

Possible role of radon in prebiotic chemistry and in early evolution of Life on Earth

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Abstract. Radon in the environment of early Earth was present in sites, determined by location of deposits of uranium, in very different geological formations. According to the decay of uranium-238, the total production of radon at the beginnings was twice as high as now and was continuously diminishing to the present levels. This nuclide could not play as big a role as do radioactive elements connected with the presence of high concentration of ^{235}U , which was high enough in some places to give rise to formation of natural nuclear fission reactors (e.g. Oklo phenomenon in Africa). The main role of ionizing radiation in prebiotic chemistry and biological evolution was played by low LET (linear energy transfer) radiations, as deep penetrating sources of external energy. High LET radiations are of low penetration and could act only superficially. Radon is an exception, due to its easy transfer in the air. Therefore, it could play a role already in the cases of these early organisms which exhibited the gaseous exchange of chemical compounds with the surrounding atmosphere. The action was destructive, but, on the other hand, was also mutagenic. Nevertheless, the general quantitative effect of radon on the global scale could not be larger than of other radioactive nuclides. Presented considerations are part of the chapter by the present author on the role of nuclear and radiation chemistry in astrobiology, in the monograph published by American Scientific Publishers [1].

Key words: great oxidation event • ionizing radiation • prebiotic chemistry • radon • thoron • uranium

Introduction

Radon-222 in the environment of early Earth was always present in and quite far from sites determined by location of deposits of uranium, in very different geological formations. Geological segregation of rocks and minerals has changed primary concentrations also of uranium deposits and consequently diversified distribution of sites of emission of radon. Calculation of total amount of a particular radionuclide at a chosen point on the axis of time is easy, but the estimation of possible concentrations and yields of radon billions years ago is difficult. Specificity of radon in comparison to other radionuclides consists in its gaseous state at ambient temperatures and possibility to travel far from the place of origin. It decays, therefore, in random, accidental places with emission of alpha particles of 5.49 MeV energy and also of gamma radiation of 0.510 MeV energy of quanta, of different importance for radiation chemistry and radiobiology in comparison to high LET alpha radiation. Ionizing radiation consisting of alphas of such energy results in high LET deposition of energy in the condensed matter, i.e. it means high congestion of chemical spurs at a short distance from decaying atoms of radon. From the chemical point of view, it means overlapping of the majority of ionization spurs what results in a continuity of ionization column. The yield of free radicals is low in comparison to low LET radiations like high energy gammas. The presence and effects of free radicals is

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Received: 1 July 2009
Accepted: 30 December 2009

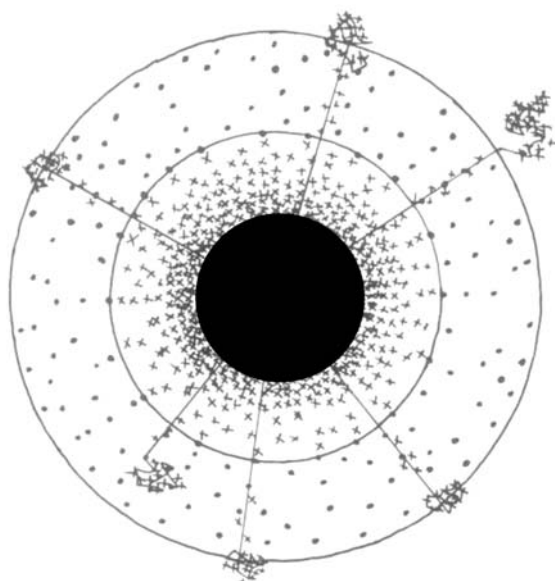


Fig. 1. Cross-section of the alpha particle track in the matter indicating the overlap (black circle) of several hundred thousands of single ionization spurs, characteristic of high LET radiations. Only a small fraction of secondary electrons escapes from the main track.

noticed only around the main column of ionized matter, allowing easy imaging of the spur by etching the appropriate polymer having decaying radon atom on its surface. Figure 1 shows cross-section of the alpha track, single ionizations overlapping into multi-ionizations. Whereas the yield of free radicals in the case of low LET radiation is ca. 80%, the yield of products from multi-ionization spurs is only 20%. Yields in the case of high LET radiations, like from radon are reversed – products of multi-ionization spurs are reaching 95% of total deposited energy. Columns of multi-ionization spurs are visualized in a popular dosimetric technique consisting in formation of zones in the surface of polycarbonate material, chemically changed in the region of ionizations and easily etched by alkaline solution afterwards.

Consideration of the role of radon in chemistry at early Earth and later in biology, is limited to radon-222, daughter of radium-226, because it has sufficiently long life time (3.28 d) to escape far from uranium location. The gaseous radioactive element penetrates any matter, is adsorbed in it and starts radiation chemistry and radiobiological phenomena if the object is alive, by high energy alpha particles. There are two similar radioactive emanations, one starting from thorium-232, i.e. radon-220 of short half-life, only 51.5 s, another, starting from uranium-235, i.e. radon-219 of half-lifetime even shorter, of 3.92 s. Both isotopes are living short and decay fully, practically in the region of the starting ore, contributing only to autoradiolysis of the system. Short-lived isotopes of radon are of low interest to our problems.

Estimations of activity of ionizing radiation on Early Earth

All approaches to the chemistry on early Earth have speculative character and are at different levels of probability

from being next to impossible to rather certain, at least basically. Radiation chemistry initiated by radionuclides belongs to the last mentioned category. However, estimation of the role of the radiation chemistry basing on ionizing radiation coming from outer space is even more difficult to analyse, both qualitatively and quantitatively for different periods of the history of Earth. That source of ionizing radiation does not belong to the present paper in spite of the fact, that during some periods of history of Earth it could have played a more pronounced role than radiation from local radionuclides. Back-extrapolation of amount of radionuclides which are still present is simple and is summarized, except for radon in a monograph [1]. There is an uncertainty as concerns short-living isotopes of lifetimes not enabling to survive till present, and these isotopes which were formed in incidents of formation of natural nuclear reactors.

The quantitative back extrapolation, of the presence of radioactive elements is important for the concentration of ^{235}U . The known half-life time of that isotope yields high values for its concentrations on the time scale of last 4.5 billion of years of Earth. Figure 2 shows the participation of uranium-235 in total uranium in the function of time, plotted back from time = 4.5 billions years before present till time = 0, i.e. now. Even later after the beginnings, the concentration was high enough in some places to give rise to formation of natural nuclear fission reactors, e.g. Oklo phenomenon in Africa, detected accidentally on the occasion of exploitation of the uranium ore, which has shown reduced concentration of uranium-235 in comparison to the present average of 0.7%. Residues at this place indicate the incident to happen ca. 1.8 billions years ago, and was of one million of years duration. Earlier, the enrichment, as we would called it in the present way, was much higher, i.e. 22%, therefore the process of self-supporting fission of chain mechanism would have been even more probable. At that time the “enrichment” in U-235 was on the level next to have an explosive character. There are no proofs for that, e.g. a crater which could have been attributed to nuclear explosion and not to meteoritic or volcanic origin. Why the nuclear reactor was not formed earlier, at more convenient high concentration of ^{235}U ? If the

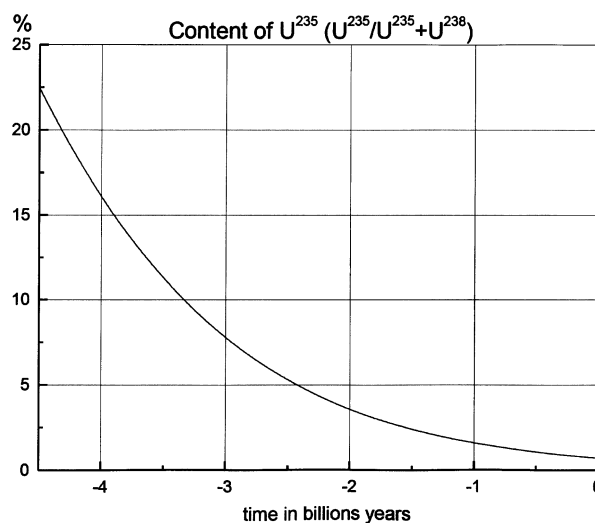


Fig. 2. Calculated content of uranium-235 in total uranium, down to the 4.5 billions years before present.

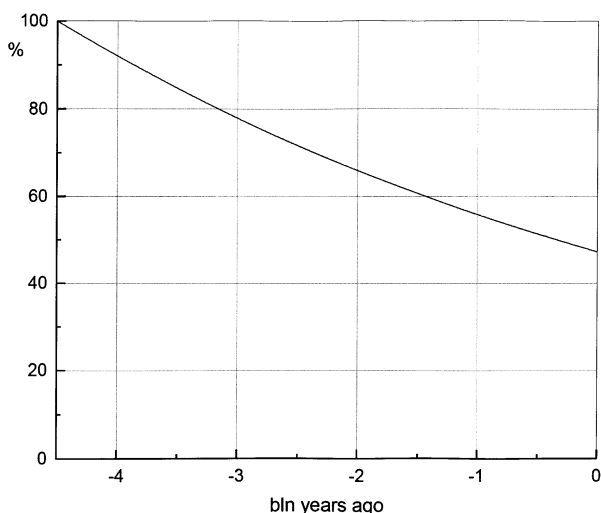


Fig. 3. Calculated decay of uranium-238, starting 4.5 billions years ago, taken as 100 but it is certain that it was high and was continuously diminishing to the present levels.

timing of Oklo-reactor is not accidental, the period of formation coincides with the Great Oxidation Event which could have been helpful in chemical oxidation of uranium making chemical concentration of uranium compounds in certain places easier.

Figure 3 shows the decay of uranium-238, much slower than ^{235}U . Therefore, the production of radon-222 did not change as dramatically during the history of planet Earth as the presence of uranium-235.

Chemical and radiobiological effects of radon at the prebiotic stage and during early evolution of Life

Estimations of the scale of radon presence in early Earth and during evolution of Life are more difficult to make. One can assume only that the production of radon was larger than now, and effects more dramatic and unexpected like today, because of appearance of radon sometimes very far from the place of origin, due to easy diffusion. Chemical, and later biological effects of radon, have to be discussed according to location. Easy penetration of radon even from deep underground deposits into the atmospheres was causing ionization of components of ancient mixture of mainly reductive properties, causing chemical reactions between them in the direction similar to reactions occurring in the primitive atmosphere during electric discharges. It is a generally accepted reaction of formation of aminoacids, so called Millers soup. Ionization of the atmosphere could trigger electric discharges, therefore locating the prebiotic products in the region of uranium deposits. Internal alpha-irradiation of dioxygen containing air, of similar to present day composition, yields completely different products with dominating ozone and nitrogen oxides. In that case exact measurements are also not known, but certainly results must be quantitatively different to results of irradiations by low LET radiations.

As concerns chemical reactions triggered by radon in aqueous reservoirs: Uranium deposits can occur at the bottom of seas or lakes and radon dissolved in water (solubility $230 \text{ cm}^3/\text{l}$ at 20°C) can travel not only by diffusion but by more rapid convection, to places of preferred

adsorption, resulting in emission of alpha particles in any material. The decay of radon taking place in solution during the transfer is accompanied by high LET radiolysis of water, i.e. production of molecular hydrogen and hydrogen peroxide. H_2 is of low reactivity, but H_2O_2 is reacting with high rate constant with reducing species, among them with products of electric discharge reactions in the atmosphere above water. Formation of reactive, highly oxidating reagent – hydrogen peroxide in otherwise oxygen free aqueous solution could start unexpected reactions. Iron was for the first ca. 2 billion years exclusively on the second oxidation level, reacting with the rate constant of $60 \text{ l/mol}\cdot\text{s}$ with H_2O_2 and producing in the result even more reactive OH radical and iron (III) ions. This reaction is known as Fenton reaction now. The presence of primitive organic compounds in the zone of radon presence could start centers of new chemistry, even chain reactions. These oxygenation reactions were unique in the pre-oxygen periods of prebiotic chemistry and in periods of anaerobic life. The advent of presence of oxygen in oceans and in the atmosphere (Great Oxidation Event) diminished the importance of hydrogen peroxide formed from water by alpha-radiolysis.

Contribution of radon to chemical reactions in the gas phase has to be divided into the preoxygen-in-air period and the oxygen containing air of more or less 20% O_2 after the Great Oxidation Event, 2.4 billions years ago. In the primary, dioxygen free world, the high LET radiation emitted by decaying radon could produce molecular products resulting from highly congested multi-ionization spurs characteristic of high LET. The exact composition of the pre-dioxygen world atmosphere is not known; components assumed by most of authors are nitrogen, carbon dioxide, water vapor, hydrogen, ammonia, sulfur dioxide, perhaps other compounds in minor concentrations. Products can be similar to these obtained in electric discharge experiments, and also there is no possibility to obtain homochiral compounds. Quantitative determination of radiation yields of products has not been done yet, as far as it is known. The experiment on chemistry of early Earth atmosphere containing radon would be difficult and expensive.

Chemistry induced by radons-alphas, deposited in solid organic matter

The main role of ionizing radiation in prebiotic chemistry and biological evolution was played by low LET radiations, as deep penetrating sources of external energy. High LET radiations are of low penetration and could act only superficially. Radon is an exception, due to its easy transfer in the air. It can initiate radiation induced reactions in solid, micro- and macroporous media. It can penetrate deep into solid aqueous media like non-living clathrates and living matter consisting in 90+ % of water. Therefore, it could play a role already in cases of these early organisms which exhibited the gaseous exchange of chemical compounds with the surrounding atmosphere or solution. The action of radon radiation was destructive, but on the other hand was also mutagenic, contributing to evolution, by the radiation damage of information carrying elements of cells.

Primary ionizations due to the absorption alpha particles are independent of the chemical composition of surroundings of the site of ionization. However, chemical reactions, secondary after the first single- and multi-ionizations depend strongly on the composition of the medium, especially on oxygen content. Therefore, these reactions are dramatically different whether they happen before or after the Great Oxidation Event. Small changes of oxygen concentrations and content after the event are not important. Before the Event, products of radiolysis were meeting mostly reducing or rather neutral reactive redox species. After the Event, already at low, far from final content of dioxygen in water and air, products of radiolysis, especially the dry and hydrated electron were reacting with high rate constant, especially in the case of hydrated electron, with dioxygen, forming reactive ion-radicals, mainly O_2^- .

Was radon involved in the Great Oxidation Event? High LET radiation emitted by radon as alpha particles of 5 MeV energy are producing especially high, in comparison to low LET radiation, local concentration of hydrogen peroxide in aqueous systems. As the penetration of radon is high in any system, one can assume, that it could also reach the anaerobic bacteria living close to the surface, creating oxidative conditions, mutating organisms which produced species in which oxygen was playing the main role. Important was the initiation only. New species formed, gaining the field did not need radon any more.

Presented considerations are a continuation of the chapter by the present author on the role of nuclear and radiation chemistry in astrobiology, in a monograph, by American Scientific Publishers [1].

Conclusions

Radon-222 was present always in the history of Earth, at two times higher amount of production at the beginnings, according to the amount of uranium-238. Production of thoron and radons-219 and -220 was much

higher, but the shorter half-lifetime did not allow for efficient action outside the site of origin. The availability of radon-222 in the milieu is determined by the chemistry of uranium ore and its location in the crust. These conditions were changing during the geological ages, especially with the advent of Great Oxidation Event. Emission of radon caused radiation induced chemical changes in the atmosphere, in aqueous systems and solids. In spite of short range of alpha particles, common for high LET radiations, radon was influencing these living organisms which had the exchange of air. The general quantitative effect of radon on the global scale cannot be large, but specific places of high concentration could have been significant. For instance, formation of highly reactive hydrogen peroxide in aqueous systems created locally significant amounts of free oxidative OH radicals, via the reaction with iron II, present before the Great Oxidation Event. Radiation effects induced by decay of radon were less important in Earth dominated later by dioxygen, except of radiobiological effects.

Acknowledgment. International collaboration is acknowledged. The author was Member of Management Committee in COST Action D-27 Prebiotic Chemistry and Early Evolution (2004–2008) and is presently Member of MC in the continuation of European COST Action, this time named Systems Chemistry CM0703 (2009–2012). The research was supported by the Polish Ministry of Science under the 619/E-76/SPB/COST/T-09/DWM/64/2003-2006 grant. The support is continued under the grant no. 365/N-COST-2008-2012.

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