Journal of Environmental Radioactivity 180 (2017) 77–81

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: www.elsevier.com/locate/jenvrad

Detailed effects of particle size and surface area on ^{222}Rn emanation of a phosphate rock

Gustavo Haquin[a,b,*], Zohar Yungrais[b], Danielle Ilzycer[b], Hovav Zafrir[c], Noam Weisbrod[a]

[a] Zuckerberg Institute for Water Research, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev (BGU), Sede Boqer, Israel
[b] Radiation Safety Department, Soreq Nuclear Research Center, Yavne, Israel
[c] Geological Survey of Israel, Jerusalem, Israel

ARTICLE INFO

Keywords:
Radon emanation
Recoil
Specific surface area
Radium distribution
Particle size distribution

ABSTRACT

The dependency of radon emanation on soil texture was investigated using the closed chamber method. Ground phosphate rock with a large specific surface area was analyzed, and the presence of inner pores, as well as a high degree of roughness and heterogeneity in the phosphate particles, was found. The average radon emanation of the dry phosphate was 0.145 ± 0.016. The emanation coefficient was highest (0.169 ± 0.019) for the smallest particles (< 25 μm), decreasing to a constant value (0.091 ± 0.014) for the larger particles (> 210 μm). The reduction rate followed an inverse power law. As expected, a linear dependence between the emanation coefficient and the specific surface area was found, being lower than predicted for the large specific surface area. This was most likely due to an increase in the embedding effect of radon atoms in adjacent grains separated by micropores. Results indicate that knowledge of grain radium distribution is crucial to making accurate emanation predictions.

1. Introduction

Radon (^{222}Rn) is a radioactive noble gas produced by the alpha decay of radium (^{226}Ra), a member of the radioactive decay chain of ^{238}U, present in almost every natural material. ^{222}Rn and its progeny in the atmosphere are the most important contributors to the health risks, such as lung cancer, associated with radiation exposure from natural sources (UNSCEAR, 2008). Its widespread occurrence in nature and its unique characteristics, among them its half-life of 3.825 days, makes it particularly suitable for use in tracking time-varying environmental and geophysical phenomena (Etiope and Martinelli, 2002; Barbosa et al., 2015).

Due to the law of conservation of linear momentum, ^{222}Rn atoms have an initial recoil energy of 86 keV that facilitates their release from solid particles into fluid-filled pore space, a process called emanation (Tanner, 1964). Only a fraction of the ^{222}Rn atoms generated in soils—0.024 to 0.40 in soils from Central Europe and Japan, respectively (Sakoda et al., 2010b)—escape the solids grains in which they are generated and further migrate by diffusion and/or advection to the subsurface air or water phases.

Radon emanation consists of two main components: (1) diffusion emanation, i.e., diffusion in grains and diffusion from inner into outer pores; and (2) recoil emanation, i.e., alpha recoil from outer and inner particle surfaces (Sakoda et al., 2011). The diffusion coefficients of ^{222}Rn in solid mineral grains having a specific density of 2700 kg·m^{-3} are extremely small, in the range of 10^{-31} to 10^{-69} m·s^{-1} (Nazaroff, 1992); thus, the main component of ^{222}Rn emanation is alpha recoil (Bossus, 1984).

The birthplace of the ^{222}Rn atom in the solid grain and the recoil direction can determine whether the ^{222}Rn atom escapes to the pore space or stays in the grains. The distance a^{222}Rn atom recoils depends on the specific density and the composition of the grain mineral. For minerals, it is in the range 20–70 nm; for quartz, a common mineral, it is 34 nm (Ziegler et al., 1985; Sakoda et al., 2010a).

^{222}Rn atoms that escape to the pore space would have been created at a distance shorter than the recoil range from the grain surface. Thus, the radium distribution within a grain, particle size and surface area crucially affect the recoil emanation coefficient in minerals. ^{222}Rn emanation from several soils, minerals rocks and other materials was experimentally measured, and its dependence on environmental factors, such as water content and temperature, and on soil characteristics, such as grain size, radium distribution, surface area and recently on fission track density, was investigated (Stranden et al., 1984; Nazaroff, 1992; Garver and Baskaran, 2004; Iskandar et al., 2004; Barillon et al., 2005; Somlai et al., 2008; Sakoda et al., 2011; Girault and Perrier, 2011, 2012; Hassan et al., 2011; Eakin et al., 2016; Krupp et al., 2017).

* Corresponding author. Zuckerberg Institute for Water Research, Jacob Blaustein Institutes for Desert Research, Ben-Gurion University of the Negev (BGU), Sede Boqer, Israel.
E-mail address: gustavo@soreq.gov.il (G. Haquin).

http://dx.doi.org/10.1016/j.jenvrad.2017.10.004
Received 6 February 2017; Received in revised form 25 September 2017

To date, mechanistic models were developed for describing the emanation process and its dependence on the environmental and physical properties of the solids (Bossus, 1984; Semkow, 1990, 1991; Semkow and Parekh, 1990; Morawska and Phillips, 1993; Sasaki et al., 2004a; Barillon et al., 2005; Adler and Perrier, 2009; Sakoda et al., 2010a).

Generally, they could not predict the emanation coefficient because they lacked information about the complex geometry of grains, the pore size distribution, the radium distribution in the solid grains, and the diffusion component of the emanation coefficient (Sakoda et al., 2011). Radium distribution in minerals, either on the surface or uniformly distributed within the grain, is affected by the sample history.

A theoretical analysis of the influence of the mineral inner structure and the type of radium distribution on the emanation coefficient was performed by Morawska and Phillips (1993). The emanation coefficient from a single spherical grain without inner pores was proportional to the surface to volume ratio for a uniform radium distribution and almost constant for a surface radium distribution (Morawska and Phillips, 1993). For spherical particles with an inner network of channels, known as the near-pore distribution model, the emanation for a surface radium distribution was represented by the sum of the probabilities of ^{222}Rn to be emanated from the inner pores and from the spherical outer surface, being the porosity of the mineral an influencing factor on the emanation coefficient for a homogeneous radium distribution (Morawska and Phillips, 1993). Sakoda et al. (2010a) developed a model of ^{222}Rn emanation as a function of grain size based on a uniform radium distribution (to a certain depth) in multiple grains packed in a face-centered cubic structure. The results of this model showed that for dry conditions and at low moisture conditions (< 25%), emanation increased to a constant value with increasing grain size as similarly predicted by other models (Sun and Furbish, 1995; Sasaki et al., 2004b; Barillon et al., 2005; Sakoda et al., 2010b).

The relation between ^{222}Rn emanation and the specific surface area (SSA) as measured by gas adsorption was derived by Semkow (1991) for a uniform radium distribution using a fractal model to describe the roughness of the emanating surface. In this model, the emanating power is related to the recoil range and the fractal dimension of the surface. Bossus (1984) showed a clear relation between emanation power and the SSA in brick and mineral samples. The average probability of a radon atom generated at a distance shorter than the recoil range to emanate is lower than 25% and directly proportional to the surface area. The average pore size, the shape of the surface, and lattice defects may also affect radon emanation power (Bossus, 1984). For low SSA values, a linear dependence of the emanation coefficient was observed for different materials (Bossus, 1984). For higher SSA values, the emanation coefficient tended to a saturation value due to the increase in the surface roughness, leading to an enhancement of the embedding effect (Barillon et al., 2005).

In contrast to the influence of temperature and humidity, the effect of grain size and surface area have not been well understood and experimental results have been inconsistent, although they are two of the most important soil properties (Bossus, 1984; Markkanen and Arvela, 1992; Sakoda et al., 2008). Indeed, while a few experimental and theoretical studies found that ^{222}Rn emanation decreases with decreasing grain size (Barillon et al., 2005; Sakoda et al., 2010a), other studies found the opposite, i.e., that the emanation coefficient increases as the grain size decreases (Markkanen and Arvela, 1992; Morawska and Phillips, 1993; Garver and Baskaran, 2004; Breitner et al., 2010; Krupp et al., 2017).

In this work, we aimed to experimentally investigate the influence of grain characteristics, namely particle size and specific surface area, on ^{222}Rn emanation. We measured particle size distribution (PSD), SSA, ^{226}Ra concentration and ^{222}Rn emanation from samples of dry ground phosphate rock. We evaluated the major contributors to radon release in an attempt to derive, from experimental results, the influence of grain structure, specifically surface roughness and inner pores, and radium distribution on radon emanation.

2. Materials and methods

2.1. Sample characteristics

The material used in this research was ground phosphate rock originating from an open pit ore in the Negev Desert, Israel. The porosity of the sample was determined by direct methods measuring gravimetrically the bulk and grain volumes. The ground mineral was oven dried at 105 °C for 24 h to a constant weight and then weighed; next, the grain volume was determined by the mass displacement method using tap water at 20 °C. The phosphate powder was sieved into ten size fractions by mesh 70 to 550 corresponding to particles larger than 210 μm to smaller than 25 μm. Each size fraction was split into three samples of at least 50 g each for SSA, ^{226}Ra and ^{222}Rn analyses.

2.1.1. Particle size distribution and specific surface area

The PSD of the ground mineral was determined by laser diffraction, as the optical data was transformed into PSD using either the Mie theory or the Fraunhofer theory depending on the particle size (ISO 13320, 2009). The measurements were performed in the Soil and Sedimentology Laboratory at the Geological Survey of Israel by the wet dispersion method using a Mastersizer 2000 (Malvern Instruments Ltd., UK) instrument. The instrument reports results as the volume-equivalent sphere diameter, which is the diameter of a sphere having the same volume as the measured particle.

SSA was determined following the Brunauer, Emmett and Teller (BET) theory by which the powder SSA is determined by the physical adsorption of a gas on the solid surface and by calculating the amount of gas adsorbed as a monolayer on the surface. The BET equation relates the equilibrium pressure (P) and saturation pressure (P_0) of adsorbates at the temperature of adsorption, the quantity of adsorbed gas (W) and the quantity of monolayer adsorbed gas (W_m). The BET equation range of applicability is always limited to a part of the nitrogen isotherm, usually below a relative pressure of $P/P_0 \sim 0.3$ (Sing, 2001). Samples were vacuum dried at 100 °C prior to being exposed to nitrogen at 77.35 K to ensure monolayer absorption. Once at equilibrium, the sample was heated; as temperature increased, nitrogen molecules were released from the pores and the pressure rose. Multipoint BET curves related the measured changes in the monolayer adsorbed nitrogen weight (W_m) to the relative pressure (P/P_0) as temperature rises. C, the BET constant, is derived from the slope $s = \frac{C-1}{W_m C}$ and the intercept $i = \frac{1}{W_m C}$ of the linear regression of multipoint BET curve, and used to calculate the sample SSA. The measurements were performed in the Physical Chemistry Laboratory at IMI TAMI Ltd. using a Nova 3000 analyzer (Quantachrome, USA).

2.2. Radium activity concentration

The ^{226}Ra activity concentration was measured by high resolution gamma spectrometry in which the radioactive elements were identified and quantified by their full energy photon peaks (Gilmore, 2008). Samples were dried overnight at 105 °C, homogenized and closed in standard plastic containers of ~40 ml volume, sealed with a silicon resin and left for three weeks before measurement to achieve a secular equilibrium of ^{226}Ra and its progeny. The sealing efficiency of the container was previously determined by measuring the leaked ^{222}Rn from a standard sample containing high ^{226}Ra activity, resulting in a negligible leak. The low yield 186 keV gamma peak of ^{226}Ra and the high yield gamma rays (352, 609, 1120 and 1764 keV) of ^{222}Rn progenies were used for identification and quantification. The ^{226}Ra activity concentration C_{Ra} was calculated by averaging the activity concentrations calculated using the above gamma peaks by the expression (Gilmore, 2008):