Alfa-radiolysis of methane with radon-222 and radon-220 (thoron)

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ABSTRACT

Atmospheric methane is rapidly lost when it enters humid subterranean critical and vadose zones (e.g., air in soils and caves). Because methane is a source of carbon and energy, it can be consumed by methanotrophic methane-oxidizing bacteria. As an additional subterranean sink, it has been hypothesized that methane is oxidized by natural radioactivity-induced radiolysis that produces energetic ions and radicals, which then trigger abiotic oxidation and consumption of methane within a few hours. Using controlled laboratory experiments, we tested whether radiolysis could rapidly oxidize methane in sealed air with different relative humidities while being exposed to elevated levels of radiation (more than 535 kBq m^{-3}) from radon isotopes ^{222}Rn and ^{220}Rn (i.e., thoron). We found no evidence that radiolysis contributed to methane oxidation. In contrast, experiments with moist soils in the same apparatus without added radon isotopes confirmed biodegradation of methane by methane-oxidizing bacteria.

EXTERNAL LINK

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Fig 1.pdf Fig 2.pdf

PROTOCOL STATUS

Working

SAFETY WARNINGS

Be aware of radiation health hazards when working with radon, uranium ore, and thorium compounds.

Overview of experimental approaches

1 The authors of this study belong to two teams that had no knowledge of each others' experiments at Indiana University (IU) and Royal Holloway University of London (RHUL). After completion of all experiments, the two groups decided to jointly report their complementary results. Work at IU afforded superior analytical control on radon isotopes and could accurately measure higher dose rates, whereas the more gas-tight experimental setup at RHUL provided more straightforward evidence for the inability of natural radiation levels to rapidly oxidize atmospheric methane (CH_4) at its natural atmospheric abundance. The following steps refer to experimental details at IU and RHUL. Figures 1 and 2 (attached) describe the two setups:

Figure 1: Experimental re-circulatory setup for separate testing of ^{222}Rn and ^{220}Rn at various conditions (Indiana University). Approximately 6 L of air was re-circulated in a sealed apparatus to assess the loss of CH_4 with or without added radiation from radon isotopes and their radioactive progeny. At the beginning of each experiment, the trapped air was slightly enriched in CH_4 (and CO_2, except for experiments with soils), followed by hourly measurements of gas concentrations over a few days to weeks. Radon ^{222}Rn was generated by uranium ore while charcoal retained ^{220}Rn (**a**). The air intake of the 3-neck 5-L glass flask was directed to the bottom of the flask with a plastic insert to facilitate the mixing of air (**b**); thorium carbonate is not shown. Depicted components of the apparatus (**c**) are not drawn to scale.

Figure 2: Gas-tight terrarium experiments at natural atmospheric abundance of methane (Royal Holloway University of London). (**a**) A hermetically sealed glass terrarium (without plants or animals) was filled with laboratory air containing CH_4 at natural atmospheric abundance. A radon monitor provided data on ^{222}Rn abundance, while an AlphaLab Air Ion Counter measured the concentration of negative ions. After ~6 hours into the RHUL experiment #1, the placement of a beaker filled with deionized, warm water elevated the relative humidity to > 85 %. At the same time, two fragments of pitchblende (containing uraninite as a radiation source) were placed into the terrarium to generate ^{222}Rn. Tedlar® bags in the terrarium are not shown in the photograph. (**b**) Diagram of the sampling procedure to collect < 1-L aliquots of air from the terrarium in RHUL experiment #2. This experiment lasted for 76 h and 50 min and reached a ^{222}Rn-based radiation level in excess of 50 kBq m^{-3} after 5 h.

Apparatus at Indiana University for active, time-resolved measurements of gas concentrations with circular flow

2 We constructed an experimental apparatus to assess the loss of CH_4 in an active (i.e., with pumping of air) and time-resolved manner with or without added radiation from radon isotopes and their progeny (see attached Figure 1). A 5-L round-bottom borosilicate glass flask with three standard tapered 24/40 ground glass ports (one closed with a glass stopper) was connected with 9 mm o.d. Pyrex® glass tubes and short segments of Tygon® tubing to a SARAD® RTM 2200 gas-analytical instrument with internal pumps (SARAD®, Dresden, Germany, with an Axetris® laser OEM Module LGC F200 methane detector, Axetris® AG, Switzerland). The use of pumping qualifies this method as active and time-resolved in contrast to passive measurements of radon that integrate over time [*Meisenberg et al.*, 2017]. Approximately 6 L of air was re-circulated in the sealed apparatus that included (i) a glass tube with thorium carbonate to generate ^{220}Rn (also called thoron), and (ii) a glass tube containing uranium ore to generate ^{222}Rn, with an overlying layer of coconut charcoal to limit the escape of co-produced, short-lived ^{220}Rn. The uranium ore derived from an undisclosed New Mexico mine and is part of the mineral collection at the Department of Earth and Atmospheric Sciences at Indiana University. The use of gas-permeable plastic tubing and conduits was minimized. Optional pinch clamps directed flow and could isolate the uranium ore.

We conducted a number of experiments to assess the importance of α-radiation intensity, relative humidity, and the presence or absence of soil on CH_4 dynamics (see steps below for further details). Moisture is critical for the emanation efficiency of radon isotopes from solid sources (i.e., the escape of noble gas radon atoms from the interior of minerals into H_2O-containing pore space *via* recoil subsequent to radioactive decay of parental nuclides; e.g., *Markkanen and Arvela* [1992]; *Morawska and Phillips* [1993]) and for stabilizing ions and radicals in air. Individual experiments differed in terms of their optional use of moist soil (freshly collected from a lawn on the north side behind the Department of Earth and Atmospheric Sciences at Indiana University), a suspended wet tissue, thorium carbonate, and gas flowing through the tube containing uranium ore. The trapped ~6-L volume of air was initially spiked with CH_4 from natural gas to ~70 ppmv and with CO_2 to ~5,000 ppmv (except for experiments with soil) to distinguish it from room air and to increase the analytical precision during the time-series of measurements that lasted over a few days to weeks. Elevated CO_2 concentrations are typical for many cave environments [*Fernandez-Cortes et al.*, 2015].

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Discriminating between α-radiation from radon Rn-222 versus thoron Rn-220 and their progeny at Indiana University

3 Whereas radon ^{222}Rn with a half-life of 3.83 days is relatively homogeneously distributed in cave air, the much shorter lived thoron ^{220}Rn with a half-life of only 55.6 s cannot travel far from its parent nuclei residing in minerals [*Meisenberg et al.*, 2017], thus thoron's highest concentrations in cave air are near cave walls and the floor. The higher α-decay energy of ^{220}Rn (6.3 MeV) relative to ^{222}Rn (5.49 MeV) prompted us to design experiments for separate examinations of the ability of both radon isotopes to trigger the oxidation of CH_4. The more energetic α-decay of thoron ^{220}Rn should ionize air more efficiently than ^{222}Rn. A mean thoron ^{220}Rn concentration equivalent up to 208 kBq m^{-3} (n = 18) was produced *in-situ* in the glass apparatus by placing 6.4 g of a dry, porous co-precipitate of thorium carbonate and nickel carbonate (prepared with a weight ratio 100 : 22 according to *Tebboth* [1948]) into the receiving port of the 5-L glass flask (Figure 1). Large signal strengths from ^{220}Rn decay in some experiments precluded quantification of small simultaneous ^{222}Rn decay signals. In other experiments, ^{222}Rn decay measuring up to 327 kBq m^{-3} was produced *in-situ* in the glass apparatus by placing a 9-cm layer of uranium ore chips into a vertically mounted 35-mm i.d. glass tube

that was plumbed into the circuit parallel to a 9-mm o.d. glass tube and could be isolated by two pinch clamps (Figure 1). Another pinch clamp could block the 9-mm bypass and force all flow through the tube with uranium ore. Escape of co-produced thoron from ore was reduced by using a 25-mm layer of coconut charcoal (6-14 mesh, Fisher Scientific) into the upper part of the glass tube as a filter [*Wang et al.*, 2011]. The resulting adsorption of ^{220}Rn on charcoal increased the residence time in the glass tube and let ^{220}Rn decay before it could enter the 5-L glass flask. Depending on the relative humidity of individual experiments and the emanation efficiency of radon isotopes from solid substrates containing parental isotopes, the signal strength of ^{222}Rn decay rose up to 327 kBq m^{-3} (experiment #9) while the ore's ^{220}Rn contribution in the glass flask remained insignificant <10 Bq m^{-3} (experiments #7 and #8). Detailed data are available in the supporting information of our manuscript [*Schimmelmann et al.*, in review].

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Basics of active time-series measurements at Indiana University

4 We quantified the concentrations of ^{222}Rn, ^{220}Rn, CH_4 and CO_2 during experiments at an air flow rate of ~0.2 L min^{-1} once every hour while operating the diffusion pump in the SARAD® RTM 2200. This small flow rate is inadequate for accurate measurements of ^{220}Rn owing to its short half-life of only 55.6 sec [*Hursh*, 1966] and partial decay under conditions of slow flow into the measurement chamber. ^{220}Rn radiation intensity was either measured *via* α-spectroscopy at a faster flow rate of 1 L min^{-1} in 10-min increments ($n \geq 10$) while temporarily operating the more powerful membrane pump, or values from flow rates of ≤ 0.2 L min^{-1} with the diffusion pump were doubled to adjust for fast ^{220}Rn decay (see supporting information of *Schimmelmann et al.* [in review] for detailed control experiments and graphed data). α-Spectroscopic measurements of ^{222}Rn abundance were not affected by flow rate and were based on a 'slow measurement' algorithm that uses ^{218}Po and ^{214}Po daughter decay as proxies for ^{222}Rn [*SARAD® GmbH*, 2017]. Ultrapure nitrogen gas and Scotty gas mixtures (Sigma-Aldrich) were used for calibration of gas concentrations with precisions of ± 1 ppmv for CH_4 and ± 100 ppmv for CO_2 (± 95 % confidence intervals).

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Humidity and temperature effects at Indiana University

5 Elevated relative humidity fosters the stabilization of ions in air *via* attachment to clusters of water molecules and may enhance the ability of ions to trigger oxidative degradation of CH_4 (discussed by *Fernandez-Cortes et al.* [2015]). Therefore, we logged humidity in the apparatus along with temperature, air pressure, flow, and battery voltage on an hourly basis using the SARAD® RTM 2200. The recorded temperature in the SARAD® RTM 2200 was ~10 °C higher than the room temperature, because the internal pump and electronics generated heat. Elevated temperature resulted in artificially low recorded relative humidity. We corrected the recorded temperatures to match room temperatures and to arrive at adjusted relative humidity data. We evaluated the influence of low *versus* high humidity by either using relatively dry lab air with a relative humidity of ~50 to 56 %, or by suspending a wet paper towel into the 5-

L glass flask to raise relative humidity to ~100 %. Alternatively, humidity was elevated in some experiments by adding moist soil and/or deionized water into the bottom of the 5-L glass flask. The emanation of radon isotopes from thorium carbonate and uranium ore was enhanced at higher humidity.

The accuracy of data from the SARAD® RTM 2200 was independently evaluated *via* direct comparison with a newly manufactured and factory-calibrated Thoron Scout instrument (SARAD® GmbH, Dresden, Germany) which recorded temperature, humidity, pressure, and the concentrations of ^{220}Rn and ^{222}Rn in the air of a sealed plastic bag. The air in the bag with a volume of ~5 L received ^{220}Rn and ^{222}Rn from uranium ore and was recirculated at 1 L min^{-1} through the SARAD® RTM 2200 while both instruments were simultaneously recording data in 10-min intervals. The ^{220}Rn and ^{222}Rn data from both instruments proved to be compatible after 2 h of initial warm-up time while a small fan was employed in the plastic bag to keep the air around the Thoron Scout turbulent and homogeneous (see supporting information of *Schimmelmann et al.* [in review]).

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Influence of radiation and Methane-Oxidizing-Bacteria (MOB) on methane loss at Indiana University

6 We conducted a number of experiments to test for the effects of radiation and microbial activity on CH_4 dynamics in our experimental apparatus. Multi-day time-series of data were collected in closed-circuit air reflux mode (i) as duplicated blank experiments without added radon or thoron, (ii) with enhanced ^{220}Rn concentration in dry or moist air, (iii) with enhanced ^{222}Rn concentration in dry or moist air, and (iv) with jointly enhanced ^{220}Rn and ^{222}Rn concentrations in moist air to depict an extreme scenario where cave air had a highly elevated α-radiation level. Furthermore, (v) we tested for CH_4 oxidation after placing moist soil, which we assumed contained methanotrophic bacteria (MOB), into the 5-L glass flask, without elevated radioactivity. Certain impurities in industrially conditioned natural gas may act as MOB inhibitors, for example acetylene and carbon monoxide [*Oremland and Capone*, 1988, p. 335]. As a precaution, the CH_4 spikes in experiments employing soils were derived from gas that was collected from a natural seepage of shale gas in New York State. The flammable shale gas contained CH_4, ethane and propane in volume ratios of 77.8 : 15.3 : 6.9 [*Farhan Ul Haque et al.*, 2018]. Natural shale gas is not known to contain acetylene or carbon monoxide. Soil #1 from the bank of Pipe Creek was collected fresh near a seepage of natural gas in New York State on June 16, 2017 (Erie County, Town of Colden, 42° 41.6 N, 78° 41.2 W), kept cool during transport, and was deployed in the apparatus on June 18, 2017. Soil #2 was collected on July 11, 2017 from a grassy area behind the building of the Department of Earth and Atmospheric Sciences, Indiana University, in Bloomington, Indiana (39° 10.35 N, 86° 31.31 W), kept moist at room temperature, and was deployed in the apparatus on July 12, 2017.

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Gas-tight terrarium experiments at Royal Holloway University of London

7 Experiments at Royal Holloway University of London (RHUL) used a gas-tight glass terrarium (i.e. an aquarium without water; wall thickness 5 mm, width 3.45 cm, length 1.92 cm, height 20.3 cm, volume 13.45 L; Figure 2). The upper rim of the terrarium had been polished flat to provide an airtight seal against the 40.6 x 24.0 cm glass cover that was hermetically fitted with high-vacuum grease. The lid provided three 6-mm o.d. ports for gas connections and communication cables. Ports were sealed airtight with O-rings and vacuum grease. The first gas port connected to an external micro-diaphragm gas pump for extracting 99.9 % pure N_2 from an external 3-L Tedlar® bag at a flow rate of 3.1 L min^{-1}. Tubing guided the N_2 through the first port and a T-connector into two 3-L Tedlar® bags inside the terrarium that inflated and caused equal volume displacement of air from the terrarium through the second port into an empty 1-L Tedlar® bag for repeated gas sampling. Two fragments of uraninite-bearing pitchblende from Cornwall (England) from the RHUL mineral collection with diameters of 5 cm were placed into the terrarium as a source of radioactivity. An AlphaLab Air Ion Counter with an integrated fan was placed in the terrarium to measure the abundance of ions in air in 30-s intervals (range: 0 to $2 \cdot 10^7$ ions m^{-}

^{3}). The α-radiation was quantified on 1-h intervals with a Canary Pro monitor (Airthings, Oslo, Norway) *via* α-spectrometry in a passive diffusion chamber with an uncertainty below 8 % above 350 Bq m^{-3}. Approximate 1-L gas samples from the terrarium were collected in Tedlar® bags and were subsequently analyzed for CH_4 mole fractions in the laboratory of the Greenhouse Gas Research Group at RHUL (https://www.royalholloway.ac.uk/earthsciences/ggrg/home.aspx) with a Picarro G1301 CRDS (Cavity Ring-Down Spectrometer, Picarro Inc., Santa Clara, California, USA), which was periodically calibrated against reference gases from the National Oceanic and Atmospheric Administration (NOAA, U.S. Department of Commerce). Each sample was analyzed for 3 min with an uncertainty of ± 0.5 ppb for CH_4.

The initial RHUL experiment #1 (Figure 2a) assessed the production of negative ions and the abundance of ^{222}Rn over ~6 h (i.e. stage 1) without either pitchblende or a beaker with water in the terrarium that had been flushed initially with laboratory air, and subsequently for ~15 h in the presence of pitchblende and a beaker with 130 mL of 38 °C warm water in the terrarium (stage 2). The subsequent RHUL experiment #2 (Figure 2b) in the same terrarium included monitoring of the CH_4 mole fraction of laboratory air sealed in the terrarium where pitchblende and a beaker with 130 mL of water (initially at 38 ºC) had been placed to provide for elevated radioactivity and relative humidity. Elevated relative humidity was needed to simulate cave conditions. The AlphaLab Air Ion Counter failed to provide useful data due to static interference with Tedlar® bags. The second experiment lasted for 76 h and 50 min and reached a ^{222}Rn-based radiation level in excess of 50 kBq m^{-3} after 5 h. Approximate 1-L aliquots of air sampled from the terrarium were analytically compared with aliquots of exterior laboratory air on four occasions.