

Study of Some Limestone Samples from Sinai and Eastern Desert, Egypt.

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Abstract: Six limestone rock samples from Sinai and eastern desert; Egypt, were analyzed by X-RD spectroscopy; the mineral and chemical composition, major, minor, and trace chemical and mineral compositions were assigned for each sample. Also, atomic absorption spectroscopy was applied for the Al, Pb, Ca, Fe, K, Bi, Th, U concentrations in ppm and / or percent. The concentrations ranged from 1120 to 8600 ppm, from 27 to 38 ppm, from 28.00% to 38.80%, from 126 to 5840 ppm, and from 190 to 2500 ppm for the Al, Pb, Ca, Fe, K respectively. Concentrations of Bi, Th, and U are < DL. The samples were also analyzed for concentrations of U-238, Th-232 series and K-40 by HPGe gamma spectrometer. The concentrations ranged from 133.20 ± 0.64 Bq/kg to 263.82 ± 0.65 Bq/kg with mean average value 212.41 ± 0.64 Bq/kg for U-238, and for Ra-226 series ranged from 048.27 ± 0.42 to 243.47 ± 0.30 Bq/kg with an average of 139.63 ± 0.33 . Meanwhile; Th-232 concentrations ranged from 48.24 ± 0.22 to 08.52 ± 0.17 Bq/kg with an average of 22.97 ± 0.20 Bq/kg, concentrations for K-40, ranged from 50.86 ± 0.10 to 353.28 ± 0.10 Bq/kg with an average 151.16 ± 0.10 Bq/kg.

Key words: Limestone rock , X-RD spectroscopy, mineral and chemical composition, Sinai, Egypt

INTRODUCTION

Limestone is of great importance, because it is one of raw materials for many industries, as Iron & steel production and cement industry, as well as it is used as building material. Sinai of Egypt is mainly covered by sedimentary rocks of Paleozoic age. Some of sediments area, are of great importance especially from the mineralogical and radiological points of view. Studies applied for exploration for radioactive materials reflect the variation of uranium, thorium, and potassium concentrations in these rocks. Many studies have been concluded about the radioactivity concentrations in cement in Sinai and the eastern desert in Egypt, (Ibrahiem *et al.* 1995, 2003), (El Galy. 2008 and Ibrahiem, *et al.* 2008), studies has been done for sedimentary rocks (limestone) from Sinai & Eastern desert of Egypt to estimate chemical & mineral composition as well as radioactivity concentrations for natural radioactivity levels, for U-238, Ra-226, and Th-232 series and K-40. Also; the study of disequilibrium in radioactive series. (Ibrahiem *et al.* 2012) studied the radio hazards of natural radioactivity in the original samples. Leachates residuals and U-content rate were calculated and compared with the internationally recommended values and were found to be much higher than the world average values. The aim of this work is to make base line map for the study area, to be compared with future studies for any environmental changes due to future nuclear radioactive or accidental activities as well as geological changes.

Geology of the Study Area:

Sinai, the triangular-shaped peninsula of Egypt, is situated between Asia and Africa. The separation of the two continents caused the form and geographical shape of Sinai the way it looks today. Sinai Peninsula consists of an area of some 61,000 square kilometers. Geographical Sinai belongs to Egypt cut from its motherland by the Suez Canal. Some twenty million years ago Sinai was connected with Egypt and the Saudi Arabian Peninsula as a part of the same land formation (The Sinai of Egypt). Geologically Sinai can be roughly divided into three areas. The northern region consists of sand dunes and fossil beaches formed by the changing levels of the Mediterranean Sea during the glacial periods two million years ago. The landscape is flat and uniform, interrupted only by some vast sand- and limestone hills. The scarcely inhabited Al-Tih Plateau is the central geological area with limestone dating from the Tertiary Period. The highlands extend towards the south until it goes over into the third area consisting of granite and volcanic rocks, Limestone and sandstone sediments are replaced by granite and basalt. Both rocks are produced by volcanic activity on the bottom of the ocean from the Precambrian (The Sinai of Egypt).

Sampling and Sample Preparation:

Six sediment rock samples were collected from different areas of Sinai; Wadi Tayeba (Long. $33^{\circ} 08'$, Lat. $29^{\circ} 04'$), Wadi. Feiran (Long. $33^{\circ} 24'$, Lat. $28^{\circ} 46' 30''$) and from eastern desert Wadi el Hoytate (Long. $33^{\circ} 56'$, Lat. $26^{\circ} 05'$) as shown in Fig (1).

Samples were grounded and passed through a 1mm sieve; samples were dried to 95°C for 24 hours in order not to lose the volatile polonium or cesium. The dried fine grained samples were packed in polyethylene

Marinelli beaker for gamma spectroscopy, and then stored for up to four months to reach secular equilibrium between radium-226 and thorium-232 and their progenies.

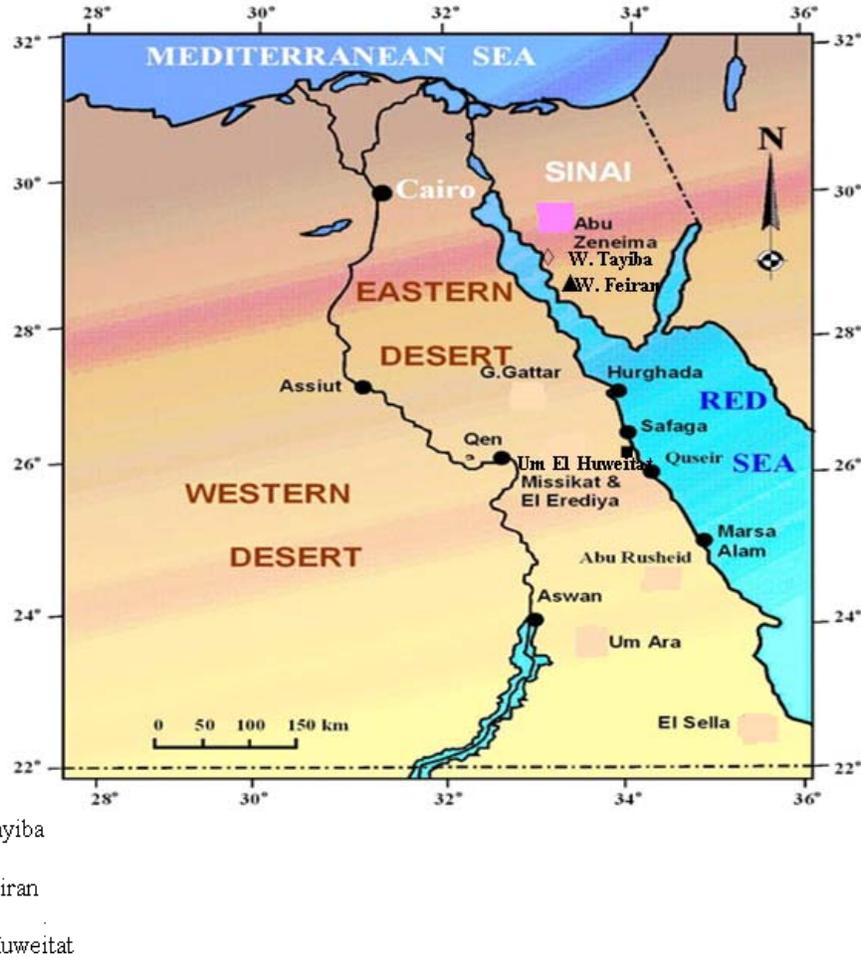


Fig. 1: Location Map of the Collected Samples.

Measurements:

10 gms. of the dried sample were analyzed by X-RD for the chemical and mineral composition, also 10 gr of the dried sample were analyzed by atomic absorption for the Al, Pb, Ca, Fe, K, Bi, Th, U concentrations in ppm and/or percent. Also; samples were analyzed for concentrations of U-238, Th-232 series and K-40 using the gamma spectrometer based on high pure germanium detector "HPGe" with relative efficiency of 20% and FWHM 4.2 keV at 1461 keV, the measurements were done four to twenty four hours. Table (1) represents energies used for the determination of concentrations of the different nuclei in U-238, Ra-226 and Th-232 series as well as K-40 concentrations.

After analyzing the spectrum, count rates for each detected photo peak were used to calculate the specific activity (A) for each detected nuclide using the following equation :(D, Amrani, M. Tahtat, 2001).

$$A = \frac{C}{M \beta \epsilon} \tag{1}$$

Where *c* is the net counting rate of a specific gamma ray (count per second), *M* is the mass of the samples (*kg*), β is the transition probability of gamma-decay and ϵ is the detector efficiency at the specific gamma-ray energy.

Table 1: Concentrations of Radioactivity Series and K-40.

Series or nuclide	Progeny	Energy(keV)	γ %
^{238}U	^{234}Th	63.29	4.10
$^{226}\text{Ra} - \text{series}$	^{214}Pb	295.09	20.10
		351.87	38.30
		609.31	49.90
		1120.27	16.20
$^{232}\text{Th} - \text{series}$	^{214}Bi	1764.49	16.00
		583.10	33.00
		2614.48	35.90
^{40}K		1460.80	11.00

RESULTS AND DISCUSSION

Table (2a) gives the X-RD results, which revealed the major, minor and trace minerals. Results show that the major mineral is calcite (CaCO_3) and ankerite $\text{Ca}(\text{Fe}^{++}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$, with additional minor and trace concentrations. Table (2b) is a review of the chemical composition of each mineral and its, description which reflects the condition of its formation (Leet L., et al, 1982).

Table 2a: The mineral composition of samples analyzed by XRD spectrometer.

Sample code No.	Major	Minor	Trace
1	Calcite	-----	Quartz, Lavenite
2	Calcite	Quartz	Laveite, Albite
3	Calcite, Ankerite	-----	Mullite, Ankerite, Jadeite
4	Calcite, Ankerite	Quartz	Albite
5	Calcite	Brushite	Gypsum, Sepiolite, Quarts, Halite, Albite
6	Calcite	-----	Mullite

Table 2b: The mineral and its chemical composition and description.

MINERAL	CHEMICAL COMPOSITION	DESCRIPTION
Albite	Sodic Plagioclase feldspar $\text{Na}(\text{AlSi}_3\text{O}_8)$	Tabular crystals, striations caused by twinning, Magmatic and pegmatitic rocks
Ankerite	Calcium Magnesium Carbonate in which ferrous iron replaces more 50% magnesium $\text{Ca}(\text{Fe}^{++}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$	Formed in low-grade regional metamorphism from conversion of Calcite or Dolomite or both between 80 and 120°C. Common in ore-bearing rocks as a rock forming mineral (gangue). High Fe species are found in iron ores.
Brushite	(dicalcium phosphate dehydrate) $\text{Ca}(\text{HPO}_4) \cdot 2(\text{H}_2\text{O})$	One of the most common cave minerals, in guano deposits, and in phosphorites, formed at low pH by reaction of phosphate-rich solutions with calcite and clay.
Calcite	Calcium Carbonate CaCO_3	Usually in crystal or coarse fine granular aggregates extremely varied-over 300 different form, Found in sedimentary, igneous, and metamorphic rocks.
MINERAL	CHEMICAL COMPOSITION	DESCRIPTION
Gypsum	Hydrous Calcium Sulfate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	The most common sulphate mineral. Found as both massive material, including the alabaster variety; and clear crystals, the selenite variety; and, parallel fibrous, the satin spar variety. Typically colourless to white, transparent crystals, thick tabular to lenticular, sometimes prismatic.
Jadeite	$\text{Na}(\text{AlFe}^{+++})\text{Si}_2\text{O}_6$	Strongly metamorphosed sodium-rich serpentinous rocks
Mullite	$\text{Al}_{4+2x} \text{Si}_{2-2x} \text{O}_{10-x}$ $x \sim 0.4$	Remelted Tertiary-aged clays. Colourless, white, yellow, pink, red, gray
Quartz	Silicon oxide SiO_2	Sedimentary, metamorphic, and igneous rocks.
Sepiolite	clay mineral, a complex magnesium silicate $\text{Mg}_4(\text{Si}_6\text{O}_{15})(\text{OH})_2 \cdot 6\text{H}_2\text{O}$	Secondary mineral associated with serpentine. Can precipitate from alkali saline waters in arid environments

Table (3) represents concentrations of Al, Pb, Ca, Fe, K, Bi, Th, and U measured by Atomic Absorption Analyzer. Results give concentrations of Al ranging from 1120 ppm (sample no. 4) to 8600 ppm (sample no. 2), concentrations of Pb. ranging from 27 ppm (sample no. 4) to 38 ppm (sample no. 2), concentrations of Ca ranging from 28.00% (sample no. 5) to 38.80% (sample no. 6), concentrations of Fe ranging from 126 ppm (sample no. 4) to 5840 ppm (sample no. 2), concentrations of total K ranging from 190 ppm (sample no. 6) to 2500 ppm (sample no. 2) concentrations of Bi, Th, and U are lower than the detection limit (DL)

Table 3: Concentrations of Al, Pb, Ca, Fe, K, Bi, Th, and U measured by Atomic Absorption Analyzer.

Samp. No.	Elements	Al	Pb	Ca	Fe	K	Bi	Th	U
	DL	2	1	0.01	2	2	10	5	10
	Units	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm
1		1800	34	38.16	2930	386	<10	<5	<5
2		8600	38	32.80	5840	2500	<10	<5	<5
3		2000	29	37.60	1950	1180	<10	<5	<5
4		1120	27	33.68	1260	325	<10	<5	<5
5		1920	35	28.00	1300	560	<10	<5	<5
6		2160	31	38.80	1470	190	<10	<5	<5

In this study, U-238 is in secular equilibrium with its daughter Th-234 and Pa²³⁴, samples were stored to four months. In order to measure Ra-226 concentrations, Pb-214 and Bi-214 were taken for the concentration measurements. For Th-232 its daughters Pb-212 and Tl-208 were used to measure the concentrations. The 1460.8 keV gamma transition was used for the concentration of K-40, (Dionisio Uendro Carlos et al, 2004),

Table (4) represents the concentrations in Bq/kg of the different radionuclides in the samples. The radioactivity of the samples, as shown in table 4, for U-238 concentrations ranged from 133.20±0.64Bq/kg (sample 3) to 263.82±0.65 (sample 4) Bq/kg with mean average value 212.41±0.64 Bq/kg, also for Ra-226 ranged from 48.27±0.42 Bq/kg (sample 3) to 243.47±0.30Bq/kg (sample 4) with mean average value 139.63±0.33 Bq/kg.

Meanwhile; for Th-232 series the highest value was 48.24±0.22 Bq/kg (sample 2) and the lowest value was 8.52±0.17 Bq/kg (sample 5) with an average value 22.97±0.20 Bq/kg, for K-40 activities ranged from 50.86±0.10 Bq/kg (sample 4) to 353.28±0.10 Bq/kg (sample 2) with average value 151.16±0.10Bq/kg.

Table 4: The specific radioactive concentrations in Bq/kg dry weight for Sinai samples and eastern desert.

Sample	The specific radioactive concentrations in Bq/kg			
	²³⁸ U	²²⁶ Ra	²³² Th	⁴⁰ K
1	166.10±0.65	178.98±0.28	15.23±0.21	101.42±0.10
2	253.59±0.64	148.71±0.30	48.24±0.22	353.28±0.10
3	133.20±0.64	048.27±0.42	23.47±0.21	261.92±0.10
4	263.82±0.65	243.47±0.30	26.89±0.22	050.86±0.10
5	229.40±0.64	124.48±0.28	08.52±0.17	085.58±0.10
6	228.33±0.64	093.86±0.28	15.44±0.21	053.91±0.10
Mean	212.41±0.64	139.63±0.33	22.97±0.20	151.16±0.10

Table (5) gives a comparison between concentration of natural radioactivity from present study and that given by (Ibrahiem et al 2000), Bq/kg dry weight.

Table 5: Comparison between concentrations of natural radioactivity, Bq/kg dry weight.

Study	U-238 series	Ra-226 series	Th-232 Series	K-40	Bq/kg
Present work	212.41 ±0.64	139 ±0.33	23.0 ±0.20	151.16± 0.10	184.12
Ibrahiem et al 2000	121±10	44.5±3.5	< DL	52.3±8.3	---

Radium equivalent from the equation (Kumar et al., 2003)

$$Ra_{Eq} = C_{Ra} X I + C_{Th} X C_2 + C_K X C_3 \tag{2}$$

Where:

C_{Ra} is concentration Bq/kg from ²²⁶Ra series.

C_{Th} is ²³²Th concentration by Bq/kg, C_2 is conversion factor.

C_k is ⁴⁰K concentration by Bq/kg, C_3 is conversion factor

Table (5) shows that radium equivalent are lower than 370Bq/kg, the permissible limit so it can be used as raw material for iron & steel production or cement industry as well as building materials is the permissible dose.

Conclusion:

- Results of the analysis by X-RD shows that the major concentration for the samples are Calcite and Ankenite, with additional minor and trace concentrations.
- The concentrations of the samples of Al, Pb, Ca, Fe, K, Bi, Th, and U were measured by Atomic Absorption Analyzer.

- The gamma-ray results can be considered as a base line monitoring for natural background radioactivity levels, this facilitate comparative study between these results and those which might occur after construction of nuclear power, or other future nuclear activities as well as nuclear accident.
- The U-238 activity concentrations of the samples are high than those of Ra-226, Th-232, and K-40.

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