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# Multi-proxy approach ($^{2}H/H$, $^{18}O/^{16}O$, $^{13}C/^{12}C$ and $^{87}Sr/^{86}Sr$) for the evolution of carbonate-rich groundwater in basalt dominated aquifer of Axum area, northern Ethiopia

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ABSTRACT

Isotopic and chemical composition of groundwater from wells and springs, and surface water from the basalt-dominated Axum area (northern Ethiopia) provides evidence for the origin of water and dissolved species. Shallow (depth < 40 m) and deep groundwater are distinguished by both chemical and isotopic composition. Deep groundwater is significantly enriched in dissolved inorganic carbon up to 40 mmol $l^{-1}$ and in concentrations of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$ and $Si(OH)_4$ compared to the shallow type.

The $\delta^{2}H$ and $\delta^{18}O$ values of all solutions clearly indicate meteoric origin. Shifts from the local meteoric water line are attributed to evaporation of surface and spring water, and to strong water–rock interaction. The $\delta^{13}C_{DIC}$ values of shallow groundwater between −12 and −7‰ (VPDB) display the uptake of $CO_2$ from local soil horizons, whereas $\delta^{13}C_{DIC}$ of deep groundwater ranges from −5 to +1‰. Considering open system conditions with respect to gaseous $CO_2$, $\delta^{13}C_{DIC}$ = +1‰ of the deep groundwater with highest $PCO_2 = 10^{-0.9}$ atm yields $\delta^{13}C_{CO2(gas)} \approx -5$‰, which is close to the stable carbon isotopic composition of magmatic $CO_2$. Accordingly, stable carbon isotope ratios within the above range are referred to individual proportions of $CO_2$ from soil and magmatic origin. The uptake of magmatic $CO_2$ results in elevated cations and $Si(OH)_4$ concentrations. Weathering of local basalts is documented by $^{87}Sr/^{86}Sr$ ratios of the groundwater from 0.7038 to 0.7059. Highest values indicate Sr release from the basement rocks. Besides weathering of silicates, neoformation of solids has to be considered, which results in the formation of, e.g., kaolinite and montmorillonite. In several solutions supersaturation with respect to calcite is reached by outgassing of $CO_2$ from the solution leading to secondary calcite formation.

## 1. Introduction

The chemical composition of groundwater is controlled by complex reactions at gas–liquid and solid–liquid interfaces, which depend on the natural surrounding and potential anthropogenic impact. In natural systems, the uptake of gaseous $CO_2$, which generates acidic solutions and favors the dissolution and transformation of minerals and rocks, is highly relevant (e.g. Clark and Fritz, 1997; Dietzel and Kirchhoff, 2002; Schofield and Jankowski, 2004; Godderis et al., 2009). As a result of $CO_2$ uptake, elevated concentrations of dissolved solids can be found in groundwaters. High partial pressure of $CO_2$ is either gained from magmatic $CO_2$ or degradation of organic carbon.

Regardless of the origin of $CO_2$, the individual solid–liquid reactions and the chemical evolution of groundwater strongly depend on the amount of $CO_2$ uptake and the mineralogical composition of associated rocks. Accordingly, the geochemical composition of groundwater along a flow path is influenced by the spatial variation of minerals and rocks, and by the initial composition of the recharged solution. Geochemical processes associated with groundwater evolutions have been studied by various authors (e.g. Frape et al., 1984; Kebede et al., 2005; Elango and Kannan, 2007; Shand et al., 2009), where chemical and isotope approaches were successfully applied to decipher the evolution of a wide range of groundwater compositions.

Recently, hydrochemical and isotopic evidence was widely used to identify the hydrogeological and hydrochemical conditions in volcanic aquifers of Ethiopia (e.g. Kebede et al., 2005, 2007; Ayenew et al., 2007; Demlie et al., 2008). Most of these studies were focused on flow paths, recharge conditions, and the chemical evolution of groundwater in the Ethiopian Rift System. In this geological setting elevated concentrations of dissolved inorganic carbon (DIC)

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are obviously linked to volcanic activities (e.g. Demlie et al., 2008). Unlike the rift valley system (Kebede et al., 2005; Demlie et al., 2008), the composition and evolution of groundwater in the northern highlands of Ethiopia, which is dominated by flood basalt aquifers, is barely known.

Therefore, the present study is focused on the main groundwater aquifers of the Axum area, located in the northern highlands of Ethiopia, which are used for drinking water. Hydrochemical and isotope data elucidate the origin of water and dissolved species for individual types of groundwater. Special emphasis is given on the source of $CO_2$ in the local groundwater and its control on solution composition.

## 2. Geological setting

The study area is characterized by hilly topography and flat plateau surfaces with average elevation of 2100 m a.s.l. The elevation is 2600 m at the headwater of the highest mountain peak in the north of Axum and decreases towards the south. Geomorphological features throughout the study area suggest that the landforms were developed mostly due to volcanic activities and Quaternary sediment deposits (Fig. 1).

The basement rocks display geochemical characteristics typical for intra-oceanic-island-arc systems (Tadesse et al., 1999). The Precambrian basement is part of an extensive low-grade metavolcanic and volcanoclastic sequence that is intruded by granitoid plutons predominantly composed of granodiorite (Tadesse et al., 2000). The sedimentary rocks unconformably overlay the basement rocks. The sedimentary sequence of the study area exhibits some fine grained and maturity-quartz sandstone (Avigad et al., 2007). The sedimentary succession of Mesozoic age consists of the Adigrat sandstone, the Hintalo carbonate sequence and the Amba Aradam sandstone formation. While exposed over vast area of the northern region, these sedimentary sequences appear to pinch out towards Axum (Getaneh, 2002).

The sedimentary rocks are overlain by basaltic lava flows and pyroclastic rocks caused by several episodes of volcanic eruption (see Fig. 1). Widespread volcanic activity during the Tertiary covered large parts of the Ethiopian Plateau including the study area by rapid outpouring of fissural basalts. Diverse magma types display distinctive spatial evolution and differentiation (Pik et al., 1999). Beside fissural basalt, a widespread volcanic hypabissal igneous terrain exists in the area forming steep cliffs. These volcanic rocks belong to the Axum–Adwa trachyte–phonolite plugs and extend to the trachyte–rhyolitic rocks in Eritrea (Zanettin et al., 2006). The Quaternary sediments, partly covering the study area, are mainly derived from the surrounding highlands.

## 3. Hydrogeological condition

Axum area is located on the main hydrogeological water – divide of two major drainage systems: the Mereb River and the Tekeze River basins. The basins have wide drainage coverage. However, about 300 $km^2$ is considered by this research, which is assumed to be the most important groundwater resources development area for the town of Axum.

The volcanic terrain and associated sedimentary deposits represent a complex aquifer system. Shallow aquifers are mostly confined to sediments of low aquifer productivity with poor surface water infiltration and to weathered top layers of the volcanic rocks. Deep aquifers may be rather related to fractured basaltic rocks. The highly fractured and weathered basalts provide good permeability due to secondary porosity with a well–interconnected fracture network. Pumping tests conducted in the well field of the study area indicate significant circulation of groundwater along major conduits of tilted blocks of basalt (Devecon Engineers and Architects, 1995). The fractured basalt can be filled with clay minerals, which in turn may locally reduce the productivity of the basaltic aquifer. In some cases, the spatial variability in chemical composition of groundwater reflects unconnected aquifers. The underlying basement rocks are characterized by low permeability except in the upper weathered horizons.

Groundwater recharge preferentially occurs at the unconfined area in the elevated topography that consists of fractured phonolite and trachyte volcanoes. Similar to the trap series of volcanoes in the highlands (Ayenew et al., 2008), the volcanic plugs have high transmissivity, low storativity, and localized fault-controlled groundwater flow direction. The flow behaviour within the deep aquifer is likely to be controlled by localised fractures related to faulting and the emplacement of intrusive bodies. In highly faulted and fractured areas the hydraulic conductivity can rise (Ayenew et al., 2008).

## 4. Sampling

Water samples were collected from wells and springs as well as from surface water for chemical and isotope analyses (see sampling sites in Fig. 1). Several solutions were collected twice, during autumn and winter of 2008 and 2009 (Tables 1 and 2). A third sampling campaign was conducted in summer 2009 to collect samples for additional isotope analysis. The groundwater collected from wells is different in depth ranging from 10 to 150 m and comprise mostly active municipal wells. Sampling was carried out close to the well heads. Prior to sample collection, inactive wells had been pumped until constant conductivity was reached to ensure sampling of primary groundwater.

All samples were filtered through 0.45 $\mu$m membranes in the field and subsequently separated in different aliquots. The solutions were stored in cleaned polyethylene (HDPE) bottles after rinsing several times with the sampled solution. Samples for cation and silica analysis were preserved by adding ultra-pure 6 N $HNO_3$ to the water samples, while those used for anion analysis were not acidified. Samples for stable isotope analyses of water ($^2H/H$ and $^{18}O/^{16}O$) were collected in HDPE bottles. For stable carbon isotope analyses ($^{13}C/^{12}C$) of dissolved inorganic carbon (DIC) 1 ml solution was injected into a 10 ml gas tight vial using a syringe and hollow needle. Previously the vials were flushed with He gas and preloaded with six droplets of phosphoric acid in the Lab. At selected sites, water samples for strontium isotope analysis ($^{87}Sr/^{86}Sr$) were collected in 50 ml HDPE bottles.

Representative rock samples comprising sedimentary and volcanic rocks were collected from the study area for chemical and mineralogical analyses.

## 5. Analytical methods

Field data of water samples, including pH, electrical conductivity and temperature, were recorded during sampling. Total alkalinity was measured *in situ* by titration with 0.1 N HCl using methyl orange as indicator. Dissolved cations (Na, K, Mg, Ca, Fe and Sr) and silicic acid were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer 4300). Anions (F, Cl, $SO_4$ and $NO_3$) were measured by ion chromatography (IC; Dionex 600). The quality of water analyses was checked from cation–anion balance by the relative deviation from charge balance ($\Delta_{meq} = 100 \cdot (\Sigma_{meq+} - \Sigma_{meq-})/(\Sigma_{meq+} + \Sigma_{meq-}) < 6\%$).

Isotopic composition of DIC was analysed using a fully automated peripheral continuous-flow gas preparation device (Gasbench II), which was connected to a Finnigan DELTA$^{plus}$ XP mass spectrometer. Analytical setup is comparable to that used in