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Gamma activity and geochemical features of building materials: estimation of gamma dose rate and indoor radon levels in Sicily

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Abstract

A high-purity germanium detector has been used to measure the abundance of radium (Ra), thorium (Th) and potassium (K) in building materials used in Sicilian dwellings. The measurements were performed to evaluate which material was suitable for the construction of an enclosure, which would have a low background emission. The materials examined in this work showed concentrations of ^{226}Ra, ^{232}Th and ^{40}K dramatically variable depending on the lithologies, particularly in the case of blocks, sands and aggregates commonly used in building materials in Sicily. The results are discussed and a criterion is indicated to reduce the radiation dose to humans. Since radon inlet is a major health problem, all the radiometric data and the geochemical features have been used to determine the radon exhalation, which arises from the disintegration of ^{226}Ra in soils and walls of houses. From our experimental data it can be seen out that one of the geochemical parameters, Total Alkali (TA), may be an appropriate index to select materials of low radiological risk. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Building materials; Radium equivalent; Radon exhalation

1. Introduction

Building materials are the main source of indoor gamma radiation, beside terrestrial and cosmic radiation. All stone-based building materials contain radioactive nuclides. ^{226}Ra and ^{232}Th, and their progenies, and ^{40}K, are the most important.

Even though radon inlet into houses is a complex process involving building materials, soil, gas, water, and weather related factors, ^{226}Ra in construction materials may be in some cases the predominant source.

Much of the radon is released from the radium trapped in the mineral grains in building materials. The gas then escapes into the air because the radon diffusion length is comparable to the material thickness. This contribution depends on radium concentration, which is generally low in materials of normal activity (~40 Bq kg^{-1}) (UNSCEAR, 1993).

The radon diffusion length in soil is estimated to range from 1 cm in moist clay soil to 2 m in well-drained gravel soils. The radium concentration in worldwide surface soil is relatively uniform, except in some well-defined areas that have a naturally higher concentration, such as some felsic volcanic soils and in some uranium mining regions.

However, in buildings with high-radium levels, the radon exhalation from building materials may become of major importance. The knowledge of radioactivity levels of materials used in the buildings and in ceramic industries is therefore important in the assessment of possible radiological hazards to human health. This

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knowledge is essential for the development of standards and guidelines for the use and management of these materials.

Sicily is an island with several specific geological characteristics and many lithotypes are present, offering a variety of peculiarities for building materials.

This work presents data concerning the concentration of the natural radionuclides in relation to the lithological and chemical features of natural quarried materials used as block or to obtain by-products and artificial building materials used in the construction of Sicilian dwellings. Additionally, the same characteristics in imported materials, used in dwellings, are also examined. A theoretical model has been used to estimate the contribution of such materials to the indoor dose rate and to the radon air concentration.

2. Experimental

A complete investigation of building materials to obtain estimation of γ dose rate and indoor radon concentration requires that all the most commonly used materials be monitored. The data presented in this paper are related to 66 samples quarried in Sicily collected at 30 sites selected from the most common lithologies. Seven cements and six sands were investigated since they are also of essential importance in the house building trade. To extend the study to all types of locally used materials, 28 building materials imported from other areas have also been included.

The samples of natural origin were chosen from among the eight most representative lithologies of the island. The seven cements, produced in Sicily, were mixtures of local rocks and had various compositions. The imported materials were materials like marbles and granites, mostly used for non-structural purposes.

The specific activities were evaluated by γ-ray spectrometry on samples crushed or milled into a powder with a particle size of less than 5 μm. Samples were dried and sealed into a "Marinelli" beaker. Measurements were performed after 20 days to be sure that secular equilibrium between ^{226}Ra, ^{222}Rn and its daughters had been reached. Spectrometry measurements of γ-activity were carried out using an HPGe detector, whose relative efficiency was 32% and which had a resolution of 1.8 keV. It was calibrated against a standard soil (NBS SRM 4353) containing all the radionuclides of interest. The activities of ^{226}Ra and ^{232}Th were computed from the ^{214}Bi 609 keV and ^{228}Ac 911 keV lines, respectively. If secular equilibrium in the materials examined does exist, the measured values of ^{226}Ra should correspond to those of ^{238}U.

The minimum detectable activity, for a 1000 min counting time, ranged between 3.2 and 8.9, 0.26 and 0.61, 0.59 and 1.8 Bq kg^{-1}, for ^{40}K, ^{228}Ac and ^{214}Bi, respectively. Data were corrected for density, which ranged between 0.6 and 1.6 g cm^{-3}.

Lithological and geochemical features of the materials were also determined. Mineralogical and chemical compositions were determined by X-ray diffractometry (XRD) and fluorescence (XRF) techniques.

3. Theoretical model

Building materials can contribute to γ-ray dose rate through inhalation of ^{222}Rn and external irradiation by other radionuclides. Measurements of the radionuclide concentrations are used to evaluate both indoor radon concentration and γ dose rate.

Exhalation of radon from these materials is of interest since the short-lived decay products of some radon isotopes are the greatest contributors to the lung dose from inhaled radionuclides. The most important isotope of radon is ^{222}Rn (radon, $t_{1/2} = 3.82$ d) and belongs to the ^{238}U natural chain. ^{220}Rn (thoron, $t_{1/2} = 55$ s) is another isotope and belongs to the ^{232}Th natural chain. Essentially, the ^{220}Rn comes out from a thin external layer of the walls, due to the relationship of half-life time to diffusion rate (0.2–0.3 m d^{-1}). The entire wall, however, contributes to the ^{222}Rn concentration in indoor air. The irradiation levels are almost entirely due to ^{222}Rn, in the case of a room with infinitely thick walls.

The transport of radon through building materials is primarily caused by diffusion and is regulated by Fick's law. The exhalation rate E_x (Bq m^{-2} h^{-1}) can then be obtained by solving the diffusion equation (Farnham, 1992; Man and Yeung, 1999).

Assuming that C_{Ra} is the concentration of ^{226}Ra (Bq kg^{-1}), λ_{Rn} (h^{-1}) is the radon decay constant, ρ is the material density (kg m^{-3}), d the wall thickness (m), and η the emanation coefficient, i.e. the fraction of radon that reaches the surface of the wall by means of the diffusion process, then the exhalation rate E_x (Bq m^{-2} h^{-1}) is

$$E_x = \tfrac{1}{2} C_{Ra} \lambda_{Rn} \rho \eta d. \quad (1)$$

The calculated exhalation rate provides the radon concentration:

$$C_{Rn} = \frac{E_x S}{\Phi}, \quad (2)$$

where S(m^2) is the surface of the room walls and Φ (m^3 h^{-1}) is the air ventilation flux (Diano and Bellecci, 1998).

The radium equivalent activities (Ra_{eq}) can be calculated (Stranden, 1979; Zaidi et al., 1999) using the formula

$$Ra_{eq} = A_{Ra} + 1.43 A_{Th} + 0.077 A_{K}, \quad (3)$$

where A_{Ra}, A_{Th} and A_K are the specific activities for the different radionuclides.

The levels of γ external radiation in buildings are important in the assessment of population exposures, as most individuals spend a large amount of time indoors. The indoor absorbed dose rates depend essentially on the type of building materials used. Country-averaged indoor-to-outdoor ratios range from 0.8 to 2.0, with an average of 1.3. An average outdoor dose rate in air of 55 nGy h^{-1} yields an average indoor absorbed dose rate in air of 72 nGy h^{-1} (UNSCEAR, 1993). Higher indoor external dose rates may arise from high concentrations of natural radionuclides in building materials. The resulting exposures, calculated with pessimistic assumptions, range between 100 and 2000 nGy h^{-1}. The annual effective dose equivalent, assuming 0.7 Sv Gy^{-1} for environmental exposures to gamma rays of moderate energy, using an occupancy factor of 0.8 and an absorbed dose rate of 80 nGy h^{-1}, is about 392 μSv.

4. Results

All the materials grouped by lithology are listed in Table 1. The number of samples, the mass percentage ranges of some major elements measured by XRF, and the common usage in dwellings are shown.

Table 2 shows the mean measured (by γ-spectrometry) specific activities of ^{226}Ra, ^{232}Th and ^{40}K of the major lithologies found in Sicily, and of the cements. The radium equivalent range (calculated by Eq. (3)), its mean value and standard deviation are also shown.

The corresponding information for building materials imported from other countries is shown in Table 3.

The calculated values Ra_{eq} are reported in the last column of Tables 2 and 3 to evaluate the relative radiological risk due to external gamma irradiation. The lowest mean values were obtained for marbles

Table 1
Materials examined, their prevalent chemical components and common usage in dwellings

Material (lithology)	No. of samples	SiO_2	CaO	MgO	Na_2O	K_2O	Typical usage
Limestone	31	0.01–9.7	29–56	0.2–22	0–0.17	0–0.4	Cement mixture, covering, blocks
Marble	8	0.05–28	22–56	0.5–22	0	0–0.13	Covering
Gypsum	5	8.2–16	61–83	2.3–7.9	0–0.05	0.3–0.6	Mixtures, internal walls
Cement[a]	7	13–24	53–69	0.65–1.4	0.02–0.3	0.09–0.9	Assembling
Basic magmatic	13	38–53	9–16	3–12	1.6–5	0.16–2	Covering, blocks
Clay	7	46–59	1.6–28	1.4–3.6	0.14–5	0.5–2.6	Cement mixture, brick, insulating
Schist	6	56–70	0.12–4	0.5–4.2	0.6–4.3	1.8–4.7	Covering, blocks
Acid magmatic	24	58–77	0.4–5.8	0–2.8	0.05–7	2.4–8.6	Covering, blocks
Silicic sand	6	78–97	0.05–9	0–0.52	0.07–0.5	0.17–0.9	Mixtures, glasses

[a] Artificial mixture of several lithologies

Table 2
Mean specific activities of radium, thorium and potassium measured by γ-ray spectrometry in the Sicilian materials used in buildings and their calculated radium equivalent specific activities. The range of radium equivalents of the samples and the mean radium equivalent of their total activity are also shown

Material	No. of samples	Mean specific activity ± S.D. (Bq kg^{-1})			Radium equivalent (Bq kg^{-1})	
		^{226}Ra	^{232}Th	^{40}K	range	Mean ± S.D.
Sedimentary						
Clay	7	34 ± 8	38 ± 17	513 ± 192	39–158	127 ± 41
Limestone	27	11 ± 8	2 ± 2	22 ± 33	0.7–38	14 ± 11
Gypsum	5	6 ± 5	2 ± 2	32 ± 43	15–31	12 ± 11
Silicic sand	6	9 ± 3	9 ± 4	156 ± 81	10–53	34 ± 14
Magmatic						
Basic	11	34 ± 25	26 ± 19	330 ± 231	21–204	96 ± 68
Acid	15	168 ± 48	157 ± 44	1303 ± 83	278–816	494 ± 107
Metamorphic						
Schist	3	39 ± 4	54 ± 12	766 ± 258	128–203	175 ± 40
Cements						
Mixture of local materials	7	38 ± 14	22 ± 14	218 ± 248	39–161	92 ± 50

Table 3
The same as in Table 2 for imported materials

Material	No. of samples	Mean specific activity ± S.D. (Bq kg^{-1})			Radium equivalent (Bq kg^{-1})	
		^{226}Ra	^{232}Th	^{40}K	Range	Mean ± S.D.
Sedimentary						
Limestone	4	9 ± 13	3 ± 3	45 ± 76	6–30	16 ± 14
Magmatic						
Basic	2	11 ± 12	15 ± 18	217 ± 272	10–89	49 ± 56
Acid	11	74 ± 34	106 ± 89	1424 ± 436	173–768	335 ± 160
Metamorphic						
Marble	8	4 ± 12	0.9 ± 3.6	16 ± 20	1–23	6 ± 7
Schist	3	52 ± 33	50 ± 26	925 ± 499	87–305	194 ± 108

(6 Bq kg^{-1}) and the highest for acid magmatic rocks (494 Bq kg^{-1}). These values are correlated with the values of Si and total alkali (TA) in the two lithologies. TA is the cumulated concentration of Na_2O and K_2O.

The radium equivalent values vs. SiO_2, CaO and total alkali (TA) content are shown in Figs. 1a, b, c, respectively. The positive correlation between Ra_{eq} and TA seems to indicate that TA can be used to give some indication of the radiological impact. It is worth noting that, for values of TA lower than 5%, the Ra_{eq} level is smaller than 150 Bq kg^{-1}, for all samples. A less definitive correlation is observed in the SiO_2 and CaO cases. A dashed line at 150 Bq kg^{-1} has been drawn, as a guide and to conservatively discriminate among different materials radiological impact.

Tables 4 and 5 show the minimum and maximum values of the radon exhalation rate, calculated from Eq. (1), for the different building materials, both for locally quarried and imported materials. The densities used in the calculations are mean values for the lithologies and are reported in the literature (Bellanca, 1969). The lowest exhalation rate value has been found in marbles (0.01 Bq m^{-2} h^{-1}) and the highest one in acid magmatic rocks (79 Bq m^{-2} h^{-1}).

5. Discussion

Radium equivalent concentration is the quantity representative of external γ irradiation dose associated with a material.

The data in Tables 2 and 3 show large variations in radium equivalent activities in some samples, even within the same lithotypes. This result suggests that it is advisable to monitor the radioactivity levels of building materials anytime they come from a new supplier. The value of Ra_{eq} should be smaller than 370 Bq kg^{-1}, in order to limit the external exposure dose due to gamma rays to 170 nGy h^{-1} (Beretka and Mathew, 1985).

The conservative model based on infinitely thick walls without windows and doors assumes, as a safety criterion, that

$$\frac{A_{Ra}}{370} + \frac{A_{Th}}{260} + \frac{A_K}{4810} < 1. \quad (4)$$

Fig. 2 clearly shows that only in the case of acid magmatic samples, mostly used on volcanic islands, does the criterion index exceed the safety level of 370 Bq kg^{-1}.

The estimate of world average indoor dose rate (80 nGy h^{-1}) from specific activities of the radionuclides can be obtained using the dose rate per unit specific concentration in materials of 0.461, 0.623, 0.041 nGyh^{-1} per Bq kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, and assuming specific activities of 50, 50, and 500 Bq kg^{-1} for ^{226}Ra, ^{232}Th and ^{40}K, respectively, for standard materials (UNSCEAR, 1993). Using the data of Tables 2 and 3 and assuming that only one material is used in the dwelling, the dose rate values are between 0.32 and 376 nGy h^{-1} for enclosures totally made of limestone and acid magmatic rocks, respectively.

The correlation of radium equivalent and the principal chemical parameters used to characterize materials is noteworthy (Fig. 1).

It is known that Si is an index used to recognize the magmatic differentiation (Bellia et al., 1996), and could be used to select materials of low radiological impact only in geological areas of prevalent magmatic origin. CaO is totally uncorrelated. The TA values show a significant positive correlation with radium equivalent. Geological knowledge indicates that Na and K increase coherently with the most common evolution processes in sedimentary, metamorphic and magmatic rocks, and we suggest it as a good safety index in all building materials except for a very few cases.

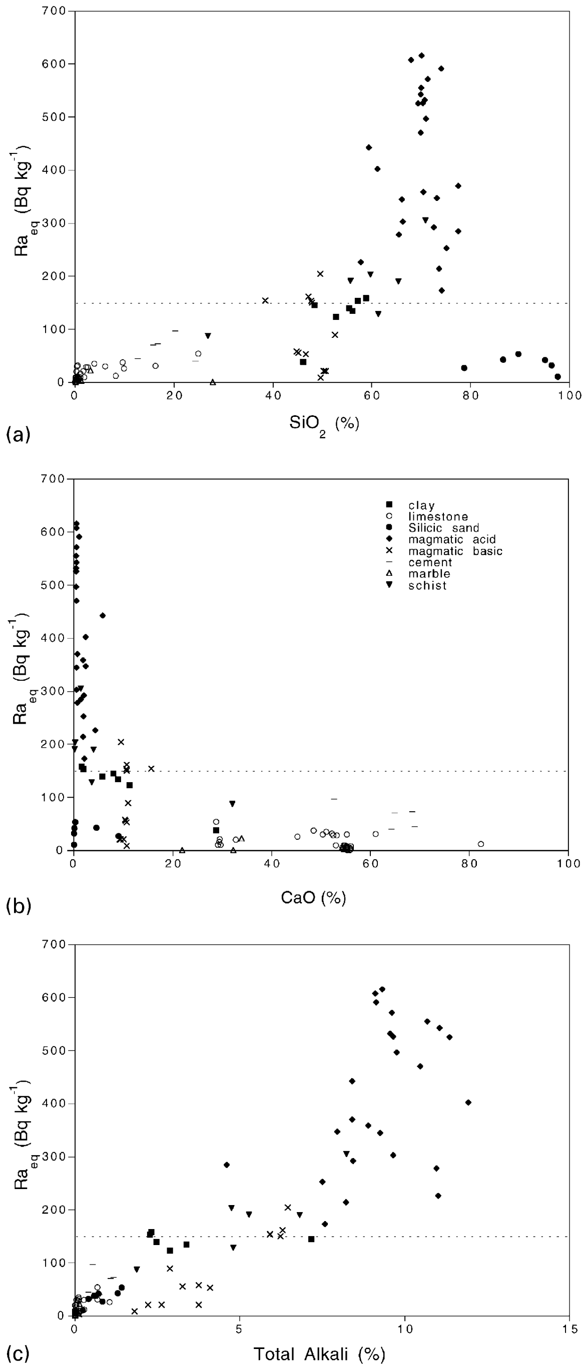

Fig. 1. Calculated radium equivalent from experimental specific activities of primordial radionuclides vs. two major chemical components (Si, Ca oxide weight%) and total alkali (Na + K oxide weight%) (Dashed line is at $150\,\mathrm{Bq\,kg^{-1}}$).

The obtained indoor radon values are to be compared with the $200\,\mathrm{Bq\,m^{-3}}$ limit, defined as the action limit internationally recommended (ICRP, 1993), where it is assumed that the indoor occupancy factor is 7000 h per year and the equilibrium factor within radon decay progenies is 0.4.

The equation relating the average radon concentration C_{Rn} ($\mathrm{Bq\,m^{-3}}$) and the average radon supply ($\mathrm{Bq\,s^{-1}}$) into a building with an average ventilation flow Φ ($\mathrm{m^3\,h^{-1}}$) is

$$C_{\mathrm{Rn}} = \frac{S_{\mathrm{a}} + S_{\mathrm{b}} + S_{\mathrm{s}}}{\Phi}, \tag{5}$$

where S_{a}, S_{b} and S_{s} indicate the average radon supplies from outside air, radium in building materials and radium in soil, respectively.

If we assume a weak contribution to radon indoor concentration due to the influx of outside air and that the geological composition of soil is of the same nature as the building materials, we can use Eq. (5) with $S_{\mathrm{b}} = E_x S$ (see Eq. (2)).

The calculated exhalation rate can be used to estimate the indoor radon concentration in the limit of a cavity with an air exchange of Φ. Then if we assume a surface area of the room walls, $S = 100\ \mathrm{m}^2$, a ventilation flow of $10\,\mathrm{m^3\,h^{-1}}$, we obtain a range from a minimum of $0.1\,\mathrm{Bq\,m^{-3}}$ for a marble enclosure to a maximum value of about $800\,\mathrm{Bq\,m^{-3}}$ for walls made of acid magmatic blocks.

Data obtained in this study are in agreement with the values of indoor radon concentration measured using an integrative sampling detector, alpha particle track etch detector and LR115 films, by our group in a previous survey in the volcanic island of Pantelleria where the houses are built with thick blocks of basalt (basic magmatic), in the north-west part of the island, and with blocks of trachytes, rhyolites (acid magmatic) in the remaining villages. The mean of the values measured were respectively, 100 and $250\,\mathrm{Bq\,m^{-3}}$ (Brai et al., 1991).

The geological nature of most of the materials used in residential areas in Sicily is sedimentary, mainly limestones with a low ^{226}Ra content. Moreover, the aggregates and cements locally produced are essentially a mixture of sedimentary rocks. The values of specific activities of Sicilian cements are lower than the pozzolanic cements used in other regions of Italy (Battaglia et al., 1990).

In the case of limestone, the minimum and maximum values of the indoor radon concentration were, respectively, 1 and $140\,\mathrm{Bq\,m^{-3}}$. A survey carried out by alpha track techniques to measure indoor radon concentration in Palermo, Sicily, gave a mean value of $20\,\mathrm{Bq\,m^{-3}}$ (Brai et al., 1991), less than one-half of the Italian mean value.

The theoretical values were obtained under the worst possible conditions of the parameters on which both exhalation rate and indoor radon concentration depend. It is therefore perfectly safe to assume that the estimated value refers to a hypothetical maximum since under the

Table 4
^{226}Ra-specific activity and emanation and density values of the Sicilian materials. In the last column the estimated exhalation rates are reported

Material	^{226}Ra specific activity ($Bq\,kg^{-1}$)	Mean emanation (fraction)	Density ($10^3\,kg\,m^{-3}$)	Exhalation ($Bq\,m^{-2}\,h^{-1}$)
Sedimentary				
Clay	21–42	0.04	2–2.7	2.7–7.4
Limestone	0.4–30	0.23	1.1–2	0.16–22
Gypsum	0.6–13	0.08	2–2.4	0.15–4.1
Cement				
Concrete	12–40	0.15	1.4–1.6	4.1– 16
Magmatic				
Basic	5–64	0.01	2.7–2.7	0.22–2.8
Acid	55–225	0.08	2.4–2.7	17–79
Metamorphic				
Schist	34–42	0.02	2.6–3	2.9–4.1

Table 5
The same as in Table 4 for imported materials

Material	^{226}Ra specific activity ($Bq\,kg^{-1}$)	Mean emanation (fraction)	Density ($10^3\,kg\,m^{-3}$)	Exhalation ($Bq\,m^{-2}\,h^{-1}$)
Sedimentary				
Limestone	1–29	0.23	1.1–2.4	0.4–26
Magmatic				
Basic	2–20	0.01	2.7–3.2	0.08–1.0
Acid	16–153	0.08	2.5–2.7	5.2–54
Metamorphic				
Marble	0.6–10	0.005	2.4–3	0.01–0.25
Schist	19–86	0.02	2.6–3	1.6–8.7

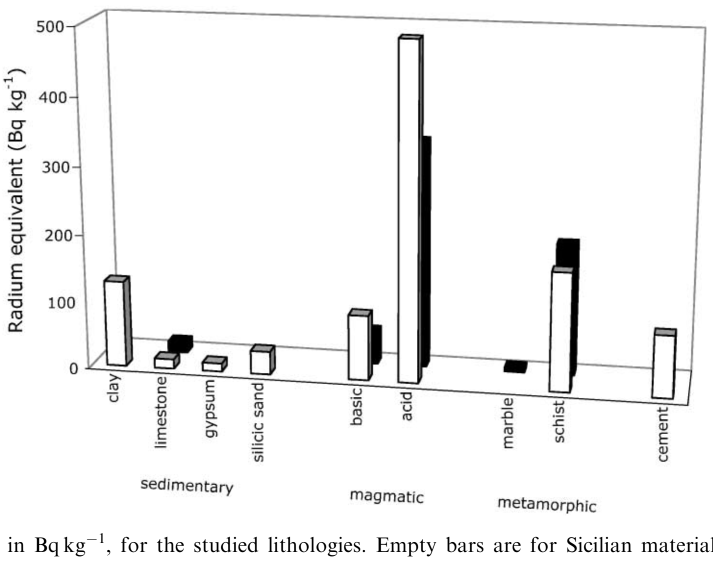

Fig. 2. Radium equivalent, in $Bq\,kg^{-1}$, for the studied lithologies. Empty bars are for Sicilian materials, filled ones for imported materials.

real conditions the contribution of the building materials in Sicily will be considerably smaller.

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