韓國環境保健學會誌
Journal of Environmental Health Sciences
Original Article

pISSN 1738-4087 eISSN 2233-8616
J Environ Health Sci. 2023; 49(5): 251-261
https://doi.org/10.5668/JEHS.2023.49.5.251

Radiological and Geochemical Assessment of Different Rock Types from Ogun State in Southwestern Nigeria

Olabamiji Aliu Olayinka[1]* and Alausa Shamsideen Kunle[2]

[1]Department of Physics, Lead City University, [2]Department of Physics, Olabisi Onabanjo University

ABSTRACT

Background: This paper deals with the study of natural radioactivity in rocks from Ogun State in Southwestern Nigeria. The aim is to determine radiation emissions from rocks in order to estimate radiation hazard indices.

Objectives: The following objectives were targeted: 1. To determine radiation emissions from each type of rocks; 2. To estimate radiation hazard indices based on the rocks; 3. To correlate the activity concentrations of radionuclides with major oxides.

Methods: The samples were analyzed using a NaI (Tl) gamma ray spectrometric detector and PerkinElmer AAnalyst 400 AAS spectrometer.

Results: The activity of ^{40}K, ^{226}Ra, and ^{232}Th were found in order of decreasing magnitude from pegmatite>granite>migmatite. In contrast, lower concentrations were found in shale, phosphate, clay stone, sandstone and limestone. The mean absorbed doses were 125±23 nGyh^{-1} (migmatite), 74±13 nGy/h (granite), 72±13 nGyh^{-1} (pegmatite), 64±09 nGyh^{-1} (quartzite), 45±16 nGyh^{-1} (shale), 41±09 nGyh^{-1} (limestone), 41±11 nGyh^{-1} (clay stone), 24±03 nGyh^{-1} (phosphate), and 21±10 nGyh^{-1} (sandstone). The outdoor effective dose rates in all rock samples were slightly higher than the world average dose value of 0.34 mSvy^{-1}. The percentage composition of SiO_2 in the rock samples was above 50 wt% except for in the limestone, shale and phosphate. Al_2O_3 ranged from 4.10~21.24 wt%, Fe_2O_3 from 0.39~7.5 wt%, and CaO from 0.09-46.6 wt%. In addition, Na_2O and K_2O were present in at least 5 wt%. Other major oxides, including TiO_2, P_2O_5, K_2O, MnO, MgO and Na_2O were depleted.

Conclusions: The findings suggest that Ogun State may be described as a region with elevated background radiation. It is recommended that houses should be constructed with good cross ventilation and residences should use home radiation monitoring instruments to monitor radon emanating from walls.

Key words: Background radiation, geochemical assessment, rock types, Ogun State, Southwestern Nigeria

Received July 17, 2023
Revised August 30, 2023
Accepted September 8, 2023

Highlights:

- Exposure to ionizing radiation should be reduced among general public, patients, and radiation workers in Ogun State, Nigeria.
- The level of ^{40}K, ^{238}U (^{226}Ra), ^{232}Th and SiO_2, Al_2O_3, Fe_2O_3, P_2O_5, CaO, K_2O, TiO_2, MnO, MgO and Na_2O were measured by NaI (Tl) and Atomic Absorption Spectrometer (AAS) respectively in rocks which are the major source of natural ionizing radiation.
- Elevated background radiation was observed in Ogun State, Nigeria and the level of activity concentrations were dependent on geology, rock-type and mineral composition.

***Corresponding author:**
Department of Physics, Lead City University, Ibadan, Oyo State 110115, Nigeria
Tel: +234-080557150364
E-mail: olabamiji.olayinka@lcu.edu.ng

I. Introduction

Exposure of the general public, patients, and radiation workers to ionizing radiation must be limited to minimize the risk of harmful biological effects. In 1954, the National Committee on the Radiation Protection (NCRP) proposed a concept that radiation exposure should be kept as low as reasonably achievable (ALARA) concept. This concept is accepted by all regulatory agencies including International Commission on Radiological Protection (ICRP), the World Health Organization (WHO), and the European Commission (EC). When human body is exposed to ionizing radiation, it damages living systems by ionizing atoms composing of the molecular structures, causing abnormalities in the functioning of the living cell and

consequently health issues. Rocks are the building blocks of the earth lithosphere (crust and mantle) embedded with long lived natural radionuclides (^{40}K, ^{238}U (^{226}Ra), ^{232}Th) and other solid minerals.[1] The concentrations of natural radionuclides depend on the local geological setting, the process of rock formation and lithological characteristics of a location.[1]

In Nigeria, there has been increase in the demand for dwellings across the major cities due to rapid population growth and urbanization. Majority of modern houses built in many cities in Nigeria contain 60~80% crushed rocks aggregate because of the strength and availability of the rocks in lieu of gravels that were popularly used in the past. However, the popular and general name for every quarried rock is granite, whereas there are various rocks crushed to different sizes or forms in commercial quantities to produce blocks for wall casting, flooring, external and internal decoration in various dwellings. Moreover, crushed rocks are processed to other products such as tiles, interlocks, bricks used for building construction. Despite the wide use of these rocks in building construction, study of the radioactivity levels of different types are not taken seriously; the building engineers and contractors are usually concerned with strength of rocks without due consideration of radiation emission from different types of the rocks. The radiological risk to individual in buildings constructed with crushed rocks may be high depending on the sources and the levels of natural radionuclides[2-4] have studied the radioactivity in rocks and soil matrices from parts of Ogun State, particularly Abeokuta identified as high background radiation area.[5] The aim of the present study is to measure the activity concentrations of ^{40}K, ^{238}U (^{226}Ra) and ^{232}Th and geochemistry of major oxides: SiO_2, Al_2O_3, Fe_2O_3, P_2O_5, CaO, K_2O, TiO_2, MnO, MgO and Na_2O in rocks. The following objectives were targeted: i. to determine radiation emission from each type of the rocks ii. to estimate radiation hazard indices due to rocks iii. Correlate the activity concentrations of radionuclides and major oxides.

II. Materials and Methods

1. Study area

The Nigerian geological basement complex is located from between Latitude 4°N and 15°N and Longitude 3°E and 14°E between the Pan African mobile belt in-between the West African and Congo Craton.[6] Nigeria geology is broadly classified into three major litho-petrological components, which are, the Basement Complex, Younger Granites, and Sedimentary Basins. The Precambrian Basement Complex, is made up of the Migmatite-Gneiss Complex, the Schist Belts and the Older Granites. The Younger Granites comprise several Jurassic magmatic ring complexes centered on Jos and other parts of north-central Nigeria. The Sedimentary Basins, containing sediment fill of Cretaceous to Tertiary ages, comprise the Niger Delta, the Anambra Basin, the Lower, Middle and Upper Benue Trough, the Chad Basin, the Sokoto Basin, the Mid-Niger (Bida-Nupe) Basin and the Dahomey Basin.[6,7]

The basement complex of Southwestern Nigeria lies between latitudes 7°N and 10°N and longitudes 3°E and 6°E. The region is on the crystalline basement rocks comprising the amphibolite, migmatite gneisses, granites and pegmatite. Other important rock units found in region are the schist comprising biotite schist, quartzite schist, talc-tremolite schist, and the muscovite schist. The states of the southwestern part of Nigeria including Lagos, Osun, Oyo, Ogun, Ondo and Ekiti are situated on basement complex. In terms of lithological setting, Osun and Oyo States belong to crystalline basement complex region, Ondo and Ekiti State belong to post-cretaceous region that comprises shale and sandstone, Ogun State belongs to basement complex (undifferentiated) region and Lagos State belongs to geological area of post-cretaceous.[8]

2. Sample collection

The geological map (Fig. 1) and features of rocks found in Ogun State have been carefully studied prior to the sample collection. Identification and classification of the rock along with physical examination of the rocks was carefully carried out by

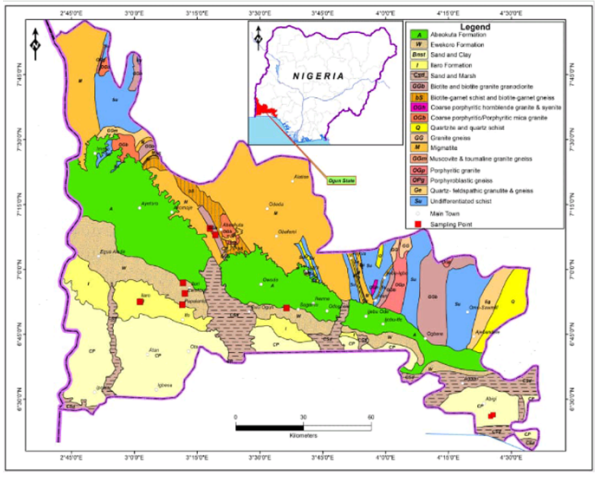

Fig. 1. Geological map of Ogun State showing the study areas

https://doi.org/10.5668/JEHS.2023.49.5.251

a geologist from Earth Sciences in Olabisi Onabanjo University. The weathered interface materials on the rocks were removed with sledge hammer and chisel before the samples were collected. The sampling was carried out randomly at 5 locations from each rock site. Ten different rocks were identified; five representative samples of each rock were collected to make a total of 50 samples for the study. The rock samples collected from each site were labeled for easy identification. The samples were then taken to the laboratory at the Department of Geology, University of Ibadan for crushing and pulverizing. The natural radioactivity levels in the samples were measured at the Radiation and Health Physics Research Laboratory at the Department of Physics, Federal University of Agriculture Abeokuta, while geochemical analyses of major oxides were performed at Geology Department, University of Ibadan.

3. Sample preparation for spectrometry analysis

Each rock sample was crushed, pulverized and homogenized. The sample was then dried and sieved with a <0.16 mm mesh-size sieve before dried in an electric temperature-controlled oven at 110°C temperature for 4 hours to remove moisture. 200 g each of the dried samples was carefully weighed using an electronic balance with a sensitivity of 0.01 mg into a gas-tight radon impermeable, cylindrical polyethylene container of 2 cm uniform base diameter and sealed. The container was substantially fit to sit on the 5 cm×5 cm NaI (Tl) detector used for the study. The rock samples in the containers were then kept for 4 weeks to allow for a state of secular radioactive equilibrium between ^{222}Rn and its short-lived decay products (^{214}Pb and ^{214}Bi).

4. Sample preparation for geochemical analysis

3 g of each pulverized rock sample was set aside for geochemical analysis. 0.2 g was taken with the aid of a weighing machine and digested with 5 mL of concentrated hydrogen fluoride (HF) and a mixture of prepared solution of nitric acid and hydrochloric acid (ratio 3:1). The sample was stirred and heated inside a fume cupboard containing water bath, the water was allowed to boil at 100°C before the counting time of two hours for the sample to be steamed. The sample was filtered into another graduated cylinder of 100 mL so as to have the stock solution for the analysis. Thereafter, the stock solution of the sample was diluted with distilled water and made up to 50 mL (representing stock solution, ×50-dilution factor). The dilution was done to prevent the analyzing machine from being damaged.

5. Determination of activity concentrations

A 5 cm×5 cm solid NaI (Tl) gamma-ray spectrometric manufactured by ORTEC and coupled to a Digital-based multichannel analyzer (MCA) was used to count the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th. The detector has a poor energy resolution of about 8% at energy of 0.662 MeV. This is considered adequate to distinguish the gamma energies of interest in the study. In addition, the photons emitted by the samples would sufficiently be discriminated if the emission probability and energy were high enough and the surrounding background continuum was low enough.

However, the activity concentration of ^{214}Bi determined from its 1.76 MeV gamma ray peak was chosen to provide an estimate of ^{226}Ra in the rock samples, while that of the daughter radionuclide ^{208}Tl determined from its 2.61 MeV gamma ray peak was chosen as an indicator of ^{232}Th. The activity concentration of ^{40}K was determined from 1.46 MeV gamma-rays emitted during the decay of ^{40}K. The standard reference

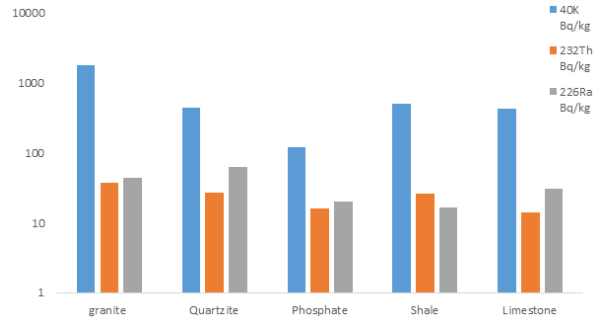

Fig. 2. Activity concentrations ^{40}K, ^{226}Ra and ^{232}Th in different rock samples

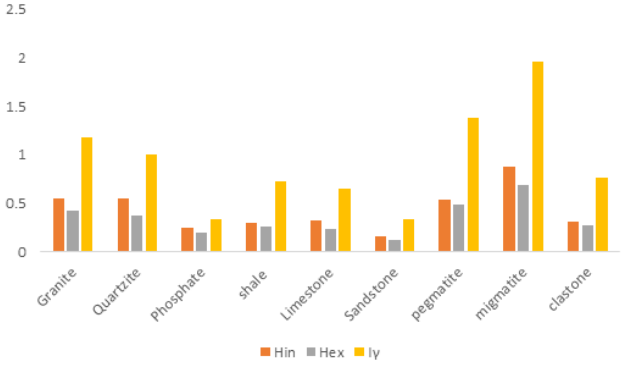

Fig. 3. Internal hazard index (H_{in}), External hazard index (H_{ex}), Gamma representative index (I_{γ})

sample used for efficiency calibration was from Rocketdyne Laboratories California, USA, traceable to a mixed standard gamma source (Ref No 48722-356) by Analytic Inc., Atlanta, GA, USA.

Equation (1) shows the usual relationship between activity concentration and the count rate under the photo peak of a given gamma-ray spectrometry detector.[2)]

$$C = \frac{C_n}{\varepsilon_p I_\gamma m_s} \quad (1)$$

Where C is the activity concentration of the radionuclides (^{40}K, ^{226}Ra and ^{232}Th) in the sample (Bqkg^{-1}), C_n is the count rate under the photo peak, ε_p is the detector efficiency at a specific gamma-ray energy, I_γ is the absolute transition probability of the specific gamma-ray and m_s is the mass of the sample.

An empty container of the same geometry with sample container was counted for the same time to take care of the background radiation count and determination of the radionuclide detection limits. The detection limits (DLs) which describes the operating capability of the detector without the influence of any sample were determined using[9)] model.

The detection limits (DLs) obtained in the present study were 0.12, 0.14 and 0.40 Bqkg^{-1} for ^{40}K, ^{226}Ra and ^{232}Th respectively. The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th less than the corresponding values of the DLs is referred to as below detection limit (BDL). One-half of each DL is considered for calculating the mean activity concentrations of the radionuclides and the radiological parameters.[10)]

6. Radiological assessments of the rock samples

6.1. Outdoor absorbed and effective dose rates

The quantity of absorbed dose is the amount of energy per unit mass absorbed by irradiated object. Absorbed dose is the energy responsible for damage in living organism. The absorbed dose rate (nGyh^{-1}) at 1 m above the ground in air is calculated using the expression given by equation (2).[11)]

$$D_R=0.462A_{Ra}+0.64A_{Ra}+0.0417A_K \quad (2)$$

Where D_R is the absorbed dose rate in nGyh^{-1}, A_{Ra}, A_{Th} and A_K are the respective activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K measured in Bqkg^{-1}. However, annual effective dose is used to assess potential long-term effects that might occur in future due to ionizing radiation exposure of the general public. The annual effective dose E_D (mSvy^{-1}) to the public due to absorbed dose rate in air can be calculated using equation (3).[12)]

$$E_D=D_R\times8760\times0.2\times0.7 \quad (3)$$

Where E_D is the effective dose in mSvy^{-1}, D_R (nGyh^{-1}) is the dose rate in air, 8760 is the time in hour for one year, 0.2 is the outdoor occupancy factor and 0.7 in the conversion factor.[11)]

6.2. Radium equivalent activity (Ra_{eq})

The radium equivalent activity (Ra_{eq}) is used as a common index to compare the specific activities of samples. It provides a useful guideline in regulating the safety standards on radiation protection of the general public and obtained as the sum of the weighted activities of ^{226}Ra, ^{232}Th and ^{40}K (Bqkg^{-1}) based on the estimation for which 10 Bqkg^{-1} of ^{226}Ra, 7 Bqkg^{-1} of ^{232}Th and 130 Bqkg^{-1} of ^{40}K will deliver the same gamma dose rate.[13)] The radium equivalent was calculated through the use equation (4).

$$Ra_{eq}=C_{Ra}+1.43C_{Tn}+0.077C_K \quad (4)$$

Where C_{Ra}, C_{Th} and C_K are the activity concentrations (Bqkg^{-1}) of ^{226}Ra, ^{232}Th and ^{40}K, respectively.

6.3. External radiation hazard index (H_{ex})

External hazard index (H_{ex}) is used to measure the external hazard due to the emitted natural gamma radiation. The external hazard index, H_{ex} estimates the potential radiological hazard posed by the different rock samples for the external gamma dose of materials to 1.5 mGy/year. It is another criterion to assess the suitability of a material. A safety criterion for materials used for building construction is that $H_{ex} \leq 1$.[12)] External hazard index is also calculated using equation (5).

$$H_{ex} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (5)$$

Where C_{Ra}, C_{Th}, C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively.

6.4. Internal radiation hazard index (H_{in})

In addition to the external hazard index, there is also a threat to the respiratory organs due to ^{222}Rn, the gaseous short-lived

https://doi.org/10.5668/JEHS.2023.49.5.251

Table 1. Activity concentrations, absorbed and effective dose rates of natural radionuclides

Rock type	^{40}K (Bqkg^{-1})	^{232}Th (Bqkg^{-1})	^{226}Ra (Bqkg^{-1})	Outdoor absorbed gamma dose (nGyh^{-1})	Outdoor effective dose (mSv/yr)
Granite	1,790.1±58.7	BDL	BDL	33.5	0.04
	1,799.7±67.3	55.3±20.7	57.8±11.4	93.9	0.12
	1,701.4±67.7	42.9±11.7	66.8±32.2	86.6	0.11
	1,764.8±30.2	47.8±31.1	47.1±50.6	83	0.1
	1,764.3±75.1	38.2±21.9	46.3±32.1	76.5	0.09
Mean±σ	1,764.1±38.4	36.9±21.5	43.6±25.8	74.7±13	0.09±0.03
Quartzite	449.2±62.7	29.3±28.9	61.3±2.7	64.7	0.08
	460.8±17.4	27.8±7.1	65.4±22.8	66.9	0.08
	435.2±66.7	27.2±31.0	55.9±67.3	61.1	0.07
	444.9±54.1	24.4±20.7	71.4±32.3	66.4	0.08
	448.4±20.9	26.7±11.2	62.8±25.2	64.8	0.08
Mean±σ	447.7±9.2	27.1±1.8	63±5.7	64.7±09	0.07±0.01
Phosphate	121.8±11.1	10.2±10.6	21.3±9.1	21.2	0.03
	127.3±16.8	20.8±11.3	19.9±8.6	27.4	0.03
	116.2±19.8	15.3±4.9	20.6±4.3	24.3	0.03
	122.7±16.7	18.2±2.3	19.8±11.5	25.5	0.09
	122.1±11.8	15.7±9.4	20.3±9.4	24.6	0.03
Mean±σ	122.0±3.9	16.0±3.9	20.4±0.6	24.60±03	0.04±0.01
Shale	505.8±77.4	BDL	BDL	21.7	0.03
	500.2±42.3	30.5±11.8	20.2±9.4	49.2	0.06
	501.1±43.6	35.3±15.6	20.6±11.2	52.4	0.06
	511.9±63.5	33.1±18.4	20.5±4.5	51.5	0.06
	504.9±16.2	32.7±16.7	20.6±3.3	51	0.06
Mean±σ	504.8±4.6	26.3±14.8	16.4±9.1	45.1±16	0.05±0.01
Limestone	435.7±69.8	14.1±7.6	28.8±7.3	40.3	0.05
	438.2±45.4	13.8±4.5	30.4±2.1	40.9	0.05
	440.8±23.3	15.3±5.9	33.2±5.3	42.9	0.05
	422.3±50.6	14.1±3.4	30.8±2.9	40.9	0.05
	433.7±57.4	13.7±2.3	31.4±11.1	41.3	0.05
Mean±σ	434.1±7.1	14.2±0.6	30.9±1.6	41.2±09	0.05±0.00
Sandstone	273.7±96.1	5.2±2.1	10.7±5.0	20.2	0.02
	278.2±56.3	4.9±1.2	18.2±6.1	23.7	0.03
	267.8±81.7	5.3±1.1	16.3±9.2	21.8	0.03
	279.2±79.6	5.1±1.5	8.9±5.2	19.4	0.02
	274.7±44.7	4.9±1.3	13.1±7.2	21.3	0.03
Mean±σ	274.7±4.5	5.1±0.2	13.4±3.8	21.2±1.65	0.02±0.01
Pegmatite	1,085.8±92.1	BDL	BDL	45.9	0.06
	1,090.1±88.6	64.9±4.9	22.9±8.5	95.5	0.12
	1,086.7±61.8	67.2±9.8	23.4±3.6	96.9	0.12
	1,084.7±88.2	61.7±7.8	24.3±5.8	94.6	0.12
	1,086.6±20.7	65.3±7.8	22.7±8.6	95.7	0.12
Mean±σ	1,086.8±2.0	51.8±29.0	18.7±10.4	85.7±22.2	0.10±0.03
Migmatite	1,759.8±16.3	32.2±4.3	68.1±27.6	124.8	0.15
	1,762.4±34.1	33.6±5.2	67.3±1.4	125.8	0.15
	1,791.7±64.6	33.1±63	70.7±11.8	127.7	0.16
	1,698.4±50.6	34.4±2.4	69.3±4.8	123.3	0.15
	1,752.7±43.1	32.9±7.1	68.7±11.2	125.5	0.15
Mean±σ	1,753.0±33.9	33.2±0.8	68.8±1.2	125.4±23	0.15±0.01
Clay stone	431.2±14.5	BDL	BDL	18.6	0.02
	432.7±22.0	38.3±12.1	15.2±11.0	48.2	0.06
	451.8±16.2	34.2±15.3	11.9±10.2	45.2	0.06
	472.3±17.7	35.8±18.1	13.7±11.9	48.4	0.06
	446.7±21.4	35.7±11.2	14.4±3.4	47.2	0.06
Mean±σ	446.9±16.7	28.8±16.1	11.1±6.2	41.52±11	0.05±0.02

decay product of ^{226}Ra. The internal hazard index (H_{in}) is defined generally to reduce the maximum permissible concentration of ^{226}Ra to half the value appropriate for external exposure alone.[14] Internal exposure to radon and its progeny products is quantified by estimating the internal hazard index using the model provided by the equation (6).[15]

$$H_{in} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_K}{4810} \quad (6)$$

Where C_{Ra}, C_{Th}, C_K are the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K respectively. If the maximum concentration of ^{226}Ra is one-half that of the normal acceptable limit, then H_{in} will be less than one. For safety precautions in the use of materials in the construction of dwellings, the criterion demands that $H_{in} \leq 1$.

6.5. Representative gamma index ($I\gamma$)

The gamma index (I_γ) is used as screening tool for identifying materials that might be a threat to human health. The representative gamma index (I_γ) used to estimate the level of γ - radiation hazard associated with the natural radionuclides in specific investigated samples. It is calculated using equation (7).[16]

$$I_\gamma = \frac{C_{Ra}}{150} + \frac{C_{Th}}{100} + \frac{C_K}{1500} \quad (7)$$

Where C_{Ra}, C_{Th} and C_K, are the activity concentrations (Bqkg^{-1}) of ^{226}Ra, ^{232}Th and ^{40}K respectively.

III. Results and Discussion

1. Activity concentrations of the radionuclides in the rock samples

The activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in different rock samples from Ogun State are presented in Table 1. The average activity concentration of ^{40}K, ^{226}Ra and ^{232}Th were 1,764.1±38.4, 36.9±21.5, 43.6±25.8 Bqkg^{-1} respectively for Granite, 447.7±9.2, 27.1±1.8, 63±5.7 Bqkg^{-1} respectively for Quartzite, 122.0±3.9, 16.0±3.9, 20.4±0.6 Bqkg^{-1} respectively for Phosphate, 504.8±4.6, 26.3±14.8, 16.4±9.1 Bqkg^{-1} respectively for Shale, 434.1±7.1, 14.2±0.6, 30.9±1.6 Bqkg^{-1} respectively for Limestone, 274.7±4.5, 5.1±0.2, 13.4 ±3.8 Bqkg^{-1} respectively for Sandstone, 1,086.8±2.0, 51.8 ±29.0, 18.7±0.4 Bqkg^{-1} respectively for pegmatite, 1,753.0 ±33.9, 33.2±0.8, 68.8±1.2 Bqkg^{-1} respectively for migmatite and 446.9±16.7, 28.8±16.1, 11.1±6.2 Bqkg^{-1} for Clay stone. According to,[12] the recommended world average value of ^{40}K, ^{226}Ra and ^{232}Th for rocks are 500 Bqkg^{-1}, 30 Bqkg^{-1} and 35 Bqkg^{-1} respectively. From the result, granite, pegmatite and migmatite have values slightly higher than the recommended values, on the other hand, quartzite, phosphate, shale limestone and sandstone have average values lower than the[12] recommended values. The elevated level of natural radionuclide in granite, pegmatite and migmatite is because they are igneous rock, meanwhile other rocks fall into sedimentary and metamorphic rock. A similar report from the study area have been reported by several authors.[17-20] In addition, the results show that there are clear differences in concentration of ^{40}K, ^{226}Ra and ^{232}Th in various rock samples, this is graphically shown in Fig. 2 this implies that distribution of natural radionuclide greatly depends on rock type and consequently radiation risk due to individual rocks varies. As could be seen from Table 1, ^{40}K has the highest value in all the entire rock samples, however, ^{232}Th was highest in pegmatite and the least was recorded in sandstone. The highest value of ^{226}Ra was recorded in migmatite and quartzite with values 71±12 and 71±32 respectively. The trend of increment in the average concentration of ^{40}K indicated that granite>migmatite>pegmatite>quartzite>shale>clay stone>limestone>sandstone> phosphate whereas ^{226}Ra decreased in the trend as from clay stone<sandstone<shale<pegmatite<phosphate<limestone<granite<quartzite. Moreover, the

Table 2. Comparison of activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th (Bqkg^{-1}) in some rocks from other places within Nigeria

Location	Material type	^{226}Ra	^{232}Th	^{40}K	References
Oguta	Soil	47.89	55.37	1,023	[19]
Imo State	Soil sample	20.69	25.04	88.41	[21]
Ogun	Rock	42.33	128.7	453.3	[20]
Ogbomoso	Stone dust	27.87	16.69	175.85	[22]
Ekiti	Concrete block	47.9	63.8	572.6	[23]
Ekiti	Rock	18.7	39.8	351.1	[23]

trend of increment in the average values in the concentration of ^{232}Th was found as pegmatite>granite>migmatite>clay stone>quartzite>sandstone>phosphate>limestone>sandstone. The results show that natural radioactivity is more pronounced in the rocks that are igneous in nature this is an indication that igneous rocks have higher radiation risk when used for building construction even though it is the hardest types of rocks. The concentrations of the three natural radionuclides are independent of each other, there is no similarities in the concentration. ^{226}Ra and ^{232}Th have the most detrimental radiation effect on humans. Numerous studies undertaken by authors within and outside the world is shown in Table 2, 3[1,15,19-29] and are comparable with the present study.

2. Geochemistry of major oxides in the rock from the study area

The major element oxides composition of rocks from the study area measured (in weight %), are presented in the Table 4. A smooth and systematic variation in chemical composition of major elements in the rock samples were observed, this showed that the elemental composition of rocks depends greatly on magma composition, fractional crystallization process by which the rock is formed and geographical location.[17] The percentage composition of SiO_2 in the rock samples is above 50 wt% in all the rock samples from the study areas except in limestone, shale and phosphate. Al_2O_3 content in all the samples from the study areas ranged from 4.10~21.24 wt% while Fe_2O_3 and CaO content ranged from 0.39~7.5 wt%, 0.09~46.6 wt% respectively. In addition, sodium oxide (Na_2O) and potassium

Table 3. Average values of activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in Bqkg^{-1} in some rocks from different countries of the world

Country	Material type	^{226}Ra	^{232}Th	^{40}K	References
Slovak	Granitic rock	77.3	91.4	929.3	24)
Egypt	Granite	40	12.5	47.1	25)
Czech	Rock	386.2	55.0	1,244.0	1)
Bangladesh	Rock	25.5	37.4	884.0	26)
India	Granites	34.06	79.05	933.6	27)
Ghana	Granites	356	161	1,796.0	28)
Pakistan	Cement	111.2	33.2	199.1	15)
Kenya	Rock	195.6	409.5	915.6	29)

Table 4. Major elemental oxides composition of rocks from the study areas (weight %)

Rocks	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	P_2O_5	K_2O	MnO	MgO	Na_2O
Quarzite	90.10	4.10	1.70	-	1.30	-	-	-	-	-
Quartzite	89.10	4.90	1.80	-	1.39	-	-	-	-	-
Pegmatite	72.71	15.99	0.45	0.02	0.22	0.38	3.68	0.01	0.06	5.56
Pegmatite	72.07	15.16	0.39	0.01	0.09	0.28	8.42	0.05	0.10	2.76
Granite	69.37	13.98	3.86	0.01	2.58	0.38	3.58	0.21	0.09	3.01
Granite	59.21	9.86	12.97	0.97	5.99	0.81	3.38	0.16	0.07	2.13
Migmatite	68.38	15.87	4.50	0.55	4.07	0.01	2.89	0.11	2.31	4.03
Migmatite	57.22	16.23	7.18	0.84	6.56	0.21	1.39	0.10	3.81	3.38
Shale	47.54	20.68	4.49	2.66	2.31	0.02	0.92	0.01	7.08	0.64
Phosphate	31.70	12.44	0.26	0.86	10.09	31.66	2.43	0.04	6.49	0.65
Limestone	8.55	2.00	2.32	-	46.63	-	0.91	-	1.14	0.98
Limestone	8.65	2.10	2.72	-	47.63	-	0.51	-	1.04	0.38
Schist	65.38	15.87	4.50	0.55	4.07	0.13	2.89	-	2.31	4.03
Clay stone	56.38	21.24	7.65	1.04	3.45	0.23	0.94	0.02	1.46	1.28
Sandstone	57.18	21.24	7.65	1.06	3.45	0.23	0.94	0.02	0.46	1.28

oxide (K_2O) are also present in at least 5 wt%. Other major oxides including TiO_2, P_2O_5, K_2O, MnO, MgO and Na_2O were depleted in the rock samples from the study area. This is a clear indication that samples analyzed in the present study were formed from igneous origin as a result of basement complex lithology of the area.

3. Correlation between activity concentrations and major oxides in the rocks

The results of the Pearson correlation coefficients between the activity concentrations of ^{40}K, ^{226}Ra, ^{232}Th and major elemental oxide SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, P_2O_5, K_2O, MnO, MgO and Na_2O in rock samples are presented in Table 5. The analysis revealed that SiO_2 had significant positive correlation with ^{226}Ra and ^{232}Th at 0.05 levels. Similarly, MgO had a very strong positive correlation with ^{232}Th at 0.01 levels while CaO had negative correlation with ^{226}Ra and the remaining of the major element did not show any significant correlation with activity concentration. The positive correlation between SiO_2 and ^{226}Ra and ^{232}Th is an indication that the rock collected the study areas derived their origin or formed from either melting of the igneous material or sediment materials or a mixture. This further supports the strong association between SiO_2, ^{226}Ra and ^{232}Th which is an indication that their presence in the rock may be under similar geochemical influence.[30] SiO_2 concentration exhibited high degree of negative correlation with CaO indicating calcite and quartz mineral in a rock sample may possibly not coexist. In contrast, there is a negative correlation between ^{40}K and (SiO_2, ^{226}Ra, ^{232}Th), implying that ^{226}Ra and ^{232}Th have dissimilar geochemical behavior with ^{40}K.

4. Absorbed and effective dose rates in rocks from the study area

Table 1 shows the absorbed dose and annual effective dose rates obtained in the rock samples from the study area. The mean absorbed dose in is 74±13 nGy/h (granite), 64±09 $nGyh^{-1}$ (quartzite), 24±11 $nGyh^{-1}$ (phosphate), 45±16 $nGyh^{-1}$ (shale), 41.2±09 $nGyh^{-1}$ (limestone), 21±10 $nGyh^{-1}$ (sandstone), 72 $nGyh^{-1}$ (pegmatite), 125±23 $nGyh^{-1}$ (migmatite) and 41±11 $nGyh^{-1}$ (claystone). These average values obtained in granite, quartzite, pegmatite, migmatite were higher than the world recommended average value of 59 $nGyh^{-1}$ [12] whereas the average values obtained in sandstone, limestone, phosphate, shale were below the world recommended. The outdoor annual effective dose rates in all rock samples were slightly higher than the world average dose of 0.34 mSv/yr to individual from outdoor radiation exposure.[31]

5. Radiological assessment of the rock samples from the study area

Radium equivalent, internal hazard and external hazard indices are parameters, used as a safety standard in radiation protection for the general public. Table 6, shows all the values Radium equivalent, internal hazard and external hazard indices in the rock samples. All the values of radium equivalent in the rock samples are within the recommended value of 370 Bq/kg. In

Table 5. Pearson correlation matrix of activity concentrations and major oxides granite

	K	Ra	Th	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	P_2O_5	KO	MnO	MgO	Na_2O
K	1												
Ra	−0.806	1											
Th	−0.602	0.845*	1										
SiO_2	−0.472	0.819*	0.886*	1									
Al_2O_3	−0.231	0.479	0.321	0.708	1								
Fe_2O_3	0.420	−0.743	−0.772	−0.955**	−0.828*	1							
TiO_2	−0.134	−0.331	−0.666	−0.731	−0.406	0.730	1						
CaO	0.504	−0.814*	−0.796	−0.979**	−0.825*	0.971**	0.633	1					
P_2O_5	0.520	−0.779	−0.790	−0.968**	−0.808	0.946**	0.601	0.989**	1				
KO	−0.716	0.710	0.723	0.792	0.664	−0.844*	−0.415	−0.828*	−0.852*	1			
MnO	0.755	−0.639	−0.763	−0.509	0.065	0.316	0.130	0.427	0.493	−0.565	1		
MgO	−0.612	0.712	0.932**	0.693	0.018	−0.513	−0.485	−0.570	−0.599	0.585	−0.916*	1	
Na_2O	−0.458	0.679	0.660	0.908*	0.903*	−0.949**	−0.561	−0.964**	−0.973**	0.872*	−0.339	0.431	1

*Correlation is significant at the 0.05 level (two-tailed), **Correlation is significant at the 0.01 level (two-tailed).

Table 6. Radium equivalent, internal, external hazard and gamma representative indices

Rock type		Ra_{eq} (Bq/kg)	H_{in}	H_{ex}	I_{γ}
Granite	Range	62.3~199.5	0.17~0.70	0.17~0.54	0.54~1.48
	Mean	156.18	0.542	0.42	1.176
	Std	54.38	0.22	0.15	0.37
Quartzite	Range	129.9~142.2	0.5~0.57	0.35~0.38	0.95~1.03
	Mean	137.66	0.542	0.37	1.00
	Std	4.78	0.03	0.01	0.03
Phosphate	Range	45.5~141.4	0.18~0.44	0.12~0.38	0.14~0.43
	Mean	70.74	0.248	0.188	0.332
	Std	39.85	0.11	0.11	0.11
Shale	Range	40.4~111.1	0.11~0.36	0.11~0.30	0.35~0.83
	Mean	94.36	0.3	0.254	0.718
	Std	30.28	0.11	0.08	0.21
Limestone	Range	83.2~88.9	0.30~0.33	0.22~0.24	0.63~0.67
	Mean	85.36	0.314	0.23	0.644
	Std	2.14	0.01	0.01	0.02
Sandstone	Range	39.0~48.4	0.13~0.18	0.11~0.13	0.31~0.37
	Mean	43.12	0.152	0.118	0.334
	Std	3.62	0.02	0.01	0.02
Pegmatite	Range	85.1~203.6	0.23~0.61	0.23~0.55	0.73~1.56
	Mean	177.54	0.53	0.478	1.374
	Std	51.71	0.17	0.14	0.36
Migmatite	Range	248.6~256.8	0.86~0.89	0.67~0.69	1.93~2.00
	Mean	252.4	0.87	0.68	1.966
	Std	3.04	0.01	0.01	0.02
Claystone	Min	96.1~103.2	0.29~0.32	0.26~0.28	0.73~0.78
	Mean	100.775	0.31	0.2725	0.76
	Std	3.32	0.01	0.01	0.02

Std: Standard deviation, Ra_{eq}: Radium equivalent, H_{in}: Internal hazard index, H_{ex}: External hazard index, I_{γ}: Gamma representative index.

addition, the external, internal and gamma hazard indices were less than unity except in granite, migmatite, pegmatite and quartzite as shown in Fig. 3.

IV. Conclusion

This study has measured the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th and geochemistry of major oxides SiO_2, Al_2O_3, Fe_2O_3, P_2O_5, CaO, K_2O, TiO_2, MnO, MgO and Na_2O in different rock samples collected from Ogun State. The results of the analysis of data obtained from activity concentrations showed that the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th are higher in granite, pegmatite, migmatite, and quartzite as a result of their similar characteristics of igneous origin but concentration of ^{40}K, ^{226}Ra and ^{232}Th are lower in shale, phosphate, clay stone, sand stone and limestone because they did not form from original rock but through either sedimentation or metamorphism. However, the activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in rocks depend on geology, rock-type and the mineral composition like SiO_2 which was found to be above 50 wt% in all the rock samples from the study areas except limestone. The mean annual effective dose due to radiation from rocks was comparable to the recommended safe limit, and the radiological hazard indices were slightly higher than the recommended international safe limits. Hence, the findings suggest that Ogun State could be described as a region having elevated background radiation. To avert potential radiation-related health issues, it is recommended to exercise care and subject the materials to international safety limits standard when building residences using rocks sourced from Ogun State. The

results could be used by the government, local authorities can use to regulate the use of rocks with elevated radiation risk in building construction. Further investigation is also suggested in quarry sites to monitor radiation dose due to inhalation of dust by the workers and the public. It is recommended that residence in Ogun State should use home radiation monitoring instrument to monitor radon emanation from walls.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

References

1. Malczewski D, Dziurowicz M, Kalab Z, Rösnerová M. Natural radioactivity of rocks from the historic Jeroným Mine in the Czech Republic. *Environ Earth Sci.* 2021; 80(18): 650.
2. Jibiri NN, Akomolafe IR. Radiological assessment and geochemical characterization of the sediments of Awba Dam, University of Ibadan, Nigeria. *Radiat Prot Environ.* 2016; 39(4): 222-232.
3. Okedeyi AS, Gbadebo AM, Arowolo TA, Mustapha AO, Tchokossa P. Measurement of gamma-emitting radionuclides in rocks and soils of Saunder quarry site, Abeokuta, Ogun State, Nigeria. *J Appl Sci.* 2012; 12(20): 2178-2181.
4. Usikalu MR, Fuwape IA, Jatto SS, Awe OF, Rabiu AB, Achuka JA. Assessment of radiological parameters of soil in Kogi State, Nigeria. *Environ Forensics.* 2017; 18(1): 1-14.
5. Alausa SK. Radioactivity in farm soils and food crops grown in Jos and Abeokuta, Nigeria and its associated cancer risks [dissertation]. [Ibadan]: University of Ibadan; 2012.
6. Rahaman MA. Review of the basement geology of Southwestern Nigeria. In: Kogbe CA. editor. Geology of Nigeria. Jos: Rock View (Nigeria) Ltd.; 1989. p.41-58.
7. Solomon AO, Ike EE, Ashano EC, Jwanbot DN. Natural background radiation characteristics of basalts on the Jos Plateau and the radiological implication of the use of the rock for house construction. *Afr J Nat Sci.* 2002; 5(2): 345-351.
8. Kitto ME, Fielman EM, Hartt GM, Gillen EA, Semkow TM, Parekh PP, et al. Long-term monitoring of radioactivity in surface air and deposition in New York State. *Health Phys.* 2006; 90(1): 31-37.
9. Alausa SK, Odusote OO. Radiological health impact due to activity concentrations of natural radionuclides in the soils from two major areas in Ijebu-North Local Government, Ogun State, Nigeria. *Nucleus.* 2013; 50(4): 293-299.
10. Odongo WOG, Chege M, Hashim N, Tokonami S, Chutima K, Rotich C. Determination of activity concentration of natural radionuclides and radiation hazards' assessment of building materials in high background radiation areas of Homa and Ruri, Kenya. *Scientific World Journal.* 2021; 2021: 9978619.
11. United Nations Scientific Committee on the effects of Atomic Radiation (UNSCEAR). Report to the General Assembly A/55/46. New York: United Nations; 2000.
12. Alnour IA, Wagiran H, Ibrahim N, Laili Z, Omar M, Hamzah S, et al. Natural radioactivity measurements in the granite rock of quarry sites, Johor, Malaysia. *Radiat Phys Chem.* 2012; 81(12); 1842-1847.
13. Prasad NG, Nagaiah N, Ashok GV, Karunakara N. Concentrations of 226Ra, 232Th, and 40K in the soils of Bangalore region, India. *Health Phys.* 2008; 94(3): 264-271.
14. Xinwei L, Lingqing W, Xiaodan J, Leipeng Y, Gelian D. Specific activity and hazards of Archeozoic-Cambrian rock samples collected from the Weibei area of Shaanxi, China. *Radiat Prot Dosimetry.* 2006; 118(3): 352-359.
15. Alausa SK, Omotosho OO. Natural radioactivity in farm soils and major food crops grown in Ayetoro, Ogun State, Southwestern Nigeria. *Int J Low Radiat.* 2017; 10(4): 285-303.
16. Papadopoulos A, Christofides G, Papastefanou C, Koroneos A, Stoulos S. Radioactivity of granitic rocks from Northern Greece. *Bull Geol Soc Greece.* 2010; 43(5): 2680-2691.
17. Al-Hamzawi AA. Natural radioactivity measurements in vegetables at Al-Diwaniyah governorate, Iraq and evaluation of radiological hazard. *J Al-Nahrain Univ Sci.* 2017; 20(4): 51-55.
18. Isinkaye MO, Emelue HU. Natural radioactivity measurements and evaluation of radiological hazards in sediment of Oguta Lake, South East Nigeria. *J Radiat Res Appl Sci.* 2015; 8(3): 459-469.
19. Adewoyin OO, Maxwell O, Akinwumi SA, Adagunodo TA, Embong Z, Saeed MA. Estimation of activity concentrations of radionuclides and their hazard indices in coastal plain sand region of Ogun state. *Sci Rep.* 2022; 12(1): 2108.
20. Clarke DB. Granitoid rocks. London: Chapman & Hall; 1992.
21. Eke BC, Ukewuihe UM, Akomolafe IR. Evaluation of activity concentration of natural radionuclides and lifetime cancer risk in soil samples at two tertiary institutions in Owerri, Imo State, Nigeria. *Int J Radiat Res.* 2022; 20(3): 671-678.
22. Ajayi JO, Jere P, Balogun BB. Assessment of radiological hazard indices of building materials in Ogbomoso, South-West Nigeria. *Environ Nat Resour Res.* 2013; 3(2): 128-132.
23. Fasae KP. Natural radioactivity in locally produced building materials in Ekiti State, Southwestern Nigeria. *Civ Environ Res.* 2013; 3(11): 99-112.
24. Alharbi WR, El-Taher A. Elemental analysis and natural radioactivity levels of clay by gamma ray spectrometer and instrumental neutron activation analysis. *Sci Technol Nucl Install.* 2016; 2016: 8726260.
25. Mibei G. Introduction to types and classification of rocks. Available: https://gogn.orkustofnun.is/unu-gtp-sc/UNU-GTP-SC-28-0205.pdf [Accessed 20 Feb 2023].
26. Dina NT, Das SC, Kabir MZ, Rasul MG, Deeba F, Rajib M, et al. Natural radioactivity and its radiological implications from soils and rocks in Jaintiapur area, North-east Bangladesh. *J Radioanal Nucl Chem.* 2022; 331(11): 4457-4468.
27. Prakash MM, Kaliprasad CS, Narayana Y. Studies on natural radioactivity in rocks of Coorg district, Karnataka state, India. *J Radiat Res Appl Sci.* 2017; 10(2): 128-134.

28. Turhan S, Baykan UN, Sen K. Measurement of the natural radioactivity in building materials used in Ankara and assessment of external doses. *J Radiol Prot.* 2008; 28(1): 83-91.
29. Otwoma D, Patel JP, Bartilol S, Mustapha AO. Radioactivity and dose assessment of rock and soil samples from Homa Mountain, Homa Bay County, Kenya. Paper presented at: XI Radiation Physics & Protection Conference; 2012 Nov 25-28; Cairo, Egypt. p. 107-116.
30. International Commission on Radiological Protection (ICRP). 1990 recommendations of the International Commission on Radiological Protection. Pergamon Press; 1991.
31. Shiklomanov IA. World fresh water resources. In: Gleick PH. editor. Water in crisis: a guide to the world's fresh water resources. New York: Oxford University Press; 1993. p.13-24.

〈Author information〉

Olabamiji Aliu Olayinka (Doctor),
Alausa Shamsideen Kunle (Professor)