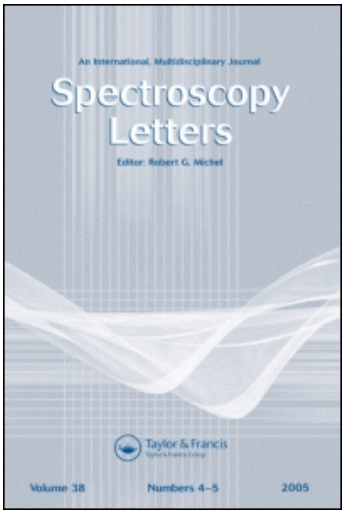

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Determination of the Uranium Content in Some Natural Formations in Morocco by Use of Nuclear Analytical Methods

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ABSTRACT In this work, we report the measurement of uranium content in some natural formation samples in Morocco. Such results are used in several studies concerning the earth sciences and the environment such as geochronology, archaeology, geophysical and geophysical studies, and prospecting of radioactive pollution. The analyses were carried out on some natural deposits such as corals, fossil shells of mollusks, phosphates, travertines, lichens, and on impure carbonate deposits. Measurements were realized by alpha-spectrometry for fossil shells of mollusks, corals, travertines, and impure carbonates, by gamma spectrometry using a well detector with NaI scintillation for phosphates, and by neutron activation for lichens. Isotopic $^{234}U/^{238}U$ ratios were also measured and are discussed.

KEYWORDS corals, impure carbonates, lichens, natural radioactivity, phosphates, shell mollusks, travertine, uranium

INTRODUCTION

The natural radioactivity present in our environment comes primarily from the radioelements of the natural radioactive families (^{238}U, ^{235}U, ^{232}Th), and from potassium-40 and rubidium-87. The distribution of these radioelements in the natural environment depends on their physicochemical state and their geochemical behavior according to the reigning natural conditions. The natural samples—having formed their skeletons starting from water solutions and containing initially mainly uranium without its descendents—after their formation can be exposed to inland water-currents, which can bring quantities of radioactive or stable elements comparable to or exceeding the concentrations incorporated initially. These concentrations can constitute, in certain cases, chemical and/or radioactive pollution. In this work, we are interested in the measurement of uranium content in coral samples, fossil shells of mollusks, continental impure carbonate, phosphate, and lichen samples.

The results obtained for corals, fossil shells of mollusks, travertines, and impure carbonates are used to determine the ages of certain formations using the $^{230}Th/^{234}U$ radiochemical dating[1–9] method. The open systems

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are dated by using isochronal methods based on uranium and thorium radioisotope activities and activity ratios.[10–13]

Phosphates are the most important minerals in Morocco, and it is recognized that Moroccan soil contains the most important reserves of phosphates in the world.[14,15] Phosphate-bearing rocks are an economical material used in the manufacture of phosphoric acid and fertilizers. In phosphate rocks, radioactive elements such as ^{235}U, ^{238}U, and their decay products may be present in high concentration.

Lichens are widely used to assess atmospheric pollution by heavy metals and radionuclides. The general advantage of the biomonitoring approach is the ease of sampling and no requirement for expensive equipment, the high sensitivity of detection, as well as the availability of samples with a wide geographic distribution.[16] Lichens are also good radionuclide bioaccumulators.[17] For example, lichens were used to assess radionuclide fallout after the Chernobyl accident.[18,19]

MATERIALS AND METHODS

The samples analyzed in this work were 6 corals, 120 fossil shells of mollusks, 87 samples of phosphates, 7 travertines, 4 lichens, and 15 samples of impure carbonates of continental origin. The coral samples, which were taken at the Mediterranean coast to a 300-m depth, included species of *Ophelia* and *Pertoza*, *Madrupora oculta*, and *Dasmosmilia lyman*. The samples of fossil shells of mollusks, which were taken on the Atlantic coast at the High Atlas in the north of the town of Agadir, were analyzed in order to study the variation of the seawater level in the past according to the climate changes. These included species of *Thais*, *Mytilus perna*, *Patella*, *Cardium ringens*, *Ostrea*, *Cymbium*, *Cymatium*, *Dosinea*, *Conus*, *Littorina*, *Turritella*, *Donax*, *Cardita*, *Mondenta*, *Trochatella*, *Chlamys*, *Lima*, and *Lutraria*.

The phosphate samples were taken from several locations of the Layer of Gantour region rich in phosphates. The phosphate measurements were realized in order to establish a distribution map of the radioactivity in Moroccan phosphates and to study its environmental impact.

The travertine samples come from the Korifla valley in the region of Wadi Bou Regreg in the western north of the Central Moroccan Plate. The results were used to date the abundant wet phases in this locality.[12]

The impure carbonate samples came from the littoral cuts between Safi and El Jadida and from the continental cuts in the Abda-Doukkala plain. These samples were analyzed in order to correlate the influence of the changes of climate on the littoral and the continental cuts. The lichens, which can be used as bioindicators of pollution for the sea–continent interface, were collected in the area of Rabat-Salé.

The analytical techniques employed in this work are

(i) Alpha spectrometry based on advanced separation and purification of uranium as described by Choukri and by Semghouli.[4,12] This procedure was used for corals, shells of mollusks, travertine, and impure carbonates.
(ii) Gamma spectrometry using a well detector with scintillation NaI(Tl). The technique used to analyze the phosphate samples is described in Ref. 14.
(iii) Neutron activation analysis using the k_0-quasi-absolute method (INAA-k_0) for the lichen samples as described in Ref. 16.

RESULTS AND DISCUSSION

The analysis results of the mollusk shell samples are given in the histograms of Figs. 1 and 2. Those of phosphates are given in the histogram of Fig. 3. The results obtained on the corals, travertines, lichens, and deposits of continental carbonates are given in Table 1. The results of fossil shells of mollusks and phosphates are presented in histograms because the number of measured values allows a statistical study.

The results obtained show that the uranium concentrations vary from one formation to another as they can vary for the same formation. For the corals, and except for only one sample whose content is relatively high, the concentrations are about those usually measured in the coral samples in various areas of the world, which is about 3 ppm.[1,3,4] The $^{234}U/^{238}U$ ratios are also of the order of those generally found in coral samples (of about 1.16).[4] Any different value would indicate that the sample was recrystallized, and consequently it would not check

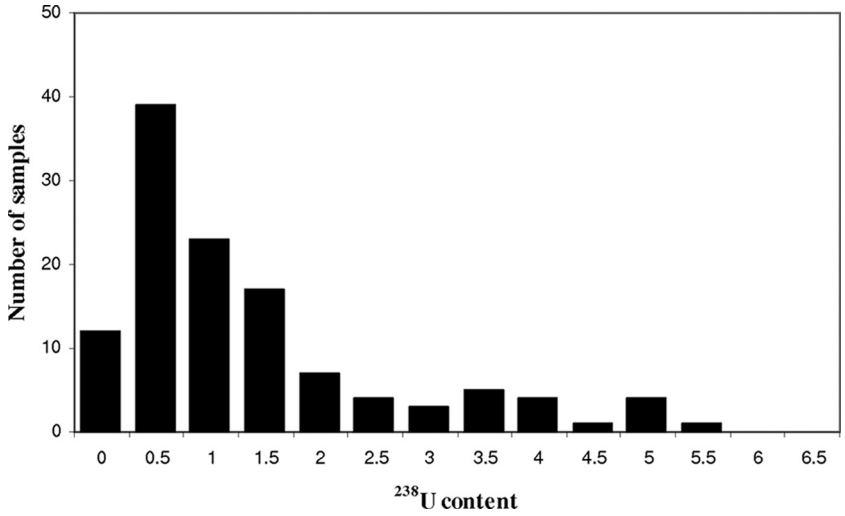

FIGURE 1 **Histogram of uranium repartition in 120 shell mollusk samples.**

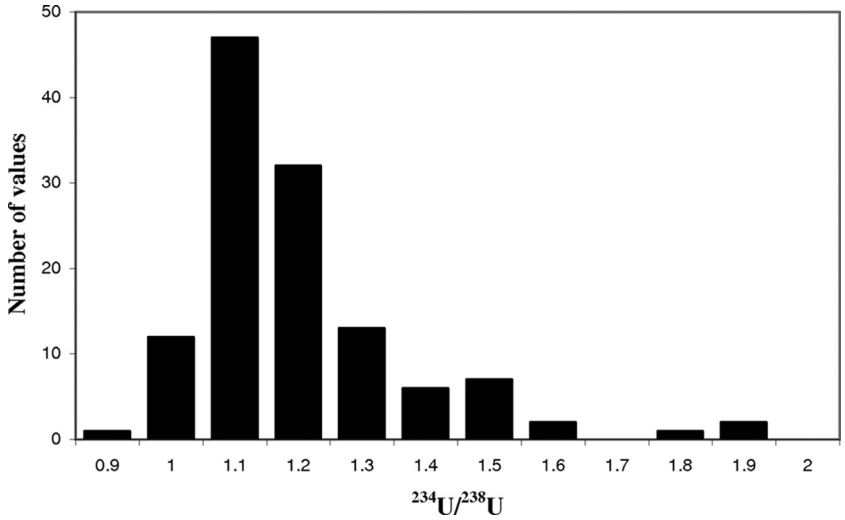

FIGURE 2 **Histogram of $^{234}U/^{238}U$ ratio repartition in 120 shell mollusk samples.**

the criterion of the closed system so that the dating is reliable and consequently it would not check the criterion of the closed system that is the necessary condition so that the dating is valid.

The mollusk shell samples are generally considered less reliable than the corals because of their opening systems.[4,8,10,12,13,20] Except for the Holocene sea level, ^{238}U and initial $^{234}U/^{238}U$ activity ratios vary for the older levels in wide intervals, independently of species and calcite contents of samples.[4,8,20] The relatively high ^{238}U contents and $^{234}U/^{238}U$ activity ratio in older mollusk shell samples are due eventually to a postincorporation of secondary uranium from seawater or from continental waters drained away by rivers. This incorporation leads to a rejuvenation of mollusk shell ages and is responsible for the wide dispersion of their apparent ages according to the mode and the timing of uranium introduction.[8,21] The analyzed mollusk shells belong to three climatic episodes, the Holocene dated to 6 ka (6000 years) approximately, The Ouljien (corresponding to the stage 5e) dated to 125 ka approximately, and the Harounien (corresponding to the stage 7 and/or 9) dated between 180 and 350 ka.[4,8,9,22] The ^{238}U contents measured in the recent samples are all weak, about one-tenth ppm, whereas the older samples present variable contents going from one-tenth ppm to more than 5 ppm, which explains why the Holocene samples did not have sufficient time to incorporate secondary

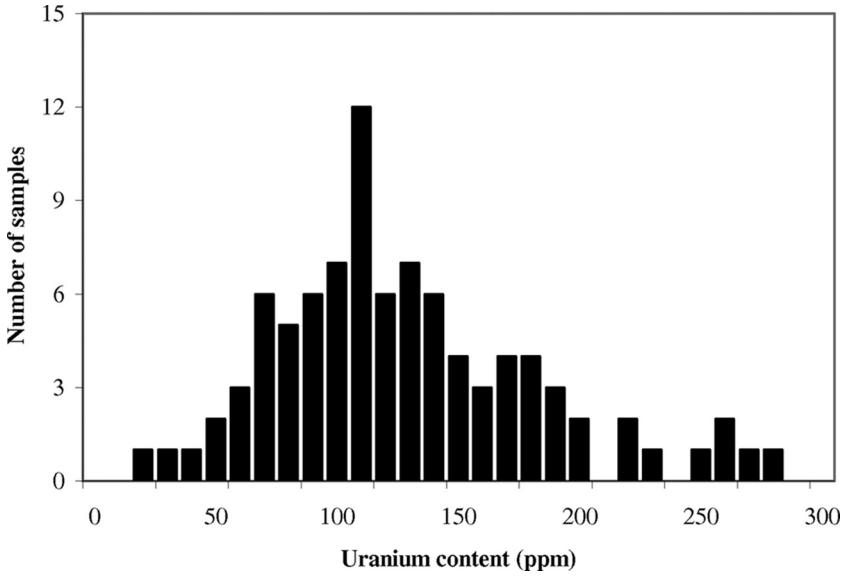

FIGURE 3 **Histogram of uranium repartition in 87 phosphate samples.**

uranium brought by continental or marine-current water. The relatively high values of $^{234}U/^{238}U$ ratio measured in the old samples confirm that the shells present an open system that can incorporate uranium of continental origin.

We cannot draw a conclusion for lichen samples because of the reduced number of analyses, and because they present low uranium contents. The travertine and impure carbonate samples present generally weak but variable uranium concentrations. They can reach, in certain cases, relatively important values as is the case for the first travertine sample where ^{238}U is about 2.84 ppm and for the two impure carbonate samples where the contents are about 2.15 and 5.96 ppm. Uranium contents and $^{234}U/^{238}U$ ratio are used to determine ages of impure carbonate samples using isochronal methods.

For phosphate samples, the concentrations vary between 20 and 280 ppm with an average value of about 120 ppm. They are higher than those of the other natural formations as has been already mentioned in the literature.[23–25] These results show

TABLE 1 **Uranium Concentrations in Travertines, Lichens, Corals, and Impure Carbonates**

Deposit	^{238}U (ppm)	$^{234}U/^{238}U$	Deposit	^{238}U (ppm)	$^{234}U/^{238}U$
Travertines	2.9±0.1	1.0±0.2	Impure	1.4±0.2	1.2±0.1
	0.5±0.1	1.6±0.1	continental	0.2±0.1	1.3±0.1
	0.2±0.1	1.3±0.2	carbonates	1.1±0.1	0.7±0.1
	0.5±0.1	2.2±0.1		6.0±0.2	1.4±0.1
	0.3±0.1	1.9±0.2		0.3±0.1	1.5±0.3
	0.6±0.1	2.2±0.1		0.2±0.1	2.3±0.2
	0.6±0.1	2.0±0.2		0.4±0.1	4.0±0.4
Lichens	0.4±0.2	—		1.0±0.1	1.2±0.1
	0.4±0.2	—		0.3±0.1	1.0±0.1
	0.5±0.2	—		1.6±0.1	0.9±0.4
	0.8±0.2	—		0.4±0.2	1.3±0.1
Corals	3.8±1.0	1.2±0.1		0.7±0.1	1.4±0.4
	3.6±0.1	1.2±0.1		1.1±0.2	1.7±0.1
	5.1±0.1	1.2±0.1		2.1±0.2	1.4±0.1
	3.7±0.2	1.±0.1		0.7±0.1	1.1±0.1
	3.6±0.1	1.1±0.1		2.7±0.2	1.0±0.1
	3.6±0.2	1.2±0.1		0.8±0.1	1.1±0.1

that phosphates are a big reservoir of fissile material uranium, even if it is in small concentration. The derived phosphate products such as fertilizers and phosphogypsum could contain radioactivity that pollutes the environment.

The three techniques used in this work (alpha spectrometry for fossil shells of mollusks, corals, travertines, and impure carbonates, gamma spectrometry using a well detector with scintillation NaI for phosphates, and neutron activation for lichens) can give results with precision, which can be improved by using very precise conditions (weight of the sample, detector used, time of counting). In this work, we were interested especially in the contents of the uranium in various natural formations in Morocco knowing that the precision of measure could change from one method to another. The large number of measurements allows us to have a general idea about the contents of the uranium in each studied formation independent of the technique used.

CONCLUSIONS

The results obtained show that:

1. The unrecrystallized Moroccan corals present uranium contents and $^{234}U/^{238}U$ ratios comparable with those habitually found in coral samples throughout the world and which are distributed around an average value of 3 ppm for ^{238}U and 1.16 for $^{234}U/^{238}U$.
2. The fossil shells of mollusks present dispersed uranium concentrations and $^{234}U/^{238}U$ ratios. Their variation does not follow any tendency according to the locality of sampling or of the species. This dispersion is responsible for the unreliability of measured radiochemical ages given by fossil shells of mollusks.
3. The phosphate samples coming from the Layer of Gantour present variable uranium contents between 20 and 280 ppm with an average value of about 120 ppm. These contents are comparable with those generally found in apatite phosphate samples known by their retention of uranium.
4. The other formations (travertines, lichens, and deposits of carbonates) present generally small quantities of uranium and can reach, in some cases, values comparable with those of coral and fossil shells of mollusks.

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