



Redox control on trace element geochemistry and provenance of groundwater in fractured basement of Blantyre, Malawi



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ABSTRACT

Assessment of redox state, pH, environmental isotope ratios ($\delta^{18}\text{O}$, $\delta^2\text{H}$) coupled with PHREEQC speciation modeling investigations were conducted to understand trace element geochemical controls in basement complex aquifer in Blantyre, Malawi. Groundwater in the area is typical Ca–Mg–Na–HCO₃ type suggesting more of carbonate weathering and significance of carbon dioxide with dissolution of evaporites, silicate weathering and cation exchange being part of the processes contributing to groundwater mineralization. The significance of pH and redox status of groundwater was observed. The groundwater redox state was mostly O₂-controlled with few exceptions where mixed (oxic–anoxic) O₂–Mn(IV) and O₂–Fe(III)/SO₄ controlled redox states were modeled. More so, some of the main trace element species modeled with PHREEQC varied with respect to pH. For instance vanadium(III) and vanadium(IV) decreased with increase in field pH contrasting the trend observed for vanadium(V). The isotopic composition of the sampled groundwater varied between -5.89‰ and -3.32‰ for $\delta^{18}\text{O}$ and -36.98‰ and -20.42‰ for $\delta^2\text{H}$. The $\delta^2\text{H}/\delta^{18}\text{O}$ and $\delta^{18}\text{O}/\text{Cl}^-$ ratios revealed that groundwater is of meteoric origin through vertical recharge and mixing processes. The *d*-excess value approximated the *y*-intercept of GMWL of 10 (*d*-excess = 9.269, SD = 1.240) implying that influence of secondary evaporative processes on isotopic signature of the study area is minimal. Thus, there is evidence to suggest that groundwater chemistry in the studied aquifer is influenced by inherent processes with contribution from human activities and furthermore, the water originates from rainwater recharge. With such results, more studies are recommended to further constrain the processes involved in mineralization through isotopic fractionation investigations.

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1. Introduction

Groundwater geochemistry is controlled by various factors. These factors include pH, availability of mineral sources, weathering processes, temperature, reduction/oxidation (redox) reactions and anthropogenic input. Each factor plays an inherent role in groundwater mineralization or may be induced by human activities.

Groundwater is a primary resource for domestic and agricultural purpose in rural communities. Groundwater exploitation may increase the levels of natural contaminants or inject additional parameters into the aquifer. Besides, evapotranspiration mostly in arid and semi-arid regions increases the potential for evaporate increase in groundwater through leaching processes. Processes controlling groundwater mineralization in these areas

requires proper evaluation in order to effectively manage and conserve groundwater (Xie et al., 2013).

Groundwater chemical composition is generally influenced by mineral dissolution within the aquifer matrix, evaporation and anthropogenic activities or combination of these processes (Ghabayen et al., 2006; Fass et al., 2007).

Whenever redox processes are involved in groundwater, they can mobilize or immobilize potentially toxic elements from geogenic materials (Smedley and Kinniburgh, 2002). Consequently, redox processes enhance degradation or preservation of anthropogenic contaminants (Bradley, 2003). Mobilization and degradation of chemical elements in groundwater may generate undesirable by-products such as dissolved ferrous iron (Fe²⁺), hydrogen sulfide (H₂S) and methane (CH₄) (Chapelle and Lovley, 1992).

Determining the kind of redox processes that occur in an aquifer, documenting spatial distribution and understanding how they affect concentrations of natural or anthropogenic contaminants, is central to assessing and describing the chemical quality of groundwater (Christensen et al., 2000; McMahon and Chapelle, 2008).

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Then again, isotopic investigation has proven useful in ascertaining the origin of groundwater. In recent years various studies have been conducted on stable isotopes elsewhere (Dindane et al., 2003; Ako et al., 2012; Amer et al., 2012; Hamed and Dhahri, 2013; Xie et al., 2013) and results have been very significant to hydrological assessments of groundwater.

Various studies done in basement complex of Malawi have documented the effect of hydrolysis of aluminosilicate, evaporite dissolution, cation exchange and carbonate weathering (Msonda et al., 2007; Wanda et al., 2013) and anthropogenic contamination (Mkandawire, 2008; Kanyerere et al., 2012; Msilimba and Wanda, 2013). However, not much has been done on redox processes and isotopic investigation in the complex (Mapoma and Xie, 2014). Therefore, the foremost objective of the present study was to investigate how redox processes affect trace element chemistry in the fractured basement complex of rural Blantyre. Subsequently, we analyzed and assessed the provenance of groundwater in the fractured basement aquifer through stable oxygen and hydrogen isotope concentrations. The study results will contribute to better groundwater management and conservation in rural Blantyre district.

2. Geological and hydrological setting of the study area

The location of the study area is illustrated in Fig. 1 which is within Blantyre district: where Blantyre district is located at 15°42'S and 35°E coordinates. The site elevation and coordinates of each sampling point are indicated in Table 1 under Section 4. The lithology of the area is characterized by crystalline basement complex mostly of metamorphic and igneous rocks of Pre-cambrian to lower Palaeozoic age (Carter and Bennett, 1973; Chilton and Smith-Carington, 1984). The study area is on the eastern edge of the southern branch of the East African Rift Valley where prominent faults occur. The basement is fractured enough for potential

aquifers to exist for groundwater exploitation (Mapoma and Xie, 2014). The major aquifer lithological units are syenitic granites, charnockitic and ultra-basic gneisses, schistis, granularite and quartzites (Mkandawire, 2004; Monjerezi and Ngongondo, 2012).

The lithofacies of the study area are mainly dark grey gneisses strongly enriched in amphibole and pyroxene. Charnockitic gneisses (calcium–iron–magnesium) and syenitic gneisses (abundance of feldspar) have been identified in the area (Dill et al., 2005). Common mineral bearing rocks present in this area include quartz, feldspar, amphibole, hematite, hydrobiotite, kaolinite, calcite, gypsum, vermiculite, goethite, halloysite and smectite (Dill et al., 2005). The presence of such mineral phases determines the abundance (or trace existence) of elements in the study area.

Various mechanisms controlling mineralization of elements in basement complex have been studied (e.g. Monjerezi et al., 2011; Wanda et al., 2013). Of significant are cation exchange, rock–water interaction, carbonate and silicate weathering and hydrolysis. Oxidic conditions in fractured basement promote redox reactions that may mobilize redox sensitive elements such as Fe, Mn and V. Some of the mineral end members identified to be of significance in the entire basement complex that are involved in trace element geochemistry include aluminosilicates, evaporites (anglesite, barite and celestite), carbonates (cerussite, siderite, strontianite and witherite), oxides (cassiterite, cuprite, hematite and karelianite), sulfides (chalcopyrite and galena), mineral alloys e.g. electrum (Ag–Au alloy) and hydroxides (garnierite and nickeliferous limonite) (Monjerezi et al., 2011; Wanda et al., 2013; Mapoma et al., submitted for publication-b).

Aquifer recharges from higher grounds and groundwater discharge in surface depressions (Fig. 1). Although there are variations in groundwater flow direction on a small scale dependent on landscape geodynamics, it can be generalized that the flow is from the east in the uplands (shire highlands) towards the west into Shire Valley (part of Zambezi Valley). Fig. 2 is a conceptualized cross

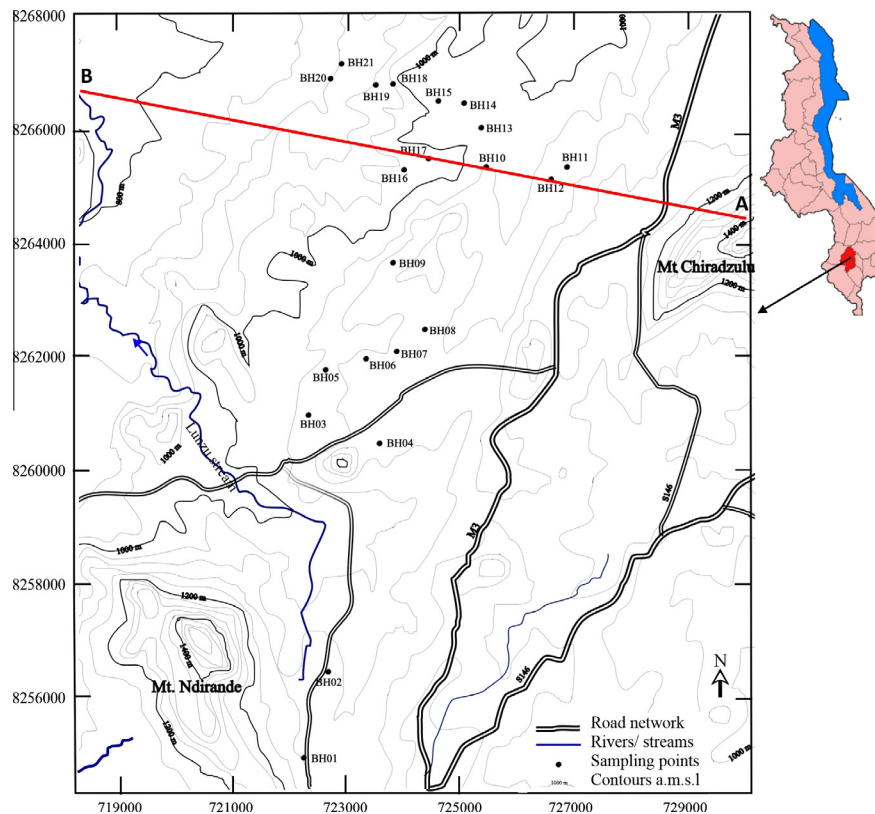


Fig. 1. Location of the study area in the shire highlands of Blantyre showing sampling points and geological features.

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