

NOTES

**Examples of the variability of disequilibrium and the emanation factor
in some uraniferous materials**

A. A. LEVINSON

Department of Geology, University of Calgary, Calgary, Alta., Canada T2N 1N4

AND

C. J. BLAND

Department of Physics, University of Calgary, Calgary, Alta., Canada T2N 1N4

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UNIVERSITY OF UTAH
RESEARCH INSTITUTE
EARTH SCIENCE LAB.

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The U_3O_8 and eU_3O_8 contents, and the activities of ^{226}Ra and ^{214}Bi , have been determined for samples from two distinctly different geological and environmental localities (Thailand and southern Africa). In both cases, most of the samples show significant disequilibrium. On the basis of these data, the potential difficulties which would be encountered if gamma ray spectrometers (either airborne or surface) were used in the exploration for uranium in these situations are discussed.

Using the same data, as well as information from the literature, it is shown that only a limited, variable, and unpredictable amount of ^{222}Rn produced during the decay of ^{238}U (and its daughters) escapes from geological material; this amount is called the emanation factor (E). Thus, in attempting to use ^{222}Rn for exploration purposes, not only must the short half-life (3.8 days) and other problems be considered, but at least of equal importance is the amount of ^{222}Rn which can escape from any sample.

On a déterminé les teneurs en U_3O_8 et en eU_3O_8 et les activités du ^{226}Ra et du ^{214}Bi pour des échantillons de deux localités de géologie et de milieu de dépôt différents (Thaïlande et sud de l'Afrique). Dans les deux cas, la plupart des échantillons montrent un déséquilibre significatif. En se basant sur ces données, on discute les difficultés potentielles qu'on rencontrerait si on utilisait les spectromètres de rayons gamma (aéroportés ou en surface) pour l'exploration de l'uranium dans ces conditions.

En utilisant les mêmes données en plus de l'information déjà publiée, on montre que seulement une quantité limitée, variable et imprévisible de ^{222}Rn produite durant la désintégration de ^{238}U (et de ses filles) peut s'échapper des matériaux géologiques; on désigne cette quantité sous le terme de facteur d'émanation (E). Ainsi, si on tente d'utiliser le ^{222}Rn pour l'exploration, non seulement doit-on considérer sa courte demi-vie (3.8 jours) et d'autres problèmes, mais aussi, et avec autant d'emphase, la quantité de ^{222}Rn qui peut s'échapper d'un échantillon donné.

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Introduction

The importance of disequilibrium in the search for, and mining of, uranium has been known for many years. Recently Levinson and Coetzee (1978) reviewed the subject with particular emphasis on the implications of disequilibrium in the exploration for uranium ores in the surficial environment. However, there have been very few studies which have presented quantitative data on this phenomenon of practical interest to exploration geologists.

Hansink (1976) published one of the few quantitative studies on the practical importance of disequilibrium in the mining (not exploration) of uranium, based on a roll-front type of deposit in the Powder River Basin, Wyoming. He verified previous reports which indicated that the altered por-

tions of roll-front deposits are depleted in uranium, whereas material from the front and unaltered sides of the deposit are enriched. By comparing the uranium content determined chemically (by fluorometry) with that obtained radiometrically he was able to establish that the 'disequilibrium correction factor', D , ranged from 0.80 to 3.0 in the deposit, with an overall average of 1.20. The disequilibrium correction factor, D , is defined as the ratio of chemically determined uranium to that determined radiometrically.

In this paper we will also discuss the 'emanation factor', E , which is equal to the amount of radon emitted by a rock compared to the total amount of radon which is in equilibrium with radium in the rock (expressed in percent). An alternative defini-

ELEMENT	ATOMIC NUMBER
Uranium	92
Protactinium	91
Thorium	90
Actinium	89
Radium	88
Francium	87
Radon	86
Astatine	85
Polonium	84
Bismuth	83
Lead	82

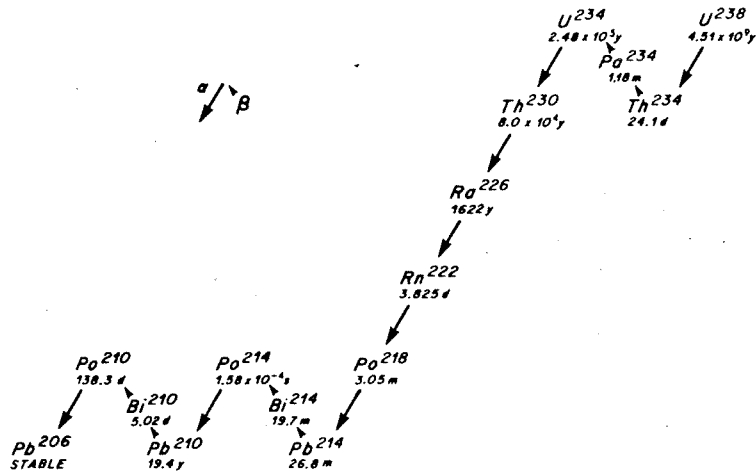


FIG. 1. The principal nuclides in the ^{238}U series decay chain.

tion would be the escape-to-production rate of radon (in percent).

Figure 1 presents the nuclides and their relative positions in the ^{238}U decay series.

Description of the Sample Occurrences

Samples from two distinctly different geological, geographical, and climatic regions were selected for this study.

Samples from Thailand

These samples originated from a part of Thailand for which very little detailed geological information is available. The area is predominantly dry, although in the vicinity there is sufficient seasonal rainfall for the cultivation of rice.

Samples 1-5, and 6-9, are soil samples which were obtained on the surface from two different traverses about 1.5 km apart. The first traverse was about 50 m in length and the samples were collected from a cliff face. The second traverse was about 125 m in length within a trench. Both traverses were conducted on what is assumed to be a similar geological horizon, in a downdip direction, on a porous sandstone believed to be Mesozoic in age. The sandstone is considered to be nonmarine based on the combination of cross-bedding, conglomeratic pods, and the presence of some tree stumps, branches, and other carbonaceous matter. Evidence of some oxidation, such as 'leaching', has been observed and it is from this oxidized zone that the samples were taken.

Samples from Southern Africa

These samples originated from near-surface (maximum depth of 7 m) boreholes in an extremely arid region (average rainfall is 55 mm) in

southern Africa. Uranium is found in a mineral form (as boltwoodite, carnotite, and zippeite) and also adsorbed on to clays and carbonaceous material. The uranium values are selectively concentrated in certain horizons characterized by high carbonaceous and diatomaceous earth contents, high moisture, and low densities. The deposit was emplaced about 40 000 years ago, and because of this young age and the fact that the movement of uranium and its daughter products is an active process at this time, disequilibrium among the nuclides in the uranium series is prevalent. Further details on this deposit, including pertinent isotope data (e.g., $^{234}\text{U}/^{238}\text{U}$ ratios), may be found in the report by Ralston *et al.* (1978).

Analytical Method

Samples were crushed to approximately 100 mesh and homogenized prior to the determination of the uranium content. The Thailand samples were assayed for uranium by fluorometry at Loring Laboratories, Calgary, and uranium in the southern African samples was measured by alpha spectrometry (Prof. R. S. Harmon, Michigan State University).

We measured portions of each sample for ^{226}Ra by the following procedure. Portions of 1 g were fused with a sodium carbonate flux and dissolved in HCl. Barium carrier was added and BaSO_4 precipitated. The precipitate was purified by taking up in alkaline EDTA solution and reprecipitated by the addition of acetic acid. Finally, the precipitate was filtered on a 2.5 cm diameter filter disc which was then mounted on a plastic disc. After drying, the disc was placed under a 400 mm² surface barrier detector in a vacuum chamber. Losses of the

TABLE 1. Analytical data and calculated eU₃O₈, D, and E for the soil samples from Thailand

Sample No.	U ₃ O ₈ (ppm) (fluorometry)	²²⁶ Ra activity (pCi/g)	²¹⁴ Bi activity (pCi/g)	eU ₃ O ₈ *	D†	E‡ (%)
1	12.2	36.6	33.0	128.2	0.10	10
2	101.0	61.2	61.2	214.3	0.47	0
3	152.0	270.9	284.4	948.6	0.16	—
4	7.8	30.2	27.6	105.7	0.07	9
5	3.3	10.1	9.6	35.4	0.09	5
6	24.6	17.8	15.6	62.3	0.39	12
7	44.7	34.7	29.4	121.5	0.37	15
8	52.4	13.5	13.4	47.3	1.10	1
9	18.9	19.1	21.6	66.9	0.28	—

*eU₃O₈ based on ²²⁶Ra activity and the fact that 100 ppm U (118 ppm U₃O₈) should yield an activity of 33.6 pCi/g at equilibrium.

†D, the disequilibrium correction factor, is the ratio of the amount of U₃O₈ determined chemically to the amount of eU₃O₈ determined radiometrically. To be consistent with Hansink (1976), eU₃O₈ has been determined from the ²²⁶Ra activity.

‡E, the emanation factor, is the ratio of the amount of radon (²²²Rn) emitted by a rock to the total amount of radon in equilibrium with radium (²²⁶Ra) within the rock. E may be calculated from the ²¹⁴Bi/²²⁶Ra activity ratios, at equilibrium, as ²¹⁴Bi is a prompt daughter of ²²²Rn. Because the ratio (²¹⁴Bi/²²⁶Ra) × 100 is the amount of ²²²Rn (in percent) which did not escape from the rock, E is the difference between this percentage and 100. Dashes (—) represent negative values and must result from analytical errors.

barium carrier during the chemical procedure were monitored by the use of ¹³³Ba tracer which can be measured by the gamma ray spectrometer (an ORTEC™ Ge(Li) detector of 15% efficiency compared to a standard 3 in. × 3 in. NaI detector). The surface barrier detector was used to measure the alpha particle spectrum from ²²⁶Ra. The radium is distributed throughout the BaSO₄ precipitate which on the disc has a thickness of no more than 1 mg cm⁻². This is approximately four times less than the range of alpha particles emitted by ²²⁶Ra (energy 4.78 MeV) and a well defined peak is exhibited in the pulse height spectrum. Corrections for the geometrical factor, overlap of counts from daughter activity, and background counts were made by calibration using a standard radium solution (Radiochemical Centre, Amersham, U.K.). Replicate analyses from further portions of the same samples revealed that the dominant source of error depended on counting statistics. Longer counting times, however, give rise to the grow-in of daughters and corresponding corrections have to be made. The optimum counting time was found to be 4 h. Errors quoted are derived from the standard deviation of the Poisson distribution.

The remaining portions of the samples (about 40 g) were kept in an air-conditioned laboratory for 1 month in open dishes. At the end of this period each sample was placed in a sealed plastic bottle of 4.5 cm inside diameter to a height of 4 cm. The bottle was placed on the entrance window (4.9 cm diameter) of the Ge(Li) gamma ray detector. The integrated counts in the 1.76 MeV gamma ray peak from ²¹⁴Bi were compared with counts in the same interval from a 4% U standard (USAEC New Brunswick Laboratory). Fortunately the matrices of the standard and the samples were very similar

as regards density and gamma ray absorption. The latter aspect was checked by mounting a ⁸⁸Y isotope point source above each sample and the standard, and monitoring the absorption of the 1.84 MeV gamma ray line. Minor corrections (a few percent) for differences in self-absorption were made. In all the radiometric measurements the counting intervals were sufficiently long to reduce the statistical error to 1% or less. Replicate measurements yielded values well within these limits.

Results

Table 1 presents the analytical data determined (U₃O₈, and the activities of ²²⁶Ra and ²¹⁴Bi), as well as the calculated eU₃O₈, D, and E values, for the soil samples from Thailand. Figure 2 graphically presents the comparison between uranium determined chemically and radiometrically. Clearly, the

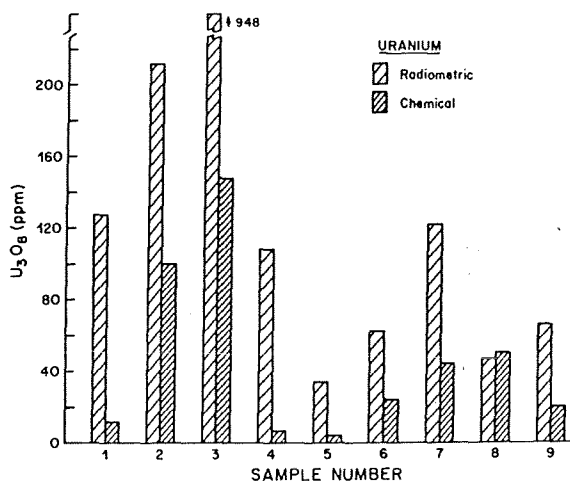


FIG. 2. Comparison between uranium determined chemically and radiometrically on the soil samples from Thailand.

TABLE 2. Analytical data and calculated eU_3O_8 , D , and E for the samples from southern Africa*

Sample No.	U_3O_8 (ppm) (alpha spectrometry)	^{226}Ra activity (pCi/g)	^{214}Bi activity (pCi/g)	eU_3O_8 (ppm)	D	E (%)
578	83	54	12.5	190	0.44	77
579	37	59	12.2	207	0.18	79
580	243	59	17.8	207	1.2	70
581	2128	108	84.1	379	5.6	22
582	579	48	21.2	169	3.4	66
583	2672	247	138.3	867	3.1	44
584	578	59	16.3	207	2.8	72
585	1884	98	26.7	344	5.5	73

*All notes in the footnote to Table 1 are applicable here.

results show that, except for sample 8, all samples are strongly depleted in uranium (D ranges from 0.07–0.47).

Table 2 presents the analytical and related data for the borehole samples from southern Africa. In this case, D values are both less than 1, indicating depletion of chemical uranium by comparison with that determined radiometrically (samples 578 and 579), and greater than 1, indicating the reverse situation (samples 580–585). As shown by Ralston *et al.* (1978): (1) this deposit is young in age (it formed about 40 000 years BP), hence the daughter ^{214}Bi has not had time to 'grow-in', and (2) fluctuations in the water table in this arid region have caused separation of the uranium isotopes ^{234}U and ^{238}U from other long-lived isotopes, specifically ^{230}Th and ^{226}Ra , because of the different mobility rates of the individual nuclides within the uranium decay series. The first observation, that is, the young age

of the samples, explains the high D values in samples 580–585, whereas groundwater fluctuations, analogous to leaching, explain the low D values (similar to those in Table 1) in samples 578 and 579. Figure 3 graphically presents the comparison between uranium determined chemically and radiometrically.

Discussion

The data presented in Tables 1 and 2, obtained from samples collected in two distinctly different geological and environmental localities, have important practical implications which exploration geologists frequently overlook. The most important implication, of course, is that high gamma activity does not necessarily reflect uranium mineralization at a particular site. Conversely, low gamma activity does not confirm the absence of mineralization. Owing to their different mobility characteristics in various geochemical environments uranium, radium, and other isotopes in the decay series may become separated, i.e., disequilibrium may occur (Levinson and Coetzee 1978). Only direct analysis for uranium by some appropriate method (e.g., fluorometry, delayed neutron activation) can conclusively confirm the presence or absence of this element. Disequilibrium may be manifested by the almost complete removal of uranium in some cases (samples 1, 4, and 5 in Table 1) or by an excess of this element by comparison with radiometric measurements (samples 580–585 in Table 2). The problem is particularly difficult in those cases where the degree of disequilibrium varies over short distances.

Another very important concept to consider in the concept of disequilibrium is the volume (or scale of sampling) within which the disequilibrium occurs. If it is smaller than the sampling volume, then disequilibrium will be of no practical significance. A case in point would be an airborne survey in which the movement of the nuclides may be tens of metres, but the disequilibrium problem is

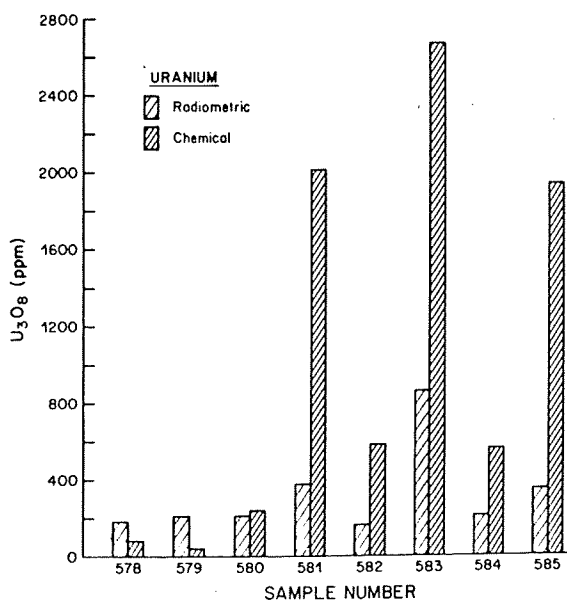


FIG. 3. Comparison between uranium determined chemically and radiometrically on borehole samples from southern Africa.

minimized by the large sample volume examined by an airborne gamma ray spectrometer. On the other hand, if movement of nuclides was only a few centimetres but only 1 g of sample was analyzed, then disequilibrium will certainly be indicated.

The E values in Table 1 are particularly significant from the point of view of the use of radon in the exploration for uranium. Inherent in the use of radon is the concept of its mobility, that is, its ability to move as a gas for various distances upward (some claim distances of hundreds of metres) before it decays by virtue of its half-life of 3.8 days. However, the very similar activity ratios for ^{226}Ra and ^{214}Bi in Table 1 indicate that very little migration, or emanation, of ^{222}Rn took place because if it did, ^{214}Bi activity values would be lower than those for ^{226}Ra . (There was a 1 month interval between the analysis of the ^{226}Ra activity and ^{214}Bi activity and in this period the samples were exposed to the air.) The lack of radon mobility is reflected in the E values which range from 0–15% or, in other words, only a maximum of 15% of the ^{222}Rn emanated from the samples.

The emanation factor, E , for the samples from southern Africa range from 26–79% and, in this situation, the use of radon for exploration purposes would appear to be feasible, at least on a qualitative basis.

The fact that radon has an emanation factor, E , which must be considered by all exploration geologists, is rarely mentioned in the exploration literature. However, it is well known by those concerned with the environmental aspects of radon in the mining of uranium. Among the many studies on the radon emanation characteristics, or the ability of radon to escape from rock and mineral samples, those of Barretto (1975) and Austin (1975) will illustrate the point we are trying to stress, i.e., that in most cases only a small percentage of the ^{222}Rn generated in rocks can emanate and be available for detection by alpha counting. Barretto (1975) showed that rocks have a wide range of radon leakage with values ranging from 1–20%; the stronger emanations were found among granites and conglomerates whereas basic and calcareous rocks showed the lowest values. Accessory minerals, even though high in uranium, show low radon emanations (generally less than 2%). Austin (1975) found that the emanation from about 800 samples from 100 mines and drilling areas in the United States averaged about 21% and ranged from 1–91%; the average values of samples from the mining areas he studied ranged from 8–57%. Summarizing Soviet experiences, Perel'man (1977, p. 95) states that the mean emanation factor for acid igneous rocks is close to 10%, but granites in

faulted and fractured zones are characterized by a factor of 25% (up to 32%). He states that sedimentary rocks generally emanate little radon (6%) but under favourable circumstances the factor may rise to 20%. The presence of uranium minerals in either igneous or sedimentary rocks increases the emanation factor drastically and, in some cases, the factor may reach 92%, but averages 20–40%.

The factors controlling the emanation of ^{222}Rn are complex and most are difficult to quantify. However, most workers (e.g., Barretto 1975; Austin 1975) will agree that mineralogy of the ore, particle size of the minerals, porosity and permeability of the ore, uranium distribution in a mineral (accessory) or rock, and the type of rock are all positively related to radon emanation. Other factors, such as ore grade, geologic age of the rock, and moisture content, have been considered in connection with the emanating power in specific instances, but the evidence for their influence is inconclusive.

From the above excerpts from the literature, as well as from the E values in Tables 1 and 2, it is clear that the use of radon for exploration purposes will be limited, in the first instance, by the amount of ^{222}Rn which can emanate from a sample. Other factors, such as the distance ^{222}Rn can migrate before it decays (half-life 3.8 days), diurnal variations, etc., must also be considered when using this element for exploration purposes.

Acknowledgments

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