# RADON ISOTOPES AT WAIRAKEI

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**SUMMARY** - We report the presence of the short lived radioactive noble gas $^{220}$Rn (half-life 56 seconds) in geothermal steam at Wairakei. It is detected by a radiochemical separation of Pb, and gamma spectrometry. Measured levels of $^{220}$Rn and the longer lived $^{222}$Rn are interpreted as reflecting processes taking place near the feed zones of the sampled wells.

## 1. INTRODUCTION

Radon is a radioactive noble gas which forms by radioactive decay. Its two isotopes are $^{220}$Rn and $^{222}$Rn with half lives of 56 seconds and 3.8 days respectively, corresponding to mean lifetimes of 81 s and 5.5 days. $^{220}$Rn is formed by decay of $^{232}$Th through a chain of other radioisotopes, its immediate precursor being $^{224}$Ra. Similarly, $^{222}$Rn is formed from $^{238}$U, with its immediate precursor being $^{226}$Ra. When these isotopes are generated close to rock surfaces in contact with geothermal fluid they may escape into the fluid. Studies of their concentrations may shed light on field processes occurring in the weeks before sampling in the case of $^{222}$Rn and minutes before in the case of $^{220}$Rn.

It has long been known that $^{222}$Rn is associated with geothermal steam (Kruger, 1979, George et al., 1980, Rich and Szalinksi, 1981, Balcazar et al., 1991). The geothermal field at Wairakei has been the object of several studies of its radioactivity, particularly the $^{222}$Rn content of its steam (Home and Kruger, 1979, Robertson and Matthews, 1978, Whitehead, 1980, 1985, Matthews, 1981).

The short-lived isotope $^{220}$Rn has been reported along with $^{222}$Rn in steam from fumaroles and geothermal waters (Belin, 1959, Kamada, 1961a, 1961b, Lin and Chen, 1983, Yamashita et al., 1987, Hashimoto and Kubota, 1989, Nakahara et al., 1990). Some of the reports showed quantities of $^{220}$Rn in the order of a thousand times those of $^{222}$Rn.

The present paper gives details of a short investigation of the content of $^{220}$Rn in the Wairakei field and discusses possible reasons for the observed levels with reference also to $^{222}$Rn measurements.

## 2. EXPECTED CONCENTRATIONS

Radon levels at Wairakei can be estimated fkom knowledge of their precursor concentrations. Given typical TVZ $^{232}$Th and $^{238}$U concentrations in rock of 5 and 1 mg.kg$^{-1}$, the $^{220}$Rn and $^{222}$Rn activities (ie the radioactive decay rates) in rock would be approximately 4700 and 2900 Bq.kg$^{-1}$ respectively. This assumes that equilibrium between the various naturally occurring radioactive isotopes has been achieved. For the decay of $^{232}$Th and $^{238}$U this takes in the order of 30 years and $10^6$ years respectively if only those isotopes are present at the start of the process, and rather less otherwise. Under the assumptions of rock density of 2500 kg.m$^{-3}$, 10% porosity, and that all the radon is leached into static liquid water, the resulting activities of $^{220}$Rn and $^{222}$Rn in the water would then be about 1 X 10$^5$ and 7 X 10$^4$ Bq.kg$^{-1}$ respectively. If the radon is leached into steam rather than liquid water the activities will be a factor of 83 times greater (Home and Kruger, 1979). Note that the assumption that all the radon is leached is particularly suspect for the short lived $^{220}$Rn.

Under flow conditions, ie when fluid is withdrawn from the field, the activities are reduced by dilution. Calculations based on a simple model (see Appendix) suggest that the reduction is small for fluid residence times significantly greater than the mean lifetimes with respect to radioactive decay of the isotopes, say 20 days for $^{222}$Rn and 5 minutes for $^{220}$Rn. In the limit of very short fluid residence times the absolute activities are greatly reduced with respect to the activities under static conditions. At the same time the $^{220}$Rn to $^{222}$Rn activity ratio increases by a factor of about 6000, ie the ratio of their respective lifetimes.

Phase changes complicate the situation because at any point in the system where boiling occurs the radon will flash into the steam phase, thus enriching the steam phase with respect to the liquid phase by an unspecified amount. Non-homogeneity of the field, especially in the region of a feed zone, will also result in complications. For example, if in the last few minutes of travel to the well the fluid is not in intimate contact with the rock, little radon would be extracted into the fluid. While this would have a negligible effect on the amount of $^{222}$Rn present the activity of $^{220}$Rn could reduce significantly.

## 3. METHODS

It is obviously quite difficult to determine in the field a radionuclide such as $^{220}Rn$ with a half-life of less than a minute. Even though indirect methods have been devised, they are not simple. Most previous workers have used a portable liquid scintillation device (eg Yamashita et *al.*, 1987) which is not available to the present authors. Instead, steam samples were collected and allowed to stand for about five minutes. During this time the $^{220}Rn$ in the collection vessel decays completely into $^{212}Pb$ which has a 10.6 hour half-life. The $^{212}Pb$ is relatively easily detected but with rather low sensitivity. The extraction of the $^{212}Pb$ was carried out in the GNS laboratory at the Wairakei Geothermal Centre.

Weighed evacuated 250 ml flasks were prepared, containing 50 ml of 1M NaOH, 0.5 ml of saturated EDTA and 200 mg of Pb as the nitrate. The EDTA complex of Pb is stronger in alkaline conditions than acid, and prevents precipitation of Pb as a hydroxide. Steam was condensed in the evacuated flasks by the standard method trapping the radon in the flask along with any other non-condensible gases. The $^{220}Rn$ then decayed into $^{212}Pb$ and because of the presence of non-radioactive Pb was retained in solution rather than precipitating or adsorbing onto the flask walls. The steam also contains *some* $H_2S$ which was absorbed by the NaOH forming the sulphide ion. Despite the removal of Pb in the form of its EDTA complex, the very low solubility product of PbS caused some Pb to precipitate. Collection was continued only until flocculation began, because $^{212}Pb$ might have been lost by adsorption onto the walls of the collecting flask if the Pb concentration had fallen too low. Five minutes of collection was usually adequate. A further delay of five minutes was allowed to enable essentially all the trapped $^{220}Rn$ to decay into $^{212}Pb$. At that stage the flask was opened and air bubbled through the hot liquid; this removed residual $^{222}Rn$ because one of the decay products of $^{222}Rn$ interferes in the subsequent assay and should be minimised. Some water samples were collected from the liquid waste stream for $^{226}Ra$ and $^{224}Ra$ analysis; they were stored in plastic bottle8 with Ba solution added.

The Rn sampling flasks were transported back to the laboratory within a few hours, weighed, and the contents emptied into a beaker. Additional sulphide was added to confirm further precipitation of PbS occurred, i.e. that a reasonable amount of Pb had remained available as a carrier during sampling. The precipitate, which contained the $^{212}Pb$ formed from the $^{220}Rn$, was isolated by filtration on glass fibre filter paper, washed with water and acetone, and weighed to determine the chemical yield of Pb. It was then counted under a standard *geometry* on a HPGe detector with portable cryostat. The $^{212}Pb$ was determined through the gamma ray it emits at 238 keV.

Most assays were for $^{220}Rn$, but a few were performed for $^{222}Rn$ by allowing its decay product $^{214}Pb$ to accumulate. In this case the flask was not vented after collection. Initially there is negligible $^{214}Pb$ present, but it accumulates rapidly to an equilibrium value in the closed flask which may be opened after several hours and Pb precipitated. The remainder of the analysis proceeds as for $^{220}Rn$. The $^{214}Pb$ was determined through the gamma ray it emits at 241 keV.

Some liquid samples were assayed for $^{226}Ra$ and $^{224}Ra$, the precursors of $^{222}Rn$ and $^{220}Rn$. Sufficient Ba solution was added to allow precipitation of about 2.5g of barium sulphate which co-precipitates the chemically similar Ra. This was also counted in the HPGe detector. $^{226}Ra$ and $^{224}Ra$ were detected through emissions at 186 keV and 241 keV respectively.

## 4. RESULTS

The results are given in Table 1, with one standard deviation propagated counting errors only.

## 5. DISCUSSION

The results are preliminary and subject to large errors but some semiquantitative discussion is useful.

A possible explanation for the presence of $^{220}Rn$ in the samples is that it is generated from $^{224}Ra$ dissolved in the liquid water phase. If this were the *case* the $^{224}Ra$ activity in the liquid phase would be comparable with that of the $^{220}Rn$. In the two wells where it was measured however, the $^{220}Rn$ to $^{224}Ra$ ratio is more than 1000. This result is typical of groundwaters in general (eg Krishnaswami *et* al., 1982). These results for $^{224}Ra$ are the first reported for Wairakei waters. The measured activities are similar in magnitude to the $^{226}Ra$ results which are already available (Stewart *et al.*, 1993). The assumption must be that Ra remains fixed in the rock and Rn is being generated in and emitted from rock surfaces.

The activities found in liquid dominated wells such as WK74, WK86 and WK107 are in the order of one percent of the theoretical maxima for static liquid water calculated earlier. In view of the short lifetime of $^{220}Rn$ this is an indication that Significant leaching of radon from the rock into the water *occurs* on a time scale of minutes.

Figs 1a and 1b show the data for which both $^{220}Rn$ and $^{222}Rn$ activities are available. *As* Fig 1a illustrates, the higher activities of both Rn isotopes occur in wells which are either steam dominated or contain some *steam*, *As* explained in section 2 this correlation between steam and high radon activity is expected. *The* correlation *between* radon and $CO_2$ contents found by Whitehead (1980) *occurs* for similar reasons. WK108 and WK118 however have a very low $^{220}Rn$ content (neither being shown in Fig 1 as the $^{222}Rn$ activity was not measured). Presumably this is an indication that in the last few minutes at least of its travel to the feed zone the fluid has little contact with rock containing the radon precursors. This could be because of transport through fissures rather than a porous medium. Further determinations, especially on wells with high steam content, would be helpful.

**Table 1.** Results of analyses for radon and radium in geothermal *steam*. The Rn results are expressed per weight of condensed steam, the Ra results per weight of liquid water. Note that units for Rn are kBq.kg$^{-1}$ and for Ra Bq.kg$^{-1}$. In the well number column, S signifies steam dominated, L liquid dominated, and SL a combination. Results in parentheses are from Stewart *et al.* (1993). For conversion to older units, note that 1 $\mu$Ci = 37 kBq. Negative values of $^{220}$Rn are related *to* background effect.

| Well number | $^{220}$Rn (kBq.kg$^{-1}$) | $^{222}$Rn (kBq.kg$^{-1}$) | $^{224}$Ra (Bq.kg$^{-1}$) | $^{226}$Ra (Bq.kg$^{-1}$) |
|---|---|---|---|---|
| | | | | |
| WK24 L | 0.30f0.28 | | | |
| WK26B L | 0.025±0.013 | (0.48) | | |
| WK30 L | <0.035 | (0.031) | | |
| WK59 L | 3.02f0.36 | | 4.9f2.1 | 4.9±0.8 |
| WK71 L | <0.035 | (0.035) | | |
| WK74 L | 1.65f0.52 | (0.41) | | |
| WK81 L | 1.20±0.17 | 0.0094±0.0046 | | |
| WK107 L | 1.35f0.58 | (0.20) | | |
| WK116 L | -1.2f1.0 | (0.2) | | |
| WK52 SL | 18.3f2.5 | 3.824f0.073 | 4.1f1.3 | 7.6f1.1 |
| WK86 SL | 1.50f0.46 | (0.13) | | |
| WK108 SL | -0.039±0.019 | | | |
| WK65 S | 7.1±1.5 | 6.85±0.16 | | |
| WK80 S | 2.61±0.50 | (5.1) | | |
| WK118 S | -0.01±0.046 | | | |
| WK216 S | 5.10±1.5 | (2.0) | | |

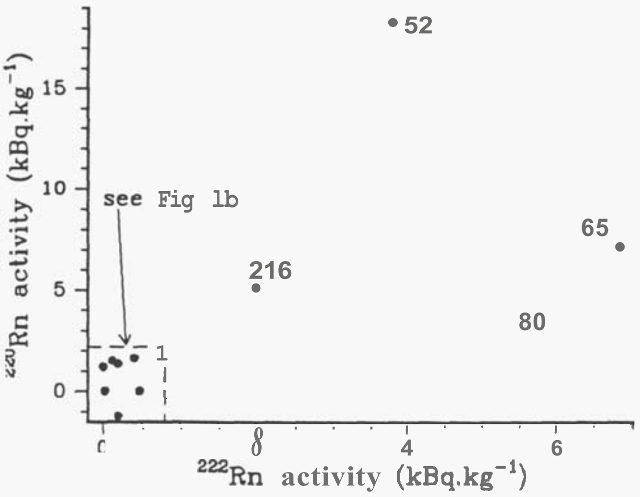

Figure 1a - All results

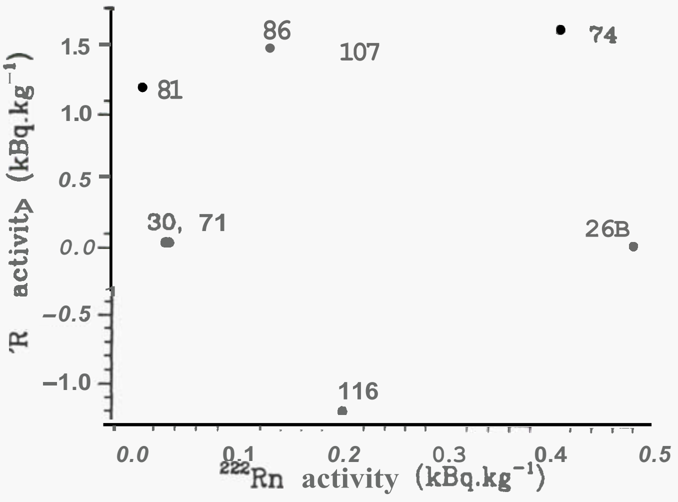

Figure 1b - Low activities

As described earlier the absolute amounts of the isotopes and their ratio can be due to a number of factors. It may well be that the values shown for WK74, WK86 and WK107 (see Fig 1b) are in the typical range for wells fed by liquid water although more measurements would be needed to confirm this. The wells which give low values of one or both of the isotopes are of interest. In the case of WK81 for example the $^{220}$Rn value is in the typical range but the $^{222}$Rn value is very low. Presumably the feed to this well comprises the residual from a boiling process which stripped radon from liquid water at a time before discharge intermediate between the lifetimes of the two isotopes. For WK26B and WK116 the $^{220}$Rn content is very low, indicating that the discharge has not been in contact with Rn generating rock for at least several minutes immediately prior to discharge. A combination of these explanations could explain the very low concentration of both isotopes in WK30 and WK71.

Much more data is needed to back up these interpretations. The most satisfactory continuation of this research would be an enlarged programme of analyses for both $^{220}$Rn and $^{222}$Rn, preferably with improved precision.

## 6. CONCLUSIONS

$^{220}$Rn has previously been found in fumaroles and this paper reports it for the first time in steam from an operating geothermal field. It does not depend on the $^{224}$Ra content in the water and originates directly from rocks. The $^{220}$Rn to $^{222}$Rn ratio was shown to be highly variable, probably reflecting boiling processes and conditions near the feed zone of the wells.

## 7. ACKNOWLEDGMENTS

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## APPENDIX

### Radon activity in discharge

Consider a model in which fluid with zero activity of radon enters a region in which radon is produced uniformly at a rate θ per unit concentration of its precursor isotope in the rock. Then consider the path of the fluid to a discharge point as a succession of n sub-regions in which radon is produced by radioactive decay and depleted by the combined effects of decay and flow. If the time of travel to the discharge point is T the mean residence time in each sub-region will be T/n. Let the sub-regions be labelled j where j = 1,..n starting the numbering from the discharge point. Each sub-region considered alone would reach a steady state radon activity $A_j$ given by stirred tank reactor theory as

$$\frac{\theta}{1+\frac{}{T}}$$

where t is the mean lifetime of the particular radon isotope with respect to radioactive decay.

The radon activity in the discharging fluid will then be the *sum* of the activities *A*, each reduced by the decay of the radon isotope in the time taken to reach the discharge point from the subregion. For subregion j the time taken is jT/n so the contribution of the jth subregion to the discharge activity is

$$\Delta A_j=\frac{\theta}{1+\frac{nt}{T}}\exp\left(-\frac{T}{t}\frac{j}{n}\right)$$

For a large number of sub-regions the total activity in the discharge becomes

$$A=\lim_{n\to\infty}\sum_{j=1}^{n}\Delta A_j$$

Thus the discharge activity for varying values of t/T *can* be calculated.