Article

Determination of Uranium in Rocks and Soils of South Cameroon by γ -ray Spectrometry

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Analytical results of uranium concentration in rocks and soils collected in the area of Lolodorf of South Cameroon where a radiometric anomaly had been found by previous investigation are reported. The analysis has been carried out by γ -ray spectrometry using a Ge detector. Radioactivity concentration of ^{235}U was determined by comparing peak count rates of samples with those of natural uranium standard sample. Radioactivity concentration of ^{238}U was calculated from the ^{235}U radioactivity concentration by assuming that the isotopic composition of ^{235}U is 0.7200% of natural abundance. Difference of γ -ray self-absorption between the samples and uranium standard was accurately corrected by using a mass attenuation coefficient of samples and standard measured by using an external γ -ray source. The radioactivity concentrations in rocks ranged from 0.92 ± 0.02 to 228 ± 14 Bq/kg (^{235}U) and 20 ± 5 to $4\,868 \pm 307$ Bq/kg (^{238}U), while radioactivity concentrations in soils ranged from 3 ± 1 to 63 ± 2 Bq/kg (^{235}U) and 71 ± 19 to $1\,346 \pm 38$ Bq/kg (^{238}U). The γ -ray dose rates in air at 1 m above the ground surface due to the high uranium concentration in soil samples were ranged from 33 ± 9 to 622 ± 18 nGy/h. The highest uranium concentration of about 0.04% in rock was found in the analysis. These results show that the uranium content in the studied areas is significantly high and the studied areas have a potential for uranium mining.

Key Words : uranium, radioactivity concentration, gamma ray dose rate, gamma ray spectrometry, Ge detector, soil, rock

1. Introduction

The Lolodorf area located at the South Cameroon (Fig. 1) was suspected to have uranium ore deposits. The French Office of Geological and Mining Research carried out geological and radiometric studies in this area to evaluate the mineral potential of the location under study from 1978 to 1985¹⁾. The radiometric study has consisted of helicopter-borne radiometric survey using a portable NaI(Tl) spec-

trometer to identify high uranium abundance area. It was found that the γ -radiation level of Lolodorf area was relatively higher than the other area. The geological aspect of this study has reported the presence of alkaline syenite which is a coarse-grained intrusive igneous rock of the same general composition as granite but with quartz either absent or present in relatively small amounts (<5%). On the other hand, Lolodorf area is in rural district and over 80% of the population is engaged in agriculture.

Fig. 1 A map of Cameroon including sampling site of Lolodorf.

The main objective of this study is determination of uranium concentration in rocks and soils in this area to evaluate possibility of uranium mining and external radiation exposures of inhabitants from uranium nuclides and their decay product nuclides of this area.

Since their chemical robustness of rock and soil, γ -ray spectrometry²⁾ using a Ge detector of non-destructive method was chosen for the analysis among the many analytical methods. Although uranium has 3 radionuclides ^{234}U , ^{235}U and ^{238}U in the nature abundance of 0.0055%, 0.7200% and 99.2745%, respectively, ^{235}U is the most suitable nuclide for the measurement

since the other nuclides are low natural abundance or no γ -ray emission. Decay products of ^{238}U such as ^{234}Th , $^{234\text{m}}\text{Pa}$, ^{214}Pb and ^{214}Bi can also be used for the measurement of uranium, however, radiochemical equilibrium condition of the nuclides in the samples must be corrected. In addition, emanation of ^{222}Rn , which is precursor of ^{214}Pb and ^{214}Bi , from sample affects for the measurement of ^{214}Pb and ^{214}Bi . Thus, we selected ^{235}U as the measurement nuclide.

Since ^{235}U emits low energy γ -rays of less than 200 keV, self-absorption of the measurement γ -rays with sample matrices is significant. The analysis has been performed by correcting

the sample self-absorption accurately by using a mass attenuation coefficient of the samples and standard measured by an external γ -ray source method. We report analytical results of ^{235}U and ^{238}U radioactivity concentration in soil and rock samples collected from Lolodorf area of South Cameroon by γ -ray spectrometry, and γ -ray dose rates of the area due to ^{238}U calculated from the analytical results of soils.

2. Experimental

2.1 Sampling and sample preparation

The soil and rock samples were collected from Ngombas and Bikoue regions in Lolodorf area of South Cameroon where uranium and potassium anomalies were found in previous radiometric investigation. A total area of the two sampling regions was 125 and 88 km² at Ngombas and Bikoue, respectively. The two sampling regions were divided into 7 (Ngombas) and 6 (Bikoue) sites of equal area. Each

site was 18 km² and 15 km² for Ngombas and Bikoue, respectively. The each site was further divided into 5 cells of area 3.5 km² and 3.0 km² for Ngombas and Bikoue, respectively. A 500 g of soil was collected from the center of each cell, and then the 5 samples of same site were mixed well. A 500 g of soil was taken from the mixture for the analysis. A 500 g of rock was collected at the center of the sampling site when the accessibility allows it. However, only soils were collected in the sampling sites at No. 2 (Ng-02), 3 (Ng-03) and 5 (Ng-05) of Ngombas where rock does not exist on the surface. All sampling site centers are located in inhabited or agricultural area and are shown in the Fig. 2. Contaminated vegetation and organic matter were removed from the collected samples. Rock and soil samples from a total of 13 sites were collected as shown in the figure.

All samples were brought to the laboratory and dried overnight at a temperature of 250°C.

Fig. 2 A map of sampling site of Lolodorf in Cameroon.

The sampling sites show with filled triangles together with codes on the map.

After cooling, the rock samples were crushed into small pieces and then homogenized. The samples were taken by weighing 110 g and 130 g on average for soil and rock, respectively, into a cylinder shaped polystyrene sample container of 86.0 mL volume and 55.5 mm internal diameter.

2.2 Standard samples

A natural uranium standard and uranium ore standard samples prepared by Dr. Yonezawa of IAEA are used for standardization of uranium contents and to check accuracy of the analytical method, respectively. A natural uranium standard solution (^{235}U : 9.644 Bq, ^{238}U : 209.5 Bq) was prepared from Natural Uranium Radioactivity Standard (NIST SRM-4321C) by diluting with 2M HCl into a sample container same as the samples. A uranium ore standard sample was prepared by weighing 105.47136 g (dry weight) of Reference Materials of Uranium Ore (IAEA-RGU-1) into the same type of sample container.

2.3 γ -ray spectrometer

A γ -ray spectrometer consisted with an n-type Ge detector (CANBERRA model GR3019) and a multi-channel analyzer (CANBERRA Inspector 2000) was used for the measurement. The energy resolution of 1 332.5 keV γ -ray line from ^{60}Co was found to be 1.85 keV at full width of half-maximum (FWHM) with the relative efficiency of 34.9%. The detector was shielded with lead shield (CANBERRA model 777) with 1 mm thick Sn and 1.5 mm thick Cu graded liner of the inside to absorb characteristic X-rays of Pb. γ -ray energy range was adjusted to 0–2 000 keV and calibrated using a mixed γ -nuclides source of ^{241}Am , ^{109}Cd , ^{57}Co , ^{139}Ce , ^{137}Cs , ^{88}Y and ^{60}Co . Stability of energy resolution, de-

tection efficiency and peak position of the spectrometer were checked by measuring a point source of ^{152}Eu for 1 200 seconds before and after measurement of the samples and standards. The rock and soil samples were measured for 16 and 6 hours, respectively. The obtained γ -ray spectra were analyzed by a γ -ray spectrum analysis program CANBERRA Genie 2000.

2.4 Measurement of mass attenuation coefficient of the samples for self-absorption correction

The source is set at the top of the sample container of the sample using a stand-alone source support, and then γ -ray spectrum is measured at identical position of the sample measurement for a period until interested peak height becomes larger than ten thousand counts. Same measurement is carried out for an empty sample container. A linear attenuation coefficient μ is obtained from peak area of major γ -ray lines of ^{210}Pb , ^{133}Ba and ^{152}Eu for sample and empty container using equation (1),

$$\mu = \frac{\ln(R_s/R_0)}{-h} \quad (1)$$

where R_s is peak count rates of a sample, R_0 is peak count rate of an empty container, h is sample height (cm) in this case 3.6 cm. When sample has identical energy γ -ray peak with the external γ -ray source in a spectrum, γ -ray peak counts of the sample must be subtracted from peak counts of external γ -ray source spectrum of the sample. A mass attenuation coefficient μ_m is obtained dividing the linear attenuation coefficient by a density ρ (g/cm^3) of the sample.

Fig. 3 γ -ray spectra of rock and soil samples compared with natural uranium standard.

a: Natural uranium standard sample

b: Soil sample Bi-01 collected from Bikoue

c: Rock sample Ng-01 collected from Ngombas

3. Results and discussion

3.1 γ -ray spectrum of the samples

γ -ray spectra at low energy region of rock, soil and uranium standard samples are shown in Fig. 3. γ -ray peaks of 109.1, 143.7, 163.4, 185.7 and 205.3 keV from ^{235}U together with γ -rays from decay products of ^{235}U , ^{238}U and ^{232}Th , and decay γ -rays from ^{40}K were detected from the samples. Determination of uranium radioactivity concentration by γ -ray spectrometry has been carried out by measuring either direct γ -rays from ^{235}U or decay γ -rays from ^{234}Th (half-life: 24.10 day), ^{234}Pa (half-life: 6.75 h) or $^{234\text{m}}\text{Pa}$ (half-life: 1.17 min), which are decay products of ^{238}U since ^{238}U has no direct γ -ray emission. However, a method which measuring γ -rays from decay products of ^{238}U has to be

measured after stand for more than one month to be radio-equilibrium of the measurement nuclides and ^{238}U . Thus we selected the method which measures direct γ -rays from ^{235}U , for the analysis.

Decay γ -rays of ^{235}U with high emission probability shown in the parentheses are 185.7 (57.2%), 143.5 (10.98%), 163.3 (5.08%), 205.3 (5.01%) and 109.2 (1.54%) keV. Although 185.7 keV γ -ray is the highest intensity, it cannot be used for the analysis due to spectral interference with 186.2 keV γ -ray of ^{226}Ra . Thus we used γ -rays of 143.5, 205.3 and 109.2 keV for the analysis. Since variation of the analytical results by 163.3 keV γ -ray is larger than that of the other γ -rays, this γ -ray peak was not used for the analysis. Radioactivity concentration of ^{238}U was calculated from that of ^{235}U by assum-

ing isotopic composition of ^{235}U and ^{238}U in natural abundance.

3.2 γ -ray self-absorption correction of the samples

A uranium 2M HCl solution was used as a standard for the analysis. On the other hand, γ -ray absorption between samples and standard is so diverse because of their differences in density and chemical composition. Soil and rock samples have higher density than standard and are consisted with elements of higher atomic weight such as Si, Al and Fe than the standard. Thus self-absorption difference of γ -rays between sample and standard, especially at low energy region is significant. Furthermore, γ -ray self-absorption among the samples is not identical due to differences of density and sample amounts. The self-absorption of γ -rays in samples and standard is accurately corrected by a method developed by Yonezawa³⁾. The method is based on a correction using correction factors for γ -rays which are obtained from experimentally measured mass attenuation coefficients of the samples and standards.

The self-absorption correction factor C_{Ab} for a sample at measurement γ -ray energy relative to the standard is obtained from equation (2),

$$C_{Ab} = \frac{(\mu_m)_c \rho_c 1 - e^{-(\mu_m)_c \rho_c h}}{(\mu_m)_s \rho_s 1 - e^{-(\mu_m)_s \rho_s h}} \quad (2)$$

where $(\mu_m)_s$ and $(\mu_m)_c$ are mass attenuation coefficients for sample and chemical standard, respectively, at measurement γ -ray energy, ρ is density (g/cm^3), h is sample height (cm), in this case 3.6 cm, and subscripts s and c stand

Fig. 4 An example of calculated and measured mass attenuation coefficients of uranium standard sample (2M HCl solution), soil sample (Bi-01) and rock sample (Ng-01). The horizontal axis show from ln 3.8 (44.7 keV) to ln 6.0 (403.4 keV).

for sample and chemical standard, respectively. The $(\mu_m)_c$ and $(\mu_m)_s$ for the measurement γ -ray are calculated by using the following equation (3),

$$\mu_m(E, Z) = A(Z) \cdot E^{3.5} + B(Z) \cdot \exp \{0.408 (\ln E) - 0.066 (\ln E)^2\} \quad (3)$$

where $A(Z)$ and $B(Z)$ are obtained from the least square fitting of experimentally measured mass attenuation coefficients to equation (3), E is measurement γ -ray energy (keV) and Z is an average atomic number of the sample. The equation (3) was obtained experimentally by Satoh et al.⁴⁾. The input data of mass attenuation coefficients of samples and standards for equation (3) were obtained experimentally by using an external γ -ray source method according to Gilmore²⁾. A mixed radionuclide point source of ^{210}Pb - ^{133}Ba - ^{152}Eu was used as the γ -ray source. Detail of the correction method will be described elsewhere³⁾.

Figure 4 shows a plot of experimentally ob-

Fig. 5 An example of sample self-absorption correction factors of soil sample (Bi-01) and rock sample (Ng-01).

tained mass attenuation coefficients and fitted curves to equation (3) of uranium standard (2M HCl solution), soil sample (Bi-01) and rock sample (Ng-01). Figure 5 is a plot of self absorption correction factors for soil sample (Bi-01) and rock sample (Ng-01) which obtained from the equation (2).

3.3 Analytical results of the reference material

A reference material of Uranium Ore (IAEA-RGU-1) was analyzed to evaluate accuracy of the presented method. The analytical results are tabulated in Table 1 together with IAEA reference values^{(5), (6)}. The analytical results of radioactivity concentration of ^{235}U and ^{238}U , and elemental uranium concentrations of the present method are in agreement within 4%.

3.4 Analytical result of rock and soil samples

Analytical results of radioactivity concentration of ^{235}U and ^{238}U and uranium concentration in 11 rock samples and 13 soil samples are listed in Table 2. The table shows analytical results and their average values. The ^{235}U radioactivity concentrations in the table are average of those obtained from 109.1, 143.7 and 205.3 keV γ -ray lines. Average values and corresponding standard deviation of all rock and soil samples are shown in

the table as well.

The highest uranium concentrations in rocks are 104 ± 9 and $2\,204 \pm 194$ Bq/kg for ^{235}U and ^{238}U , respectively, and 179 ± 16 mg/kg for U in the Bikoue region. In the Ngombas region, these values are 228 ± 14 and $4\,868 \pm 307$ Bq/kg for ^{235}U and ^{238}U , respectively, and 395 ± 23 mg/kg for U. The highest mass concentrations of U are equivalent to 0.02% and 0.04% for the Bikoue and Ngombas regions, respectively, and they suggest that the studied area has a high possibility of uranium deposit. Further geological investigation is desired for uranium mining.

Due to the high uranium concentration of rocks in the studied area, the highest uranium concentrations in soils are 63 ± 2 and $1\,346 \pm 38$ Bq/kg for ^{235}U and ^{238}U , respectively, and 110 ± 3 mg/kg for U in Bikoue while these values are

Table 1 Analytical results of uranium ore reference material (IAEA-RGU-1)

	Obtained value*	IAEA reference value	Deviation, %
^{235}U , Bq/kg	235 ± 13	228 ± 2	+3
^{238}U , Bq/kg	5149 ± 190	4940 ± 30	+4
Elemental U, mg/kg	415 ± 17	400 ± 2	+4

*Uncertainty show standard deviations of the γ -ray counts.

Table 2 Analytical results of rock and soil samples

Sampling site*	Rock			Soil		
	^{235}U , Bq/kg	^{238}U , Bq/kg	U, mg/kg	^{235}U , Bq/kg	^{238}U , Bq/kg	U, mg/kg
Bi-01	41±5	863±113	71±9	23±3	496±55	40±4
Bi-02	0.92±0.20	20±5	2.1±0.4	29±3	628±55	51±4
Bi-03	9±1	186±29	15±2	6±1	121±28	10±2
Bi-04	104±9	2204±194	179±16	36±4	767±76	62±6
Bi-05	76±3	1625±80	132±6	63±2	1346±38	110±3
Bi-06	1.2±0.1	25±3	2.0±0.3	29±1	621±27	50±2
Ng-01	76±7	1628±148	133±12	21±3	446±55	36±4
Ng-02	—	—	—	7±2	159±50	13±4
Ng-03	—	—	—	3±1	71±19	6±1
Ng-04	228±14	4868±307	395±23	3±1	72±23	6±2
Ng-05	—	—	—	4±1	74±19	6±1
Ng-06	27±4	584±82	47±7	18±1	377±28	31±2
Ng-07	86±8	1829±161	140±13	31±3	668±63	54±5
Mean	63±72	1383±1460	112±118	21±17	450±370	37±30

*The codes “Bi” and “Ng” mean Bikoue and Ngombas, respectively, of sampling regions.

Uncertainties show standard deviations of the γ -ray counts.

31 ± 3 and 668 ± 63 Bq/kg for ^{235}U and ^{238}U , respectively, and 54 ± 5 mg/kg for U in Ngombas. The uranium concentration of the Bikoue region is higher than that of the Ngombas region.

3.5 γ -ray dose rate

About 45 thousand people are living in the Lolodorf area and about 80% of the population is engaged in agriculture. Since soil contains high uranium concentration in the area (63 ± 2 and 1346 ± 38 Bq/kg for ^{235}U and ^{238}U , respectively, in Bikoue and 31 ± 3 and 668 ± 63 Bq/kg for ^{235}U and ^{238}U , respectively, in Ngombas), radiation dose exposure of the inhabitants must be evaluated. Thus, γ -ray dose rate (nGy/h) at 1 m high was calculated using the conversion dose coefficient of ^{238}U (0.462 nGy/h^{-1} per Bq/kg^{-1})^{7), 8)} and ^{238}U concentration (Bq/kg) in soil samples. The results are shown in Table 3. The γ -ray dose rate at 1 m above the ground

surface of Bikoue region is higher than that of Ngombas region since their higher uranium concentrations. Moreover, average γ -ray dose rate 208 ± 171 nGy/h at 1 m height is higher than the recommended maximum value $57 \text{ nGy/h}^{9)}$ which takes into account the absorbed dose rate due to ^{238}U , ^{232}Th and ^{40}K . Table 4 shows comparison of uranium concentration in soils and γ -ray dose rate which calculated from the uranium concentration in all over the world⁸⁾. The uranium concentration and γ -ray dose rate of the Lolodorf area are higher than those of the other area in the world. Further study on health impact of the high γ -ray dose rate to inhabitants of this area is desired.

4. Conclusions

Radioactivity concentrations of uranium nuclides in rocks and soils collected from Lolodorf area in South Cameroon where radiation anomaly had been confirmed in previous investiga-

Table 3 γ -ray dose rates in air at 1 m above the ground of the analyzed soil sample areas

Sapling site	γ -ray absorbed dose rate in air, nGy/h
Bi-01	229 $\pm$ 26
Bi-02	290 $\pm$ 26
Bi-03	56 $\pm$ 13
Bi-04	354 $\pm$ 35
Bi-05	622 $\pm$ 18
Bi-06	287 $\pm$ 13
Ng-01	206 $\pm$ 26
Ng-02	74 $\pm$ 23
Ng-03	33 $\pm$ 9
Ng-04	33 $\pm$ 11
Ng-05	34 $\pm$ 9
Ng-06	174 $\pm$ 13
Ng-07	309 $\pm$ 29
Mean	208$\pm$171

*The codes “Bi” and “Ng” mean sampling sites Bikoue and Ngombas, respectively. Uncertainties show standard deviation of the γ -ray counts.

Table 4 Comparison of γ -ray dose rate among the world due to ^{238}U

Locality	^{238}U concentration (Bq/kg $^{-1}$)	γ -ray dose rate in air (nGy/h $^{-1}$)
China	33	16
Hong Kong	84	39
Costa Rica	46	22
United states	35	17
Thailand	114	53
India	29	14
Croatia	110	51
Portugal	49	23
Lolodorf in Cameroon	450$\pm$370	208$\pm$171

The ^{238}U concentrations and their γ -ray dose rate cited from UNSCEAR ⁸⁾

tion has been determined by γ -ray spectrometry. The highest uranium concentration of 179 mg/kg (0.0179%) in Bikoue and 395 mg/kg (0.0395%) in Ngomba regions were detected and they suggest that the area has high possibility of uranium deposit. Due to high uranium concentration in rocks of this area, average uranium concentration in soils of 37 mg/kg, is high and γ -ray dose rate at 1 m height due to ^{238}U series radio-nuclides of the area is higher than the other area in the world. Further stud-

ies are required on geological investigation for uranium mining and on health impact of the high γ -ray dose rate to inhabitants of this area.

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References

- 1) Maurizot, P., Abessolo, A., Feybesse, J. L., Johan, V. and Lecomte, P., Etude et prospection minière du Sud-Ouest Cameroun, Synthèse des travaux du BGRM, de 1978 à 1985 (1986)
 - 2) Gilmore, G., Practical Gamma-Ray Spectrometry Second Edition, Wiley, Chichester (2008)
 - 3) Yonezawa, C., Unpublished work in 2008
 - 4) Satoh, K., Ohashi, N., Higuchi, H. and Noguchi, M., Determination of attenuation coefficient for self-absorption correction in routine gamma-ray spectrometry of environmental bulk sample, *J. Radioanal. Nucl. Chem.*, **84**, 431-440 (1984)
 - 5) IAEA, Preparation of Gamma-ray Spectrometry Reference Materials of RGU-1, RGTh-1 and RGK-1, Report-IAEA/RL/148, Vienna (1987)
 - 6) IAEA, IAEA Analytical Quality Control Services Reference Materials Catalogue 2004-2005, p.22 (2004)
 - 7) Saito, K. and Jacob, P., Gamma ray fields in the air due to sources in the ground, *Radiat. Prot. Dosem.*, **58**, 29-45 (1995)
 - 8) United Nations Scientific Committee on the Effects of Atomic Radiation, UNSCEAR 2000 Report Vol. I, 115-116 (2000)
 - 9) United Nations Scientific Committee on the Effects of Atomic Radiation, UNSCEAR 1993 Report, Annex A, 44-45 (1993)
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