SOURCES OF RADON CONTAMINATION IN ^{14}C DATING

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ABSTRACT. We investigated the effect of radon (^{222}Rn) contamination of samples and chemicals used for sample preparation and gas purification on the ^{14}C age of samples. Radon count rate was monitored over several ^{222}Rn half-lives in a proportional counter filled with methane. We analyzed *ca.* 240 samples of fossil and recent wood, charcoal, bone, dissolved inorganic carbon in water, travertine, peat, aquatic plants, organic soil and atmospheric CO_2 for ^{222}Rn contamination. Chemicals used for gas purification (MnO_2, $Mg(ClO_4)_2$), ruthenium-coated pellets used for catalytic reduction of CO_2 to CH_4, and acids used for dissolution of calcareous samples (HCl and H_3PO_4) are also potential sources of Rn. Most geological samples contained a significant amount of Rn, as opposed to samples of wood, charcoal, aquatic plants and atmospheric CO_2. We also studied Rn contamination of water samples during tritium activity measurements in a CH_4-filled gas proportional counter. We found an increased count rate in the ^3H channel, as well as above the 20 keV region in Rn-contaminated groundwater samples.

INTRODUCTION

Radon (^{222}Rn) is produced in the Earth's crust by radioactive decay of ^{226}Ra in the ^{238}U decay series. ^{222}Rn decays by emitting α particles ($T_{½} = 3.823$ days; $E_\alpha = 4.98$ and 5.49 MeV) in secular equilibrium with its parent and short-lived non-gaseous daughters ^{214}Pb and ^{214}Bi. As a heavy noble gas it can diffuse from its point of origin to the surface and remains accumulated close to the ground. It is found more often in samples that are in contact with radioactive material containing uranium or radium. De Vries (1957) first observed the contamination of samples by ^{222}Rn in radiocarbon dating. Signals due to high-energy α particles can be discriminated, however, and it is the β particle spectra of ^{222}Rn daughters ^{214}Pb and ^{214}Bi that overlap the ^{14}C spectrum, thus contributing to the total count rate in the ^{14}C energy window in both proportional and scintillation counters (Nydal 1983; Polach and Kaihola 1988). Samples often contain traces of ^{226}Ra or are contaminated during storage or from chemicals used in preparation of the sample for radiometric counting.

Rn can be allowed to decay below the detection limits by storing the counting gas for a period of several ^{222}Rn half-lives. We also found relatively high Rn concentrations in shells and noted that Nydal (1983) detected Rn in shell samples eight weeks after sample preparation. Other methods apply gas chromatography using activated charcoal (Bruns 1979; Schoch and Münnich 1981) or slow fractional distillation at controlled temperatures (de Vries 1957), during which no isotopic fractionation is observed; these procedures are also efficient for Rn removal from CO_2 gas (Schoch and Münnich 1981). ^{222}Rn is quantitatively avoided during the dynamic vacuum condensation of benzene to be used in liquid scintillation counting (LSC) at −78°C (Hood *et al.* 1989). In accelerator mass spectrometry (AMS), there is no problem of Rn contamination because mass, rather than radioactive decay, is measured.

The routine procedure at the Rudjer Bošković Institute Radiocarbon Laboratory involves radiometric counting of the sample in the form of methane, 15 days after its preparation, repeating the measurement after a subsequent 10- to 15-day interval. We noticed a significant decrease in count rate, particularly for geological samples, even a month after methane synthesis.

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We also noticed an increase in background count rates immediately after replacing chemicals used in the preparation and purification of CO_2 and CH_4. We were prompted by these observations to make a systematic investigation of Rn effects. The aim of this study was to determine Rn concentration in various samples and in chemicals used in sample preparation. We also studied Rn contamination in water samples prepared for ^3H activity measurement.

METHODS

Radiocarbon Dating

We measure the ^{14}C ages of samples using a gas-proportional counter filled with methane. Calcareous samples were hydrolyzed in HCl, whereas H_3PO_4 was used to recover CO_2 from carbonates precipitated from water. Organic samples were combusted in a stream of oxygen purified by passage over silica gel, $Mg(ClO_4)_2$, and NaOH on asbestos. We used MnO_2 to purify the CO_2 produced by combustion. CO_2 was then hydrogenated to CH_4 over a ruthenium catalyst (0.5% Ru on Al_2O_3 pellets). The CH_4 was purified in a distillation chain charged with $Mg(ClO_4)_2$, copper turnings heated at 700°C and NaOH absorbed on asbestos. Details of our gas purification, sample preparation and counting procedures are described in Srdoč and Sliepčević (1963) and Srdoč, Breyer and Sliepčević (1971).

We monitored the progressive decrease in count rate recorded by the proportional counter, as a measure of the Rn effect. We attributed the excess count rate to the Rn contamination if 1) the count rate of the sample approached a constant value after 5 to 10 ^{222}Rn half-lives and 2) the excess count rate above the constant value dropped by a factor of 2 every 4 days.

^3H Concentration in Water

^3H activity is measured in an Oeschger-type proportional counter filled with methane, which is produced by reaction of the water sample with Al_4C_3 (Siegenthaler *et al.* 1975; Horvatinčić 1980). The count rate is constantly monitored in two energy channels: 1) 1–10 keV, where the best figure of merit is obtained; and 2) above 20 keV, *i.e.,* above the ^3H energy channel (E_{max}=18 keV). The continuous monitoring of the count rate in a high-energy channel enabled us to 1) monitor the effects of atmospheric pressure (the higher the pressure, the lower the count rate); 2) get an independent indication of gas purity (a lower count rate than standard for contaminated gas) (Krajcar Bronić, Obelić and Srdoč 1986); and 3) detect Rn in the sample. We analyzed the Rn contribution in both energy channels. The initial time t=0 is the sampling date, as opposed to the date of methane preparation in the case of the ^{14}C sample.

RESULTS AND DISCUSSION

^{222}Rn Contamination of Samples

Table 1 shows the samples tested for Rn contamination. Rn is seldom detected in wood and plant samples, and often detected in peat, charcoal and geological samples, such as travertine and groundwater. Figure 1 illustrates the Rn contamination, proportional to the initial Rn count rate, N_0, in various types of samples. Samples of annual terrestrial plants, submerged aquatic plants and tree-ring samples showed no Rn contamination. On the contrary, excavated wood samples were often contaminated by Rn. Several peat, groundwater and hot-spring travertine samples showed the highest Rn count rate, $N_0 > 20\ min^{-1}$, equivalent to ^{14}C activity >100 pMC in our system. Atmospheric CO_2 was collected by absorption in saturated NaOH solution (Obelić *et al.* 1986), and the two samples that showed slight Rn contamination were prepared immediately after collection. Samples stored in the laboratory for several weeks showed no Rn contamination, indicating a low initial ^{222}Rn content and no ^{226}Ra presence. A sample of hot-spring travertine (tufa) (Z-2147, from Varaždinske toplice spa), stored for two years in the laboratory, gave the same ^{222}Rn count rate as the sample processed immediately after collection. Thus, we concluded that the sample contained ^{226}Ra, which constantly produces ^{222}Rn.

TABLE 1. ^{222}Rn Contamination in Various Types of Samples

Sample type	No. of samples tested	No. of samples contaminated by ^{222}Rn	% samples contaminated by ^{222}Rn
Inorganic Samples			
Groundwater	42	21	50
Travertine, tufa	42	25	60
Lake sediments	19	9	47
Atmospheric CO_2	15	2	13
Organic Samples			
Wood, cellulose	60	6	10
Charcoal	13	5	39
Bone collagen	22	3	14
Peat	4	3	75
Terrestrial plants	2	0	0
Submerged aquatic plants	10	0	0
Organic soil	8	3	38
Others	7	0	0

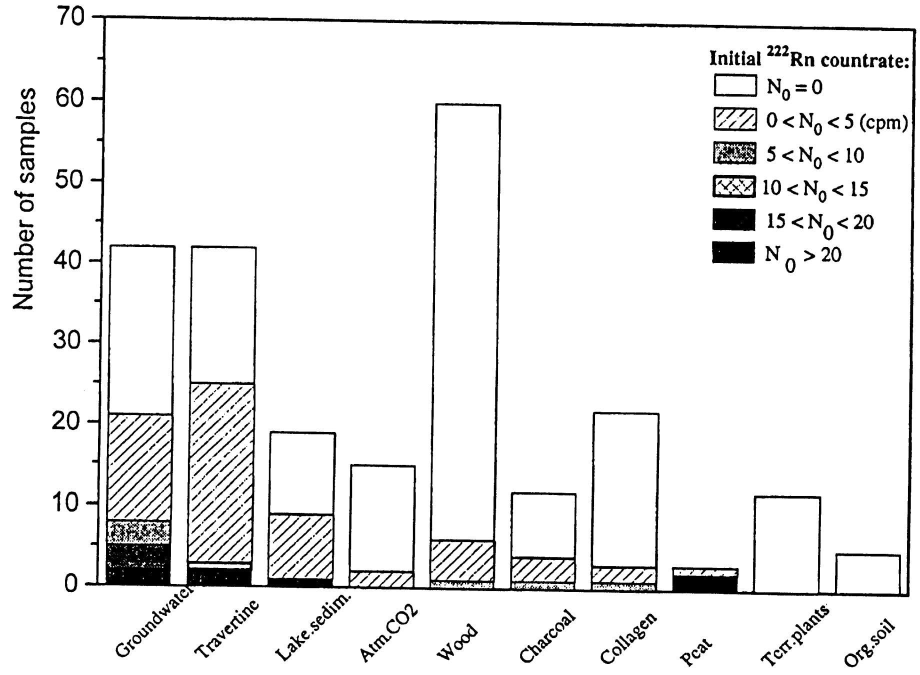

Fig. 1. Bar graph showing the number of samples tested for Rn content with various initial Rn count rates N_0 in radiocarbon samples

Figure 2 shows the logarithm of the normalized net count rate Nt/N_0 attributed to the ^{222}Rn contamination as a function of time elapsed since the methane synthesis. The data points represent the samples prepared for ^{14}C dating regardless of their composition or origin. The best fit to the data points follows the equation

$$\ln\frac{N_t}{N_0} = \ln\frac{n_t - n_\infty}{n_0 - n_\infty} = (-0.19 \pm 0.01)\cdot t + (0.01 \pm 0.01) \qquad n = 98, r^2 = 0.84 \tag{1}$$

where:

$N_t = n_t - n_\infty$	excess count rate due to Rn contamination as a function of time
$N_0 = n_0 - n_\infty$	excess count rate due to Rn contamination immediately after methane preparation (initial Rn count rate)
$n_t = C - B$	net count rate as a function of time t after the CH_4 sample preparation (C=total count rate; B=mean background count rate)
n_∞	net sample count rate after decay of Rn below the detectable limit
n_0	net sample count rate immediately after methane preparation.

The calculated half-life is (3.73 ± 0.17) days, close enough to the ^{222}Rn half-life of 3.82 days to attribute the contamination to Rn. The scattering of the data points, Figure 2, stems from the fact that the fluctuations in the sample ^{14}C count rate obliterate the Rn contamination count rate when low, either initially or after substantial decay.

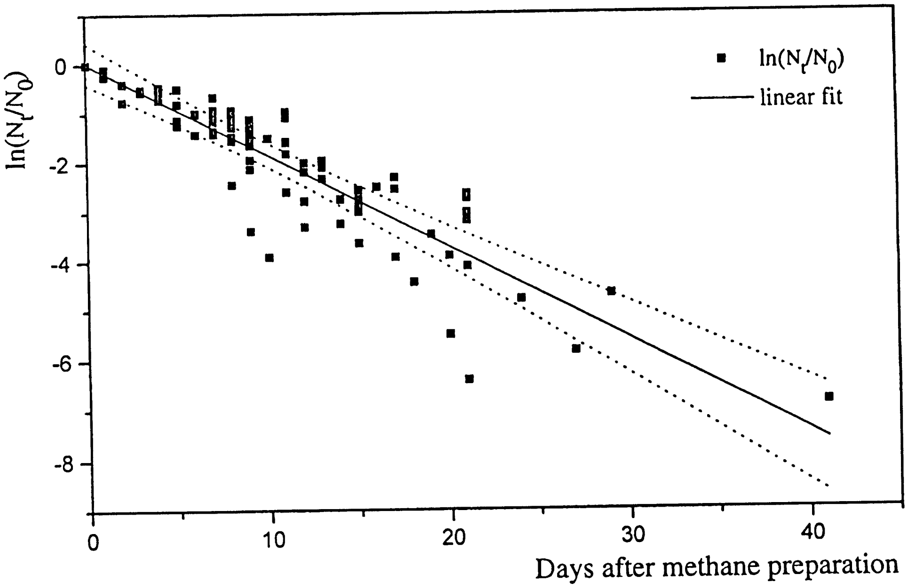

Fig. 2. The normalized net count rate attributed to ^{222}Rn contamination N_t/N_0 in radiocarbon samples as a function of time elapsed since methane preparation. —— = best fit to the data points (Equation 1).

We made detailed case studies of three significantly contaminated samples of travertine, peat and groundwater. A tufa sample from a hot spring at Varaždinske toplice spa (Z-2147) showed the highest Rn contamination. Its ^{14}C activity was 0.5 ± 0.5 pMC after ^{222}Rn decay, even though the apparent ^{14}C activity equal to 31.9 pMC was measured 14 days after the methane preparation. Figure 3 shows the count rates of Z-2147, Z-2471, peat Ellanmore (TIRI) and Z-2511, tap water (Zagreb) as a function of time. A short initial increase of the count rate is attributed to the buildup of ^{222}Rn daughters. The maximum was reached *ca.* 400 min after the counter was filled. Nydal (1983) observed the same effect, which agrees with the secular equilibrium of Rn and its daughters. The maximum count rate is followed by an exponential decrease with *ca.* (4 ± 1) days' half-life.

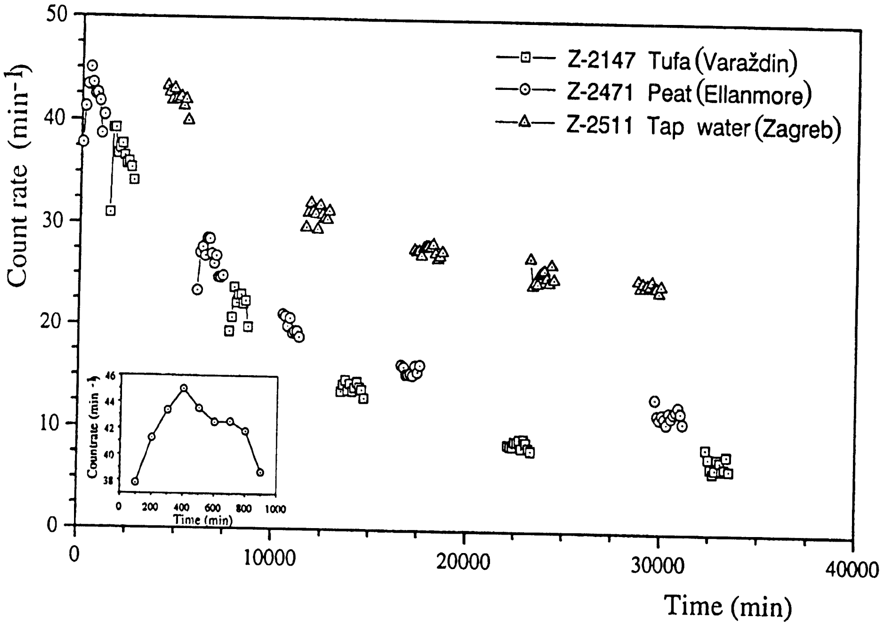

Fig. 3. The mean value of 6 subsequent 20-min counts as a function of time elapsed since methane preparation for three samples containing significant amounts of ^{222}Rn. The inset shows the increase of count rate during the initial 400 min, due to a buildup of ^{222}Rn decay products ^{214}Pb and ^{214}Bi.

When we replaced the sample contaminated with Rn with a background sample, we observed a decrease in count rate during the first few 20-min counting intervals (Fig. 4). The average half-life of the decreased count rate was *ca.* 26 min, indicating the presence of ^{214}Bi and ^{214}Pb.

^{222}Rn Contamination by Chemicals

Chemicals used for CO_2 and CH_4 preparation and purification are potential sources of Rn contamination in methane gas used for proportional counting. We investigated potential sources of Rn contamination in our system: 1) HCl or H_3PO_4 used for dissolution of carbonate samples; 2) H_2 and ruthenium catalyst (0.5% Ru on Al_2O_3 pellets, Industrie Engelhard S.p.A., Italy) used for methane synthesis; and 3) MnO_2, $Mg(ClO_4)_2$ and NaOH on asbestos used for gas purification. We tested individual gas-line fillings by preparing background samples, *i.e.*, samples that do not contain ^{14}C and are routinely used for measuring the background count rate of the ^{14}C system. The background source materials used are borehole CO_2 gas, Carrara marble and anthracite. To identify sources of ^{222}Rn contamination, we prepared background samples immediately after replacing chemicals used for methane preparation or purification. Figure 5 shows the results as a function of time after preparation.

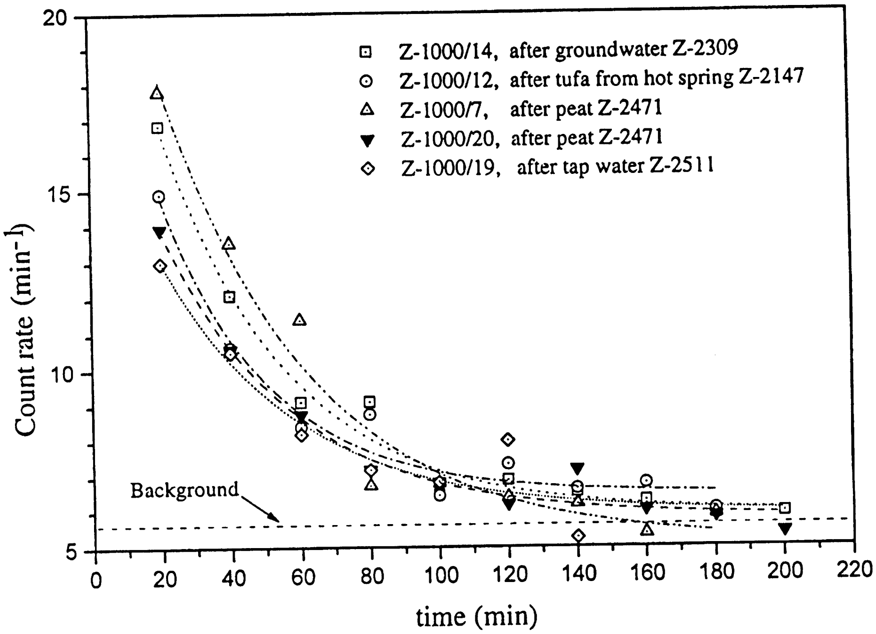

Fig. 4. The decrease of the background count rate after replacing the Rn-contaminated samples with background samples. The exponential functions fitted to the data points correspond to the decay curve of ^{214}Pb with an average half-life of 26 min.

We did not observe Rn contamination in CH_4 obtained routinely in our laboratory by reducing borehole CO_2, thus showing that the H_2, CO_2 and Ru-catalyst were not permanent sources of ^{222}Rn contamination. However, each replacement of the Ru catalyst introduced significant ^{222}Rn contamination, which required prolonged pumping and baking of the catalyst, and several hydrogenations of "dead" borehole CO_2 before it could be used for routine sample preparation (Fig. 5). We also noticed a significant increase of background count rate after MnO_2 was replaced. Carrara marble and anthracite samples prepared for routine background testing showed slight ^{222}Rn contamination, attesting to traces of ^{226}Ra in these materials. The initial ^{222}Rn count rate of these samples was equivalent to a ^{14}C activity of *ca.* 4 pMC.

It is difficult to assess the ^{222}Rn contamination of gases from commercial acids used for dissolving of calcareous samples because both acid and background sample (Carrara marble) can contain traces of ^{226}Ra and thus ^{222}Rn. Figure 5 shows the result of testing the analytical grade HCl manufactured by Merck, Germany, and Kemika, Croatia, as well as H_3PO_4 manufactured by Merck and used for dissolving Carrara marble. We observed similar degrees of Rn contamination in methane prepared from Carrara marble irrespective of the acid used for the dissolution, pointing to Carrara marble as the source of ^{222}Rn rather than the acids.

^{3}H Samples

We observed an excess count rate in the ^{3}H energy window and above 20 keV in several groundwater samples prepared shortly after sampling. The excess count rates in both windows decreased by a factor of 2 after 4 days, again identifying ^{222}Rn as the source of contamination. Figure 6 illustrates an example of ^{222}Rn contamination of a groundwater sample, and shows the excess count rate in both energy windows decreased exponentially. The contaminated groundwater sample was shelved

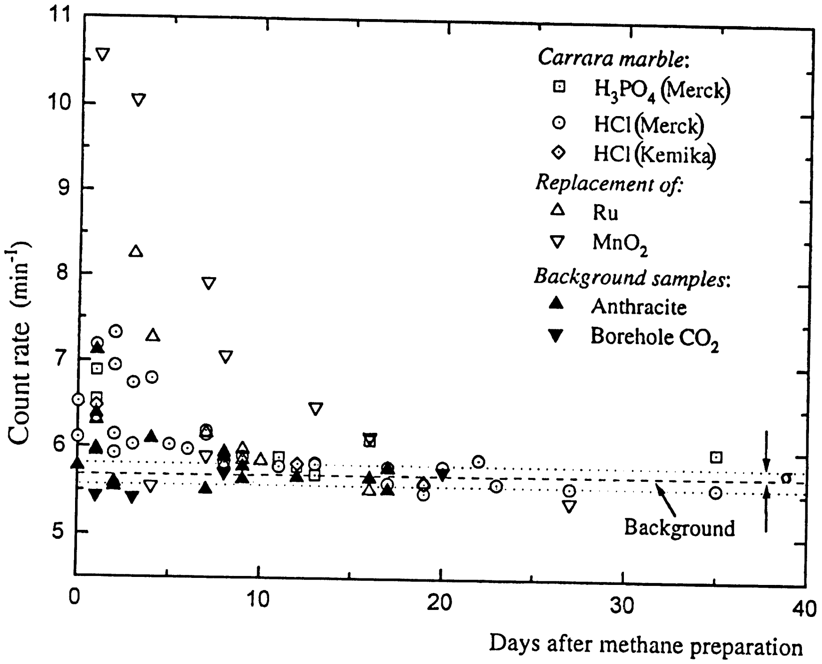

Fig. 5. Background count rates showing Rn contamination in background samples after replacement of chemicals used in CO_2 and CH_4 preparation line

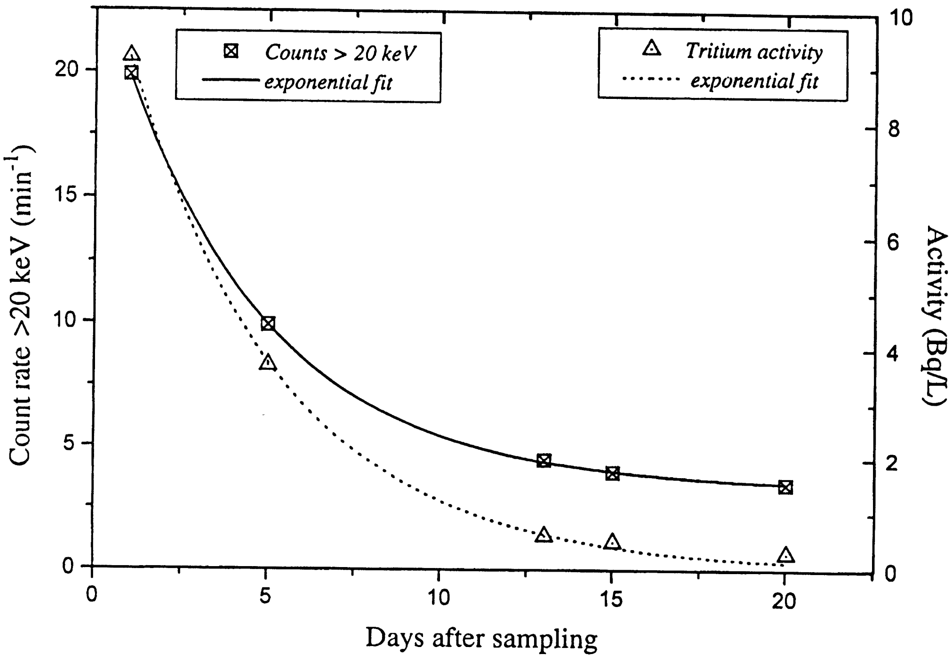

Fig. 6. Apparent ^{3}H activity measured in ^{3}H energy window (1–10 keV, right scale) and the count rate in the energy window above 20 keV (left scale) in groundwater sample (T-1583) as a function of the number of days after sample collection. Excess count rates in both windows indicated ^{222}Rn as the source of contamination.

for several weeks for further testing. No excess count rate was observed in subsequent measurements, showing that only Rn gas was dissolved in the water, not its parent ^{226}Ra, as opposed to the hot-spring travertine sample previously described.

CONCLUSION

Our study of Rn contamination of samples used in radiocarbon dating and ^{3}H activity measurements showed the following:

1. Various sample materials used for radiocarbon dating differ significantly in Rn contamination, terrestrial and aquatic plants being least affected, as opposed to geological samples.
2. Materials used in sample processing and gas purification are very often sources of Rn contamination. The ruthenium catalyst essential for methane synthesis and MnO_2 used in the CO_2 purifying line are the most serious sources of Rn contamination and must be "cleaned" prior to routine use.
3. ^{3}H activity measurements of precipitation and groundwater samples can be affected by Rn contamination if the measurement is made shortly after sampling. Samples of water should be stored for 2 to 3 weeks to allow ^{222}Rn decay before processing; we found no parent ^{226}Ra in these samples.

To minimize the Rn effect, it is advisable to shelve the gaseous methane samples for *ca.* 15 days before measurement and to repeat the measurement after 10 to 15 days; if the count rate does not decrease exceeding statistical uncertainty, the sample can be considered Rn-free. Otherwise, measurements should be repeated in *ca.* 10- to 15-day intervals until a reproducible count rate is reached. Samples of wood, terrestrial plants, aquatic plants or atmospheric CO_2 can be measured immediately after methane preparation.

The count rate recorded above 20 keV in a ^{3}H measuring system should be monitored continuously; any excess of the count rate that cannot be explained by variation of atmospheric pressure is an indicator of Rn contamination.

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