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The Effect of CO_2 on the Measurement of ^{220}Rn and ^{222}Rn with Instruments Utilising Electrostatic Precipitation

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Abstract

In some volcanic systems, thoron and radon activity and CO_2 flux, in soil and fumaroles, show a relationship between (^{220}Rn/^{222}Rn) and CO_2 efflux. It is theorized that deep, magmatic sources of gas are characterized by high ^{222}Rn activity and high CO_2 efflux, whereas shallow sources are indicated by high ^{220}Rn activity and relatively low CO_2 efflux.

In this paper we evaluate whether the observed inverse relationship is a true geochemical signal, or potentially an analytical artifact of high CO_2 concentrations. We report results from a laboratory experiment using the RAD7 radon detector, known ^{222}Rn (radon) and ^{220}Rn (thoron), and a controllable percentage of CO_2 in the carrier gas. Our results show that for every percentage of CO_2, the ^{220}Rn reading should be multiplied by 1.019, the ^{222}Rn radon should be multiplied by 1.003 and the ^{220}Rn/^{222}Rn ratio should be multiplied by 1.016 to correct for the presence of the CO_2.

Key words: radon, thoron, fumaroles, carbon dioxide, volcano.

1. INTRODUCTION

Rn isotope measurements provide a unique opportunity to study the genesis, segregation and movement of gases in volcanic systems (see references

Cigolini *et al*. 2009, D'Amore and Sabroux 1976, Giammanco *et al.* 2007, 2009, Huxol *et al.* 2012, Laiolo *et al*. 2012, Liotta *et al*. 2010, Martelli *et al*. 2008, Martinelli 1998, Neri *et al*. 2011, Perez *et al*. 2007, Tuccimei and Soligo 2008, Yang *et al.* 2011). For example, on Mt. Etna in Italy, measurements of ^{220}Rn and ^{222}Rn activity and CO_2 flux in fumarolic gases follow a general empirical relationship wherein the higher the flux of CO_2, the lower the ratio between ^{220}Rn and ^{222}Rn (Giammanco *et al*. 2007; Fig. 1). It is posited that this relationship is due to significant differences in the half-lives ^{220}Rn ($t_{1/2}$ = 55.6 s) and ^{222}Rn ($t_{1/2}$ = 3.82 days): deep sources of magmatic gas are characterized by high ^{222}Rn activity and high CO_2 efflux, whereas shallow sources exhibit higher ^{220}Rn activity and relatively low CO_2 (Giammanco *et al*. 2007).

When measuring Rn nuclides by alpha decay using the Durridge RAD7[1], ^{222}Rn is measured by its daughter ^{218}Po ($t_{1/2}$ = 3.05 min) and ^{220}Rn is measured by its daughter ^{216}Po ($t_{1/2}$ = 0.145 s), that are precipitated onto an ion-implanted silicon detector. During our measurements of CO_2 and Rn iso-

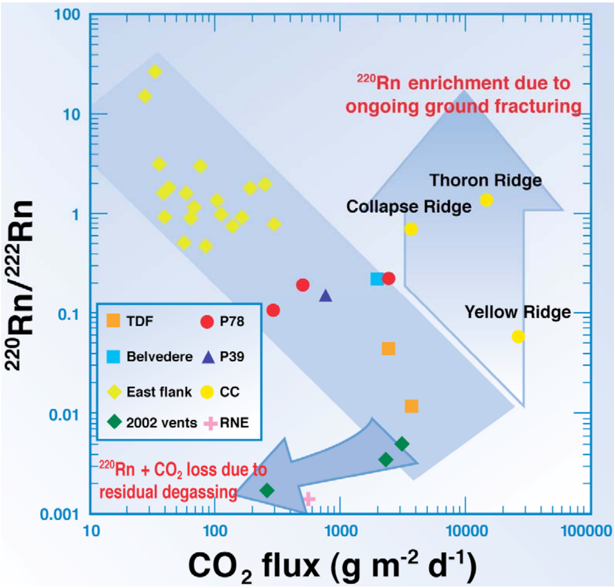

Fig. 1. ^{220}Rn and ^{222}Rn as a function of CO_2 efflux on Mt. Etna as shown in Giammanco *et al.* 2007.

[1] At present, there are a significant number of scientists, from USA, Portugal, Spain, France, Luxembourg, Italy, Pakistan, India, Thailand, Australia, New Zealand, and others, using the RAD7 to measure Rn isotopes in volcanic systems with high CO_2 around the world.

topes in Yellowstone fumaroles and thermal waters we have noticed a significant effect of CO_2 on the Rn isotope measurements. This effect is most pronounced for ^{220}Rn and is a function of CO_2 concentration. With high CO_2 the ^{220}Rn counts decrease. We theorised that the mean free path during electrostatic precipitation of the radon and thoron daughters, in flight to the alpha detector, is reduced by the denser CO_2, in volcanic gases, thus slowing down their flight, and that because of the short half-life of ^{216}Po there should be a "CO_2 effect" on the ^{220}Rn/^{222}Rn ratio. To investigate this CO_2 effect and evaluate whether the observed inverse relationship between ^{220}Rn/^{222}Rn and CO_2 in volcanic systems is a true geochemical signal, or potentially an analytical artefact of high CO_2 concentrations, we have conducted a laboratory experiment using known activities of ^{222}Rn and ^{220}Rn, with a controllable ratio of CO_2/air in the carrier gas.

One approach to solving the problem of CO_2 interference is to remove the CO_2 before making the radon and thoron measurements (Tuccimei and Soligo 2008), but this may increase the radon concentration if CO_2 constitutes a major portion of the carrier gas. An alternative, presented in this paper, is to measure the effect and apply a correction for CO_2, without disturbing the sample.

2. EXPERIMENTAL METHOD

To evaluate the effect of CO_2 on the ^{220}Rn and ^{222}Rn measurements in volcanic systems we have devised a system to produce a known concentration of radon or thoron with a controllable ratio of CO_2 to air in the carrier gas (Figs. 2-4).

2.1 Constant flow system

The first part, common to both radon and thoron setups, is a constant flow rate arrangement. A CO_2 cylinder, pressure regulator and needle valve, and a fresh-air pump and needle valve, feed a combined tubing section whose pressure is maintained above 10 psi (about 690 mbar). A pressure regulator reduces this to a controlled pressure of about 5 psi and a final needle valve determines the flow rate. With the pump running, the fresh-air needle valve open and the CO_2 cylinder shut down the flow is 100% fresh air. With the cylinder open, the regulator set above 12 psi, the CO_2 needle valve open and the fresh-air pump off, the flow is 100% CO_2. With both the CO_2 on and the fresh-air pumps on, the combined tubing section pressure must be kept above 10 psi. Adjusting the CO_2 regulator and the two needle valves feeding the combined tubing section permits any ratio of CO_2 to fresh air to be obtained, while maintaining the constant outlet flow rate (Fig. 2).

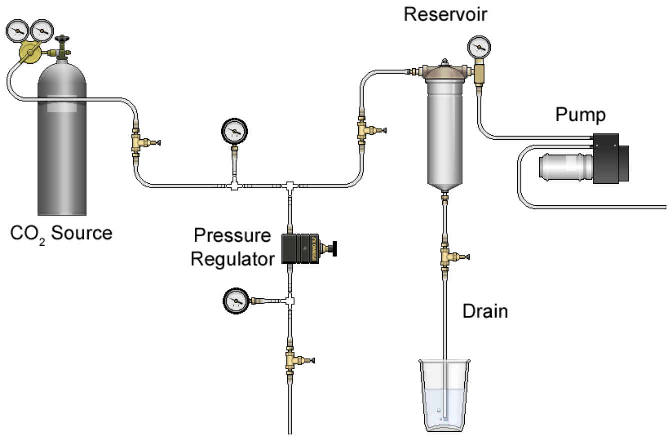

Fig. 2. CO_2-air delivery system.

2.2 Radon (^{222}Rn) delivery

A constant flow rate of gas through a steady radon source produces a constant radon concentration in the gas (Fig. 3). The source used for this experiment was a 20 kBq radium source on foil, manufactured by the Czech Metrological Institute. The output from the source was dried to eliminate the effect of humidity before delivering it to the RAD7. A flow meter on the outlet of the RAD7 was used to verify the constant flow velocity and a 0-100% CO_2 meter monitored the percentage of CO_2.

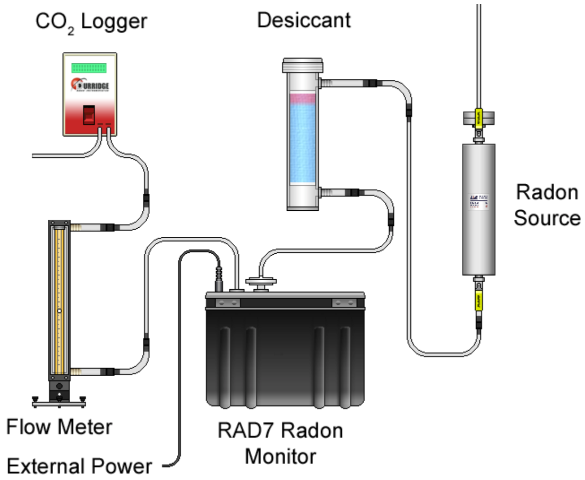

Fig. 3. System for measuring the effect of CO_2 on ^{222}Rn measurements.

It should be noted that while the radon concentration in the sample air is a function of the rate of air flow through a standard radon source, the sensitivity of the RAD7 to radon, on the other hand, is independent of the flow rate provided: (i) that it is less than 3 L/min, and (ii) that the sample acquisition time is much less than the half life of radon (3.8 days). Both criteria were satisfied in these experiments. The constant flow rate through the radon source ensured constant radon concentration in the sample.

2.3 Thoron (^{220}Rn) delivery

While the generation of the thoron sample is similar to that for radon, its delivery to the RAD7 is different because of its short half life. The system is similar to that used for standard thoron measurement and thoron calibration (Fig. 4). The thoron is injected into a sample stream where it is carried at the RAD7 pump flow rate into the RAD7. To preserve the CO_2 percentage, the flow is recirculated. Thus the equilibrium thoron concentration at the sampling point is equal to the rate of injection divided by the RAD7 flow rate, plus a proportion of the thoron, about 25%, that survives the circuit around the loop.

While with radon the sensitivity is independent of the sample flow rate, with thoron the flow rate is a critical factor. For the purpose of the experiment a relatively high and constant flow rate was maintained through the thoron source to ensure a constant thoron concentration in the RAD7. For measurements in the field, the sample acquisition time, from entering the sampling tube at the sampling point to leaving the measurement chamber in the instrument should be determined, by measuring the flow rate and the volume of the sample acquisition path, and a correction applied to the reading accordingly.

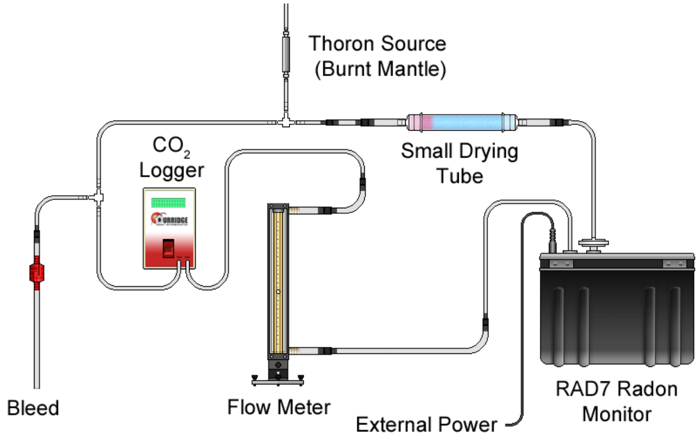

Fig. 4. System for measuring the effect of CO_2 on ^{220}Rn measurements.

3. RESULTS

3.1 Effect of CO_2 on RAD7 radon measurements

Figure 5 shows the effect of CO_2 on the RAD7 radon measurements. At 100% fresh air the radon concentration reading is 430 pCi/L. At 100% CO_2 the reading drops to 330 pCi/L. That's a decrement of 100 pCi/L or 23.3%. To correct a 100% CO_2 radon reading would require a multiplying factor of 1.3. In other words, a radon concentration reading in the presence of some CO_2 should be increased by 0.3% for every percentage of CO_2.

3.2 Effect of CO_2 on RAD7 thoron readings

Figures 6 and 7 show the effect of CO_2 on the RAD7 thoron (^{220}Rn) measurements. When the CO_2 concentration changes from 0% to 100% there is an immediate and dramatic change in the count rate in window B of the RAD7 (Fig. 6). However, the count rate in the D window (^{212}Po) continues to rise, with a 10.6 hour half life, to a level in excess of the count rate in window B. This indicates that while some ^{216}Po atoms may be prevented by the CO_2 from reaching the detector surface, some of those atoms, after decaying to ^{212}Pb, are eventually able to reach it.

The effect of CO_2 on the thoron reading is dramatic (Fig. 7). A change from fresh air to 100% CO_2 reduced the reading from 61 000 to 21 000 Bq/m^3. That's a decrement of 65.6%. In other words a thoron reading at 100% CO_2 should be multiplied by a factor of 2.9 to obtain the fresh-air

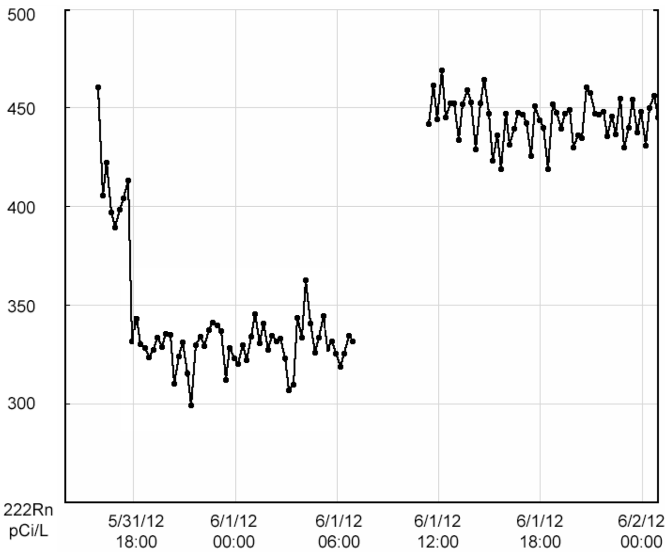

Fig. 5. Effect of CO_2 on radon measurements.

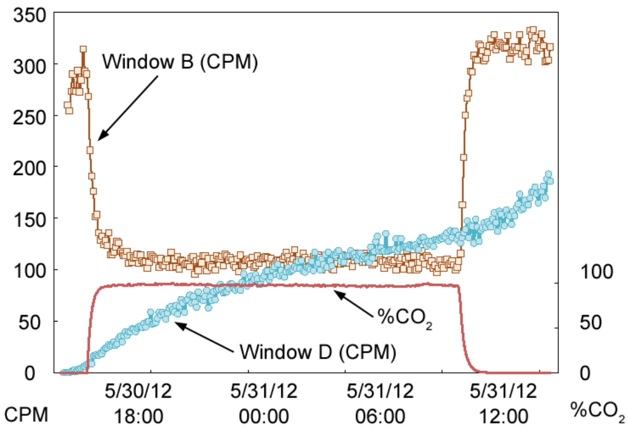

Fig. 6. Effect of CO_2 on the count rates in the B (^{216}Po) and D (^{212}Po) windows.

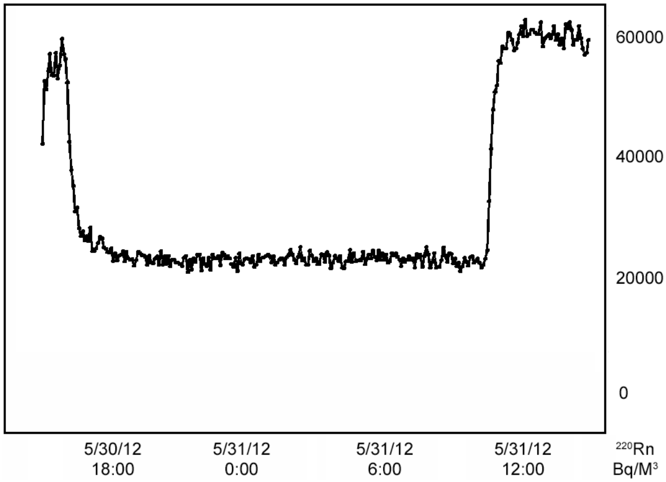

Fig. 7. Effect of CO_2 on thoron measurement.

reading. A correction of 1.9% should be added to a thoron reading in the presence of CO_2 for every percentage of CO_2 above zero.

4. CONCLUSIONS

The absolute values of ^{220}Rn and ^{222}Rn and the ^{220}Rn/^{222}Rn ratio are important parameters in both geothermal and anthropogenic systems. Based upon our laboratory experiments evaluating the effect of CO_2 on these parameters using the Durridge RAD7 alpha counting system we have determined that when Rn is measured in the presence of CO_2 the ^{220}Rn (thoron) measurement is diminished more than the ^{222}Rn reading and that therefore the $^{220}Rn/^{222}Rn$ decreases as a function of CO_2 concentration.

Our experimental measurements show that for every percentage of CO_2 above zero, the thoron reading should be multiplied by 1.019, the radon reading should be multiplied by 1.003 and the measured ratio should be multiplied by 1.016 to correct for the presence of the CO_2. Thus for the measurement of Rn isotopes with significant ambient CO_2 in both volcanic and anthropogenic systems, this correction must be applied to obtain optimal accuracy.

However, the result also indicates that this correction will modify but not nullify the analysis and conclusions of prior work (*e.g.*, Giammanco *et al.* 2007). Finally, we note that an alternative option is to scrub the CO_2 prior to the measurement of radon as was done in Tuccimei and Soligo (2008). However, the scrubbing of CO_2 prevents simultaneous measurement of CO_2 with radon and thoron, whereas the experimental results we present here suggest that a simple correction can be applied. Also, if the CO_2 concentration is high, removing it will reduce the volume of the gas and hence increase the radon concentration in the gas remaining.

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