# Pre-drill Groundwater Geochemistry in the Karoo Basin, South Africa

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#### Abstract

Enhanced production of unconventional hydrocarbons in the United States has driven interest in natural gas development globally, but simultaneously raised concerns regarding water quantity and quality impacts associated with hydrocarbon extraction. We conducted a pre-development assessment of groundwater geochemistry in the critically water-restricted Karoo Basin, South Africa. Twenty-two springs and groundwater samples were analyzed for major dissolved ions, trace elements, water stable isotopes, strontium and boron isotopes, hydrocarbons and helium composition. The data revealed three end-members: a deep, saline groundwater with a sodium-chloride composition, an old, deep freshwater with a sodium-bicarbonate-chloride composition and a shallow, calcium-bicarbonate freshwater. In a few cases, we identified direct mixing of the deep saline water and shallow groundwater. Stable water isotopes indicate that the shallow groundwater was controlled by evaporation in arid conditions, while the saline waters were diluted by apparently fossil meteoric water originated under wetter climatic conditions. These geochemical and isotopic data, in combination with elevated helium levels, suggest that exogenous fluids are the source of the saline groundwater and originated from remnant seawater prior to dilution by old meteoric water combined with further modification by water-rock interactions. Samples with elevated methane concentrations (>14 ccSTP/kg) were strongly associated with the sodium-chloride water located near dolerite intrusions, which likely provide a preferential pathway for vertical migration of deeply sourced hydrocarbon-rich saline waters to the surface. This pre-drill evaluation indicates that the natural migration of methane- and salt-rich waters provides a source of geogenic contamination to shallow aquifers prior to shale gas development in the Karoo Basin.

### Introduction

The development of unconventional hydrocarbon resources promises a new, cleaner energy alternative to coal. However, hydraulic fracturing for the extraction of shale oil and gas in the United States has sparked environmental concerns from the public. One of the most prominent concerns is the potential for contamination of groundwater from spills, leakage from poorly constructed or damaged oil- and gas-wells, and the release of wastewater during storage, transport, and disposal (Vidic et al. 2013; Jackson et al. 2014; Vengosh et al. 2014). Both the injected freshwater used during hydraulic fracturing and the water produced along with the hydrocarbons (flowback or produced water) present risks to water quality if released to the environment (Vidic et al. 2013; Warner et al. 2013; Jackson et al. 2014; Vengosh et al. 2014; Harkness et al. 2015; Lauer et al. 2016). The fluids that are used to hydraulically fracture the impermeable, hydrocarbon-rich shales are composed of a mixture of freshwater or recycled flowback water, sand, and organic chemical additives, some of which have known human health impacts (Kassotis et al. 2014, 2015; Akob et al. 2015; Drollette et al. 2015). Formation waters from hydrocarbon-rich formations (e.g., shales) constitute 60 to 100% of the flowback and produced fluids generated following petroleum well stimulation. These fluids contain high concentrations of salts, organic matter, naturally occurring radionuclides, and metals that can lead to a variety of adverse risks including salinization of water resources, radioactive soil and sediments, and indirectly, formation of disinfection byproducts in water utilities downstream from disposal sites (Warner et al. 2013;

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Parker et al. 2014; Vengosh et al. 2014; Akob et al. 2015; Harkness et al. 2015).

Delineating the presence of groundwater contamination in areas of shale gas development has been difficult because these areas often display naturally occurring saline groundwater and/or hydrocarbon-rich brine seeps that mimic the geochemistry of the produced water (Warner et al. 2012; Darrah et al. 2015a, 2015b; Harkness et al. 2017b). In this scenario, saline waters are thought to have migrated from depth episodically over geological time in response to tectonic, climatic, and hydrogeological processes via natural pathways (e.g., faults, fractures) in the subsurface, and later mixed with shallow groundwater or discharged at the surface as salt springs (Warner et al. 2012; Darrah et al. 2015a, 2015b; Harkness et al. 2017b).

The rapid expansion of hydraulic fracturing in the United States has resulted in limited or immature federal regulations associated with shale oil and gas development in light of a lack of environmental risk analysis. Attempts to study the environmental impacts of wastewater release have been stymied because: (1) there are rarely adequate baseline water quality studies in most regions targeted for shale gas development and (2) the mechanisms for subsurface migration from depth or from leaking petroleum wells are not well established. The goal of this study is to establish a database of reliable pre-drill water quality parameters for groundwater prior to unconventional drilling in the Karoo Basin, South Africa using diagnostic geochemical and isotopic tools that have proved useful in delineating contamination sources from shale gas development elsewhere (Warner et al. 2012, 2014; Harkness et al. 2017b).

The Karoo Basin in South Africa offers an ideal study area to evaluate these processes because the region is targeted for shale gas extraction in the near future, but has only been minimally developed for conventional energy extraction previously. Further, groundwater in the Karoo Basin is the primary source of both drinking and agricultural irrigation water making a baseline analysis in the region essential (Adams et al. 2001; Woodford and Chevallier 2002; Le Maitre et al. 2009; Rosewarne et al. 2013; Miller et al. 2015; Murray 2015; Swana 2016; Eymold et al. 2018). Previous work has identified natural geothermal, salt- and gas-rich springs throughout the basin and a few deep boreholes have revealed highly saline groundwater (Adams et al. 2001; Rosewarne et al. 2013; Miller et al. 2015; Swana et al. 2015; Talma and Esterhuyse 2015). To date, the geochemistry of the deep groundwater and its potential influence on shallow groundwater has not been formally evaluated. In this study, shallow groundwater, natural springs, and deep groundwater throughout the Karoo Basin were analyzed for a suite of inorganic geochemical and isotope characteristics to better understand the controls on groundwater quality prior to possible future shale gas development.

# Study Area and Methodology

#### **Geological Setting**

The Karoo Basin is located in central South Africa and spans an area of more than  $200,000 \,\mathrm{km^2}$  (Figure 1) (Aarnes et al. 2011). The dominant lithologies in this basin are part of the Karoo Supergroup, which is a thick package of sedimentary rocks that formed during the late Carboniferous to Middle Jurassic periods (Figure 2) (Johnson et al. 1996, 2006). The Karoo Basin formed as a retro-arc foreland basin behind the Cape Fold Belt (Catuneanu et al. 2005). The initial sedimentary units were deposited during a basin-wide glaciation that formed when the Gondwana supercontinent was situated over the South Pole leading to the deposition of the Carboniferous Dwyka Group (Johnson et al. 1996, 2006). The Permian Ecca Group was formed by a series of marine and deltaic deposits that make up the Lower Ecca Prince Albert and Whitehill formations and the Upper Ecca Collingham Formation (Figure 2) (Johnson et al. 1996, 2006). The Whitehill Formation is a black, organic-rich (up to 14%) total organic carbon) shale and the primary target of shale gas development in the basin (Catuneanu et al. 2005).

During the late Triassic and early Jurassic, fluvial sedimentation formed the Beaufort Group, followed by uplift of the Cape Fold Belt, which led to the aridization of the basin that formed the Stromburg Group (Veevers et al. 1994; Catuneanu et al. 2005). An intense period of Jurassic volcanic activity, which produced the Karoo dolerites, intruded into the Ecca and Beaufort sedimentary strata and formed a complex network of sills, dykes, and ring structures (Figure 1) (Aarnes et al. 2011; Talma and Esterhuyse 2015). The introduction of the dolerite dikes contributed to the generation of fractures and contact metamorphism within the sedimentary host rocks (Aarnes et al. 2011).

Groundwater in the region is found and produced primarily within relatively shallow (<200 m) fractured aquifers (e.g., the aquifer lithology varies spatially to include the Adelaide Subgroup, Tarkastad Subgroup, and Molteno, Elliot, and Clarens Fm. from the Karoo Supergroup) and the shallower fluvial deposits (Rosewarne et al. 2013). Flow is dominantly controlled by localized secondary permeability (e.g., fractured zones adjacent to dolerite dikes). Groundwater flow rates are generally slower in the unfractured matrix, and faster through the fractured zones (Adams et al. 2001; Rosewarne et al. 2013). These factors result in highly heterogeneous groundwater geochemistry and transport rates in the different aquifer regions and even within the same aquifer (Adams et al. 2001; Rosewarne et al. 2013). The highly fractured aquifer systems also allow for movement of deep water to the surface through preferential flow paths. The flow conditions and geochemistry of deeper wells (>1000 m) are not well constrained (Adams et al. 2001; Woodford and Chevallier 2002). The occurrence of thermal springs throughout the basin indicates the possible natural migration of deeper, geothermal waters (Murray 2015; Talma and Esterhuyse 2015).



Figure 1. Map of groundwater sample locations in the Karoo Basin, South Africa.



Figure 2. Stratigraphic column of the Karoo Supergroup in South Africa.

#### Site Selection and Sample Collection

In this study, eight (n = 8) sampling regions across the Karoo Basin were evaluated for gas and water geochemistry (Figure 1). The sample regions were selected based on prior knowledge of the presence of geothermal springs/artesian boreholes or the presence of deep boreholes. The study also included other nearby drinking-water or agricultural wells for comparison with a total of n = 22 samples. Samples included 2 deep boreholes (depth ranging between 1400 and 4200 m), 9 springs/artesian wells, and 11 groundwater samples from shallow boreholes (Mahed 2016; Swana 2016).

At each sample location (Figure 1), field measurements were conducted including electrical conductivity, pH, temperature, and oxidation-reduction potential (ORP) using a YSI multiprobe calibrated daily. Water samples were collected after 30 min of flushing or when the field parameters stabilized. Each sample was filtered and preserved in high-density polyethylene (HDPE), airtight bottles following USGS protocols (USGS 2011). Samples for major anions, cations, trace metals, and inorganic trace element isotopes (boron (B), strontium (Sr)) were filtered through 0.45 µm filters into HDPE bottles. Major cation and trace metal samples were acidified to a pH  $\sim$  2 in the field. Samples collected for dissolved inorganic carbon (DIC), water isotopes and tritium analyses were collected in HDPE bottles without headspace. Hydrocarbon and dissolved gas samples for concentration and isotopic analyses were collected in closed volume, flow-through, refrigeration-grade copper tubes that were flushed in-line with at least 50 volumes of sample water prior to sealing with stainless steel clamps following methods reported previously (Darrah et al. 2013, 2015a; Moore et al. 2018) and reported in detail in this issue (Eymold et al. 2018).

#### **Analytical Methods**

Measurements of water chemistry, stable water isotopes, and isotopes of dissolved salts (B, Sr) were conducted at Duke University. All samples were analyzed for dissolved anions, including fluoride (F), chloride (Cl), bromide (Br), and sulfate (SO<sub>4</sub>) by ion chromatography on a Dionex IC DX-2100 (Thermo Fisher Scientific, Germering, Germany) following standard methods. Major cations were analyzed by directly coupled plasma optical emission spectrometry and trace elements, including lithium (Li), B, and Sr were analyzed by inductively coupled plasma mass spectrometry on a VG PlasmaQuad-3 (Thermo Fisher Scientific, Cheshire, UK).

The stable isotopes of water (i.e.,  $\delta^2$ H and  $\delta^{18}$ O) were analyzed in the Duke Environmental Isotope Lab. These gases are chromatographically separated in the high temperature conversion elemental analyzer (TCEA), and carried to a ThermoFinnigan Delta + XL ratio mass spectrometer via a Conflo III flow adapter. Raw delta values were normalized offline against known vs. measured isotope values for international reference waters Vienna Standard Mean Ocean Water (VSMOW), Standard Light Antarctic Precipitation (SLAP), and International Atomic Energy Agency (IAEA)-OH16. The  $\delta^2$ H and  $\delta^{18}$ O values are expressed in per mil (‰) vs. VSMOW, with standard deviations of ±0.5 and ±0.1‰, respectively.

Isotope ratios for B and Sr were measured using thermal ionization mass spectrometry on a Thermo Scientific Triton at Duke University following previously reported methods (Warner et al. 2014; Harkness et al. 2017b). B isotope ratios were measured in negative mode using single Re filaments and expressed in per mil (%) vs. National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 951 (mean = 4.0051, n = 65) with a precision of  $\pm 0.3\%$ . Sr was pre-concentrated by evaporation in a HEPA-filtered clean hood and re-digested in 3.5 N nitric acid, then separated using Eichrom Sr-specific ion exchange resin. <sup>87</sup>Sr/<sup>86</sup>Sr ratios were measured in positive mode using single Re filaments with a precision of  $\pm 0.000006$  on repeated measurements of NIST SRM 987 (mean = 0.71062, n = 98).

Dissolved gas samples were measured by extracting the fluid from the copper sampling tubes on a vacuum line following standard methods (Darrah et al. 2013; Kang et al. 2016; Moore et al. 2018). From this gas volume, splits of samples were taken for the measurement of major gas components (e.g., N2, O2, CO2, CH4 to C<sub>5</sub>H<sub>12</sub>), noble gases (e.g., He), and stable carbon and hydrogen isotopes ( $\delta^{13}$ C-CH<sub>4</sub>). The major gas components (e.g.,  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $CH_4$  to  $C_5H_{12}$ ) were measured using an SRI gas chromatograph (GC; SRI Instruments, Torrance, California) at The Ohio State University (OSU) with standard errors of <3% (Hunt et al. 2012; Kang et al. 2016). The average external precision was determined by measurement of a "knownunknown" standard, including an atmospheric air standard (Lake Erie, Ohio Air) and a series of synthetic natural gas standards obtained from Praxair and the DCG

Partnership (Houston, Texas). The results of the "knownunknown" average external precision analysis are as follows: CH<sub>4</sub> (1.27%), C<sub>2</sub>H<sub>6</sub> (1.68%), C<sub>3</sub>H<sub>8</sub> (1.34%), N<sub>2</sub> (1.25%), and CO<sub>2</sub> (1.06%). CH<sub>4</sub> concentrations are reported as ccSTP/kg of water (the SI molar unit for gas abundance in water) at standard temperature and pressure (STP), where 1 mg/kg of gas is equivalent to 1.4 ccSTP/kg.

The abundance and isotopic composition of noble gases were determined using a Thermo Fisher Helix SFT Noble Gas MS at OSU following methods reported previously (Darrah and Poreda 2012; Moore et al. 2018; Harkness et al. 2017b). The average external precisions based on "known-unknown" standards were all less than  $\pm 1.96\%$  for noble gas concentrations with values reported in parentheses (<sup>4</sup>He [0.78%], <sup>22</sup>Ne [1.46%]). These values were determined by measuring referenced and cross-validated laboratory standards including an established atmospheric standard (Lake Erie Air) and a series of synthetic natural gas standards obtained from Praxair and the DCG Partnership. Noble gas isotopic standard errors were approximately  $\pm 0.0091$  times the ratio of air (or  $1.26 \times 10^{-8}$ ) for <sup>3</sup>He/<sup>4</sup>He ratio, and ±0.402% and  $\pm 0.689\%$  for <sup>20</sup>Ne/<sup>22</sup>Ne and <sup>21</sup>Ne/<sup>22</sup>Ne.

Procedures for analyses of stable isotopic values of carbon in CH<sub>4</sub> were described previously (Darrah et al. 2013, 2015a; Jackson et al. 2013; Harkness et al. 2017b). Using a Thermo Finnigan Trace Ultra GC separation and a dual-inlet isotope ratio mass spectrometry on a Thermo Fisher Delta V Plus, the detection limits for  $\delta^{13}$ C-CH<sub>4</sub> were 0.001 ccSTP/kg. The  $\delta^{13}$ C-CH<sub>4</sub> values are expressed in per mil vs. Vienna Peedee belemnite, with a standard deviation of  $\pm 0.1$ .

#### Groundwater Residence Time Models

Groundwater residence time estimates were calculated using a combination of  ${}^{3}H-{}^{3}He$  and radiogenic  ${}^{4}He$  in-growth techniques to determine the apparent ages using a simplistic piston-flow conceptual model following previously published methods (Schlosser 1992; Cook et al. 1996; Solomon et al. 1996; Castro and Goblet 2003; Sheldon et al. 2003; Plummer et al. 2012). Tritium active waters indicate the presence of post-1950s (Modern) water (recharged since the early 1950s). Excess  ${}^{3}He$  produced by the radioactive decay of  ${}^{3}H$  was calculated by in-growth methods using the measured  ${}^{3}He/{}^{4}He$  and  ${}^{4}He$  concentrations and noble-gas derived amounts of excess air and recharge temperatures (Schlosser et al. 1989; McMahon et al. 2015).

To evaluate the potential for in-situ radiogenic production and/or release of <sup>4</sup>He, we analyzed the U and Th in three aquifer outcrop samples (i.e., n = 2 from the Clarens Fm. and n = 1 from the Adelaide Subgroup) collected in the Karoo Basin using a Thermo Finnigan Element 2 ICP-Sector Field MS following methods developed previously (Darrah et al. 2015a; Harkness et al. 2017a).

 Table 1

 Field Parameters for Karoo Groundwaters<sup>1</sup>

Town	Date	Location	Sample Type	Sample ID	Temp (°C)	pН	EC (µS/cm)	TDS (mg/L)	ORP (mV)	DO (mg/L)
Florisbad	June 28, 2014	Florisbad Spa	Spring	FLS1	20.0	9.4	3620	2160	49	3.3
	June 28, 2014	Farm	Shallow well	FLB5	19.2	7.7	1382	822	72	4.1
Trompsburg	June 29, 2014	Vlakfontein	Deep borehole	VFB1	29.5	9.2	10190	6100	184	1.9
	June 29, 2014	Vlakfontein	Shallow well	VFB2	18.2	7.7	502	301	43	4.5
	June 29, 2014	Vlakfontein	Shallow well	VFB4	19.3	7.5	712	525	49	4.6
Aliwal North	June 30, 2014	Aliwal North Spa	Spring	ANS1	30.0	9.1	2010	1200	197	2.5
	June 30, 2014	Farm	Shallow well	ANBH1	21.6	7.5	1896	1123	45	2.2
Venterstad	July 1, 2014	Rooiwal	Artesian borehole	RWB1c	25.7	8.0	487	293	-250	1.8
	July 1, 2014	Rooiwal	Shallow well	RWB5	18.1	7.4	854	511	29	4.0
	July 2, 2014	Vaalbank	Artesian borehole	VBB1	18.2	8.4	543	322	-157	1.9
	July 2, 2014	La Rochelle	Shallow well	LRB1	17.4	7.1	1231	735	45	4.0
	July 2, 2014	La Rochelle	Shallow well	LRB2	17.3	7.5	580	345	49	4.5
Fort Beaufort	July 4, 2014	Sulphur Baths	Artesian borehole	BFB1	23.5	10	822	492	-232	1.5
	July 4, 2014	Sulphur Baths	Shallow well	BFB2	21.2	7.4	2000	1194	-220	1.5
	July 4, 2014	Rocky Ridge	Shallow well	RRB1	21.2	7.1	2490	1480	35	3.9
Cradock	July 6, 2014	Cradock Spa	Spring	CRS1	29.4	9.8	208	123	-210	1.6
	July 6, 2014	Waaikraal farm	Shallow well	DRB4	16.2	7.8	1615	963	41	4.0
Leeu Gamka	July 8, 2014	Kruidfontein	Artesian borehole	WP508	26.5	8.1	930	557	-172	4.4
	July 8, 2014	Groot Kruidfontein	Shallow well	WP502	20.3	7.9	527	316	24	5.7
	July 8, 2014	Groot Kruidfontein	Artesian borehole	WP505	23.5	8.2	1326	799	-190	1.5
Merweville	July 9, 2014	Farm	Deep borehole	SA1/66	NaN	NaN	NaN	NaN	NaN	NaN
	July 9, 2014	Farm	Shallow well	MWB2	21.5	7.1	1067	639	27	3.4

<sup>1</sup>Field Parameters not taken are indicated by NaN.

#### Results

Field water chemistry data are presented in Table 1. Groundwater pH values varied between 7.08 and 10.03 and groundwater temperatures ranged from 16.2 °C to 30.0 °C. Redox state ranged from oxidizing to highly reducing conditions, with field ORP from -232 to +197 mV. Salinity of the groundwater varied over three orders of magnitude with electrical conductivities (EC) and total dissolved solids (TDS) from 501 to 10,190  $\mu$ S/cm and 301 to 6100 mg/L, respectively. Six samples exhibited salinities above World Health Organization drinking water recommendations (1000 mg/L). However, all groundwater wells currently being used for agriculture are within acceptable limits for irrigation.

The Cl content of the samples ranged from relatively fresh (10.1 mg/L) to saline (4100 mg/L) water (Table 2). Br concentrations ranged from 0.1 to 23.4 mg/L, SO<sub>4</sub> from 1.2 to 870 mg/L and dissolved inorganic carbon (DIC as bicarbonate) from 20 to 764 mg/L. Calcium (Ca) concentrations ranged from 3.4 to 554 mg/L, magnesium (Mg) from below detection limits (b.d.l.) to 71.3 mg/L, and sodium (Na) from 17.6 to 2470 mg/L (Table 2). Cl concentrations were positively correlated to Br  $(r^2 = 0.97, p < 0.01;$  Figure 3), Ca  $(r^2 = 0.79, p < 0.01;$ p < 0.01), Na ( $r^2 = 0.84$ , p < 0.01; Figure 3), and SO<sub>4</sub>  $(r^2 = 0.70, p < 0.01)$ . Mg and DIC were positively correlated (0.91, p < 0.01), but neither correlated with Cl. Salinity (TDS) and Cl were not correlated with pH, but DIC and Mg were positively correlated with pH  $(r^2 = 0.72, p < 0.01 \text{ and } r^2 = 0.63, p < 0.01;$  Figure 4). Br/Cl ratios in the saline water samples with Cl > 200 mg/L (mean =  $1.5 \pm 0.5 \times 10^{-3}$ ) were all close to the seawater ratio of  $1.5 \times 10^{-3}$  and Na/Cl ratios (0.90 ± 0.29) were greater than the seawater ratios of 0.86 (Figure 3). The two saline samples (Cl > 3000 mg/L) from the deep boreholes had Br/Cl values close to or above the seawater ratio ( $1.6 \times 10^{-3}$  and  $2.5 \times 10^{-3}$ ) and Na/Cl <1 (0.23 and 0.93, respectively) that are typical of formation brines associated with a marine source (Warner et al. 2012; Vengosh 2014).

Overall, groundwater samples from this study area are composed of: (1) a low-salinity, Ca-Mg-HCO<sub>3</sub> water (defined as Type A); (2) a low-salinity, Na-HCO<sub>3</sub>-Cl type (Type B); and (3) a relatively high-salinity, Na-Cl water (Type C) (Figure 5). Type A water (n = 8)was found in the shallow wells (depth < 100 m) used for drinking-water or agricultural irrigation, and characterized by neutral pH (7.1 to 7.9) and oxidizing conditions (ORP > 24 mV). Types B and C water, including the deep boreholes and springs, were both alkaline (pH > 8.0) with significantly lower DIC (<250 mg/L, p<0.01) and Mg (<4.0 mg/L, p<0.01), and higher Na (>57 mg/L; p < 0.05) concentrations relative to Type A groundwater (Figures 4 and 5). Types B and C were also significantly elevated in F (2.2 to 16.1 mg/L, p < 0.01), Li (0.05 to 3.7 mg/L, p < 0.01), and B (0.4 to 7.2 mg/L, p < 0.01) compared to the Type A water (Table 2).

Three of the shallow groundwater wells contained elevated TDS (>800 mg/L) characterized by a distinctive Ca-Na-HCO<sub>3</sub>-Cl composition with pH < 8 that possibly

 Table 2

 Water Chemistry in the Karoo Groundwater<sup>1</sup>

Town	Sample ID	Water Type	Cl (mg/L)	Na/Cl	Br/Cl (×10 <sup>-3</sup> )	Ca (mg/L)	Mg (mg/L)	DIC (mg/L)	F (mg/L)	B (mg/L)	Li (mg/L)	Sr (mg/L)
Florisbad	FLS1	С	1330	0.9	1.3	102	0.1	22	5.7	2.45	0.87	3.45
	FLB5	A/C	136	1.0	2.5	97.5	49.1	444	0.9	0.37	0.07	1.68
Trompsburg	VFB1	С	4080	0.9	2.5	554	0.1	25	3.7	4.38	3.75	14.21
	VFB2	А	12.0	2.3	3.3	37.4	12.8	284	0.6	0.06	0.04	0.48
	VFB4	А	25.6	1.9	2.7	55.4	19.1	324	0.7	0.08	0.04	0.70
Aliwal North	ANS1	С	665	1.0	1.0	99.1	b.d.l	20	4.5	1.10	0.56	1.13
	ANBH1	С	546	1.1	1.0	17.9	1.5	73	3.8	0.69	0.48	0.56
Venterstad	RWB1c	В	26.9	5.8	2.8	22.2	3.2	227	2.5	0.47	0.14	0.56
	RWB5	А	20.2	3.4	3.9	73.4	28.1	465	0.4	0.13	0.04	0.75
	VBB1	В	77.3	2.2	1.9	16.5	3.1	167	3.1	0.42	0.05	0.24
	LRB1	А	48.3	1.4	2.2	108	38.9	585	0.0	0.07	0.05	1.03
	LRB2	А	10.1	4.3	4.1	54.0	19.6	339	0.3	0.05	0.04	0.51
Fort Beaufort	BFB1	В	174	1.4	1.6	4.6	b.d.l	63	16.1	1.03	0.34	0.31
	BFB2	A/C	436	1.1	1.5	81.2	37.1	403	3.4	0.94	0.19	2.31
	RRB1	A/C	524	1.1	1.7	165	71.3	622	1.3	0.36	0.05	2.07
Cradock	CRS1	В	20.9	4.2	1.7	3.4	b.d.l	55	7.0	0.48	0.16	0.06
	DRB4	А	42.3	10.4	2.0	30.0	52.3	764	1.2	0.97	0.02	0.59
Leeu Gamka	WP508	В	76.2	3.4	1.9	37.5	2.6	212	2.2	0.39	0.53	2.38
	WP502	А	24.1	4.0	1.9	39.2	10.2	236	0.9	0.12	0.11	1.70
	WP505	В	91.7	4.3	2.1	23.6	0.5	232	3.7	0.62	0.44	2.19
Merweville	SA1/66	С	3610	0.2	1.7	129	4.0	NaN	5.6	7.19	1.91	13.72
	MWB2	А	103	1.4	2.0	87.3	19.6	347	0.6	0.32	0.10	2.48

<sup>1</sup>Chemical constituents not analyzed are indicated by NaN.

results from mixing between Type A and Type C waters (discussed below) (Figure 3). These apparently Type A/C mixed groundwater samples are found in the Florisbad (FLB5) and Fort Beaufort boreholes (RRB1 and BFB2).

F concentrations in all 11 Type B and C water samples exceeded the World Health Organization's drinking-water recommendations of 1.5 mg/L (Table 2). The Type A/C mixed water from the Fort Beaufort wells (BFB2 and RRB1) with elevated salinity (Cl > 200 mg/L) were the only shallow groundwater wells with F > 1.5 mg/L. F was positively correlated to B ( $r^2 = 0.86$ , p < 0.01) and negatively correlated to Mg  $(r^2 = 0.76, p < 0.01)$  and DIC  $(r^2 = 0.76, p < 0.01;$ Figure 6). B concentrations correlated with Cl ( $r^2 = 0.77$ , p < 0.01) and concentrations exceeding 1 mg/L were primarily found in the highly saline Type C deep waters and springs. The only exception was one of the Type B artesian wells (BFB1; B = 1.02 mg/L). All the shallow groundwater wells used for agriculture had B concentrations less than 1 mg/L (up to 0.97 mg/L).

Hydrogen and oxygen stable isotope values varied between -41.6 and +4.3% for  $\delta^2$ H and between -6.7 and +0.7% for  $\delta^{18}$ O (Table 3). A comparison to the global meteoric water line (GMWL) with a slope of 8 and a local meteoric water line with a slope  $\sim 6.2$  (Miller et al. 2015) shows that all of the shallow Type A groundwater data plot along a lower slope than the GMWL (Figure 6). The Type B and C groundwater had lower  $\delta^2$ H and  $\delta^{18}$ O values with a slope close to the GMWL. The  $\delta^{18}$ O values were weakly correlated with Cl ( $r^2 = 0.40$ , p < 0.05) and displayed more negative values in the more saline waters.

Sr concentrations correlated to Cl  $(r^2 = 0.93,$ p < 0.01) and Ca ( $r^2 = 0.73$ , p < 0.01). Sr isotope ratios (87Sr/86Sr) in the groundwater varied from 0.7089 to 0.7718 (Table 3), with the highest radiogenic value in the high-salinity deep borehole sample (VFB1). The spring from Florisbad (FLS1) also yielded a highly radiogenic ratio of 0.7530 and the shallow Type A/C mixed groundwater in Florisbad (FLB5) was the only freshwater sample with  ${}^{87}$ Sr/ ${}^{86}$ Sr > 0.715. Other groundwater samples had less radiogenic  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios (0.7107 ± 0.0009; Figure 8). Sr isotope ratios correlated inversely to DIC  $(r^2 = 0.52, p < 0.05)$  and Mg  $(r^2 = 0.57, p < 0.05)$  when excluding the radiogenic samples with  ${}^{87}$ Sr/ ${}^{86}$ Sr > 0.715. Overall, higher <sup>87</sup>Sr/<sup>86</sup>Sr ratios were found in the Type C saline springs and deep boreholes, while the lowest values were found in the two shallow Type A/C mixed groundwater samples from Fort Beaufort (BFB2 and RBB1), yet these differences were not statistically significant.

B concentrations were positively correlated with Cl concentrations, and negatively correlated to Mg  $(r^2 = 0.53, p < 0.01)$  and DIC  $(r^2 = 0.57, p < 0.01)$  concentrations. B/Cl (molar) ratios in the groundwater were high compared to the seawater ratio (B/Cl =  $0.8 \times 10^{-3}$ ), with the highest values found in the Type B water (B/Cl > 0.17) and lowest values in the Type C saline springs (mean =  $5 \times 10^{-3}$ ). B isotope ratios ( $\delta^{11}$ B) were significantly and positively correlated to Mg ( $r^2 = 0.72$ , p < 0.01) and DIC ( $r^2 = 0.61$ , p < 0.05). Type B freshwater was marked by low  $\delta^{11}$ B values (5.4 to 9.3%c), which were significantly lower than the Type A freshwater



Figure 3. Concentration of chloride (Cl) vs. bromide (Br [A]; and sodium (Na) [B], in water samples from the Karoo Basin. Both axes for all figures are plotted on log scale. The seawater ratio for Br/Cl and Na/Cl are displayed as solid black lines in (A) and (B). The majority of samples display a significant correlation between Br, Na, and other brine components (not shown) with Cl, indicating mixing between a regional brine and relatively fresh meteoric water.

(26.9 to 35.1‰; Figure 8). Type C waters had intermediate values ranging from 9.5 to 29.9‰. The shallow Type A/C mixed waters had  $\delta^{11}$ B values that spanned a similar range (19.9 to 35.1). A negative relationship was observed between B/Cl and  $\delta^{11}$ B for all samples excluding the fresh Type A waters ( $r^2 = 0.66$ , p < 0.01; Figure 8).

Methane was detected in all samples with concentrations ranging from b.d.l. (0.01 ccSTP/kg) to 39.1 ccSTP/kg (Table 4). The upper limit approaches the saturation conditions for CH<sub>4</sub> in shallow groundwater (~40 ccSTP/kg). CH<sub>4</sub> concentrations exceeding 14 ccSTP/kg (n = 4) were found in the Na-Cl Type C or Type A/C mixed saline waters. There was a significant, positive correlation of CH<sub>4</sub> with Cl ( $r^2 = 0.81$ , p < 0.01) and <sup>4</sup>He ( $r^2 = 0.63$ , p < 0.01) when excluding the deep borehole sample (VFB1) (Figure 9). Borehole VFB1 contained the highest Cl content (4080 mg/L), but only 1.0 ccSTP/kg of CH<sub>4</sub>. We were unable to obtain a gas sample or field parameters from the SA1/66 deep borehole site. Carbon isotopes of methane ( $\delta^{13}$ C-CH<sub>4</sub>) ranged from -74.61



Figure 4. Concentration of magnesium (Mg) and dissolved inorganic carbon (DIC) vs. pH in water samples from the Karoo Basin. Types B and C waters are distinguished by low Mg and DIC that are explained by water-rock interactions rather than mixing between the saline Na–Cl and fresh Ca–HCO<sub>3</sub> waters.

to -49.54% throughout the study area and were also positively correlated to CH<sub>4</sub> ( $r^2 = 0.67$ , p < 0.01) and <sup>4</sup>He ( $r^2 = 0.65$ , p < 0.01) concentrations (Eymold et al. 2018).

The <sup>4</sup>He concentrations ranged from near air saturated water (ASW) values ( $\sim 48 \times 10^{-6}$  ccSTP/kg) up to 483,493 × 10<sup>-6</sup> ccSTP/kg (or approximately 1.07 × 10<sup>4</sup> times atmospheric levels) (Table 4). Measured <sup>3</sup>H concentrations ranged from b.d.l. to 3.5 tritium units (T.U.), suggesting mixing between young (Modern) and older (Pre-Modern) waters in the local groundwater system (Table 4). All except one sample contained detectable <sup>3</sup>H concentrations.

In the samples with radiogenic <sup>4</sup>He in-growth model residence times of less than 100 years, we also determined the <sup>3</sup>H-<sup>3</sup>He ages, following standard approaches (Solomon et al. 1993, 1995). For the remaining samples, ages were determined using the radiogenic <sup>4</sup>He in-growth mean residence time model described previously (Darrah et al. 2015a; Harkness et al. 2017a). In order to calibrate the radiogenic <sup>4</sup>He in-growth model, we measured the diffusional rates for <sup>4</sup>He from aquifer rocks following standard methods (Darrah et al. 2015a; Harkness et al. 2017a, 2017b). Our model assumes a 25% aquifer porosity, a 1-D



Figure 5. Ternary diagrams of Ca vs. Mg vs. Na (cations) and  $HCO_3$  vs.  $SO_4$  vs. Cl (anions) in Karoo Basin groundwater. The majority of samples appear to fall along a mixing line between two groundwater types: (1) a fresh groundwater type with a Ca-Mg-HCO<sub>3</sub> composition and (2) a saline water type with a Na-Cl composition. A subset of samples has distinct Na-Ca-HCO<sub>3</sub> water type that is not explained by mixing alone.



Figure 6. Concentrations of fluoride (F) vs. dissolved inorganic carbon (DIC) (A) and boron (B) (B), in water samples from the Karoo Basin. F correlates negatively with DIC  $(r^2 = 0.76, p < 0.01)$  and Mg  $(r^2 = 0.76, p < 0.01;$  not shown) and positively with B  $(r^2 = 0.86, p < 0.01)$  suggesting waterrock interactions as a mechanism for F enrichment in the groundwater samples.

radial diffusion model, and the measured average initial [<sup>4</sup>He] of 22,340  $\mu$ cc/kg (±1946  $\mu$ cc/kg) from the outcrop samples following standard methods (Darrah et al. 2015a, 2015b; Moore et al. 2018; Harkness et al. 2017a). From these measurements, we calculated an average <sup>4</sup>He accumulation rate of 0.402  $\mu$ cc/kg/year as compared to the standard steady-state estimate of approximately 0.500  $\mu$ cc/kg/year.

The maximum estimated mean residence times from either  ${}^{3}\text{H}{-}{}^{3}\text{H}\text{e}$  or the modeled in-growth of  ${}^{4}\text{H}\text{e}$  are reported in Table 4. The mean residence time estimates ranged from 13.2 to  $1.2 \times 10^{6}$  years (Table 4). These apparent ages span from recent recharge of Modern meteoric water (i.e., post-1950) up to Pre-Modern groundwater that was recharged during the mid-Pleistocene. We performed a crude sensitivity analysis by comparing these age estimates using a conservative approach that attempts to account for the potential for mixing of exogenous fluids or two-phase gas partitioning, which would preferentially enrich <sup>4</sup>He. This approach estimates a 33 to 143% difference in the mean residence time ages, ranging from 15.7 to  $7.45 \times 10^5$  years, when compared to the standard model that assumes a purely piston flow. Importantly, the presence of <sup>3</sup>H in all but one sample (BFB1) suggests that even waters with apparently old mean residence times (up to at least  $7.45 \times 10^5$  years) actually reflect the mixture of Modern and Pre-Modern waters near the surface.

The mean residence time of Type A waters ranged from 13.2 to  $2.35 \times 10^3$  years. On average, Type A waters were significantly younger than the other water types (mean =  $8.8 \times 10^2 \pm 6.62 \times 10^2$  years) for the <sup>4</sup>He in-growth mean residence time method and the model that attempts to correct for exogenous <sup>4</sup>He  $(7.80 \times 10^2 \pm 5.46 \times 10^2 \text{ years})$ . By comparison, the mean residence time of Type B waters ranged between 33.1 and  $1.55 \times 10^5$  years with an average of  $5.11 \times 10^4 \pm 5.02 \times 10^4$  years with the in-growth method, and  $4.03 \times 10^4 \pm 4.09 \times 10^4$  years for the model that attempts to correct for exogenous <sup>4</sup>He. Type C waters were significantly older on average and displayed mean residence times that ranged between  $1.20\times 10^5$  and  $1.20\times 10^6$  years with an average of  $7.74 \times 10^5 \pm 4.00 \times 10^5$  using the in-growth method and  $3.70 \times 10^5 \pm 2.70 \times 10^5$  years for the model that attempts to correct for exogenous <sup>4</sup>He. The three shallow mixed Type A/C wells had ages between  $1.87 \times 10^4$ and  $2.10 \times 10^5$  years, respectively, using the in-growth method, and  $1.01 \times 10^4$  and  $9.54 \times 10^4$  years, respectively, using the model that attempts to correct for exogenous <sup>4</sup>He. The age ranges for these mixed wells

 Table 3

 Water Isotope Ratios in Karoo Groundwater<sup>1</sup>

Town	Sample ID	Water Type	δ <sup>18</sup> O (‰)	δ <sup>2</sup> H (‰)	δ <sup>11</sup> B (‰)	<sup>87</sup> Sr/ <sup>86</sup> Sr
Florisbad	FLS1	С	-5.8	-37.7	23.2	0.753937
	FLB5	A/C	-3.6	-21.5	32.9	0.718000
Trompsburg	VFB1	С	-6.5	-39.1	29.9	0.771772
	VFB2	А	-3.7	-29.0	NaN	0.710670
	VFB4	А	-4.4	-28.1	NaN	0.710670
Aliwal North	ANS1	С	-5.6	-37.0	9.5	0.712076
	ANBH1	С	-6.0	-36.7	15.2	0.712105
Venterstad	RWB1c	В	-4.9	-30.9	6.5	0.710202
	RWB5	А	-4.4	-28.3	NaN	0.710450
	VBB1	В	-4.7	-32.5	5.9	0.710572
	LRB1	А	-3.3	-21.1	NaN	0.710147
	LRB2	А	-4.2	-27.3	NaN	0.710036
Fort Beaufort	BFB1	В	-6.0	-41.6	5.4	0.710050
	BFB2	A/C	-4.3	-25.5	19.9	0.708925
	RRB1	A/C	-4.0	-25.7	35.1	0.709625
Cradock	CRS1	В	-6.7	-41.5	NaN	0.709850
	DRB4	А	-1.7	-12.3	32.9	0.712325
Leeu Gamka	WP508	В	-4.3	-29.9	8.9	0.711582
	WP502	А	0.7	4.3	NaN	0.711599
	WP505	В	-4.2	-29.8	9.3	0.711169
Merweville	SA1/66	С	NaN	NaN	23.9	NaN
	MWB2	А	-4.8	-30.6	26.9	0.710562

<sup>1</sup>Isotope Ratios not measured indicated by NaN.

indicate varying contributions of older, saline water into the shallow aquifer in these areas.

#### Discussion

Our data provide an opportunity to characterize the baseline water quality in the Karoo Basin. The groundwater chemistry in the region presents a wide range of salinities and distinct water characteristics, which suggests that several independent processes control the shallow groundwater geochemistry. Although there is limited geochemical data on the deep formation water from the underlying gas-rich Whitehill Formation, previous studies have shown that formation waters from hydrocarbon-rich shales tend to be highly saline due to their marine origin (Vengosh 2014; Vengosh et al. 2014). The presence of naturally occurring saline groundwater with elevated CH<sub>4</sub> is common in shallow aquifers that reside within shale gas basins (Warner et al. 2012; Darrah et al. 2015a, 2015b; Harkness et al. 2017b). For these reasons, we hypothesize that the migration of CH<sub>4</sub>-rich, saline waters from deeper formations in the Karoo Basin could complicate the delineation of potential geogenic and anthropogenic contamination from future shale gas development in South Africa.

#### Sources of Shallow Groundwater in the Karoo

One proposed natural source for the observed relationship between  $CH_4$  and Cl (Figure 9), which has also been observed in other shale gas basins (e.g., groundwater overlying the Marcellus and Barnett shales), includes the migration of a hydrocarbon-rich brine from source rocks to shallow aquifers (Warner et al. 2012; Jackson et al. 2013; Darrah et al. 2014, 2015a, 2015b; Harkness et al. 2017b). In this scenario, it has been proposed that following the migration of hydrocarbon-rich brines, hydrocarbon gas and salt inflows are diluted by meteoric water at shallow depths. This multi-stage process leads to the paradoxical observation of Modern <sup>3</sup>H-active water in the presence of highly saline, CH<sub>4</sub>-rich groundwater with extremely long apparent mean residence times (Darrah et al. 2015a, 2015b; Harkness et al. 2017b). To test this hypothesis, we have employed a suite of geochemical tracers capable of delineating deeper sources of groundwater and mixing processes.

Stable isotopes of water provide one tracer capable of evaluating different sources of groundwater. The stable isotope values of shallow groundwater samples in this study deviate from the GMWL (Figure 3). These trends are commonly observed in groundwater recharge in arid environments (Gat and Issar 1974; Gat 1996). In contrast, the apparently deeper sources of saline groundwater (Type C) have lower  $\delta^{18}$ O and  $\delta^{2}$ H values with relationships that fall closer to the GMWL slope ( $\sim$ 8), rather than along an evaporation slope typically found in deep evaporative brines (Sofer and Gat 1975). These results indicate that meteoric water with a GMWL signature diluted the relatively high salinity end-member and reduced the original salinity of the formation waters. This suggests an open system in which freshwater recharge mixed with a Pre-Modern (likely with a mean residence time of >1,000,000 years) saline groundwater source that is



Figure 7. The stable hydrogen isotopic composition in water  $(\delta^2 H - H_2 O)$  vs. the stable oxygen isotopic composition in water  $(\delta^{18}O - H_2 O)$  of springs (squares) and boreholes (circles) from the Karoo Basin. The bold line denotes the global meteoric water line (GMWL) modeled after Craig (1961) and the dashed line denotes the local meteoric water for the Karoo basin with slope approximately 6.2 (Miller et al. 2015; Mahed 2016). The Karoo Basin samples show evidence of evaporation consistent with recharge in an arid environment as opposed to the addition of brines. The Types B and C waters have more depleted oxygen and hydrogen isotope ratios that are characteristic of older waters.

consistent with a seawater geochemical signature. The difference between the shallow groundwater with higher  $\delta^{18}$ O and  $\delta^2$ H and lower slope and the deep groundwater with both lower  $\delta^{18}$ O and  $\delta^2$ H and a slope approaching the GMWL suggests that the deep formation water was diluted with fossil groundwater recharged in wetter environmental conditions relative to the modern arid conditions that dominate modern recharge in the Karoo Basin.

Major dissolved ion chemistry provides another indication that helps to delineate the different sources of groundwater, as well as water-rock interactions in the subsurface. Overall, the groundwater analyzed in the Karoo Basin represents a mixture of  $Ca-Mg-HCO_3$ (Type A) and Na-Cl (Type C) type waters. The Type A groundwater samples are found in shallow wells across our study area with the exception of the Aliwal North region (Figure 1), and are typical of shallow



Figure 8. Isotope ratios of strontium ( $^{87}$ Sr/ $^{86}$ Sr) vs. Sr/Ca ratios (A) and of boron ( $\delta^{11}$ B) vs. B/Cl ratios (B) in Karoo Basin groundwater. The highly radiogenic  $^{87}$ Sr/ $^{86}$ Sr values in the saline deep borehole, VFB1, and in the Florisbad area are shown in the insert.

groundwater originated from the recharge of modern meteoric water. The Type C groundwater dominates both deep boreholes and was identified in a subset of thermal springs and shallow boreholes from the Florisbad and Aliwal North areas. The Type C groundwater samples displayed elevated pH, temperatures, and salinities. The resulting highly saline, Type C groundwater has a Na–Cl composition that is typical to saline formation waters originated from seawater. The Br/Cl ratios near or greater than the seawater ratio indicate a seawater (or evaporated seawater) source, in which the solute ratios have been maintained even after significant dilution from fossil meteoric water.

The relatively enriched  $\delta^{11}$ B values in Type C water further support a marine source. Yet, higher B/Cl (0.005) and lower  $\delta^{11}$ B values (9.5 to 23.2%) in Type C water compared to seawater ( $\delta^{11}$ B of 39% and B/Cl=0.0008) imply modifications of the original B isotope ratios through water-rock interactions with a depleted <sup>11</sup>B source. Potentially, the water-rock interactions were intensified by the elevated temperatures that characterize the deep water; numerous studies have shown that geothermal waters are characterized by high B and low  $\delta^{11}$ B values that reflect mobilization of B from the rock sources to the aquatic phase (Williams et al. Table 4Gas Chemistry in Karoo Groundwater<sup>1</sup>

Town	Sample ID	Water Type	CH4 (ccSTP/kg)	δ <sup>13</sup> C-CH <sub>4</sub> (%)	Tritium (T.U.)	<sup>4</sup> He (×10 <sup>-6</sup> ccSTP/L)	<sup>4</sup> He/ <sup>20</sup> Ne	Terrigenic <sup>4</sup> He	Release Model Ages (Years)	Exo Release Model Ages (Years)
Florisbad	FLS1 FLB5	C A/C	32.0 3.40	-50.90 -51.60	1.6 1.3	$4.83 \times 10^5$ $7.57 \times 10^3$	1016.8 22.1	$4.83 \times 10^{5}$ $7.52 \times 10^{3}$	$\begin{array}{c} 1.20\times10^{5}\\ 1.87\times10^{4} \end{array}$	$3.99 \times 10^5$ $1.01 \times 10^4$
Trompsburg	VFB1 VFB2 VFB4	> > C <	1.21	-65.65 -72.14 NoN	0.1 1.0	$4.06 \times 10^{5}$ $1.86 \times 10^{2}$ $4.02 \times 10^{10}$	3346.4 1.2 0.3	$4.06 \times 10^{5}$ $1.43 \times 10^{2}$ $5.30 \times 10^{0}$	$1.01 \times 10^{6}$ $3.55 \times 10^{2}$ $1.22 \times 10^{1}$	$7.45 \times 10^{5}$ $5.07 \times 10^{2}$ $1.57 \times 10^{1}$
Aliwal North	ANS1 ANBH1	αυυ	20.2 35.3 39.1	-64.98 -65.61	0.5 0.1	$4.02 \times 10$ 2.35 × 10 <sup>5</sup> 1.21 × 10 <sup>5</sup>	654.6 229.0	$2.35 \times 10^{5}$ $1.21 \times 10^{5}$	$5.85 \times 10^{5}$ $3.00 \times 10^{5}$	$2.15 \times 10^{5}$ $2.15 \times 10^{5}$ $1.20 \times 10^{5}$
Venterstad	RWB1c RWB5	A B	2.91	-50.68 NaN	0.5	$3.96 \times 10^4$ 8.71 × 10 <sup>1</sup>	136.4 0.4	$3.96 \times 10^4$ $4.41 \times 10^1$	$9.85 \times 10^4$ $1.10 \times 10^2$	$6.07 \times 10^4$ 7.53 × 10 <sup>1</sup>
	VBB1 LRB1 LRB2	A A B	5.31 2.24 1.61	-49.54 -71.49 -73.14	0.6 0.5 1.2	$6.75 \times 10^{3}$ $6.23 \times 10^{1}$ $9.80 \times 10^{2}$	21.0 0.5 4.9	$6.71 \times 10^{3}$ $1.94 \times 10^{1}$ $9.37 \times 10^{2}$	$1.70 \times 10^4$ $4.83 \times 10^1$ $2.33 \times 10^3$	$9.48 \times 10^4$ $6.87 \times 10^1$ $2.20 \times 10^3$
Fort Beaufort	BFB1 BFB2 RRB1	B A/C A/C	0.01 23.5 3.67	NaN -55.36 -55.88	0 4.0 0.5	$7.12 \times 10^{1}$ $8.45 \times 10^{4}$ $1.02 \times 10^{4}$	0.2 252.0 60.8	$2.83 \times 10^{1}$ $8.45 \times 10^{4}$ $1.01 \times 10^{4}$	$7.04 \times 10^{1}$ $2.10 \times 10^{5}$ $2.51 \times 10^{4}$	$3.31 \times 10^{1}$ $9.54 \times 10^{4}$ $2.74 \times 10^{4}$
Cradock	CRS1 DRB4	A B	0.22 3.07	-72.11 -70.14	0.5 3.1	$4.12 \times 10^{2}$ $9.87 \times 10^{2}$	1.9 3.0	$3.70 \times 10^2$ $9.44 \times 10^2$	$9.18 \times 10^2$ $2.35 \times 10^3$	$8.97 \times 10^2$ $1.62 \times 10^3$
Leeu Gamka	WP508 WP502 WP505	B A B	0.07 1.14 0.27	NaN -74.45 -67.64	0.1 3.5 0.4	$1.41 \times 10^4$ $6.39 \times 10^2$ $6.25 \times 10^4$	78.3 2.4 291.2	$1.41 \times 10^{4}$ $5.96 \times 10^{2}$ $6.25 \times 10^{4}$	$3.51 \times 10^4$ $1.48 \times 10^3$ $1.55 \times 10^5$	$3.79 \times 10^4$ $1.38 \times 10^3$ $1.32 \times 10^5$
Merweville	SA1/66 MWB2	A C	NaN 1.05	NaN -74.61	NaN 1.4	$\underset{1.89\times10^{2\mathrm{s}}}{\mathrm{NaN}}$	NaN 0.9	$\underset{1.64\times10^{2}}{\text{NaN}}$	NaN 3.64 $ imes$ 10 <sup>2</sup>	$\begin{array}{c} \mathrm{NaN}\\ 3.85\times10^2 \end{array}$

<sup>1</sup>Gas constituents not analyzed are indicated by NaN.



Figure 9. Methane (CH<sub>4</sub>) vs. chloride (Cl) (A), carbon isotopes of methane ( $\delta^{13}$ C–CH<sub>4</sub>) (B), helium (<sup>4</sup>He) (C), and mean residence times (D) calculated as the average between the <sup>4</sup>He in-growth method and model that attempts to correct for exogenous <sup>4</sup>He in water samples from the Karoo Basin. CH<sub>4</sub> concentrations correlated positively with Cl ( $r^2 = 0.81$ , p < 0.01) indicating a saline source of hydrocarbon gases in the shallow groundwater.  $\delta^{13}$ C–CH<sub>4</sub> values range from biogenic (<-60%c) in low CH<sub>4</sub> water to thermogenic in CH<sub>4</sub>-rich water (>-60%c). Some of the CH<sub>4</sub>-rich samples have isotopic values indicative of mixing between biogenic and thermogenic water that then migrated to the shallow groundwater. There is a positive correlation between CH<sub>4</sub> and <sup>4</sup>He ( $r^2 = 0.63$ , p < 0.01). The higher <sup>4</sup>He concentrations in the CH<sub>4</sub>-rich water indicate migration of an exogenous source of CH<sub>4</sub> into shallow water with older, saline water.

2001a, 2001b). The higher B/Cl and lower  $\delta^{11}$ B clearly suggest more intense water-rock interactions in the Type B groundwater, which is likely related to a different source (low salinity) and longer transport times. Type A groundwater had lower B concentrations and higher  $\delta^{11}$ B values, which would reflect preferential removal of <sup>10</sup>B during adsorption of B onto clay minerals in the aquifer, a common phenomenon in shallow aquifers (Vengosh 2014).

The resulting saline, Type C groundwater, which features relatively depleted  $\delta^{18}$ O and  $\delta^2$ H values and extremely elevated amounts of <sup>4</sup>He, likely stems from an exogenous source of relatively old groundwater that migrated into the shallow aquifers in these areas (Miller et al. 2015; Swana et al. 2015; Eymold et al. 2018). Further, the presence of exogenous fluids elucidates the potential pathways that allow for the migration of the deep formation waters to the shallow aquifers (Figure 3). Based on the coexistence of high salinity groundwater and the

intense zones of fracturing located near the intrusion of the dolerite sills, we hypothesize that the fracture zones near dolerite sills have provided preferential pathways for the transmission of deeper, saline waters to the shallow aquifers. The presence of springs and artesian boreholes with depleted  $\delta^{18}$ O and  $\delta^{2}$ H values and highly elevated <sup>4</sup>He concentrations indicates a significantly longer mean groundwater residence time ages for fluids located near dolerite sills or within a dolerite ring structures, which further supports this hypothesis.

The <sup>87</sup>Sr/<sup>86</sup>Sr ratios in groundwater throughout the study area can provide further information about the sources of solutes from water-rock interactions within the formation lithologies. Highly radiogenic ratios >0.715 were found in the deep borehole from Trompsberg, VFB1, and the groundwater in the Florisbad area, FLS1 and FLB5. These samples were collected from the only area where the Ecca Group underlies the surficial sediments and the basement rocks are present at shallower depths

(Figure 1). The higher Sr isotope ratio in the shallow Type A/C mixed groundwater well (FLB5) was associated with higher Cl (135 mg/L) than the other freshwater wells, high Br/Cl  $(2.5 \times 10^{-3})$ , and lower Na/Cl (0.94)similar to the saline spring at this site  $(1.3 \times 10^{-3})$  and 0.93, respectively). This observation indicates possible influences from the deep saline water, albeit with smaller contributions, in the FLB5 well. Outside of the Florisbad area, the <sup>87</sup>Sr/86</sup>Sr values were not correlated with Cl, indicating that the Sr isotopes do not mimic the original saline water source in the Karoo groundwater. Instead, <sup>87</sup>Sr/<sup>86</sup>Sr values observed in the groundwater mimic the isotopic range reported for Karoo Permian sediments in the shallow lithologies (De Villiers et al. 2000). Sr isotope ratios correlated negatively with both DIC ( $r^2 = 0.52$ , p < 0.02) and Mg ( $r^2 = 0.57$ , p < 0.01) concentrations. These relationships suggest that retention of DIC and Mg in the alkaline water are occurring in formations with more radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr values, consistent with the expected isotope ratio of the felsic volcanics in the basement rocks. Water-rock interactions with the mafic dolerites (0.7046 to 0.7094) result in overall lower <sup>87</sup>Sr/<sup>86</sup>Sr values in the migrated Type C and B waters compared to the deep formation water, but are still more radiogenic that the shallow freshwaters with <sup>87</sup>Sr/<sup>86</sup>Sr values similar to Karoo sedimentary rocks ( $\sim 0.7125$ ).

The groundwater geochemistry and residence time models support mixing of the deep, saline Type C groundwater into the shallow aquifers in some of the study regions. The shallow Type A/C mixed wells displayed relatively high Cl (135.6 to 524 mg/L) and Br/Cl ratios  $(\text{mean} = 1.6 \times 10^{-3})$  as compared to the other Type A waters (Figure 3). The three saline groundwater samples fall along the Br-Cl mixing line between the deep saline water and the fresh shallow water (Figure 3). The mixing of deep saline water into the shallow aquifers results in water geochemistry with overall lower pH (<8), and higher Ca/Cl (mean = 0.36), Mg/Cl (0.29), and DIC/Cl (0.66) than the migrated Type C saline waters observed in springs or artesian wells (pH > 8,Ca/Cl = 0.08, Mg/Cl = 0.001, and DIC/Cl = 0.02). These mixed Type A/C samples displayed mean residence times between  $1.01 \times 10^4$  and  $2.10 \times 10^5$  years, further indicating mixing of an older, saline source into the shallow wells. The shallow Type A/C mixed wells in the Florisbad area (FLB5) also exhibited an elevated <sup>87</sup>Sr/<sup>86</sup>Sr of 0.71837. While this value is not nearly as radiogenic as the saline spring (0.75394) or deep borehole (0.77177) in Florisbad, it does indicate an overall influence of more radiogenic groundwater in this region.

The two mixed samples from the Fort Beaufort areas (BFB2, RBB1) had the lowest <sup>87</sup>Sr/<sup>86</sup>Sr ratios observed in the groundwater, with values close to the ratio in modern seawater (0.7093). These lower values point to additional water-rock interactions that increased Na/Cl, but lowered <sup>87</sup>Sr/<sup>86</sup>Sr ratios, possibly from interactions with the Karoo basalts that have lower <sup>87</sup>Sr/<sup>86</sup>Sr values (0.7046 to 0.7094) during migration from depth (De Villiers et al. 2000). The shallow Type A/C mixed waters

show how groundwater geochemistry can vary depending on the subsurface dynamics and source waters in specific locations within the Karoo Basin.

B elemental and isotopic ratios further constrain the ambiguous samples that display a mixture between Type A/C waters. The B/Cl ratios  $(7 \times 10^{-3})$  and  $\delta^{11}$ B values (19.9%) in one of the Fort Beaufort wells (BFB2) mimic the values found in the saline Type C water (mean =  $5 \times 10^{-3}$  and 20.3%, respectively). The other groundwater well (RBB1) has higher  $\delta^{11}B$  (35%) and lower B/Cl  $(2 \times 10^{-3})$ , which could be derived from preferential adsorption of the lighter B isotope, causing higher  $\delta^{11}B$  and lower B/Cl values as the high B water migrated into the fresh groundwater. The saline water likely mixed into the shallow groundwater over a longer period of time, which allowed for more waterrock interactions in addition to dilution; these processes altered the chemistry from those observed in the springs. The mixing of high salinity water from depth into the shallow aquifers produced water geochemistry that is distinct from migrated, older saline waters with residence times over  $1.20 \times 10^5$  years that discharge as springs and provides evidence for natural (geogenic) contamination of the shallow aquifers from deep saline brines.

The six Type B springs and boreholes are distinctly different from the deep boreholes and saline springs. The Type B samples are characterized by low salinity (TDS < 1000 mg/L) with low Br and Cl concentrations and pH > 8. However, compared to Type A freshwater samples, they have lower  $\delta^2 H$  and  $\delta^{18} O$  values (-4.0 to -6.7 and -29.8 to -41.5, respectively)(Figure 3), and a wider range of <sup>4</sup>He concentrations (71 to  $62,532 \times 10^{-6}$  ccSTP/kg). The corresponding mean residence times range from Modern (33.1 years) to Pre-Modern  $(1.55 \times 10^5 \text{ years})$  (Eymold et al. 2018). These data suggest either mixing of an older, deeper freshwater source into the Type A shallow groundwater or longer residence times for the Type B groundwater. The pH, Mg, and DIC concentrations in the Type B freshwater are statistically different from the Type A waters, but similar to the saline Type C waters. Type B samples were also collected near dolerite intrusions, indicating possible natural pathways for migration of these waters from greater depths. The pH, Mg, and DIC anomalies in these Type B samples are likely due to similar water-rock interactions that the deep saline waters experience at depth or during migration to the shallow aquifer.

The correlation between high pH and peculiarly low levels of Mg and DIC suggests water-rock interactions that consume Mg and DIC, while releasing hydroxide (OH<sup>-</sup>) to the residual water (Figure 4) (Swana et al. 2016). Weathering of silicate minerals such as olivine, which is highly abundant in the dolerite rocks, is known to catalyze these types of reactions (Matter and Kelemen 2009; Olsson et al. 2012). CO<sub>2</sub> reactions with olivine would lead to initial increases in Mg and HCO<sub>3</sub> in groundwater. When the concentrations of these components exceed mineral saturation levels, magnesite (MgCO<sub>3</sub>) is precipitated, leaving a paucity of Mg and DIC. Although this scenario would require high  $CO_2$  fluxes, one would expect elevated  $CO_2$  to be associated with the intrusion of the dolerites throughout this region. In essence, this process mimics a natural carbon sequestration process.

#### **Deep Groundwater Proxies for Produced Water**

The two deep boreholes provide the best insight into the geochemistry of deep waters in the Karoo Basin. The deep groundwater is brackish (Cl from 3600 to 4080 mg/L) with a Type C Na-Cl water type. The Br/Cl ratios are higher than the seawater ratio of  $1.5 \times 10^{-3}$ and Na/Cl ratios are lower than 1, which are a typical of deep formation waters from a marine source (Warner et al. 2012; Vengosh 2014). However, the fluids produced from these two boreholes were sourced from two different formations, and both boreholes produce fluids from beneath the target shale formations in the Ecca Group. Although the waters are not directly drawn from the shale formations, the geochemistry of these two samples indicates a seawater source, which is likely consistent with the source of formation waters in the overlying Ecca Group.

VFB1, the shallower well (1434 m) was drilled to metamorphosed felsic basement rocks, while the SA1/66 borehole is deeper (4175 m) and draws from the Dwyka Group made up of late Carboniferous glacial till deposits. While both samples are composed of a Na-Cl water type, VFB1 had higher TDS, Br/Cl, Na/Cl, Ca/Cl, and SO<sub>4</sub>/Cl ratios, but lower Sr/Ca and B/Cl ratios. VFB1 has likely experienced a greater degree of evaporation that would increase TDS and Br/Cl ratios (Vengosh 2014), while interactions with the glacial till deposits could enrich the Sr and B concentrations in SA1/66. Both deep boreholes had elevated B isotopes (>20%), which are derived from an enriched marine value of  $\delta^{11}B \sim 39\%$ , and modified by water-rock interactions as indicated by the higher B/Cl ratios compared to seawater. This range of  $\delta^{11}$ B values is similar to produced water from U.S. formation waters in shale gas basins (Williams et al. 2001b, 2015; Warner et al. 2014).

VFB1 had a remarkably radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.77177 that is higher than the range reported previously for shale gas produced waters globally (Chaudhuri 1978; Moldovanyi et al. 1993; Chapman et al. 2012; Warner et al. 2012; Capo et al. 2014; Lauer et al. 2016). The ratio measured in VFB1 is consistent with interactions with felsic igneous rocks and confirms water-rock interaction with the metamorphosed volcanic basement rocks of the Karoo Basin. FLS1 is located in the Florisbad area, where surficial sediments overlie the Ecca Group. The Ecca Group sits on top of the metamorphosed felsic volcanic basement rocks and other acidic Archaen granites and gneisses. The felsic igneous basement rocks in Florisbad are shallower than in all the other areas sampled, suggesting a shorter pathway for migration of thermal fluids from the basement formations into the overlying aquifers. The Sr isotope ratios reported from permeable formations underlying or overlying shale formations in the United States are also radiogenic, with values ranging from 0.7095 to 0.7130 (Chaudhuri 1978; Moldovanyi et al. 1993; Warner et al. 2012; Capo et al. 2014). Therefore, we conclude that Sr isotopes are best used to identify deep waters that have interacted with the basement and migrated from depth to near-surface with little water-rock modifications, as seen in the FLS1 spring with <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.75394.

#### Geochemistry of Naturally Occurring Methane

Elevated concentrations of CH<sub>4</sub> (>14 ccSTP/kg) were only associated with the saline groundwater found in the Type C waters and the more saline Type A/C waters, suggesting that the CH<sub>4</sub> migrated to the shallow subsurface along with the saline groundwater. However, the deep borehole in Trompsburg (VFB1), with unusually high salinity and extremely elevated <sup>4</sup>He concentrations, only had a CH<sub>4</sub> concentration of 1 ccSTP/kg, showcasing the lack of a direct link with elevated amounts of Cl (Figure 7). As discussed elsewhere in this issue, these processes may be related to secondary hydrocarbon degradation (Eymold et al. 2018).

Sources for hydrocarbon gas within groundwater can be biogenic (microbially produced) or thermogenic, or result from subsurface migration from an exogenous source of biogenic or thermogenic gas (Darrah et al. 2015a, 2015b). CH<sub>4</sub> concentrations and C isotope ratios of CH<sub>4</sub> ( $\delta^{13}$ C-CH<sub>4</sub>) were correlated with <sup>4</sup>He concentrations, indicating an exogenous source of thermogenic CH<sub>4</sub>. The Type A waters with low CH<sub>4</sub> and <sup>4</sup>He concentrations had more depleted  $\delta^{13}C-CH_4$  values (-74.61 to -70.14%) consistent with a biogenic CH<sub>4</sub> source in shallow, fresh groundwater. Type C waters, on the other hand, had higher  $\delta^{13}$ C-CH<sub>4</sub> values associated with higher CH<sub>4</sub> and <sup>4</sup>He concentrations consistent with a thermogenic source. The range of isotope ratios ( $\delta^{13}C-CH_4 = -65.61$ to -50.9%) in the samples with CH<sub>4</sub> > 14 ccSTP/kg suggests a mixture of both biogenic and thermogenic gas in the saline groundwater (Eymold et al. 2018). The Type B waters had a range of isotope ratios between biogenic (-72.11%) and thermogenic (-49.54%), with the more thermogenic signatures found in samples with  $CH_4 > 1$ ccSTP/kg. The isotopic signatures for CH<sub>4</sub> and the presence of quantifiable levels of ethane in the CH<sub>4</sub>-rich water, along with higher <sup>4</sup>He concentrations and residence times, implies a mixture of thermogenic and biogenic gases that was ultimately emplaced in these shallow groundwater (Eymold et al. 2018).

# Water Quality and Potential Human Health Risks in Karoo Groundwater

The migration of deep groundwater presents possible water quality risks for human health and agricultural consumption. If the dolerite intrusions are providing a pathway for mixing of deep formation water into shallow aquifers, interactions with the dolerites may produce some of the distinct geochemistry observed in the migrated water types. Types B and C waters had significantly elevated F concentrations compared to Type A. Dissolved F is usually associated with volcanic rock sources, and alkaline conditions favor dissolution of Frich minerals. While the concentrations of F are much lower than observed in the East African Rift Valley, similar patterns, such as higher F in Na-rich and Mgpoor groundwater, have been observed there (Rango et al. 2009, 2010). Previous studies have pointed toward baseexchange reactions between Na and either Ca or Mg as reactions that can cause the enrichment of F, as well as reactions of DIC and water with volcanic rocks at high pH (Rango et al. 2009, 2010). Interactions of the alkaline Type B and C groundwater with the igneous basement rocks or the dolerite intrusions would promote mobilization of F into the groundwater.

The high F in both the fresh Type B and saline Type C waters that were located in close proximity to dolerite intrusions supports the hypothesis for interactions with dolerites during groundwater transport, rather than interaction with the basement igneous rocks. The strong correlations with Mg, DIC, and B are consistent with exchange reactions or precipitation of MgCO<sub>3</sub> that triggers the release of soluble F and B from the dolerite rocks. The high F concentrations in groundwater with lower  $\delta^{11}$ B values and low F concentrations in the shallow groundwater with enriched  $\delta^{11}$ B values further support interactions with dolerites as the main source of fluoride.

The presence of elevated naturally occurring F and B concentrations in both the springs and artesian boreholes discharging deep water and groundwater wells impacted by mixing with saline water presents potential public health concerns in cases where this groundwater will be used for drinking water or agricultural purposes. This study only sampled a select group of wells and does not address the possible distribution of these geogenic contaminants throughout the Karoo Basin. Future studies should further expand the monitoring of water quality in other areas of the Karoo Basin to evaluate the potential for naturally occurring contaminants to impact human health and to evaluate if these contaminant levels will be affected by the incipient development of unconventional resources. Future studies should also be mindful of the natural contamination found in this baseline study.

# Conclusion

By combing a suite of inorganic and isotope tracers, we have provided information regarding sources of salinity and  $CH_4$  to the pre-drill baseline groundwater quality in the Karoo Basin. The shallow fresh groundwater is a  $Ca-Mg-HCO_3$  water type recharged in the modern arid climate of the Karoo. Deep saline, Na-Cl waters discharge at the surface in springs, but also flow to shallow aquifers used for agriculture and drinking water. The saline water end-member was likely sourced from formation water originated from fossil seawater and diluted with fossil meteoric water recharged under wetter climate conditions. In addition, an older fossil freshwater end-member with chemistry distinct from the shallow modern freshwater and deep, saline water is found in springs and wells throughout the region. The Karoo dolerites produced fractures during intrusion that could provide pathways for migration of deep water. The saline springs, artesian freshwater wells, and mixed groundwater wells were all located within a dolerite ring or near dolerite sills, supporting the hypothesis that the intrusions provide conduits for the upward migration of groundwater from greater depths. The samples with elevated CH<sub>4</sub> concentrations are strongly associated with the Na-Cl end-member. The migration of saline water from depth and the interactions of migrated fluids with volcanic intrusions contribute elevated levels of geogenic contaminants (CH<sub>4</sub>, B, F) to the shallow groundwater. However, both the fresh and saline shallow groundwater found throughout the basin presented relatively high B and Sr isotope signatures with ranges that are similar to the deep formation waters reported in this study and found in shale gas basins in the United States; these similarities may complicate the use of these tracers in attempts to identify contamination from potential future development. The presence of geogenic contaminants and hydrocarbon and isotope ratios similar to those in produced water from shale gas basins in the Karoo groundwater highlights the importance of a comprehensive pre-drill study in areas slated for shale gas exploration.

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