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Radon emanation coefficient study of a geological sample (*)

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Summary. — The radon atom can escape from the material it was formed in by direct recoil or by diffusion. It then enters either an inter or intra-granular space. Next, the radon atom can migrate by diffusion or convection in order to reach the atmosphere. The emanation coefficient is defined as the ratio between the number of radon atoms that escape from the matrix and the total number produced in the entire material. We propose to define a protocol in order to measure this emanation coefficient by a differential gammametric method. This method consists in determining the concentration of the short, half-life progenies of radon (essentially lead-214 and bismuth-214) through measuring their gamma-ray intensities in a hermetic cell before and after radioactive equilibrium. The first gamma measurement results give us the quantity of radon trapped in the solid matrix. A second analysis, after 13 days, gives the total production of the progenies, and thus the total radon in the sample. The measurements of a sample that is both dried and saturated are necessary to estimate the radon emanation potential. The influence of the fluid in the porous space is discussed in a theoretical way. This approach is applied to a geological sample and compared with the experimental results.

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1. – Introduction

In the models proposed in the literature (Simopoulos *et al.*, 1986; Semkov, 1990; Morawska *et al.*, 1992) the direct recoil is the most important mechanism in radon emanation for the mineral phases. Therefore, the alpha disintegration of radium charges the atom with a kinetic energy of 86 keV allowing it to escape from the crystalline structure in which it was formed and to finish its run in the porous space.

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Apart from the determination methods of the emanation coefficient, such as the effluent ones (Nielson *et al.*, 1994; Pellegrini, 1997), another method exists called gamma differential (Nielson *et al.*, 1982). This one is rather simple to use because it only requires two measurements of activity during a relatively short time lapse of 13 days after an equilibrium setting stage. Thus, a large number of samples can be analyzed routinely. However, this method presents some limits that we will develop here.

2. – Gammametric Differential Method

2·1. *Principle.* – The first measurement at time $t_{\mathrm{ini}} = 0$ gives the quantity of radon in the solid mineral matrix. The second one at time $t_{\mathrm{f}} = 13$ days gives the quantity of radon produced in the entire sample. These quantities are determined indirectly by measuring the gamma-ray intensities issued by the short half-life progenies of radon (essentially lead-214 and bismuth-214), which are in radioactive equilibrium with it. We consider that the concentration of radium-226 is constant during the experiments because its period is relatively long (1620 years). Taking into account the period of ^{222}Rn (3.82 days), the equilibrium between radon and radium is reached at 99% only after 21 days. But 90% of this equilibrium is reached after 13 days; we consider this rate to be satisfying in our case. The short half-life progenies, like ^{214}Bi and ^{214}Pb, are in equilibrium with radon after only three hours, because their radioactive periods are 19.7 and 26.8 minutes, respectively.

2·2. *Emanation coefficient expression.* – At time $t_{\mathrm{ini}} = 0$, the initial activities of ^{214}Pb and ^{214}Bi are expressed by A_{ini}. With time, the variation of the Bi or Pb activities is expressed by

$$\begin{cases} A(t) = A^0_{\mathrm{Ra}} \sum\limits_{i=1}^{n} C_i \exp[-\lambda_i t_{\mathrm{f}}] + A_{\mathrm{ini}} & \text{with } j \neq i\,, \\ C_i = \dfrac{\prod\limits_{k=2}^{n} \lambda_k}{\prod\limits_{j=1}^{n} (\lambda_j - \lambda_i)}\,, & \end{cases} \tag{1}$$

A_{ini}: ^{214}Bi or ^{214}Pb activity at time $t_{\mathrm{ini}} = 0$ (Bq),

$A(t)$: ^{214}Bi or ^{214}Pb activity with time (Bq),

A_{Ra}: ^{226}Ra activity (Bq),

n: element n in the decay chain of the radium ($n = 4$ for ^{214}Pb, $n = 5$ for ^{214}Bi),

λ_i: decay constant of the element i (s^{-1}).

Thus, by definition, the expression of the emanation coefficient is: $\eta = \dfrac{A(13d) - A_{\mathrm{ini}}}{A(13d)}$.

2·2. *Measurement protocol.* – The measurement stage requires first the equilibrium setting of radon with radium in the sample. In a dry medium, the sample is degassed under a suction-hood for 13 days, then the sample is immediately placed in a Teflon cell and sealed air-tightly. In a water-saturated medium, the sample is placed in a holder, through which water circulates during 13 days. Next, the water-saturated sample is dried immediately and placed in a Teflon cell and sealed in the same way. Here, we have used a Hyper Pure Germanium semi-conductor, P-type detector with a useful volume of 70 cm^3. The maximum standard deviation for the experimental results is 5.1%.

3. – Application

We have determined the emanation coefficient of a reference sample, UTS4 (Uranium Tailings Sample, "Energy, Mines and Resources Canada"), in both dry and

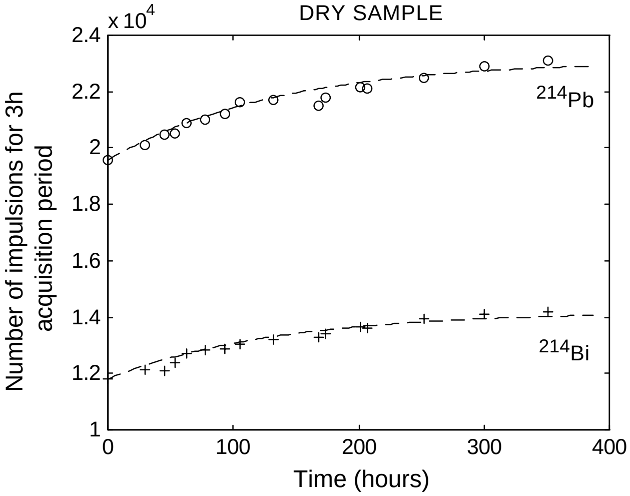

Fig. 1. – Evolution of the average number of calculated (solid line) and experimental counts of ^{214}Pb and ^{214}Bi detected in a dry sample (crosses).

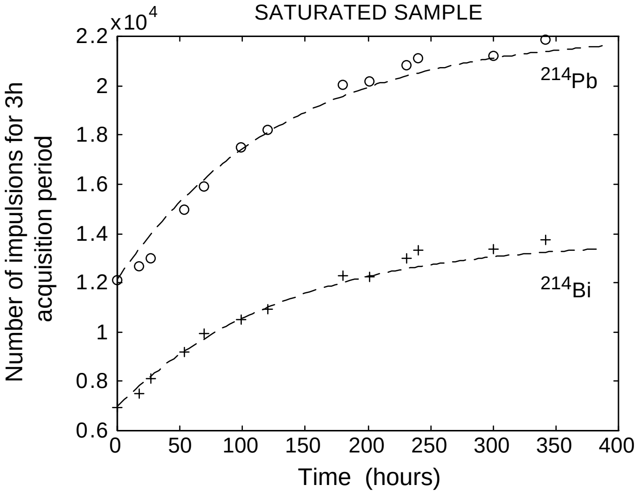

Fig. 2. – Evolution of the average number of calculated (solid line) and experimental counts of ^{214}Pb and ^{214}Bi detected in a water-saturated sample (crosses).

TABLE I. – *Experimental emanation coefficients* (η) *for the dry and saturated* UTS4 *sample.*

	η(%)	
	With ^{214}Bi	With ^{214}Pb
Dry sample	16.8 ± 0.9*	15.4 ± 0.8*
Water-saturated sample	49.5 ± 2.5*	45.4 ± 2.3*

* Standard deviation.

saturated media (table I). Figures 1 and 2 represent the evolution of the number of calculated counts from the integration of eq. (1) (solid line) and the experimental counts (points and crosses) detected for ^{214}Bi and ^{214}Pb over a three-hour acquisition period.

First, these results show that the sample treatment does not modify the measured activity of radium. Therefore, after 13 days, the Bi, Pb and Ra activities are identical in both a dry and a water-saturated sample. These results also show the importance of the fluid contained in the porous space. Effectively, the initial activities of Bi and Pb are distinctly greater in the saturated sample than in the dry one. Furthermore, the experimental points line up with the calculated points from eq. (1), give or take 5.1%.

4. – Discussion on the fluid influence

In order to verify the experimental results, we have developed a simple model concerning the UTS4 sample (fig. 3). The mercury porosity technique determined a porosity rate of 43%, and this allowed us to estimate the pore diameter distribution. The sample has two pore size families. The first family of pores has a diameter between

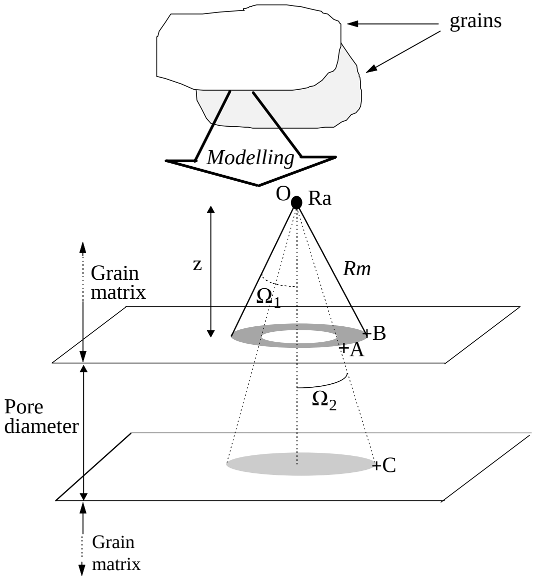

Fig. 3. – Modelling of the porous space.

0.3 and 5 μm, and the other between 5 and 100 μm. The sample contains a very small quantity of pores with a diameter less than 0.3 μm. Consequently, the porosity of the sample is essentially inter-granular. The calculated emanation coefficient will be assigned by the proportion of each pore size determined above.

5. – The model

Here, a simple radon emanation model is presented. It includes only the direct recoil phenomenon, which is the most important one.

The space between the two parallel planes, which are filled with either air or water, represent the pore. Given a radium atom that disintegrates at point O, the radon atom will stay trapped between the two planes if it is emitted in a determined space by two solid angles: Ω_1 and Ω_2. The maximum range of the atom in the matrix is R_m (OB). Ω_1 is defined as the maximum solid angle beyond which the radon atom has no probability of leaving the matrix because it has lost all of its recoil energy. Ω_2 is the minimum solid angle at which the insertion probability of the radon atom in the neighbouring grain is equal to 1. Consequently, P (eq. (2)) represents the probability that one radon atom from the matrix will stay trapped in the porous space. Knowing the lost energy in the matrix (E_m) and the one lost in the pore filled with air or water (E_p), we can obtain these two solid angles for each height z. For each height z, Ω_1 is defined as $E_\mathrm{m} = 86$ keV and Ω_2 is defined as $E_\mathrm{m} + E_\mathrm{p} = 86$ keV. Consequently, the trapping probability (P) in the pore is expressed as

$$P = \frac{1}{4\pi}(\Omega_1 - \Omega_2)\,. \tag{2}$$

This model allowed us to calculate this trapping probability for two cases of the radium distribution in the material: first, homogeneous ($0 < z < R_\mathrm{m}$) and second, on the surface ($z = 0$) of the grain for both a dry (fig. 4) and water-saturated sample (fig. 5).

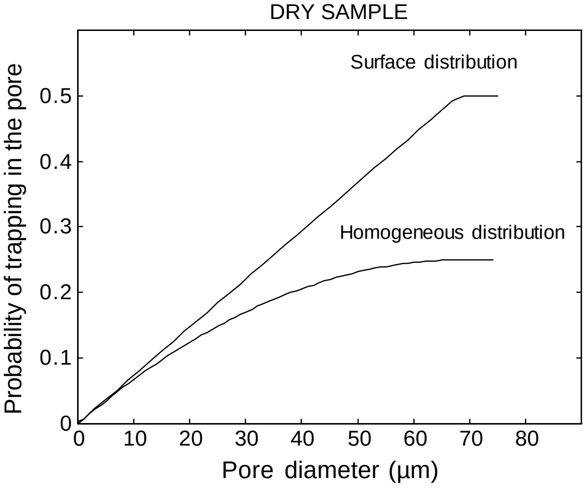

Fig. 4. – Calculated probability of trapping for a dry sample with surface and homogeneous radium distribution.

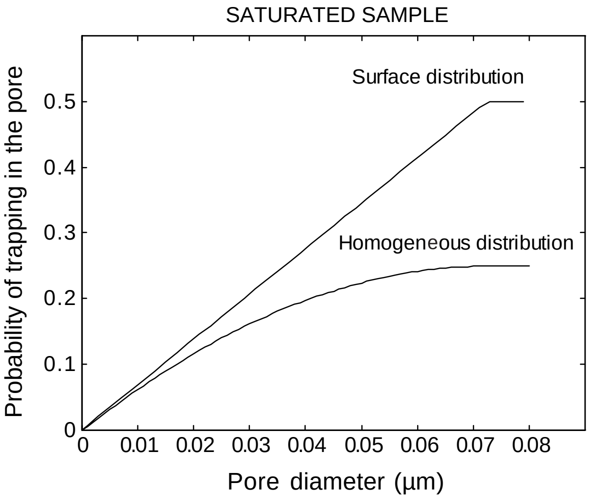

Fig. 5. – Calculated probability of trapping for a water-saturated sample with surface and homogeneous radium distribution.

The calculation for a homogeneous distribution is made for the surface layer with an R_m thickness. The results obtained for each height z are integrated in order to reach a maximum coefficient of 0.25. For a dry sample, the insertion phenomenon in the neighbouring grain is very important for pores with a diameter between 0.3 and 5 μm (low emanation coefficient for the first family of pore sizes). This phenomenon is not negligible for the pore diameters between 5 and 100 μm (high emanation coefficient for the second family of pore sizes). For a water-saturated sample, the emanation coefficient is at a maximum for a pore diameter less than 0.06 μm. Consequently, the emanation is at a maximum for this sample because it only presents a small number of pores with a size less than 0.1 μm. The maximum average ranges of the atom were determined as: 72 nm in water, 35 nm in the solid matrix of the sample and 68 μm in air (SRIM).

The experimental and theoretical results are summarized in the following table II:

TABLE II. – *Calculated and experimental emanation coefficients* (η) *for a distribution of radium on the surface of the grains for the* UTS4 *sample.*

	η(%)	
	Calculated	Experimental
Dry sample	11.6	16.1 ± 0.8*
Water-saturated sample	50	47.5 ± 2.4*

* Standard deviation.

It is difficult to limit the surface layer from which we can determine if the radium distribution is on the surface or not (Morawska *et al.*, 1992). However, the experimental results, when compared with the calculated values, define essentially a surface distribution of the radium in the grain. The theoretical values of 11.6 and 50% are close to the experimental values of 16.1 and 47.5%.

6. – Discussion and conclusion

The differential gammametric method allows for the determination of the emanation coefficient of most geological samples. Indeed, the technique used has high sensitivity and allows for radium activity in the order of $0.1\,\mathrm{Bqg}^{-1}$ to be measured. However, for samples with a low emanation coefficient, high accuracy is needed because the coefficient is determined by taking the difference between two measurements for which the standard deviation is 5.1%. We estimate that this technique does not allow us to determine a coefficient less than 10%. This coefficient is generally at a minimum for a dry sample and at a maximum when the same sample is completely water-saturated. Therefore, the radioactive equilibrium of ^{226}Ra and ^{222}Rn is not set in the same way as long as the fluid in the pore is water or air. For a dry sample, the phenomenon of inserting the atom in the neighbouring grain is very significant. On the contrary, for a water-saturated sample, this insertion phenomenon is more limited. The results obtained show that it is necessary to do a study in both a dry and a completely water-saturated medium to estimate the variation range of the emanation coefficient of a geological sample.

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