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Research paper

Fluoride concentrations in the arid Namaqualand and the Waterberg groundwater, South Africa: Understanding the controls of mobilization through hydrogeochemical and environmental isotopic approaches

Tamiru Abiye*, Grant Bybee, Joyce Leshomo

School of Geosciences, University of the Witwatersrand, Private Bag X3, P.O.Box Wits, 2050 Johannesburg, South Africa

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ABSTRACT

A comprehensive survey was conducted to understand the high concentration of fluoride in the groundwater systems of Namaqualand and Waterberg regions, as well as its association with the host rock composition in these areas. A variety of hydrogeochemical and environmental isotope methods were applied including major ions, 18-oxygen, 2-hydrogen and 3-hydrogen. Felsic igneous rocks, primarily granites were found to be the primary source of fluoride in the groundwater. This was facilitated by high evaporation processes as a result of the aridity of both regions. The occurrence of thermal groundwater systems, in these areas, was controlled by high geothermal gradient that has facilitated the release of fluoride from minerals under alkaline pH conditions. The results indicate that the concentration of fluoride in cold groundwater of the arid Namaqualand is ≈4 times greater than the fluoride concentration in the thermal groundwater system in the Waterberg region. High fluoride concentration in the groundwater has been related to long residence time of groundwater due to enhanced water-rock interaction process, where the tritium level usually falls below 1.7T.U., indicating substantially long circulation time within the aquifers. Extreme fluoride concentrations (about 38 mg/L) in the Namaqualand groundwater can be linked to the facilitation by high evaporative rates.

1. Introduction

The occurrence of high concentrations of fluoride within the groundwater supply has health impacts for humans exposed to this water for long periods of time (WHO, 1984). In South Africa, communities in the northern and western parts of the country that consume groundwater with high concentration of fluoride have mottled teeth (McCaffrey, 1998; McCaffrey and Willis, 2001; Ncube, 2002). These areas are characterized by an arid and semi-arid climate with erratic rainfall where surface water resources are generally scarce, making groundwater a primary water source for local users. Similarly, in the East African Rift, human exposure to high fluoride concentrations in groundwater was also identified as major health problem (Abiye, 2010a, 2010b). Therefore, as a result of global water quality problems it is essential to conceptualize the spatial distribution of fluoride in water supply, especially in arid regions, in order to design an appropriate water management strategy.

The presence of high fluoride concentrations in groundwater is one of the most important health and geo-environmental related issues in different parts of South Africa. At low doses, fluoride is beneficial to both bone and dental development, while prolonged consumption of high fluoride is also known to damage neurons and the brain, as well as the reproductive system, particularly as the level and period of exposure increases (Whitford, 1997; WHO, 2004; Jacks et al., 2005; Vithanage and Bhattacharya, 2015a, 2015b; Kut et al., 2016). However, drinking water containing fluoride with a concentration of 1 mg/L is considered ideal for dental health of children less than 10 years of age (WHO, 1984, 2004). The WHO guideline for maximum fluoride concentrations in drinking water is 1.5 mg/L. Concentrations above 2 mg/L results in permanently mottled teeth, while concentrations above 4 mg/L can cause skeletal fluorosis (WHO, 1984, 2004). This problem is frequent in the East African Rift (Abiye, 2010b). Studies show that high fluoride content in water can increase the corrosion of pipes leading to high risk of lead accumulation in the blood (Furi et al., 2011). Studies also suggest that ingestion of high concentrations of fluoride is known to cause severe skeletal fluorosis and extreme bone deformity in several parts of the world, such as China (Genxu and Guodong, 2001; Lin et al., 2004), India (Kumar et al., 2001; Jacks et al., 2005; Das et al., 2016), Kenya (Moturi et al., 2002), Israel (Kafri et al., 1989) and Ethiopia (Alemayehu, 2000; Alemayehu et al., 2006; Abiye, 2010a, 2010b; Furi

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* Corresponding author.
E-mail address: tamiru.abiye@wits.ac.za (T. Abiye).

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et al., 2011). Even though groundwater contains high fluoride, different techniques are available for fluoride removal from drinking water (Jacks et al., 2005; Vithanage and Bhattacharya, 2015a, 2015b; Maity et al., 2017). Although the prevalence of dental and skeletal fluorosis in South Africa has been recognized long ago, only a few local studies have been carried out that laid a foundation for fluoride research (McCaffrey, 1993; McCaffrey, 1998; McCaffrey and Willis, 2001; Ncube, 2002).

Many of the world's high-fluoride districts are underlain by igneous and metamorphic rocks, e.g. parts of India, Sri Lanka, Senegal, Ghana, Cameroon, Tanzania, South Africa, in the southern part of South America and Scandinavian regions (Vasak and Kukuric, 2006; Brindha, and Elango, 2011). On the other hand, Plio-Quaternary felsic volcanic rocks have been associated with the high fluoride content in the groundwater system of the East African Rift (Abiye, 2010a, 2010b; Furi et al., 2011). The average fluoride concentration in the crystalline rocks ranges from 100 ppm to over 1000 ppm, owing to the presence of a large proportion of fluoride bearing minerals. In different parts of the world, fluoride concentration in crystalline rock aquifers has been reported to be higher than 0.5 mg/L and up to 40 mg/L (Jacks et al., 2005; Chae et al., 2007; Fantong et al., 2010; Reddy et al., 2010; Vikas et al., 2013). Fluoride-rich groundwater from granitic aquifers has also been reported in India (Saxena and Ahmed, 2001).

Even though South Africa is located on a stable tectonic plate, it is well endowed with thermal springs, which are controlled by the natural geothermal gradients and associated deep faults. A number of thermal springs have been developed for recreational purposes, with facilities including swimming pools, jacuzzis and spas fed by water from thermal springs (Olivier et al., 2008).

Fluoride has long been recognized as a water-related health concern where a number of studies have been conducted mainly focusing on the water quality aspects. However, the main objective of this study is the assessment of the natural variations of fluoride in relation to different hydrogeological and tectonic settings. Here we assess how fluoride concentrations in groundwater are controlled by lithology, hydrogeochemical variables and structures in groundwater of the Waterberg and Namaqualand regions, South Africa (Fig. 1). In this study, a comparative approach was followed where fluoride containing aquifers in the thermal (Waterberg) and cold groundwater systems (Namaqualand) have been assessed to identify the control process for fluoride concentration in groundwater.

2. Geological setting and fluoride occurrence

The occurrence of high fluoride in groundwater has been related to geogenic sources. Among the primary magmatic minerals, biotite and muscovite are known to contain about 1 wt% of Fluoride, while, the Fluoride content is higher in accessory minerals such as fluorapatite (~3.8 wt%), topaz (~11.5 wt%), and fluorite (~48 wt%). On the other hand, minerals such as cryolite may contain up to 54 wt% fluoride (Garcia and Borgnino, 2015). Villiamite (NaF) may contribute considerably to fluoride concentration in groundwater associated with certain peralkaline intrusive bodies, such as the Lovozero Massif in Russia (Kraynov et al., 1969). Fluoride reacts readily with calcium to form CaF_2, which is reasonably insoluble and was found to be an important indicator for fluoride removal from groundwater (Hem, 1985).

Fluoride occurs most abundantly in nature as fluorite (CaF_2), fluorapatite ($3Ca_3P_2C_8CaF_2$), cryolite (Na_3AlF_6), apatite ($Ca_5(PO_4)_3F$), muscovite and biotite, amphiboles $(Ca, Na)_2(Mg,F, Al)_5(Si, Al)_8O_{22}(OH)_2$, topaz ($Al_2SiO_4(OH\text{-}F)_2$) and fluocerite ($X_2OF_4$ (X = Ce, La, Di)) (Pan and Fleet, 2002). Cryolite is less abundant than fluorite in South Africa, while fluorspar is associated with phosphate bearing rocks and it is also widely associated with granite and dolomitic formations (Ncube, 2002).

Studies suggest that the most important geological formation that contains fluoride in the Karoo sediments includes tillites (in the range of 1 mg/L), volcanic rocks and dolerites (in the range of 3 mg/L), granites and gneisses (about 10 mg/L) (Fayazi, 1994). This could suggest the importance of the contribution of deep seated dolerite dykes and granitic intrusion in contaminating the non-fluoride bearing sediments and rocks through hydrothermal activity. In the Karoo sediments, such as shale and sandstone, groundwater was identified with high fluoride content as a result of detrital fluorapatite as the main source (McCaffrey, 1998; McCaffrey and Willis, 2001).

Mineralogically, dolomites and sandstones do not contain fluoride and hence, the presence of fluoride in these rocks can only be attributed to interaction with the thermal water.

McCaffrey (1998) and McCaffrey and Willis (2001) reported that fluorine content of rocks in the Waterberg region is excessively high (Table 1), which guarantees its constant release into the groundwater.

The Pilanesberg Alkaline Complex, to the west of the Waterberg thermal region is characterized by alkaline igneous rocks, and has been mined for fluorite at a small scale (Johnson et al., 2006). The local community largely relies on groundwater that is obtained from the crystalline aquifers, where the mean borehole yield is about 1 L/s and

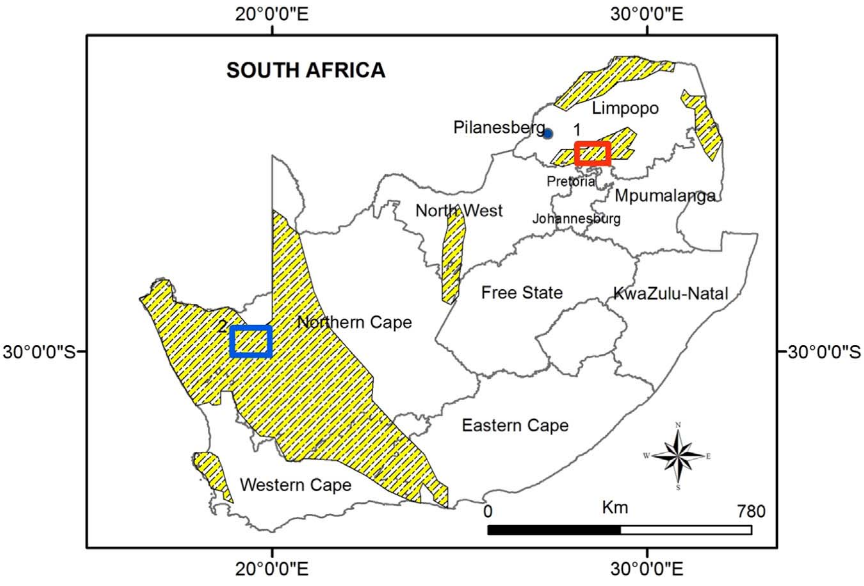

Fig. 1. Location map of the study area. 1: Waterberg thermal region, 2: Namaqualand, and the shaded areas represent spatial distribution of fluoride > 1.5 mg/L in South Africa as reported by McCaffrey (1998).

Table 1
Fluorine content in selected rocks (Source: McCaffrey, 1998 and McCaffrey and Willis, 2001).

Lithology	Fluoride (ppm)
Bushveld granite	163–3350
Amphibolite	104–1400
Granitic gneiss	240–2800
Dolomite	110–400
Rashoop granophyre	127–1060
Rusternberg norite	153–205
Nepheline Syenite (Pillanesberg)	3300–16400
Sandstone	≈900

the mean borehole depth is in the range of 52 m. Springs also discharge at a rate of less than 0.1 L/s. According to McCaffrey (1993), in the Pilanesberg Alkaline Complex, two types of groundwater occurrence were identified, with the shallow circulating low fluoride cold groundwater overlying the deep circulating thermal groundwater (29 °C) enriched with fluoride. The same study also indicated that the pH of groundwater with fluoride concentration of 1.3 mg/L to 79 mg/L ranges from 7 to 10.4, where higher values were associated with high fluoride concentration. High fluoride concentration in groundwater is characterized by electrical conductivity values reaching 1900 µS/cm, with high sodium and low calcium concentrations. High fluoride groundwater, in the Waterberg region (this study) is hosted by the Bushveld Igneous Complex (BIC), which is composed of mafic rocks of the Rustenburg layered suite (dunite and pyroxenite, norite, gabbro and anorthosite), the Lebowa and Nebo granites, the Rashoop granophyre suite and the Rooiberg Group volcanic rocks (basalts, rhyolites, dacites and basaltic andesites) (Johnson et al., 2006). The northern part of the BIC, particularly in the Limpopo Province is dominated by the Lebowa granite overlain by the sandstones of the Karoo Supergroup (Fig. 2). These rocks have been intersected by strike slip faults that brought together the BIC and the Karoo Supergroup sediments. In the southern thermal region of the Limpopo Province (Waterberg region), the main aquifer that hosts thermal water is the Nebo and Lebowa granites that are overlain in parts by the Waterberg Group sandstone. Some thermal springs emerge from the Waterberg sandstone and Karoo sediments with provenance at depth within the granitic aquifer e.g. the Bela Bela thermal zone (Fig. 2). The long-term weathering of rocks and leaching

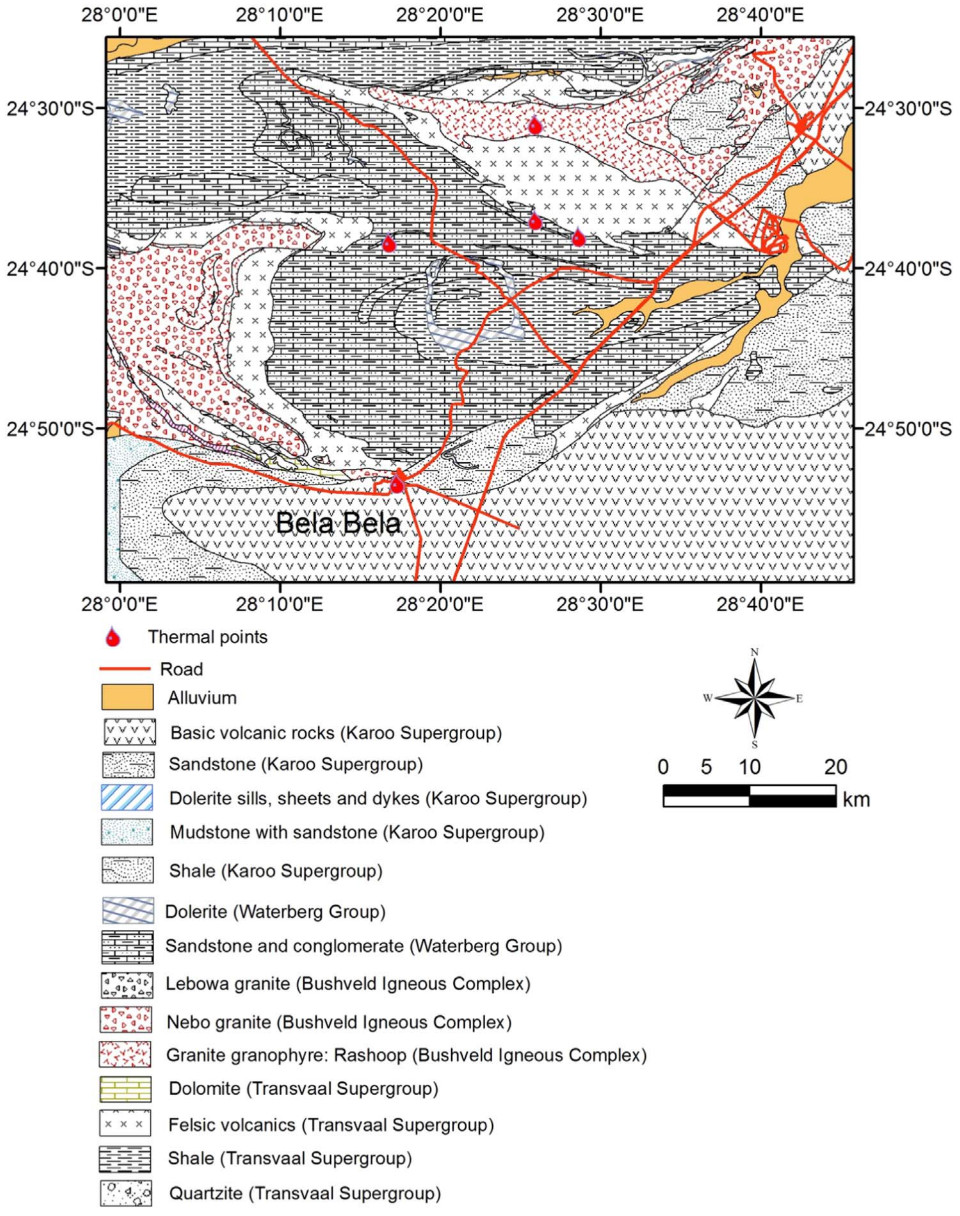

Fig. 2. Simplified geological map of the Waterberg region with prominent thermal centres (Geological data obtained from Council for Geosciences).

of fluoride from felsic igneous rocks primarily plays an important role in the release of fluoride from minerals, which is facilitated by hydrothermal fluids into the groundwater. According to Vasak and Kukuric (2006), the Bushveld Igneous Complex was identified as a medium fluoride concentration zone, comparable to the East African Rift volcanic aquifers. However, the East African Rift volcanic aquifers contain as much as 180 mg/L of fluoride (Abiye, 2010a, 2010b), which implies the presence of fluoride enriched groundwater more than that of South Africa. Elevated fluoride levels are peculiar to diverse crystalline rocks of South Africa (Fig. 1). Fluorite mineralised veins within the igneous rocks provided particular potential sources of dissolved fluoride (McCaffrey, 1998; McCaffrey and Willis, 2001). In the Northern Cape and the North West Provinces, fluorosis was identified as a severely debilitating illness resulting from excessive consumption of fluoride, where some residents have mottled teeth, in addition to skeletal fluorosis (McCaffrey, 1998; McCaffrey and Willis, 2001).

The Namaqualand region is covered with the basement rocks of the Namaqua Province, the volcano-sedimentary rocks of the Gariep Complex in the northwest and a Phanerozoic cratonic cover (Tankard et al., 1982; Visser, 1989). The central zone of the Namaqua Province is characterized by deformed heterogeneous group of gneisses and intrusions of medium to high grade metamorphism and comprised of metasedimentary, metavolcanic and intrusive rocks (Tankard et al., 1982). The area in general is dominantly underlain by granites and granitic gneisses. These rocks are overlain by the intrusive rocks of the Jurassic age that are covered by sediments of the Tertiary and Quaternary ages (Fig. 3).

These rocks are also characterized by wide spread mineralization. The climatic aridity in the area is manifested through extremely low mean annual rainfall that ranges between 3 and 36 mm/year and potential evaporation of 2200–3000 mm/year (Leshomo, 2011). Owing to high evaporation process, the Namaqualand region is characterized by widespread salt pans (Leshomo, 2011; Abiye and Leshomo, 2013, 2014). The aquifer systems are mostly limited to fault-controlled valleys occurring throughout the Namaqualand region where groundwater, within the lower most unweathered basement rocks, is stored in interconnected systems of fractures, joints and fissures.

On the other hand, the Waterberg thermal springs are located in the lower-central section of the Limpopo River basin, which is characterized by mean annual rainfall of about 480 mm (Waterberg district municipality, 2009) with an evaporation that ranges between 1600 and 2000 mm (FAO, 2004).

In the East African Rift, fluoride concentration in groundwater was attributed to the precipitation of calcium in the form of carbonate as well as continuous release of fluoride from felsic pyroclastic rocks in the alkaline pH condition (Abiye, 2010b; Furi et al., 2011). Fluoride is also commonly associated with volcanic activity and fumarolic gases in tectonically active rift systems (Abiye, 2010b). As magma ascends and decompresses, its volatile species exsolve into a vapour phase with the dominant hydrogen fluoride gas diffusing into aquifers. The calcalkaline volcanoes, typical of the continental rift in East Africa (Gasparon et al., 1993), hot spot, and continental arc (Andes) or island arcs (Japan), produce relatively fluorine-rich lavas (Rosi et al., 2003). In these aquifers, high fluoride concentration was associated with the active and sub-active regional thermal fields and felsic volcanic rocks within high geothermal zones (Alemayehu, 2000; Alemayehu et al., 2006; Abiye, 2010b; Furi et al., 2011).

3. Thermal water distribution in South Africa

A number of thermal springs with temperatures up to 64 °C were reported in the Western Cape Province, where occurrence of springs was linked to deep faulting (Diamond and Harris, 2000). Similarly, the Shu-Shu thermal springs in the KwaZulu Natal Province with temperature of 52 °C to 53 °C were related to deep faulting (Gravelét-Blondin, 2013). The thermal springs in Swaziland and in adjacent KwaZulu Natal Province have discharge temperature that ranges between 25 °C and 52 °C (Robins, 2013). In general, eighty seven thermal

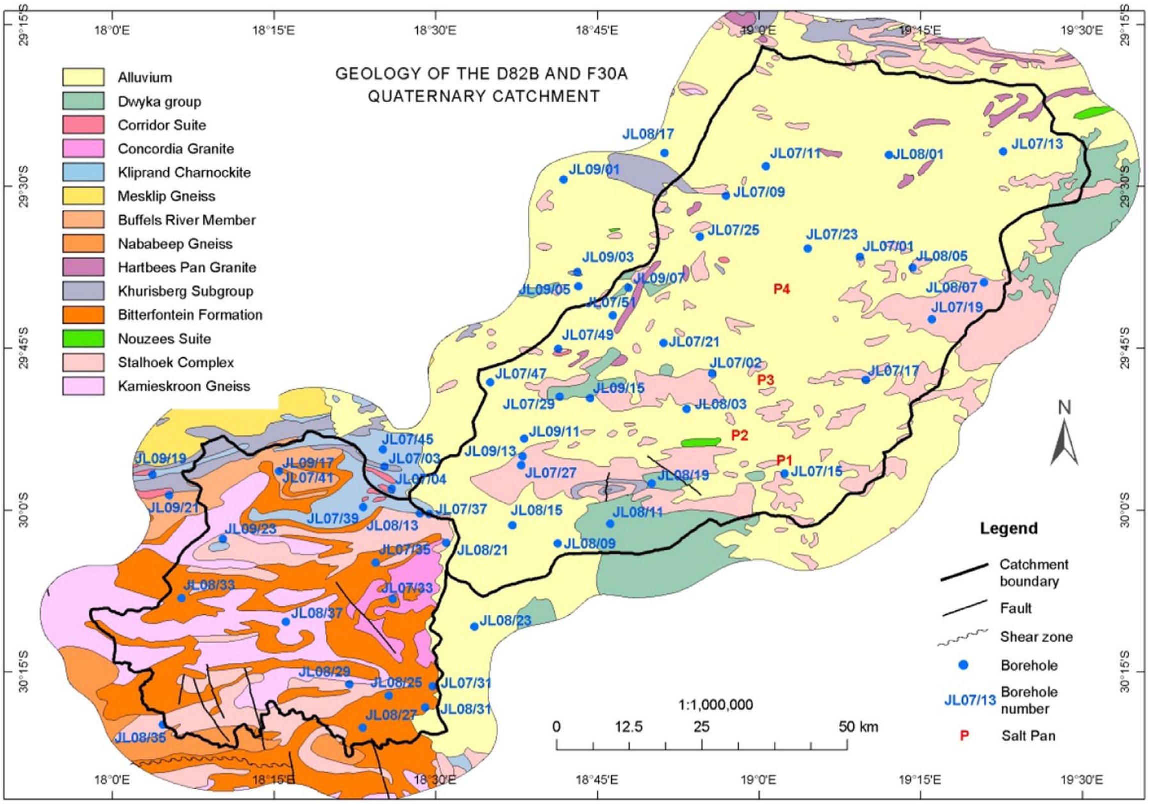

Fig. 3. Simplified geological map and borehole sampling position in Namaqualand ((Geological data obtained from Council for Geosciences).

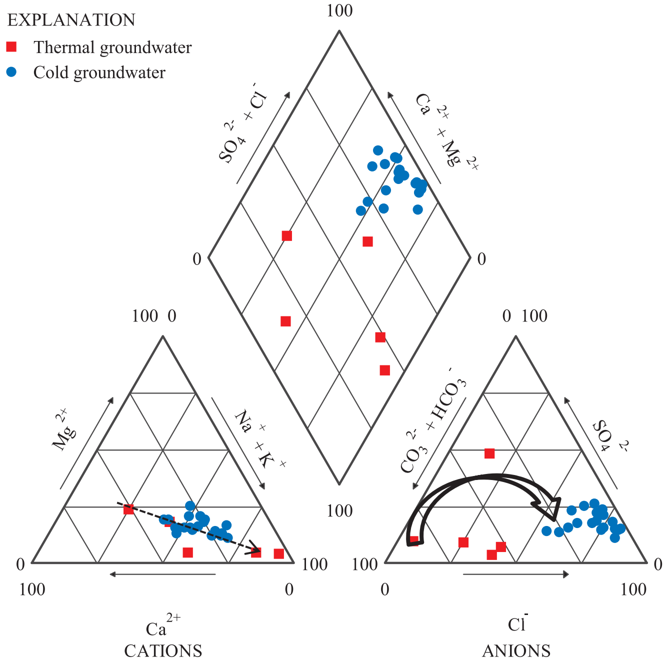

Fig. 4. Piper plot for the thermal and cold groundwater.

springs, with temperatures ranging from 25 °C to 67.5 °C were documented to date in South Africa (Tshibalo et al., 2015). On the other hand, about 803 areas were identified as fluorosis endemic (Thole, 2013). At least 28 thermal springs and boreholes were located in the Limpopo Province and are limited to two zones: the Waterberg in the south and the Soutpansberg in the north (Olivier and Jonker, 2013). The main focus of this study is limited to the southern Waterberg region (Fig. 2).

The main hydrostratigraphy in the Waterberg region, which is located at the centre of the BIC, hosts thermal water within the underlying granitic aquifer that are overlain by the fractured rhyolites, sandstone of the Waterberg Group and Karoo sediments. The overlying rocks play an important role in recharging the thermal system through dispersed fracture and deep transecting faults. Fluoride concentration is high in the felsic rocks of the BIC, with values that range between 2.0 mg/L to 10 mg/L (McCaffrey and Willis, 2001). The well-known thermal springs in the area are the Warmbath, Loubad, Vischgat, Die Oog, Rhemardo, Lekkerrus, Libertas and Buffelshoek with temperature that ranges from 30 °C to 52 °C, while the temperature of the thermal springs located in the northern part of the Limpopo Province varies between 30 °C and 67.5 °C (Olivier et al., 2008, 2011).

4. Materials and methods

All relevant data were collected through repeated field exploration utilizing existing hydrogeochemical, geological and hydrogeological information. Water samples were collected systematically from the Waterberg thermal fields (Limpopo) and the Namaqualand region and were subsequently analysed.

Thermal centres that were chosen from the Waterberg thermal region include Warmbaths (Bela Bela), Libertas, Die Oog and Badseloop Jeugkamp. At each site the physico-chemical parameters such as temperature, pH, Electrical Conductivity and Total Dissolved Solids were measured in the field using an AquaRead multi-parameter probe. In order to capture the correct temperature for thermal water, a mercury-based thermometer was used.

The stable isotopes of ^{18}O and ^{2}H were analysed using the Liquid Water Isotope Analyzer-model 45-EP at the University of the Witwatersrand, South Africa. The instrument contains a laser analysis system and an internal computer, liquid auto-sampler, a small membrane vacuum pump, and a room air intake line that passes air through a drierite column for moisture removal. A 1–1.5 ml aliquot of a sample was pipetted into a 2 ml vial and closed with Polytetrafluoroethylene septum caps. A Hamilton microliter syringe was used to inject 0.75 µl of sample through a PTFE septum in the auto-sampler. The injection port of the auto-sampler was heated to 46 °C to vaporize the sample under vacuum immediately upon injection. The vapour then travels down the transfer line into the pre-evacuated mirrored chamber for analysis. Five standards with known δ^{18}O and δ^{2}H values (*5C*: δ^{2}H −9.2 ± 0.5‰, δ^{18}O −2.69 ± 0.15‰, *4C*: δ^{2}H −51.6 ± 0.5‰, δ^{18}O −7.94 ± 0.15‰, *3C*: δ^{2}H −97.3 ± 0.5‰, δ^{18}O −13.39 ± 0.15‰, *2C*: δ^{2}H −123.7 ± 0.5‰, δ^{18}O −16.24 ± 0.15‰ and *1C*: δ^{2}H −154 ± 0.5‰, δ^{18}O −19.49 ± 0.15‰) were used in the analysis procedure and the laser analyzer automatically calibrates itself and determines the stable isotope values. The laser machine is capable of providing accurate results with a precision of approximately 1‰ for δ^{2}H and 0.2‰ for δ^{18}O in liquid water samples. Tritium analyses were performed at iThemba Labs using 500 ml of the sample, which was distilled with sodium hydroxide and then enriched by electrolysis. An electric current was applied and the volume of water reduces to 20 ml. These samples were enriched by a factor of 20 and were ready for liquid scintillation in which half the volume was mixed with 11 ml of Ultima Gold.

For major ion determination, 5 thermal (from Waterberg region) and 19 cold groundwater samples (from Namaqualand) were collected. Water sampling for cation analysis was performed with 100 ml glass bottle. The samples were filtered on site with 0.45 µ filters. The samples were acidified immediately with HNO_3 acid to keep the metals dissolved and were also kept cool. Water sampling for anion analysis was performed with a 100 ml HDPE plastic bottle. The samples were filtered on site with 0.45 µ filters and kept cool in a dark place. Major ions were analysed by Dionex QIC Ion Chromatograph, equipped with an

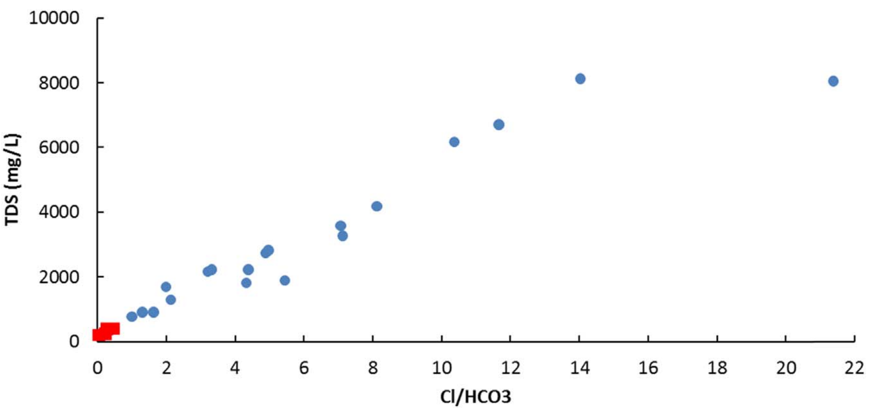

Fig. 5. The TDS vs Cl/HCO_3 plot for the thermal and cold groundwater.

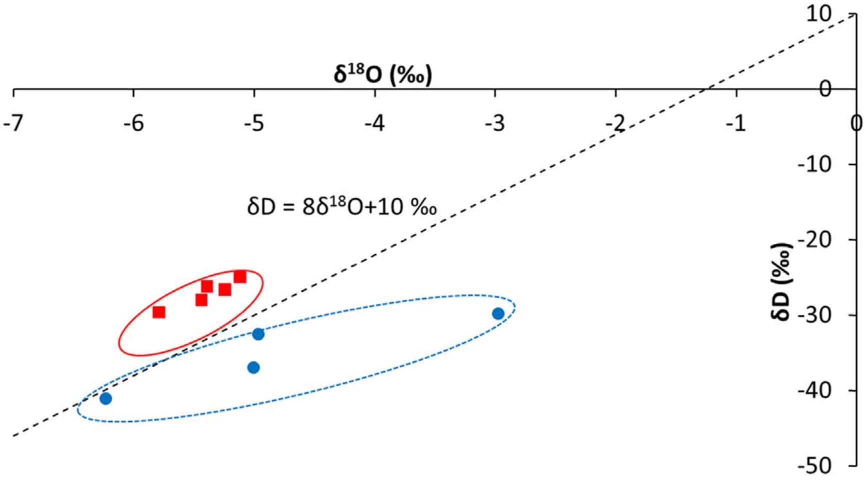

Fig. 6. Stable isotope plot for cold and thermal groundwater in relation to the Global Meteoric Water Line ($\delta D = 8\delta^{18}O + 10‰$, Craig, 1961).

Table 2
Hydrogeochemical parameters in the thermal groundwater system of the Waterberg region.

Parameter	Warmbath - spring	Warmbath- borehole	Die Oog borehole	Libertas - Spring	Badseloop Borehole
Temp (°C)	52	51	48	46	42
pH	8.82	8.51	8.60	8.06	7.83
EC (μS/cm)	556	543	317	211	480
K (mg/L)	4.50	4.80	7.00	3.70	4.90
Ca (mg/L)	4.00	12.80	32.40	21.20	40.80
Mg (mg/L)	2.40	3.10	9.20	6.20	2.80
Na (mg/L)	105.70	100.90	14.30	25.90	66.40
Cl (mg/L)	69.50	79.00	28.50	5.50	30.00
HCO_3 (mg/L)	177.00	171.00	127.00	129.00	115.00
SO_4 (mg/L)	8.80	17.90	14.00	11.20	122.60
F (mg/L)	7.80	7.70	4.50	4.90	5.10
δ2H (‰)	−26.2	−25.0	−28.0	−29.6	−26.7
$\delta\ ^{18}O$ (‰)	−5.39	−5.12	−5.44	−5.79	−5.24
3H (TU)	0 ± 0.2	1.7 ± 0.3	0 ± 0.2	0 ± 0.2	0.3 ± 0.2

automated sampler, an IonPac AG4A guard column and an IonPac AS4A analytical column.

4.1. Results and discussion

The analytical results in Table 1 show that the fluoride concentration in thermal groundwater of the Waterberg ranges between 4.5 and 7.8 mg/L and has limited alkaline pH condition (7.83–8.82). The results also indicate that groundwater temperature ranges between 46 °C and 52 °C with the Electrical Conductivity (EC) values that fall between 211 μS/cm and 556 μS/cm. The fluoride concentration in the groundwater was found to be above the World Health Organization guideline value of 1.5 mg/L for drinking water.

The data in Table 1 represent the Waterberg region, marked as number 1 in Fig. 1, and shows that groundwater temperature ranges between 46 °C and 52 °C, pH ranges between 7.83 and 8.82, Electrical Conductivity (EC) ranges between 211 μS/cm and 556 μS/cm. On the other hand, in the cold groundwater system of the Namaqualand region, marked number 2 in Fig. 1 and presented in Table 3, the fluoride concentration ranges between 1.12 mg/L and 31.8 mg/L for the pH values of 4.9 and 7.91, EC values range from 1170 μS/cm to 12,880 μS/cm with the temperature range of 17–32 °C, showing about 4 times increase when compared to the fluoride concentration in the high thermal zone of the Waterberg region.

In the Namaqualand region, climatic aridity as a result of very low annual rainfall ($\leq$ 200 mm/year) and very high ambient temperature $>$ 30 °C, has direct impact on the groundwater quality that enhances an evaporation driven concentration of salinity and chemical constituents. The main aquifers are fractured crystalline rocks where recharge is regionally controlled through fracture network besides local recharge after evaporation (Leshomo, 2011; Abiye and Leshomo, 2013, 2014). Intensive evaporation processes have been identified as a cause for the high concentration of fluoride in the East African Rift (Abiye, 2010a, 2010b), which we assume to be the case for the Namaqualand groundwater.

The Piper diagram (Fig. 4) was useful in identifying distinct clusters of thermal and cold groundwater along with the mixing and hydrochemical evolution. Cold groundwater from Namaqualand falls in the sodium chloride region, which could be due to evaporative effects, while thermal groundwater was dominated by bicarbonate owing to the shallow circulating groundwater. In both cases, sodium was the dominant cation. The diamond plot depicts salinization processes in the cold groundwater, while mixing was identified for thermal groundwater, which could be due to the mixing of infiltrated rainwater and deep circulating groundwater.

The TDS vs Cl/HCO_3 plot (Fig. 5) revealed strong linearity, which could be explained by thermal water occupying the origin of the plot as a freshwater with minimum salinity concentration. However, there is a possibility of mixing that generated salinity for the cold groundwater in the Namaqualand region primarily controlled by the evaporation process due to aridity of the area (Fig. 5). According to Abiye and Leshomo (2014), based on the Br/Cl ratio (3.22–6.67), 30% of the samples in the Namaqualand region contain chloride from marine source while the majority of them contain chloride which was derived from local source through an evaporation process. Owing to the absence of carbonate rocks in the area, evaporation due to extreme climatic aridity was a reasonable source for high Cl and bicarbonate in groundwater often characterized by high electrical conductivity (12,800 μS/cm). Evapotranspiration related fluoride concentration in groundwater has also been recorded in India (Jacks et al., 2005).

The stable isotope data for the Namaqualand and Waterberg regions were plotted in Fig. 6. The plot portrays that the Namaqualand samples fell below the GMWL, suggesting the occurrence of recharge after evaporation. The Waterberg thermal waters plotted above the line ruling out the evaporation effect.

The environmental isotope plot (Fig. 6) also suggests that thermal springs in the Waterberg area are substantially depleted with respect to $\delta^{18}O$ with the values that fall between −5.12‰ and −5.79‰, and low tritium values, 0 ± 0.2 to 1.7 ± 0.3 TU (Table 1, Table 2), indicating the presence of deep circulating groundwater that emerges as thermal water. In the Namaqualand aquifers, $\delta^{18}O$ varies between −2.98‰ and −6.24‰, while the ^{3}H values fall between 0 and 1.2 T.U. (Table 3), indicating the presence of recharge from evaporated water and deep circulating groundwater that has very low tritium content.

The spatial concentration of fluoride has also been assessed based

Table 3
Hydrogeochemical parameters in cold groundwater system of the Namaqualand region.

Parameter	JL 07-01	JL 07-02	JL 07–09	JL 07–11	JL 07–13	JL 07–15	JL 07–17	JL 07–19	JL 07–21	JL 07–23	JL 07–27	JL 07–29	JL 07–41	JL 07–47	JL 07–49	JL 07–51	JL 08-05	JL 08-07	JL-09-09
Temp (°C)	22	24	23	21	22	17	19	23	17	32	17	24	33	20	20	21	27	23	21
pH	7.29	7.91	4.90	6.72	7.11	7.64	7.78	7.20	7.22	7.17	7.92	7.42	7.27	7.42	7.10	7.22	6.27	6.22	6.84
EC (μS/cm)	3360.00	3730.00	3600.00	5820.00	2750.00	12,130.00	1490.00	4580.00	3720.00	6410.00	4620.00	3330.00	1170.00	5640.00	12,880.00	10,620.00	1380.00	2060.00	11,540.00
K (mg/l)	19.92	30.59	25.04	39.73	17.46	55.14	21.01	22.71	26.26	44.30	26.78	18.47	4.08	30.40	75.62	47.51	14.42	13.35	55.78
Ca (mg/l)	162.07	154.91	267.22	398.53	173.17	579.32	71.38	300.19	277.65	268.33	227.63	169.72	57.00	332.32	451.13	536.18	110.39	167.87	559.99
Mg (mg/l)	55.49	52.18	78.02	109.15	51.25	217.34	34.13	84.87	69.65	101.02	111.37	72.30	31.64	139.05	269.36	156.41	23.38	49.71	186.72
Na (mg/l)	350.34	605.91	303.61	652.63	318.09	1802.00	178.20	568.26	383.29	960.26	535.42	422.30	111.99	609.69	1960.35	1523.02	155.41	203.86	1895.85
Cl (mg/l)	820.78	875.27	800.15	1553.45	556.69	2591.91	308.61	1074.98	896.11	1785.41	1291.23	707.56	240.23	1638.20	4070.03	3149.20	288.96	468.47	4104.57
HCO_3 (mg/l)	190.00	200.00	250.00	220.00	280.00	250.00	190.00	220.00	270.00	220.00	260.00	130.00	240.00	230.00	290.00	270.00	223.00	220.00	192.00
SO_4 (mg/l)	210.71	309.99	433.23	602.87	290.32	666.98	103.41	468.78	306.33	792.64	366.18	372.30	83.63	296.44	993.65	1005.32	90.25	174.18	1021.98
F (mg/l)	6.00	6.05	5.70	4.87	3.68	14.15	1.81	5.46	3.72	7.95	3.46	5.10	2.03	3.24	16.23	15.26	1.12	1.28	31.80
δ2H (‰)					−36.9					−32.5							−41		−29.8
δ18O(‰)					−5.01					−4.97							−6.24		−2.98
3H(T.U.)					1.2 ± 0.3					0.2 ± 0.2							0.5 ± 0.2		0 ± 0.2

on its relation to sodium, calcium, chloride and bicarbonate (Fig. 7). The scatter plots depict the geochemical affinity of fluoride with these ions. There is a tendency of linear correlation between Na, Ca, Cl, HCO_3 and F with thermal water occupying the lower enrichment zone, while the cold groundwater displaying a mixing trend through a linear plot. This illustrates that release of fluoride into the groundwater is geologically controlled with a characteristic increase in concentration through evaporative processes rather than solely driven by thermal activity.

Since large part of South Africa are characterized by arid and semi-arid climatic conditions, evaporative processes play an important role in controlling the quality of groundwater through salinity increases as shown in Table 3. High fluoride concentrations could also be related to long residence times of groundwater in the Waterberg region, where the tritium level usually falls below 1.7 TU, indicating substantially long circulation time within the weathered granitic aquifer. Similarly, the cold groundwater from the Namaqualand region with long residence times (^{3}H value of 0 T.U) also contains the highest fluoride concentrations.

The controls on the fluoride concentration in the thermal and cold groundwater regimes show an interesting revelation. Unlike the East African Rift groundwater where the fluoride concentration in the thermal water is much higher than the cold groundwater, cold groundwater in the Namaqualand region of South Africa contains higher fluoride concentrations than the thermal Waterberg groundwater due to severe climatic aridity and strong evaporation. The role of Na, Ca, and Cl on the fluoride abundance in the thermal and cold ground water systems (Fig. 7) shows a linear mixing pattern with less saline thermal water occupying the origin in the plots. In the East African Rift system, increase in fluoride concentration was related to an increase in sodium and a decrease in calcium, owing to its precipitation as carbonate (Abiye, 2010b). However, the pattern on Fig. 7b,d revealed that calcium has not been consumed from the system through precipitation either as CaF_2 or $CaCO_3$. In this study calcium concentration increases with fluoride especially in cold groundwater system of Namaqualand (Fig. 7b) with high bicarbonate concentration (Fig. 7d), which supports the notion of strong evaporative concentration of fluoride. The East African Rift groundwater system is under strong influence of neo-tectonic related magmatic activity, which has abundantly enriched the groundwater system with fluoride (Abiye, 2010b).

5. Conclusion

The variation in the fluoride content is considered to be the result of the interplay of a number of factors that include geological and climatic setting of the areas. The results in this study revealed that fluoride is inherently associated to the felsic igneous rocks, producing concentrations above the WHO recommended limits, with further, concentration through evaporative processes rather than solely driven by thermal activity. In the arid Namaqualand region, fluoride concentration in the groundwater was ≈4 times greater than the fluoride concentration in the Waterberg groundwater. High fluoride concentration in the groundwater is also related to long residence time of groundwater due to enhanced water-rock interaction where the tritium level usually falls below 1.7 TU, indicating substantially long circulation time within the weathered granitic aquifer. Similarly, the cold groundwater from the Namaqualand region with the highest fluoride concentrations also returns the lowest ^{3}H values of 0T.U. In this study calcium displayed an increasing pattern with fluoride concentration in cold groundwater system that has high bicarbonate concentration, which supports the notion of strong evaporative concentration of fluoride in the arid Namaqualand groundwater.

An important recommendation emanating from this work is that aquifers in felsic igneous rocks, like those in the Waterberg and Namaqualand, are not ideal when the minimisation of fluoride

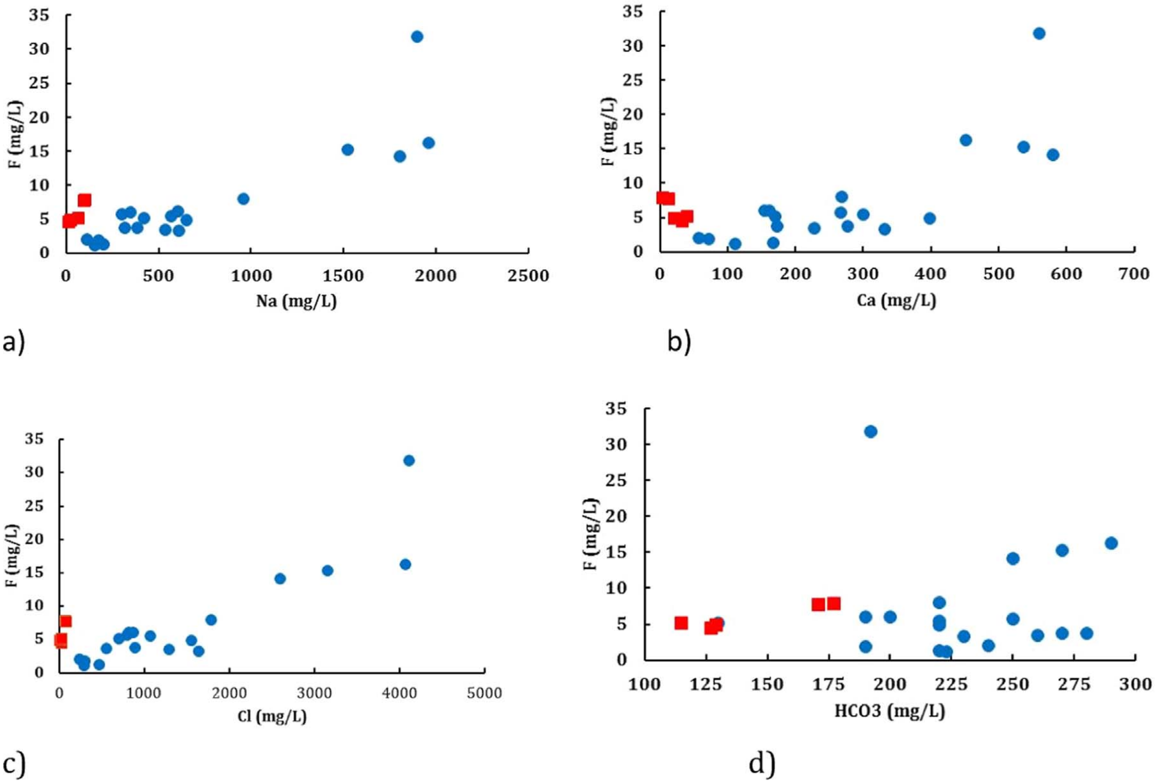

Fig. 7. Comparative binary plots, red squares represent thermal groundwater and blue solid circles represent cold groundwater.

concentration is desirable. This undesirable geogenic source is further exacerbated by high evaporation rates, as seen in the Namaqualand region. Although the resultant fluoride concentrations may not be reduced completely to the acceptable levels, low cost defluoridation techniques can be applied to ameliorate the water condition and produce resources fit for human consumption.

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