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## Characterisation of radon concentrations in Karoo groundwater, South Africa, as a prelude to potential shale-gas development.

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### Abstract

Proposed shale-gas exploration in the semi-arid Karoo, South Africa, has created the need for the development of a robust geochemical baseline, differentiating deep and shallow groundwaters. Shallow groundwater is the main source of potable water in the Karoo, and the possibility of upwards migration of poorer quality deep groundwaters is a cause for concern. Radon concentrations of nineteen groundwater samples, from eight locations in the Karoo Basin, were determined in summer and winter. Sub-thermal waters were used as an initial proxy to define deep groundwater. Radon concentrations of < 100 Bq/L were recorded for most sites, with higher concentrations in shallow groundwaters. Seasonal and geographical variations in radon provide insight into the processes controlling radon concentrations in the Karoo groundwater. The presence of uranium and radium nuclides (possibly originating in the Karoo Uranium Province), and the presence of dolerite intrusions are important for controlling radon concentrations. Negligible uranium in deep groundwater was associated with anoxic, low alkalinity, high pH, old sub-thermal waters. Discrepancies between radon concentration and chemistry of groundwater sources defined as shallow is attested to the short half-life of <sup>222</sup>Rn, which records only the last stage of the water's history. Elevated radon may be linked to seismic activity, a cause for concern considering the deep formation micro-fractures associated with hydraulic fracturing.

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## 1. Introduction

The potential for groundwater contamination in the Karoo Basin, South Africa, is high given the presence of a large uranium province, and interest in shale-gas fracking in the same region. During fracking, high-pressure fluids create fractures in the deep shale formations, releasing trapped shale gas. Contamination of shallow aquifers may occur from the upward migration of poorer quality deep groundwater along these or existing fracture networks, but at present the composition of the deep groundwater is unknown. In addition to impacts on the groundwater quality, there is also concern that radon gas emissions might spike in response to fracking, as anomalous radon peaks have been noted prior to seismic activity (Monnin and Seidel, 1992). The peaks are likely due to the formation of micro-fractures which release trapped radon gas as well as increase the reactive surface. The radioactive gas  $^{222}\text{Rn}$ , formed from the decay of  $^{226}\text{Ra}$ , itself a daughter of  $^{238}\text{U}$ , has known health risks if ingested or inhaled in high concentrations. However,  $^{222}\text{Rn}$  has a short half-life of 3.8 days, and an inert gaseous nature, making it a useful element for subsurface groundwater tracing between deep and shallow aquifers. In this study, sub-thermal ( $>25^\circ\text{C}$ ) old groundwater (a proxy for deep groundwater) and cold young groundwater (shallow groundwater) in the Karoo Basin have previously been defined on the basis of a range of geochemical parameters. The purpose of this study is to report on associated radon, radium and uranium concentrations in the deep and shallow groundwaters in order to understand how the behaviour of these elements varies between these two different groundwater systems. In particular,  $^{226}\text{Ra}$  and  $^{238}\text{U}$ , the parent isotopes of  $^{222}\text{Rn}$ , are sensitive to groundwater redox conditions and can provide insights into the characteristics of the deeper Karoo groundwater system.

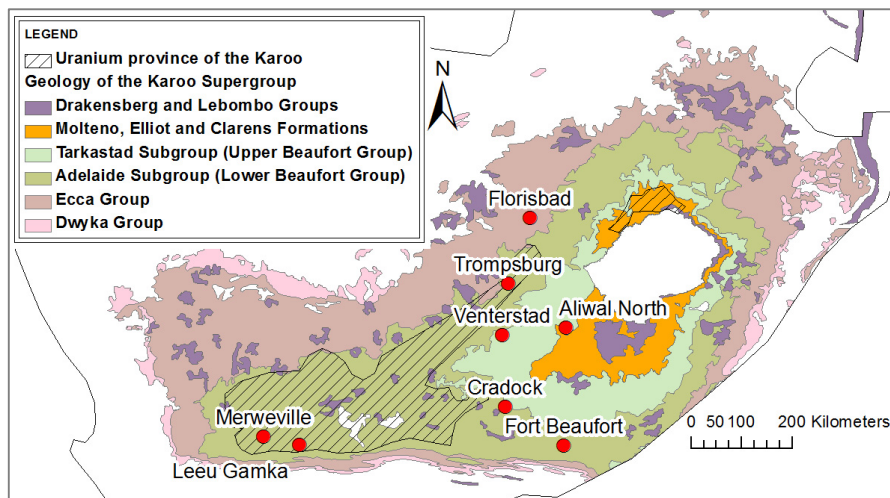


Figure 1. Geology of the Karoo Supergroup, South Africa, including sampling locations and the Karoo Uranium Province (Cole, 2008)

## 2. Karoo Basin

The Karoo Basin, consisting of Permian marine and terrestrial sediments, covers one third of South Africa. It is characterised by fractured rock aquifers with low permeability and low borehole yields. The Ecca Group is a potential source of shale gas in South Africa and is overlain by the Beaufort and Stormberg Groups, which host the Karoo uranium deposits that define a region known as the Karoo Uranium Province (Fig. 1). Fluvial-dominated uranium mineralization is highest in the Molteno Formation (Stormberg)  $>1700$  ppm, followed by the Adelaide Subgroup (Beaufort)  $>1200$  ppm, with the lowest grades occurring in the Elliot Formation (Stormberg)  $<250$  ppm. Dolerite intrusions comprise 30% of the Karoo Basin's thickness, with the thickest sills associated with the Ecca Group. These intrusions occur at an average depth of 250 m, and their high transmissivity values indicate preferential flow, a potential mechanism for the rise of deep and poorer quality groundwaters.

### 3. Methods

Nineteen sampling sites from eight locations throughout the Karoo Basin (Fig. 1) were sampled in March 2014 (summer) and July 2014 (winter). A sub-thermal spring or borehole, as well as a corresponding cold borehole, were sampled at each location. Temperature and alkalinity were measured in the field, and samples were collected for major cations,  $^{222}\text{Rn}$ ,  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , as well as  $^{14}\text{C}$ .  $^{222}\text{Rn}$  was determined using a DurrIDGE RAD7 detector. Analysis was completed six hours after sampling, and  $\alpha$ -decay corrections were not applicable. The statistical uncertainty ( $1\sigma$  level) associated with  $^{222}\text{Rn}$  concentration values (reported in Bq/L) are indicated in the data plots (Fig. 2). Uranium concentrations were analysed by ICP-MS at Stellenbosch University, South Africa. Radium was extracted on site using Mn-oxide fibres, incubated for 3 weeks, and  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activity concentrations were measured in a Canberra DSA2000 BEGe  $\gamma$ -detector, Duke University, USA with activities calibrated against CCRMP.

### 4. Discussion and results

Sample sites were classified as either deep or shallow, based on the temperature of water emanating at the collection point, Stiff diagram shape and  $^{14}\text{C}$  value (pmC between 20.2 and 94.0). Some samples did not fit within either the deep or shallow groupings and were defined as mixed. The U,  $^{222}\text{Rn}$ ,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  data are presented below for these three groups.

#### 3.1. Radon-222

In general deep (and mixed) groundwaters have low  $^{222}\text{Rn}$  (<10 Bq/L), while shallow groundwaters have higher  $^{222}\text{Rn}$  (>13 Bq/L) (Fig. 2).  $^{222}\text{Rn}$  varied slightly between the two sampling seasons (Fig. 2), with greater variability in the shallow samples.  $^{222}\text{Rn}$  concentrations do not correlate spatially with the Karoo Uranium Province as the highest  $^{222}\text{Rn}$  concentrations are located outside its boundaries. At Merweville,  $^{222}\text{Rn}$  in the shallow groundwater increased from 47 Bq/L in summer to 163 Bq/L in winter, placing it above the EPA action limit of 148 Bq/L. Merweville is located near the Colenso fault and the  $^{222}\text{Rn}$  spike may be due to local micro seismicity. The Florisbad shallow groundwater also had high  $^{222}\text{Rn}$  (152 Bq/L) in winter and this may be related to the presence of thick dolerite sills associated with the Eccia Group in this area which increases transmissivity. The deep groundwater from the Florisbad spring decreased slightly from 16 Bq/L to 9 Bq/L from summer to winter. At Leeu Gamka  $^{222}\text{Rn}$  is low, despite the proximity to the highest grade parts of the Karoo Uranium Province (Fig. 1) and this may be due to the absence of dolerite intrusions in this area and the extremely low annual rainfall (<150 mm/yr) which may account for extremely low flow velocities and thus low  $^{222}\text{Rn}$ .  $^{222}\text{Rn}$  also decreased from summer to winter in both deep (4 down to 2 Bq/L) and shallow groundwater (28 down to 14 Bq/L) but the reason for this is unknown. A deep outlier exists at Aliwal North, where the  $^{222}\text{Rn}$  concentration is high (58 Bq/L) but the water is not sub-thermal (21°C). At this site, the deep groundwater may have become retarded in the overlying Adelaide Sub-group, where the water cooled and gained  $^{222}\text{Rn}$  presumably from the local geology.

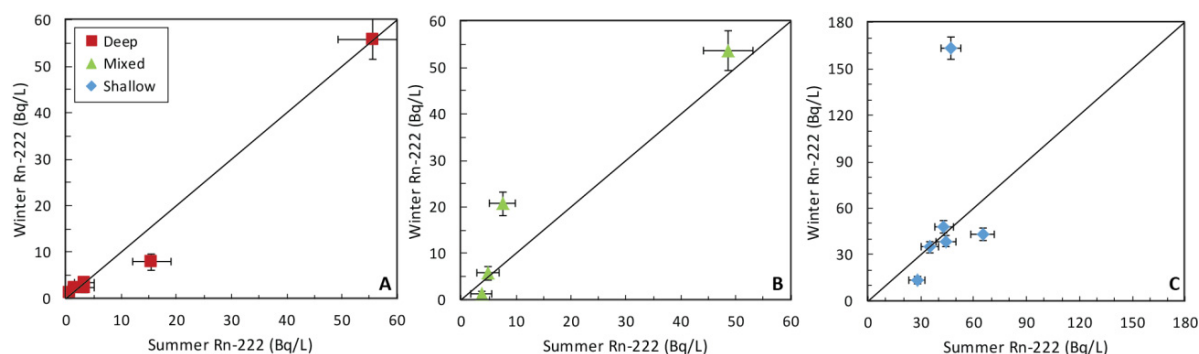


Figure 2.  $^{222}\text{Rn}$  concentrations in summer vs winter with individual uncertainty values, for (a) deep samples, (b) mixed samples and (c) shallow samples (note the difference in y-axis values). Note that the high value from Florisbad is not shown because this site was only sampled in winter.

### 3.2. Radium-226 and -228 and Uranium

$^{226}\text{Ra}$  and  $^{228}\text{Ra}$  activities of the six samples that were analysed, are  $< 0.02$  Bq/L, and show little distinction between deep, mixed and shallow groundwater.  $^{226}\text{Ra}/^{228}\text{Ra}$  ratios are  $\sim 5$  in shallow groundwater and  $\sim 2$  in deep groundwater. High  $^{222}\text{Rn}$  in comparison to its parent isotope  $^{226}\text{Ra}$ , implies that  $^{222}\text{Rn}$  is unsupported in the Karoo groundwater samples analysed. Uranium concentrations are negligible in the deep groundwater ( $< 0.005$   $\mu\text{g/L}$ ) and higher but variable in the shallow groundwater ( $\sim 2.5 - 41$   $\mu\text{g/L}$ ). Interestingly, like  $^{222}\text{Rn}$  there is not a strong correlation between uranium in the water and the Karoo Uranium Province, nor is there a correlation between uranium and  $^{222}\text{Rn}$  (Fig. 3a) and this is probably due to different processes that affect each isotope concentration.

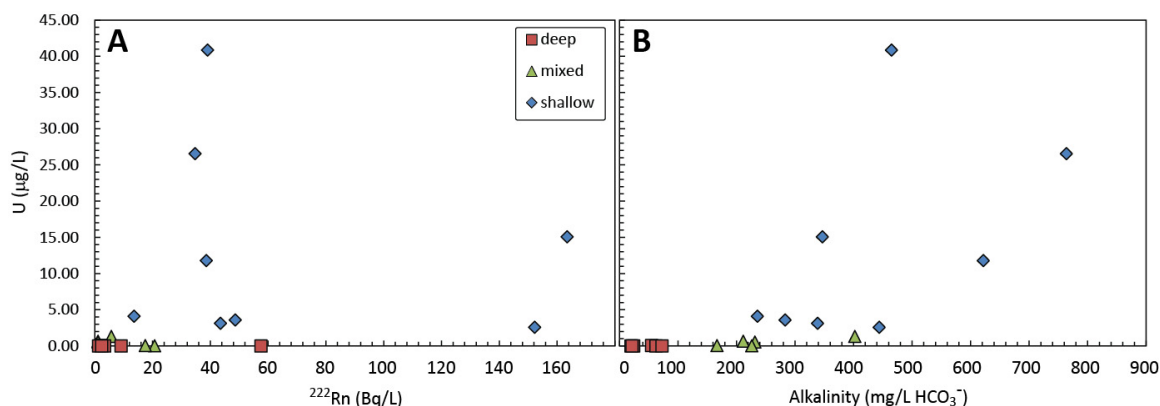


Figure 3. Uranium concentration vs (a)  $^{222}\text{Rn}$ , and (b) alkalinity for winter samples

## 5. Discussion and Conclusions

The unsupported nature of the  $^{222}\text{Rn}$ , the very low uranium and generally low  $^{222}\text{Rn}$  concentrations in the deep groundwater, suggests that the environmental conditions of the shallow and deep groundwater systems largely control  $^{222}\text{Rn}$  concentrations. In the shallow groundwater, high oxygen levels and high alkalinity (Fig 3b) increase uranium solubility in comparison to deeper groundwater.  $^{226}\text{Ra}$  is produced during decay of uranium, but is mostly adsorbed onto the aquifer because of the presence of oxic fractures, hence giving rise to the very low  $^{226}\text{Ra}$  in the groundwater.  $^{226}\text{Ra}$  decays with a half-life of  $\sim 1600$  years but in the shallow groundwater system there is enough uranium present to replenish what is lost on that time scale. Therefore  $^{222}\text{Rn}$  (unsupported by dissolved radium) remains high in shallow groundwater. In the deeper groundwater systems, the transition to more anoxic conditions is accompanied by higher pH and lower alkalinity resulting in reduced uranium solubility. There is no uranium as support for adsorbed  $^{226}\text{Ra}$  and as a result no more production of  $^{222}\text{Rn}$ . Therefore the low  $^{222}\text{Rn}$  and  $^{238}\text{U}$  in deeper groundwater is also telling us about a lack of interaction with shallow aquifer material as it moves to the surface and in particular the lack of interaction with the uranium-rich Beaufort Group. However, the  $^{222}\text{Rn}$  spike at Merweville suggests that the formation of new conduit paths (for example through induced seismic activity in response to fracking) could increase  $^{222}\text{Rn}$  concentrations in shallow groundwater. In conclusion, anoxic uranium-absent waters, originating below the Karoo Uranium Province, are a good indicator of deep groundwater in the Karoo basin.

## References

- Cole, D. (2008). A Review of Uranium Deposits in the Karoo Supergroup of South Africa. In: *American Association of Petroleum Geologists' International Conference and Exhibition*. Unpublished.
- Monnin, M. and Seidel, J. (1992). Radon in Soil-air and in Groundwater Related to Major Geophysical Events: A Survey. *Nuclear Instruments and Methods in Physics Research*, 314, pp.316-330.
- Vinson, D., Vengosh, A., Hirschfeld, D. and Dwyer, G. (2009). Relationships between radium and radon occurrence and hydrochemistry in fresh groundwater from fractured crystalline rocks, North Carolina. *Chemical Geology*, 260, pp 159-171.