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Characterisation of deep groundwater in the Karoo Basin through the use of warm springs as proxies.

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The possibility of shale-gas development in the semi-arid Karoo Basin, South Africa has created the need to develop a hydrochemical baseline for deep Karoo groundwater. In particular, it is unclear how the process of hydraulic fracturing (fracking) will affect the surrounding groundwater and environments, particularly shallow groundwater sources which are used to support local populations and agricultural activities. The first step in this process is to develop a good understanding of the characteristics of the deep groundwater and its connectivity to the shallower groundwater systems through the development of a groundwater baseline for the deeper groundwater and to critically assess how it is distinguished from the shallow groundwater system. Because no known sites accessing the deep groundwater system exist, warm springs were used as proxies for the deep groundwater because the elevated temperature of the springs is assumed to be the result only of depth of circulation. Nineteen groundwater samples were collected from eight locations throughout the Karoo Basin. At each site a deep sample was collected from a warm spring or borehole, and a corresponding shallow site was collected from a nearby shallow borehole. Following an initial assessment of the groundwater samples, three groups were identified and denoted as deep, shallow and mixed, although no constraints could be placed on what depth the deep was referring to. The shallow samples could be identified by temperatures less than 25°C, high alkalinities, the presence of Mg, $NO_3^{2-}$and U, as well as higher δ^2H and $\delta^{18}O$ values. Warmer temperatures usually above 25°C, low alkalinities less than 80mg/L HCO_3^{2-}, elevated Na^{2+} and F^- as well as lower δ^2H and $\delta^{18}O$ values were characteristic of the deep samples. The results of the mixed samples consistently fell between those of the deep and shallow samples and indicates that natural mixing occurs between the deep and shallow aquifer systems. The significant differences observed between the deep and shallow samples are the result of different controls on the groundwater chemistry. Nitrification occurs in the shallow groundwater resulting in elevated NO_3^{2-} concentrations, whereas the dissolution of fluorite in the deeper groundwater resulted in elevated F^- concentrations. The high pH, low alkalinity character of the deep groundwater is thought to in part be related to methanogenesis and this interpretation is supported by elevated $\delta^{13}C$ values for dissolved inorganic carbon. The radioactive isotopes in the deep groundwaters (^{14}C, ^{36}Cl, ^3H, ^4He) along with noble gas concentrations reflect the fact that the deeper groundwaters are older and have had longer to interact with their host rocks. In spite of

this, overall the warm springs and boreholes, as proxies for deep groundwater, suggest that the deep groundwater system is relatively good quality and would not pose a problem should it migrate upwards during fracking activities. However, further work is needed to constrain the actual composition of the deeper groundwater through the drilling of deep boreholes in appropriate locations. This is currently taking place, and the results of this study provide an important framework against which the composition of deep Karoo groundwater can be assessed