grained granite. It is a finish granite containing quartz, plagioclase, microcline, biotite, muscovite, zircon, apatite, fluorite, monazite, epidote and chlorite. It is a rather unaltered sample.

African red is a dark-red coarse-grained granite from South Africa. It contains quartz, plagioclase, orthoclase, zircon and chlorite. The feldspars are totally kaolinized and sericitized and biotite is chloritized.

Multicolour is a medium- to coarse-grained granite with a gneiss-like structure of light red and dark gray zones. It comes from India and contains quartz, plagioclase, microcline, biotite, muscovite, zircon, apatite chlorite and opaque minerals. The feldspars are slightly kaolinized and sericitized.

Baltic brown is a dark brown, coarse-grained granite, with rapakivi texture (Haapala & Rämö 1999), originating from Finland. It contains quartz, plagioclase, orthoclase, biotite, amphibole, zircon, apatite and opaque minerals. Orthoclase is kaolinized.

Gris perla is a white to light gray-coloured coarse-grained granite with, porphyritic structure. It is a Spanish granite containing quartz, plagioclase, microcline, biotite, amphibole, titanite, zircon, apatite, allanite, epidote and chlorite. It is an almost unaltered sample.

Emerald is a black, iridescence, coarse-grained quartz monzonite, originating from Norway. It is called "larvikite". It contains alkali feldspar, biotite, amphibole, clinopyroxene, apatite and opaque minerals, and it is almost unaltered.

Marina pearl is a dark blue-gray iridescence, coarse-grained quartz monzonite coming from Norway. It is a "larvikite" like the Emerald sample. It contains alkali feldspar, biotite, clinopyroxene, olivine, zircon, apatite, allanite, epidote and opaque minerals, and is unaltered.

Zimbabwe is a black medium-grained quartz monzodiorite originating from South Africa. It contains quartz, plagioclase, orthopyroxene, clinopyroxene and opaque minerals. It is unaltered.

Africa nero is a black to dark brown, medium-grained quartz gabbro originating from South Africa. It contains quartz, plagioclase, orthopyroxene and clinopyroxene. It is almost unaltered.

The natural radioactivity (^{238}U , ^{226}Ra , ^{232}Th and ^{40}K content) of the samples was measured by gamma spectrometry (Manolopoulou 1990). All samples were crushed into grains less than 400 μm in diameter, oven-dried at 60°C to constant weight, well-blended and measured using two high-resolution gamma ray spectrometry systems. The first one consisted of a HPGe coaxial detector with 42% efficiency and 2.0 keV resolution at 1.33 MeV photons, shielded by 4" Pb, 1mm Cd and

1mm Cu and the second one consisted of a LEGe planar detector with 0.7 keV resolution at 122 keV photons, shielded by 1.3" Pb, 1mm Cd and 1mm Cu. The efficiency calibration of the gamma spectrometry systems was performed with the radionuclide specific efficiency method in order to avoid any uncertainty in gamma ray intensities as well as the influence of coincidence summation and self-absorption effects of the emitting gamma photons. A set of high quality certified reference materials (IAEA, RG-set) was used, with densities similar to the building materials measured after pulverization. Cylindrical geometry (\varnothing 55 mm, h= 20 mm) was used assuming that the radioactivity is homogenously distributed in the measuring samples. The measurement duration was up to 200000 sec.

3 RESULTS AND DISCUSSION

The results of the specific activities and the average activity concentrations of ^{238}U , ^{226}Ra , ^{235}U , ^{232}Th and ^{40}K of sixteen granite samples examined are presented in tables 1 and 2, respectively, while in figure 1 the activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K of the examined samples are compared. The average activity concentrations of the natural radionuclides of granites from different countries from all over the world reported by Chen & Lin (1995), are shown in table 3, for comparison. The average activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K of the samples examined (Tab. 2) are slightly higher than those reported by Chen & Lin (1995) for the granites of different countries all over the world.

Table 1. Activity concentrations of ^{238}U , ^{226}Ra , ^{235}U , ^{232}Th and ^{40}K (Bq kg^{-1}) of granites examined.

Granite name	^{238}U	^{226}Ra	^{235}U	^{232}Th	^{40}K
1. Salvatierra	115 ± 9	118 ± 2	4.3 ± 0.6	77 ± 2	1320 ± 33
2. Rosa porriño	61 ± 5	59 ± 1	2.5 ± 0.8	109 ± 2	1420 ± 36
3. Blanco Real	96 ± 5	117 ± 1	5.3 ± 1.0	95 ± 1	1233 ± 30
4. Topazio	32 ± 5	29 ± 1	1.5 ± 0.6	44 ± 1	1327 ± 33
5. Yellow cecilia	<MDA	19 ± 1	1.0 ± 0.5	30 ± 1	1020 ± 26
6. Blanco crystal	163 ± 9	163 ± 2	7.0 ± 0.7	91 ± 2	1190 ± 30
7. Napoleon	< MDA	11 ± 2	< MDA	46 ± 1	1200 ± 30
8. Balmoral	174 ± 7	170 ± 1	7.7 ± 1.3	354 ± 3	1592 ± 39
9. African red	98 ± 5	80 ± 1	4.2 ± 1.2	121 ± 1	1421 ± 32
10. Multicolour	< MDA	11 ± 1	1.0 ± 0.5	84 ± 2	926 ± 23
11. Baltic brown	64 ± 6	60 ± 1	2.9 ± 0.7	57 ± 1	1350 ± 34
12. Gris perla	67 ± 5	70 ± 1	3.2 ± 0.5	43 ± 1	1340 ± 34
13. Emerald	50 ± 4	55 ± 1	2.5 ± 1.2	63 ± 1	1053 ± 24
14. Marina pearl	29 ± 3	35 ± 1	1.1 ± 0.5	37 ± 1	894 ± 22
15. Zimbabwe	19 ± 4	20 ± 1	< MDA	32 ± 1	332 ± 14
16. Africa nero	< MDA	1.6 ± 0.3	< MDA	< MDA	49 ± 4

MDA = minimum detectable activity; ^{238}U : 9 Bq.kg^{-1} ; ^{235}U : 1 Bq.kg^{-1} ; ^{232}Th : 1 Bq.kg^{-1}

Table 2. Average activity concentration of the natural radionuclides (Bq kg^{-1}) of granite samples examined.

Nuclide	^{238}U	^{226}Ra	^{232}Th	^{40}K
Average	61	64	81	1104
Standard deviation	56	53	79	407
Range	<MDA - 174	2 - 170	<MDA - 354	49 - 1592
MDA	9	1	2	12

MDA = minimum detectable activity

Table 3. Average activity concentrations of the natural radionuclides (Bq kg⁻¹) of 137 granite samples from different countries all over the world*.

Nuclide	²²⁶ Ra	²³² Th	⁴⁰ K
Average	42	73	1055
Standard deviation	35	51	357
Range	0.2-160	<MDA-253	<MDA-2355
MDA	0.2	4.0	36.0

MDA = minimum detectable activity

*Chen and Lin (1995)

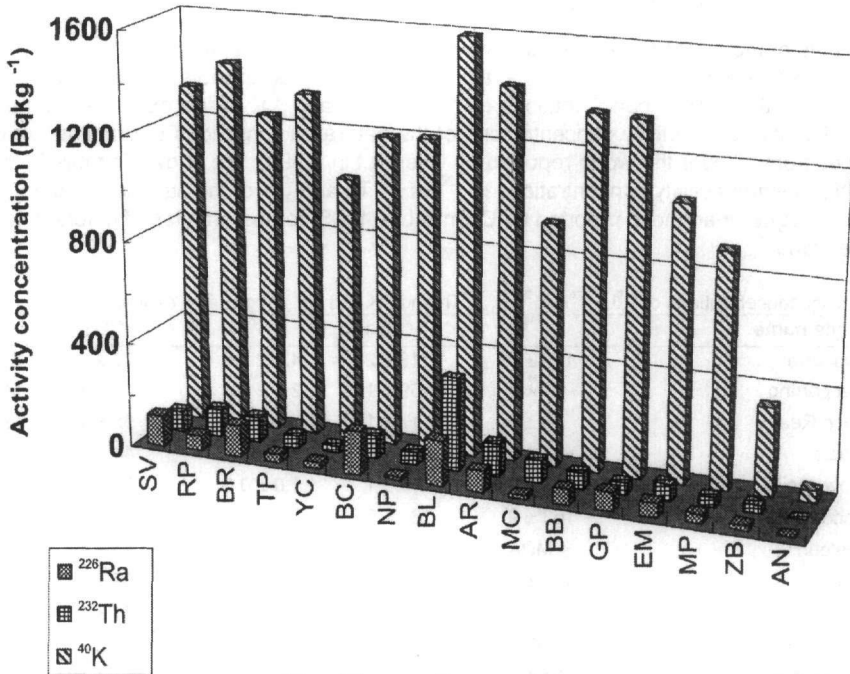


Figure 1. The activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K (Bq kg⁻¹) of the granite samples examined. SV: Salvatierra, RP: Rosa porriño, BR: Blanco real, TP: Topazio, YC: Yellow Cecilia, BC: Blanco crystal, NP: Napoleon, BL: Balmoral, AR: African red, MC: Multicolour, BB: Baltic brown, GP: Gris perla, EM: Emerald, MP: Marina pearl, ZB: Zimbabwe and AN: Africa nero.

The mean activity concentrations of ²²⁶Ra, ²³²Th and ⁴⁰K of the granite samples examined were compared to those of different building materials (Zikovsky & Kennedy 1992) and the earth's crust (UNSCEAR 2000) (Tab. 4). It is pointed out that the natural radionuclide content of granites of the present study is relatively high, just like those of all granite types referred in the literature (Chen & Lin 1995), compared to other building materials, such as concrete, brick and clay brick, gypsum, gravel, glass wool, tile, glass and wood (Fig. 2). The latter has the lowest natural radionuclide content, while some kinds of concrete; brick and tile show relatively high natural radioactivity in contrast to gypsum and glass.

In order to assess the radiological impact of granites used as building materials, the model of a cubic building 3m×3m×3m, infinite thin walls and no doors and windows (standard room model) was considered (UNSCEAR 1993).

The absorbed dose rate was determined by the following formula:

$$D \text{ (n Gy h}^{-1}\text{)} = \alpha_1 C_{40K} + \alpha_2 C_{232Th} + \alpha_3 C_{226Ra} \quad (1)$$

where:

C_{40K} , C_{232Th} , C_{226Ra} = the specific activity of ⁴⁰K, ²³²Th and ²²⁶Ra respectively, in Bq kg⁻¹

$$\alpha_1 = 0,0414 \text{ n Gy h}^{-1}/\text{Bq kg}^{-1}$$

$$\alpha_2 = 0,623 \text{ n Gy h}^{-1}/\text{Bq kg}^{-1}$$

$$\alpha_3 = 0,461 \text{ n Gy h}^{-1}/\text{Bq kg}^{-1}$$

The annual effective dose limit was considered 1 to 2 mSv.

Table 5 shows the absorbed dose rate D (nGy h^{-1}) and the annual effective dose D_a (mSv) estimated for the granite samples examined. Corresponding data for the mean soil composition (UNSCEAR 1993) are included for comparison. It is concluded that the absorbed dose for people living in dwellings made of the granites examined would be higher than the absorbed dose for those living in dwellings made of building materials having the mean soil composition except for the case of granites Zimbabwe and Africa nero. Moreover, the annual effective dose D_a (UNSCEAR 1993) exceeds the limit of 1 mSv for six samples (Tab. 5) as follows: Salvatierra (1.4 mSv), Rosa porriño (1.4 mSv), Blanco real (1.4 mSv), Blanco crystal (1.6 mSv), Balmoral (3.2 mSv), African red (1.5 mSv). However, granite, being a relatively expensive material, is only used on floors, tables, exterior walls, fire places and other decorations, and as a result, its contribution in most of the building constructions is relatively low. So, granite would contribute to the level of natural radioactivity, but it wouldn't be responsible for exceeding the 1 mSv dose limit.

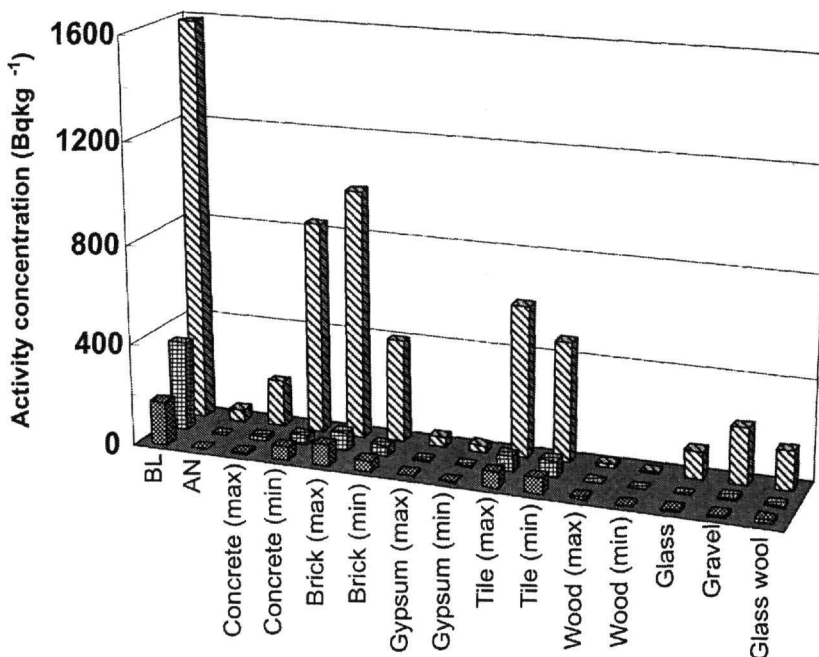


Figure 2. The activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K (Bq kg^{-1}) of the granite samples BL (Balmoral) and AN (Africa nero), having the maximum and the minimum annual effective dose D_a among the examined samples, are compared to maximum (max) and minimum (min) activity concentrations of different building materials (Zikovsky & Kennedy 1992). Symbols as in figure 1.

There has been an attempt to correlate the mineral composition of granites to the relatively high level of natural radioactivity. According to Heinrich (1958), natural radioactivity of igneous rocks is mostly attributed to the chemical composition of minerals that they contain and to a lesser extent to fluid inclusions in minerals and intergranular fluids. Some minerals contain radioactive nuclides either as basic elements in their chemical composition or as elements that substitute the basic ones. Table 5 shows the accessory minerals found in all samples that could be radioactive, according to Heinrich (1958), if they contain Uranium or Thorium compounds.

Table 4. Average activity concentrations of ^{226}Ra , ^{232}Th and ^{40}K (Bq kg^{-1}) of building materials from different countries all over the world¹ granites^{2,3} and Earth's crust⁴.

Material	Number of samples	^{226}Ra	^{232}Th	^{40}K
Concrete (UK)	21	19	11	183
Concrete (Spain)	24	30	32	204
Concrete (Canada)	13	11	17	488
Concrete (Finland)	15	53	38	838
Brick (Germany)	109	59	67	670
Brick (Canada)	6	44	59	404
Brick-clay (UK)	25	52	44	640
Brick-clay (Spain)	11	68	56	416
Brick-clay (Netherlands)	14	39	41	560
Brick-clay (Finland)	38	80	62	986
Gypsum-chemical (Canada)	3	33	31	79
Gypsum-natural (Canada)	3	4	5	40
Gypsum-natural (Finland)	1	7	1	25
Gravel (Canada)	3	10	12	222
Glass wool (Finland)	8	16	7	157
Tile (Canada)	15	61	66	476
Tile (Netherlands)	8	61	66	600
Glass (Netherlands)	2	8	2	110
Wood (Netherlands)	2	10	4	19
Wood (Finland)	2	0	1	10
Granites ²	16	61	82	1061
Granites ³	167	42	73	1055
Earth's crust ⁴	-	35	30	400

¹Zikovsky & Kennedy (1992), ²Present study, ³Chen & Lin (1995), ⁴UNSCEAR (2000).

Table 5. Potentially radioactive accessory minerals in the granite samples examined, absorbed dose rate D (nGy h^{-1}), annual effective dose D_e (mSv) for the samples and the mean soil composition.

Name	Potentially radioactive minerals	Absorbed dose rate D (UNSCEAR 1993) (nGy h^{-1})	Annual effective dose D_e (UNSCEAR 1993) (mSv)
1. Salvatierra	Tit, Zr, All	157.2	1.4
2. Rosa porrino	Zr, All	153.9	1.4
3. Blanco real	Zr, Ap, Mz	164.2	1.4
4. Topazio	Zr, Hem, Ru	95.7	0.8
5. Yellow cecilia	Zr	69.7	0.6
6. Blanco crystal	Tit, Zr, Mz	181.1	1.6
7. Napoleon	Zr	83.4	0.7
8. Balmoral	Zr, Ap, Fl, Mz,	364.8	3.2
9. African red	Zr	171.1	1.5
10. Multicolour	Tit, Zr, Ap, Py, Hem	95.7	0.8
11. Baltic brown	Zr, Ap, Py, Hem, Ilm	119.1	1.0
12. Gris perla	Tit, Zr, Ap, All	114.5	1.0
13. Emerald	Ap, Py, Hem	108.2	1.0
14. Marina pearl	Zr, Ap, Al, Py, Ilm	76.2	0.7
15. Zimbabwe	Py, Hem	42.9	0.4
16. Africa nero	-	2.8	0.0
Mean soil composition*		43.5	0.4

*UNSCEAR (1993), Tit=titanite, Zr=zircon, Ap=apatite, Fl=fluorite, All=allanite, Mz=monazite, Py=pyrite, Hem=hematite, Ilm=ilmenite.

Due to its high specific activity of ^{232}Th ($354 \pm 3 \text{ Bq kg}^{-1}$), Balmoral granite appears to have the higher annual effective dose ($D_a=3.2 \text{ mSv}$). Furthermore, monazite with high amount of ThO_2 (4.00%) has been found in its mineralogical composition. The chemical composition of monazite in this sample is shown in table 6. Consequently, the high level of natural radioactivity of Balmoral granite is attributed to its monazite content. Also, this sample contains other minerals, such as zircon, apatite and fluorite, which could contain radioactive nuclides in their chemical composition and thus contribute to the level of natural radioactivity of the sample.

Monazite has also been found in the samples Blanco real ($D_a=1.4 \text{ mSv}$) and Blanco crystal ($D_a=1.6 \text{ mSv}$). Its presence in these samples could justify the natural radioactivity caused by Thorium (Tab. 6).

Table 6. Average electron microprobe analysis of monazite of the samples Blanco real (BR), Blanco crystal (BC) and Balmoral (BL).

Sample	BR	BC	BL
Number of analyses	4	3	6
Oxides % w/w			
SiO_2	0.00	0.00	2.88
P_2O_5	30.27	34.19	30.02
Y_2O_3	13.55	33.60	3.71
La_2O_3	10.65	3.48	16.04
Ce_2O_3	21.11	7.85	28.89
Pr_2O_3	1.70	1.12	2.76
Nd_2O_3	7.89	4.33	8.27
Sm_2O_3	0.75	0.83	0.82
Gd_2O_3	0.62	2.76	1.26
Dy_2O_3	1.12	4.11	0.49
ThO_2	8.34	5.01	4.00
UO_2	1.67	0.82	0.00
Total	97.66	98.09	99.13

All the other samples of granites resulting in an annual effective dose higher than 1 mSv (Tab. 5), contain accessory minerals that, according to Heinrich (1958), could contain radioactive nuclides in the form of U- or Th-compounds. It is obvious that the rest of the samples, contain possibly radioactive minerals as well. It must be their quantity and their particular chemical composition that have a specific effect on the level of natural radioactivity of each sample.

Another interesting point is that the two red granite samples, i.e. Balmoral and African red, show relatively enhanced radioactivity. It is remarkable that most of the granite samples with high radioactivity examined by Chen & Lin (1995) were also red. As for the other highly radioactive samples, one of them was light gray (Salvatierra), two were white (Blanco real and Blanco crystal) and one was pink (Rosa porriño).

The red colour of Balmoral and African red granites is due to the more abundant minerals, the feldspars that are reddish in colour. The red colour of feldspars is due to hematite inclusions (Smith & Brown 1988). Electron microprobe analysis of feldspars in Balmoral and African red granites show relatively high amounts of Fe, as it is shown in table 7, which could justify the presence of such inclusions. According to Heinrich (1958), hematite could be radioactive, containing small amounts of Uranium. Thus, it is possible that hematite inclusions in feldspars might contribute to the level of natural radioactivity of Balmoral and African red granites.

Table 7. Average electron microprobe analysis of feldspars of the samples African red (AR) and Balmoral (BL).

Sample	BL	AR	AR
Feldspar type	Mi	Or	Pl
Number of analyses	3	2	2
Oxides %w/w			
SiO ₂	65.37	64.85	65.13
TiO ₂	0.04	0.35	0.00
Al ₂ O ₃	18.46	18.02	20.67
FeO	0.18	0.87	1.29
CaO	0.00	0.00	0.85
Na ₂ O	1.50	2.44	10.66
K ₂ O	14.16	12.54	0.58
BaO	0.14	0.44	0.33
Total	99.84	99.51	99.50

Mi = Microcline, Or = Orthoclase, Pl = Plagioclase

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