Geochemical Evolution of Fluoride and Implication for $F^-$ Enrichment in Groundwater: Example from the Bilate River Basin of Southern Main Ethiopian Rift

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Abstract: Groundwater is the most important source of drinking water. Fluoride was found in high concentrations in the groundwater from deep wells of the water supply in the southern main Ethiopian rift. The high concentration of fluoride is dominantly geogenic rather than anthropogenic in origin, as the agricultural area was not found to be contaminated with NO$_3^-$ . Knowledge of fluoride enrichment will help to provide management plans for developing deep groundwater and minimizing the health risks of exposure to fluoride. The chemical processes of fluoride were investigated in the waters in the Bilate River basin using hydrochemical and isotopic tools. The $F^-$ concentration ranged from 0.5 to 1.29 mg/L in water from shallow wells and from 0.48 to 5.61 mg/L in water from deep wells. Seventy percent of deep well samples had $F^-$ $>$ 1.5 mg/L higher than the World Health Organization potable guideline. The high fluoride concentration in the groundwater was mainly situated in the rift valley of the Bilate River basin, in contrast with low $F^-$ groundwater in the highland. The concentration of fluoride was lowest in Ca-Mg-HCO$_3^-$ type groundwater and highest in Na-HCO$_3^-$ type groundwater. Moreover, $F^-$ was positively correlated with HCO$_3^-$, Na$^+$, Na$^+$/Ca$^{2+}$ and pH in groundwater and Na$^+$/Ca$^{2+}$ ratios were increased along the flow path. Hydrogeological, hydrodynamic and hydrochemical conditions are responsible for fluoride accumulation in the deep aquifers. Strong dynamic flow in highland areas flush away weathered chemical components (e.g., $F^-$). Thus, surficial weathering is not a major controlling factor for high concentrations of Fluoride in deep groundwater but the combination of silicate hydrolysis and ion exchange mainly control fluoride enrichment in stagnant flow environments.

Keywords: fluoride; hydrochemical characteristics; water–rock interaction; geochemical modeling; bilate river basin; South Ethiopia

1. Introduction

Fluoride in groundwater is a concern for health worldwide and attracts a lot of attention, since high fluoride (>WHO limit of 1.5 mg/L) in drinking water can often cause dental ($F^- > 1.5$ mg/L), skeletal ($F^- > 4$ mg/L) and crippling ($F^- > 10$ mg/L) fluorosis [1]. More than eight million people are subjected to high fluoride groundwater in the Ethiopian rift valley [2], about 200 million in other places in the world [3–5].
In past decades, researchers have studied the geographical distribution of fluoride concentration [6–8] and its relationship with dental caries, dental fluorosis and skeletal fluorosis [9–11] in the Ethiopian rift valley. Water quality and fluoride sources were investigated in the central Ethiopian rift [12]. The occurrence of health problems related to fluoride are well documented in the Central Ethiopian rift valley, whereas hydrogeochemistry and F⁻ enrichment mechanism in the southern Ethiopian rift valley have not yet been investigated and are poorly understood.

Fluoride in groundwater is related to various rock types, that is, sedimentary rocks [13,14], igneous rock [12,15], or metamorphic rock [16,17], influenced by geochemical and climatological conditions [18]. Volcanic emissions and geothermal water are also sources of fluoride in groundwater [19–21]. Fluorine-bearing minerals like topaz, fluorite, tourmaline, muscovite, biotite, hornblende and villianmite, release F⁻ through weathering and water-rock interaction [22–24]. Besides natural sources, fluoride can be derived from anthropogenic activity including mining activities, industrial emissions and agricultural fertilizers [25–27].

The south Ethiopian rift is located in a volcanic area where there exist basalts, felsic-volcanic rocks (ashes, tuffs, pyroclastic rocks, trachyte and rhyolite) and their weathered and re-deposited fluvio-lacustrine sediments, geothermal systems also exist. Those lithotypes can release chemical components into interacting water. Hydrodynamic could control F⁻ distribution in surface water and groundwater of shallow aquifers. The roles of geothermal activity and geothermal water on pollution of surface and shallow aquifers depend on recharge mechanisms and a hydraulic relationship with groundwater in aquifers. This investigation is vital for the assessment of water quality, F⁻ mobilization and accumulation, the development of strategies for sustainable use and reducing the health risk of exposure to fluoride.

This paper aims to characterize the fluoride spatial distribution, geochemical process and enriching mechanism for groundwater in the Bilate river basin. The results provide information on the fluoride contaminants that are harmful to humans and the environment.

2. Description of the Study Area

The Bilate river basin is located in the Ethiopian rift valley lake basin within the geographic limit of 6°30'–8°10' N latitude and 37°40'–38°20' E longitude (Figure 1). It is characterized by the semi-arid climate in the rift floor and humid climate in the western highlands. Topographically, it can be divided in to the rift, escarpment and highland physiographic zone. The elevation ranges from 1200 m a.s.l to 3200 m a.s.l. Topographical effects cause considerable variability in mean yearly rainfall in the drainage basin. The annual rainfall in the rift varies from 800 in the rift to 1500 mm in the large highland parts. The mean yearly rainfall over the entire basin is 1165 mm. Rainfall is characterized by a bimodal pattern where the wet rainy seasons are March-May and July-October. The mean monthly temperature of rift floor is 22 °C and 14 °C in the highland parts. The Bilate river basin is rift-controlled, where its drainage pattern mainly governed by topography that depend on geologic structure [28,29]. The stream networks show parallel flow to the geologic structure mainly in the highland and develops dendritic drainage pattern in the lowland part (Figure 1).
3. Geological and Hydrogeological Settings

In the Southern Main Ethiopian Rift (SMER), basins are extensional and bounded by faulted escarpments, for example, [31] occurring significant slip during the Pliocene [32] with marginal deformation in the Arba Minch-Bridge of God area [33] and along the Chencha escarpment in the western rift margin [34]. In general, volcanic activity is limited within the rift depression and magmatic
processes are absent [35]. Quaternary volcanic activity occurred along the rift margins (e.g., Soddo area) and basaltic activity gave rise to the (NS directed) land bridge separating Lake Abaya from Lake Chamo, for example, see References [36,37].

The Bilate river basin is located on the western margin of the Southern MER, close to the transition zone with the Central MER, with the escarpments of Fonko-Guraghe. It extends from the northern coast of Lake Abaya, to the south, up to Akit town, to the north (Figure 1), enclosing the Soddo area. Geologic units from the lowest to the top consist of widespread Pliocene peralkaline pantelleritic ignimbrites (Nazret pyroclastics, NQS) and silicic volcanic complex (Damota volcano, ND), corresponding to predating main rifting events (~30–36 Ma), onset of main rifting events (~4 Ma), rift-margin transverse volcanism with E-W alignment of eruptive centers (close to Durame) and (Goba-Bonga) structure (~2.9 Ma) and Quaternary volcanic eruptive and sedimentation. Volcanic sediments formed on the rift floor in the Pleistocene, consisting of alluvial sands, pumiceous tuff, rhyolitic and basaltic fragments [29,30,37]. Holocene lacustrine and fluvial sediment are distributed in Lake Abaya and the Bilate and Gidabo rivers. A lacustrine delta a few kilometers wide occurs in the northern part of the Lake Abaya. The geologic units in the Soddo area were described in detail by Corti et al. (2013) [30].

The aquifers of the basin are characterized by fractured volcanic rocks, sediments and lacustrine deposits of the Tertiary and Quaternary age. Quaternary porous aquifer and volcanic fissured aquifer is a typical hydro-stratigraphic unit in the area. Quaternary deposits in the rift floor form shallow aquifers with a water yield that varies between 3 and 14 L/s [38,39]. The yield in the Quaternary volcanic aquifers varies from 2 to 5 L/s [39–41]. Weathered volcanic rock, together with locally inter-bedded gravels and alluvial deposits, form the water-yielding zones in the upland area. The Alluvium-Lacustrine Sediments, particularly in the upper Bilate river, have medium to high permeability and productivity where the groundwater well can yield up to 9 L/s with varying water table from 1.5 m to 50 m [38]. Water-bearing units in the Lake Abaya area are primarily composed of fractured and weathered basalts, ignimbrites, lacustrine and alluvial sediments. The depth of the groundwater table was found to be variable with an increasing trend from the highland towards the rift floor. The depth of the static water level in the highland and escarpment ranges from just below the land surface to approximately 40 m, while in the rift floor it can reach up to 290 m b.g.l. Generally, the flow of groundwater is along the natural morphological gradient from the west highland and escarpments eastwards the rift. However, the faults in the rift redirect the flow in some parts, so that the groundwater flows along the NE faults towards Lake Abaya. The volcanic terrain of Ethiopia is characterized by the occurrence of numerous and different yield springs that vary between 2 L/s in dry areas to 250 L/s [39]. Springs at the foot of the escarpment are largely representing shallow and deep groundwater flow, for example, Arbaminch spring yields 250 L/s [39]. The discharge of springs is progressively increasing from the highland to the mountain foot, suggesting that the rift boundary fault plays a vital role in the incidence of springs. In relation to the active fault zone, many thermal springs emerge in the area particularly in tectonically active northern Abaya in the rift floor. The thermal springs discharge within the rift floor along the north–northeast to south-southwest (NNE-SSW) trending faults [42] that emerge at varying elevations. Thermal springs in the northern lake Abaya area characterized by a temperature ranging from 35 to 95 °C and Na-HCO$_3$ type [42] with a TDS in the range of 1000–2500 mg/L.

4. Methodology

4.1. Sample Collection and Analysis

This study is based on water sample analysis together with the utilization of existing geological and hydrogeological information. Campaign for water sampling was undertaken through the area for hydrochemical and isotope analysis. The selection of the sampling locations was planned to take into consideration the representative area of the basin and the presence of complex system where cold water and thermal springs are found together. Forty-two water samples were collected in Bilattie
river basin in May 2016 and the sampling location is shown on Figure 1. Among them, 6 samples were taken from shallow wells (10–60 m), 23 samples from deep wells (60–360 m), 4 samples were cold spring waters, 3 samples were hot spring waters, 2 samples were river water and 4 samples were lake water. Before sampling, the wells were pumped to remove the stored water in the well and ensure sampling of primary groundwater. Separate samples were picked for the analysis of isotopes and major ions. Samples were stored in new 100 mL polyethylene bottles for major ions and 100 mL glass bottle for $\delta^{18}$O and $\delta$D analysis, respectively. Water temperature (T), pH and EC were measured in situ using a portable Multi-functional water quality analyzer (Multi 3430) (WTW a xylem brand, Weilheim, Germany) that was calibrated before use. Major ions (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, SO$_4^{2-}$, Cl$^-$, F$^-$ and NO$_3^-$) concentrations were measured with ion chromatography (Dionex Dx-120) (Thermo Fisher Scientific, Washington, DC, USA). Alkalinity was measured on the sampling day by Gran titration using 0.05 M HCl, while SiO$_2$ concentration was determined using colorimetry. Stable isotopic compositions of water ($\delta^{18}$O and $\delta$D) were measured with a Finnigan MAT 253 mass spectrometer (Scientific Instrument Services, INC, New Jersey, NJ, USA). Water samples were equilibrated with CO$_2$ for oxygen isotopic analysis and the Cd-reduction method was used to produce hydrogen gas for deuterium analysis. The $\delta$ notation was (VSMOW) used to report the analyzed water isotopes. The analysis was carried out at the State Key Laboratory of Geology and Geophysics, Chinese Academy of Sciences.

4.2. Mineral Speciation Modeling and Inverse Geochemical Modeling

The geochemical computer program PHREEQC [43] was used to calculate saturation indices of fluorite and calcite, activities of dissolved species in the groundwater (Ca$^{2+}$ and F$^-$). Saturation indices are widely used to evaluate the degree of equilibrium between mineral species and water. Changes in the saturation state of the minerals in water are useful for providing significant information on the various hydrogeochemical processes controlling the groundwater chemistry [44,45]. The saturation index of a mineral is calculated by following equation [46].

$$SI = \log \left[ \frac{IAP}{K_{sp}} \right]$$

where, $SI$ = saturation index, $IAP$ = ion activity product of the dissociated chemical species in solution, $K_{sp}$ = equilibrium solubility product for the chemical involved at the sample temperature. In this study, mineral saturation indices were calculated for all groundwater samples using the observed temperature and pH condition. The line of solubility product (K) used in the activity-activity diagram was constructed by using log $K_{fluorite} = \log$ Ca$^{2+} + 2 \log$ F$^-$ and the value of solubility product ($K_{fluorite}$) at 25 °C was taken from [46] and ($K_{fluorite}$) at 30 °C and 50 °C was taken from Reference [47].

Inverse geochemical modeling can determine the nature and extent of the geochemical reactions by identifying the reacting minerals and the dissolution or precipitation amount of these minerals [43,48,49]. The geochemical computer code NETPATH-WIN, capable of calculating mass transfer along groundwater flow paths [50], was used in this study. NETPATH-WIN suggests possible reactions on the basis of constraints (dissolved elements) and phases (minerals which are present and dissolved and/or precipitate), using inverse modeling techniques to construct geochemical reaction models. NETPATH-WIN produces geochemical mass balance reactions between an initial and final water composition. In the present study, the NETPATH-WIN software was run to calculate the dissolution/precipitation amount of the major aquifer minerals along a groundwater flow path in the Bilate River basin and to evaluate the effect of major hydrogeochemical processes on the F$^-$ concentration in groundwater.
5. Results

5.1. Hydrochemistry

A summary of the physico-chemical parameter of the sampled waters is reported in Table 1 by means of statistical data (minimum, maximum, average). Groundwater of the Bilate river basin presents generally low to moderate mineralization apart from hot springs, reflected in electrical conductivity measurements, which range between 112 μS/cm and 770 μS/cm. Hot spring water shows the highest value of electrical conductivity (1260 μS/cm). Groundwater temperature shows variability in the basin and ranges from 20–81 °C. Groundwaters can vary from mainly slightly acidic to slightly alkaline, with pH values ranging between 5.6 and 8.5. The minimum value was measured in shallow groundwater, while the maximum value registered corresponds to hot springs. The EC values of lake water were found to be high, reflecting the evaporation effect. In general, there is a progressive increase in temperature, EC and pH value in groundwater from the highland to the rift floor with local anomalies related to the thermal systems.

Major dissolved ions display wide variability across the basin (Figure 2). In the Bilate river basin Na⁺ is the dominant cation in groundwater followed by Ca²⁺ and K⁺. The concentration of Na⁺ in groundwater shows a diagnostic increase from highland to the rift floor while Ca²⁺ and Mg²⁺ decrease rift wards. The K⁺ concentration is normally low but shows a positive trend with groundwater temperature. HCO₃⁻ is the dominant anion in groundwater followed by Cl⁻ and SO₄²⁻. The HCO₃⁻ content is higher in the hot spring, the highest being in the hot spring water of the Abaya geothermal field. Elevated NO₃⁻ contents are observed in B1, a shallow hand-dug well, which exceeds the WHO guideline for drinking water (50 mg/L). The high NO₃⁻ is related to pollution from anthropogenic sources. Generally, NO₃⁻ and SO₄²⁻ concentrations were found to be low in groundwater and surface water (Table 1).

A Piper plot (Figure 3) of the groundwater data, classified the groundwater into different group of groundwater facies based on the dominant cations and anions: Ca–Mg–HCO₃, Ca–Na–HCO₃, Ca–Na–Mg–HCO₃, Na–Ca–Mg–HCO₃, Na–Ca–HCO₃ and Na–HCO₃. However, the dominant water types are Ca–Mg–HCO₃, Na–Ca–HCO₃ and Na–HCO₃. Water types evolved from Ca–Mg–HCO₃ to Ca–Na–HCO₃ and to Na–HCO₃ from the highland to the rift floor.

![Figure 2](image-url)  
*Figure 2. Box and whisker showing variability of chemical composition of the groundwater. Q1, Q2 and Q3 represent the first, the second and the third quartile, respectively.*

5.2. F⁻ Concentrations

The F⁻ concentrations varied from 0.5 to 112 mg/L in all water samples in the Bilate river basin. Shallow groundwater and cold spring water had fluoride concentration below 1.5 mg/L.
Deep groundwater samples had F⁻ concentrations ranging from 0.48 to 5.61 mg/L. More than 70% of groundwater from deep well contained F⁻ more than the WHO potable guideline. All hot spring water samples had F⁻ more than the WHO potable guideline with a maximum value that can reach up to 57.4 mg/L (B36). Likewise, all lake water samples had the highest fluoride concentration (Table 1) except lake water (B42), which had the lowest F⁻ concentration of 0.2 mg/L.

Table 1. Statistical summary of hydrochemical components in the study area.

|                  | Shallow Groundwater | Deep Groundwater |                  | Shallow Groundwater | Deep Groundwater |
|------------------|---------------------|------------------|------------------|---------------------|------------------|
| **Units**        | **Min**             | **Max**          | **Mean**         | **Min**             | **Max**          |
| Temperature      | °C                  | 21.8             | 26.0             | 23.7               | 21.9             | 40.6             | 27.0             |
| pH               | -                   | 5.6              | 7.1              | -                  | 6.1              | 8.2              | -                |
| EC               | µS/cm               | 197.0            | 633.0            | 400.6              | 232.0            | 770.0            | 490.9            |
| Na⁺              | mg/L                | 25.5             | 38.2             | 29.1               | 7.0              | 106.0            | 46.6             |
| K⁺               | mg/L                | 6.9              | 16.7             | 10.1               | 4.3              | 19.0             | 11.7             |
| Mg²⁺             | mg/L                | 4.1              | 10.1             | 7.7               | 0.6              | 20.5             | 7.3               |
| Ca²⁺             | mg/L                | 11.4             | 48.3             | 24.8               | 8.0              | 61.6             | 22.1             |
| Cl⁻              | mg/L                | 2.3              | 35.1             | 17.3               | 0.3              | 15.3             | 5.5               |
| SO₄²⁻            | mg/L                | 0.1              | 74.9             | 14.5               | 0.0              | 16.6             | 4.0               |
| HCO₃⁻            | mg/L                | 26.8             | 577.1            | 257.3              | 136.9            | 622.6            | 359.2            |
| NO₃⁻             | mg/L                | 2.1              | 69.5             | 20.0               | 0.2              | 17.6             | 3.7               |
| F⁻               | mg/L                | 0.8              | 1.3              | 0.9               | 0.5              | 5.6             | 2.5               |
| SiO₂             | mg/L                | 31.9             | 54.4             | 47.4               | 22.1             | 70.0             | 64.0             |
| δ¹⁸O             | -                   | -3.4             | -2.1             | -4.9              | -2.1             | -2.1             | -2.1             |
| δD               | -                   | -4.3             | 5.3              | -0.6              | -27.1            | -2.7             | -13.9            |

Cold Spring Hot Spring

|                  | Cold Spring | Hot Spring | Cold Spring | Hot Spring |
|------------------|-------------|------------|-------------|------------|
| **Units**        | **Min**     | **Max**    | **Min**     | **Max**    |
| Temperature      | °C          | 20.1       | 22.5       | 21.6       | 32.8       | 81.0       | 48.0       |
| pH               | -           | 6.1        | 6.5        | -          | 6.5        | 8.5        | -          |
| EC               | µS/cm       | 112.0      | 198.0      | 144.7      | 202.0      | 1262.0     | 840.3      |
| Na⁺              | mg/L        | 7.1        | 23.3       | 15.8       | 27.2       | 197.7      | 121.5      |
| K⁺               | mg/L        | 4.0        | 10.7       | 6.9        | 6.6        | 39.7       | 21.6       |
| Mg²⁺             | mg/L        | 1.0        | 2.7        | 1.7        | 0.3        | 4.1        | 2.1        |
| Ca²⁺             | mg/L        | 4.8        | 6.1        | 5.2        | 3.5        | 18.4       | 9.2        |
| Cl⁻              | mg/L        | 3.6        | 6.2        | 4.5        | 1.8        | 64         | 28.2       |
| SO₄²⁻            | mg/L        | 1.0        | 2.2        | 1.5        | 0.5        | 106        | 35.0       |
| HCO₃⁻            | mg/L        | 40.3       | 117.7      | 72.0       | 178.4      | 747.9      | 541.6      |
| NO₃⁻             | mg/L        | 4.2        | 23.2       | 11.0       | 2.4        | 8.9        | 5.7        |
| F⁻               | mg/L        | 0.5        | 0.7        | 0.6        | 1.7        | 57.4       | 20.2       |
| SiO₂             | mg/L        | 33.4       | 34.7       | 34.1       | 67.17      | 70.2       | 68.7       |
| δ¹⁸O             | -           | -3.2       | -2.1       | -2.6       | -3.18      | -1.9       | -2.2       |
| δD               | -           | -9.7       | -2.4       | -5.6       | -12.73     | -4.1       | -8.2       |

River Lake

|                  | River | Lake |
|------------------|-------|------|
| **Units**        |       |      |
| Temperature      | °C    | 23   | 24   | 23.5 | 23.6 | 27.8 | 26.0 |
| pH               | -     | 7.4  | 7.7  | -    | 6.97 | 10.1 | 10.1 |
| EC               | µS/cm | 83.2 | 219  | 151.1 | 187 | 26300.0 | 118468.8 |
| Na⁺              | mg/L  | 17.0 | 17.2 | 17.1 | 15   | 4250 | 2541.3 |
| K⁺               | mg/L  | 7.2  | 10.3 | 8.8  | 23   | 282  | 126.8 |
| Mg²⁺             | mg/L  | 3.1  | 6.4  | 4.8  | 0.5  | 4.3  | 2.1   |
| Ca²⁺             | mg/L  | 12.2 | 18.7 | 15.5 | 2.4  | 17.6 | 8.6   |
| Cl⁻              | mg/L  | 3.6  | 8.2  | 5.9  | 11.4 | 611.4 | 307.6  |
| SO₄²⁻            | mg/L  | 4.9  | 12.8 | 8.8  | 1.1  | 652.5 | 168.3  |
| HCO₃⁻            | mg/L  | 86.3 | 93.9 | 90.1 | 37.1 | 4114.0 | 2110.3 |
| NO₃⁻             | mg/L  | 2.1  | 15.6 | 8.9  | 1.2  | 42.0 | 11.9  |
| F⁻               | mg/L  | 0.6  | 1.9  | 1.3  | 0.2  | 112.0 | 50.2   |
| δ¹⁸O             | -     | -2.9 | -2.1 | -2.5 | 3.88 | 8.0  | 6.7   |
| δD               | -     | -4.9 | -3.7 | -4.3 | 28.81 | 51.1 | 40.5   |
Figure 3. Piper diagram showing the hydrochemical facies of groundwater and surface water in the Bilate river basin.

5.3. Spatial Distribution of Fluoride

Layers of water points, drainage pattern and topographic map were overlaid for the presence of the spatial distribution of fluoride (Figure 4). It is apparent that the $F^-$ distribution is related to topography and drainage pattern. More than 56% of the samples were low in $F^-$ for groundwater that were from shallow wells, cold spring waters and the groundwater from deep wells that are located in highland and escarpment. The $F^-$ increased from highland to lowland and the Bilate river marked the boundary between groundwater bodies of $F^- < 3$ mg/L and $F^- > 3$ mg/L. The $F^-$ distribution was classified into four zones based on the variation of fluoride concentration. The Low fluoride groundwaters (<1.5 mg/L) are located on the escarpment and highland in the western part of the area with elevations > 2000 m.a.s.l. (Area-1, AI). The groundwater of fluoride in the range of 1.6 to 3.0 mg/L was located in the central part of the area and mainly along the Bilate river (Area-2, AII). The groundwater of fluoride in the range of 3.1 to 6.0 mg/L was located in the north eastern part of the area with elevation between 1600 and 2000 m.a.s.l. (Area-3, AIII). High fluoride groundwater in the range of 6.1 and 12.0mg/L was situated in the southern part of the area with elevations between 1400 and 1800 m.a.s.l. (Area-4, AIV).
Figure 4. Spatial distribution of $\text{F}^-$ in groundwater of Bilate River basin. Note: black, brown, red and light-blue lines are used as approximate demarcation of areas with different fluoride concentration.
5.4. Stable Hydrogen (δD) and Oxygen (δ18O) Isotopes

The result of the isotopic composition of δ18O and δD are listed in Table 1 and presented in Figure 5, along with the Global Meteoric Water Line (GMWL) and the Addis Ababa Meteoric Water Line (AAMWL), given by the equation δD = 7.04 δ18O + 11.8, derived from the GNIP data base [51]. The δ18O and δD values of groundwater range from −4.9 to −1.1%, and −27.1 to 5.3‰, while the δ18O and δD values of surface water range from −2.9 to 8.0%, and −4.9 to 51.1‰. The δ18O and δD of water sample from shallow well and cold spring range from −1.12 to −3.4‰ and 5.34 to −9.65‰, respectively. The δ18O and δD value of deep groundwater ranges from −2.12 to −4.90%, and −2.96 to −27.08‰, respectively. Deep groundwater shows wide variation in δ18O and δD value compared to shallow groundwater and cold spring. Groundwaters with δ18O more depleted than −3.5‰ (Figure 5) represent deeper groundwater from eastern part of Halaba town. Groundwater from shallow wells and cold spring water lies on or above local water line and groundwater from deep wells plot below the local meteoric water line with more depleted isotopic values. Hot spring waters lies on GMWL, with a same range as groundwater of shallow wells. Lake waters deviate from the AAMWL and GMWL. It appears that the groundwater samples plot along or close to the two meteoric lines, indicating a meteoric origin for the recharge of groundwater (Figure 5).

![Figure 5. Relationship between δ18O and δD values of Bilate water types compared with the Global Meteoric Water Line (GMWL), Addis Ababa Local Meteoric Water Line (AAMWL).](image)

6. Discussion

6.1. Mechanisms Controlling Groundwater Chemistry

Different geochemical processes occur during rock-water interaction, which include dissolution/precipitation, ion exchange processes, hydrolysis, oxidation and reduction [52–55]. Gibbs diagrams, which are constructed by plotting ratio of Na+/Na+ + Ca2+ and Cl−/Cl− + HCO3− versus TDS [56], are widely used to identify natural processes such as precipitation, rock-water interaction, governing groundwater geochemistry [54,55]. As seen in Figure 6a,b, all groundwater samples were plotted on the rock-water interaction region, indicating the important roles of rock-water interaction in groundwater chemistry, and evaporation was found to be no contribution to the dissolved constituent of groundwater. Lake water samples were plotted into the evaporation dominant area, signifying the importance of evaporation in lake water chemistry.

To further understand the details of rock-water interaction in the study area, some ratio plots of major ions were conducted (Figure 6c,d). The hydrolysis of silicate could result in the release of cations such as Ca2+, Mg2+, K+ and Na+ and the balancing bicarbonate ion into the groundwater [46]. This can be understood by general relationships between the concentrations of major ions. The correlation of cationic species, [Ca2+ + K+ + Mg2+ + Na+] and [HCO3−], suggests that the cations are balanced...
mainly by the bicarbonate anion (Figure 6c) and this in turn confirms that silicate hydrolysis is the most governing hydrochemical process. In addition, if the ratio of Na$^+$ to Cl$^-$ is greater than 1, the result can be interpreted as Na$^+$ being released from a silicate mineral [57]. While if the ratio is approximately equal to 1, Na$^+$ is mainly contributed by halite dissolution, whereas less than 1 indicates derivation from anthropogenic sources. Figure 6d shows that the value of Cl$^-$ as a function of Na$^+$ in the groundwater. In this study, nearly all groundwater samples are with the ratio greater than 1, implying that silicate hydrolysis is an important source of sodium in groundwater.

![Figure 6](image)

**Figure 6.** Plot of TDS versus the weight ratios of Na$^+$/ (Na$^+$ + Ca$^{2+}$) (a), the weight ratios of Cl$^-$/(Cl$^-$ + HCO$_3^-$) (b) Gibbs [56]. Relationship between major cations species and (HCO$_3^-$) (c), plot of Na$^+$ versus Cl$^-$ (d).

Cation exchange was another significant factor that was responsible for the formation of groundwater chemistry in the Bilate river basin. The high content of Na$^+$ in groundwater from the rift areas may be related to the cation exchange that takes place in the aquifers. The Na$^+$/Ca$^{2+}$ ratio of groundwater in the rift floor is much higher than that in the highland and escarpments and the hydrochemical facies evolved from Ca-Mg-HCO$_3^-$ to Na-HCO$_3^-$. The two Chloro-Alkaline Indices CAI-I and CAI-II were used to investigate the occurrence of cation exchange reactions in this area as suggested by Shoeleller [58]. These two indices are expressed as Equations (2) and (3) (all ions are expressed in meq/L).

\[
CAI - I = \frac{[Cl^- - (Na^+ + K^+)]}{Cl^-}
\]

(2)

\[
CAI - II = \frac{[Cl^- - (Na^+ + K^+)]}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-}
\]

(3)

Both indices are expected to be positive when Na$^+$ exchanged for Ca$^{2+}$ or Mg$^{2+}$ from aquifer matrix and negative indices expected when Ca$^{2+}$ or Mg$^{2+}$ exchanged for Na$^+$ from aquifer matrix. The value of CAI-I and CAI-II for nearly all groundwater samples from Bilate river basin is negative.
(Figure 7a), indicating the cation-exchange of Ca$^{2+}$ in the water with Na$^+$ in the aquifer material takes place. The indices of shallow groundwater and cold spring water scattered in a narrow range for CAI-I and CAI-II, while deep groundwater from the Bilate river Basin revealed a very wide variation in these two indices (Figure 7a). From this, it could be inferred that deep groundwater was affected by various degrees of the cation exchange process. The cation exchange also resulted in the high Na$^+/Ca^{2+}$ ratio of deep groundwater in the rift floor (0.44 to 12.37) compared to that in the shallow groundwater (1.02 to 4.13) of the highland and escarpment. This indicated that there was an increase in such an exchange in the central basin, where significantly elevated Na$^+/Ca^{2+}$ ratios and sodium contents were observed.

![Figure 7](image_url)  
**Figure 7.** (a) plot of CAI-II vs. CAI-I of groundwater samples from the Bilattie River Basin [38] and (b) plot of F$^-$ vs. Na/Ca ratio.

### 6.2. Genesis of High Fluoride Groundwater

The formation of high fluoride groundwater in Bilate river basin displayed typical major ion chemistry that is rich in Na$^+$ and poor in Ca$^{2+}$ with relatively high pH and HCO$_3^-$ concentrations (Figure 8) as a result of geochemical processes of silicate hydrolysis and cation exchange in the aquifer as discussed above. Na$^+$ display a positive correlation with F$^-$ (R$^2$ = 0.665, Figure 8a) suggesting that hydrolysis reactions of fluoride bearing minerals could lead to simultaneous fluorine and sodium enrichment. The competitive anions, such as HCO$_3^-$, promoted the formation of high-F$^-$ groundwater under alkaline conditions in the in Bilate river basin. In this study, there was a positive correlation between F$^-$ and HCO$_3^-$ with significant coefficient (R$^2$ = 0.492, Figure 8b). Groundwater with F$^-$ concentrations (>1.5 mg/L) had HCO$_3^-$ values ranging from 150 to 750 mg/L. Moreover, the groundwater with F$^-$ concentrations (>3 mg/L) had HCO$_3^-$ greater than 400 mg/L. The highest observed groundwater HCO$_3^-$ concentration of 750 mg/L occurred with a fluoride concentration of 11.9 mg/L. This indicates that elevated HCO$_3^-$ contents favored F$^-$ release from the aquifer matrix into groundwater. For the fluoride in groundwater, fluorite bearing mineral such as fluorite may be a natural source and F$^-$ is also abundant in silicate minerals such as amphiboles, muscovite and biotite [22–24,59]. Hydroxyl and HCO$_3^-$ might be simultaneously released into the groundwater during the leaching and dissolution process of F-bearing minerals [60]. In addition, hydroxide ions provide a high exchange capacity replacing the F$^-$ within the minerals, increasing the F$^-$ content in groundwater [59,61]. In the study area, groundwater with a fluoride content >1.5 mg/L has a pH value in the range of 6.5 to 8.5 and displays a positive correlation with F$^-$ (R$^2$ = 0.28, Figure 8d). Thus, F$^-$ can be released from aquifer matrix and entered the groundwater when the HCO$_3^-$ concentrations were high under alkaline conditions, which reasonably explained why groundwater samples with elevated F$^-$ concentrations had high HCO$_3^-$ concentrations and alkalinity in the Bilate river basin.

When fluoride concentration in groundwater is mainly due to fluorite dissolution, then Ca$^{2+}$ versus F$^-$ is negatively correlated [22,62]. However, in the study area, the correlation of F$^-$ with Ca$^{2+}$

are quite weak and complex ($R^2 = 0.054$, Figure 8c). The correlation shows two different trends owing to their activity in groundwater. Cold spring water, shallow groundwater and some deep groundwater that has lower F$^-$ and Ca$^{2+}$ content shows a positive correlation and deep groundwater and hot spring water shows a negative correlation. This indicates that the dissolution of fluorite mineral is not the only source of fluoride in the groundwater. Furthermore, the rocks rich in alkali metals (such as sodium and potassium) and obsidian, both of which are common in the rift, tend to have relatively high amounts of F$^-$ [8]. In the Ethiopian rift valley, the average fluorine contents of the pyroclastic deposit range from 0.2 to 0.3% [63,64]. This supports the explanation that the high fluoride concentration of groundwater in the Bilate river basin originates mainly from silicates in volcanic rocks.

Cation exchange between Ca$^{2+}$ and Na$^+$ due to the movement of water in the aquifer may result in high F$^-$ associated with high Na$^+$ and low Ca$^{2+}$ concentration [24]. The chemical composition of groundwater resulted in the formation of different water types and can be reflective of the geochemical process that operated in a certain lithological environment. The dominant hydrochemical facies in the Bilate river basin were Na-HCO$_3$ followed by Na-Ca-HCO$_3$, Na-Ca-Mg-HCO$_3$, Ca-Na-HCO$_3$ and Ca-Mg-HCO$_3$. The removal of Ca$^{2+}$ and addition of Na$^+$ by cation exchange process often gives rise to Na-HCO$_3$. Na-Ca-HCO$_3$ and Na-HCO$_3$ were predominant and accounted for 80% in the Bilate River Basin and mainly found in the rift floor. Meanwhile, samples with high F$^-$ concentrations were Na-HCO$_3$ water type while samples with low F$^-$ concentrations were Ca-Mg-HCO$_3$ water type. This is because Na-HCO$_3$ water types are capable of releasing fluoride from fluorite mineral [62,65]. Likewise, cation exchange resulted in high Na$^+/Ca^{2+}$ in groundwater of the Bilate river basin. Meanwhile, fluoride show positive correlation with Na$^+/Ca^{2+}$ ($R^2 = 0.611$, see Figure 7b). The increasing of fluoride content with Na$^+/Ca^{2+}$ suggest the removal of Ca$^{2+}$ from a solution and the uptake of Na$^+$ from aquifer matrix in the flow process that lead to greater mobilization of fluoride.

![Figure 8](image)

**Figure 8.** (a) Plot of Na$^+$ vs. F$^-$, (b) HCO$_3^-$ vs. F$^-$, (c) Ca$^{2+}$ vs. F$^-$ and (d) F$^-$ vs. pH.

Oxygen ($\delta^{18}O$) isotopes are commonly used for tracing flow-systems as they retain information of recharge conditions and may reflect residence time of groundwater [66]. The oxygen ($\delta^{18}O$) value
of groundwater decreasing from highland to the rift floor mirrors the flow path. The change of δ18O value is accompanied by a change in a diagnostic increasing trend in electrical conductivity (EC), Na+ and HCO3− from highland to the rift floor. A regular increase in F− content is also noted with a decrease in δ18O value towards the rift floor. This is indicative of successive accumulation of F− along the groundwater flow path. Moreover, the plot of δ18O versus fluoride (Figure 9a) shows negative correlation with groundwater, indicating the water with lighter isotope had experienced longer water–rock interactions. It has been reported that isotope-depleted water contains a high-fluoride concentration [19,67]. The δ18O versus fluoride diagram (Figure 9a) show that there is a significant isotopic contrast between the shallow groundwater and deep groundwater. The deep groundwaters in the Bilate river basin are isotopically more depleted and show higher fluoride levels than those in the shallow groundwater and cold spring. The δ18O of deep groundwater is negatively correlated with fluoride content with a coefficient of 0.65 (Figure 9a). This trend is more obvious when groundwater from the deep well is considered exclusively. Groundwaters with fluoride levels greater than 3 mg/L occur only when δ18O values are lighter than −3.5‰ (Figure 9a), indicating that the enrichment of fluoride was the result of longer water–rock interaction and successive accumulation along the groundwater flow path.

An additional characteristic of the groundwater is that it has low NO3− concentrations. The nitrate concentration for all groundwater samples is less than 50 mg/L, which is the WHO drinking water guideline value for NO3−. Groundwater with a fluoride concentration greater than 3 mg/L commonly had low nitrate concentration (<10 mg/L). The highest nitrate concentration that recorded in shallow well B1 of 69 mg/L occurred with low fluoride concentration of 0.5 mg/L. The insignificant correlation between F− and NO3− (Figure 9b) with correlation coefficient of −0.13 suggests that fluoride pollution due to agricultural activity was negligible.

![Figure 9](image_url) 

**Figure 9.** (a) Plot of δ18O vs. F− and (b) NO3− vs. F−.

### 6.3. Geochemical Modeling of Water Rock Interaction

The saturation index of fluorite and calcite were calculated under the field measured temperature and pH. Fluorite is undersaturated for all water samples (Figure 10a). Nevertheless, hot springs B34 and B35 are oversaturated with respect to fluorite; precipitation of this mineral phase is a limiting factor for F− and Ca2+ species in water. Samples fall in the region of fluorite undersaturated is capable of dissolving F-bearing minerals. Figure 10b shows that fluorite would precipitate when ion activity products of Ca2+ and F− are above the fluorite equilibrium constant (Kfluorite is 10−10.57 [46]). The activities of both species were calculated using a geochemical modeling program PHREEQC [43]. Figure 10b, a logarithmic activity–activity diagram, shows two evolution trends. Trend 1 indicates that Ca2+ and F− ion concentrations increase which depict an independent origin and, in a manner, independent of fluorite dissolution. This groundwater collected from highland and escarpment area which characterized by Ca-Mg-HCO3 water type could be independent of fluorite dissolution and
is likely influenced by water type. As known, the Ca-HCO₃ water type could have lower fluoride compared to Na-HCO₃ [68]. The solubility limits for fluorite and calcite can provide a natural control on water composition because calcium, fluoride and carbonate activities are interdependent [69]. The low calcite solubility can lead to a high F⁻ concentration in groundwater. However, there is a progressive dissolution of calcite and fluorite in groundwater that collected from highland and escarpments (Figure 10a) that correspond with trend 1 in Figure 10b and there is no favorable condition that reduces Ca²⁺ activity and allowing more fluorite to dissolve. Additionally, there is strong flow dynamics because of intensely fractured and highly weathered of highland volcanic rock and the recharge in the highland is high as 250 mm/year [38]. Therefore, the available condition is not favorable for high F accumulation in groundwater from the highland and escarpment area. Trend 2 shows increasing F⁻ activity with decreasing Ca²⁺ activity where the activities of Ca²⁺ and F⁻ shift to the left along the saturation line of fluorite. Samples that follow trend 2 were mainly collected from low land. The samples did not cross the fluorite equilibrium line and this suggests that fluorite precipitation controls the upper limits of F⁻ in groundwater. The calcite is saturated in some deep groundwater (Figure 10a). The activity of Ca²⁺ will decrease with calcite precipitation as some of the deep groundwater is saturated with respect to calcite (Figure 10a). However, the calcite SI of the saturated deep groundwater oscillates around zero, suggesting conditions close to equilibrium for this mineral phase. Moreover, in the rifted part of the basin, there is low recharge, and low flow dynamics occur that can favor water rock interaction. This in turns means that the observed calcium activity is mainly controlled by the cation exchange process as discussed in Section 6.1 rather than by calcite precipitation.

An inverse geochemical model was built using the available hydrochemical data in order to evaluate the effect of geochemical process on fluoride enrichment in groundwater. The phases and constraints used in the NETPATH-WIN modeling were selected based on potential hydrogeochemical reactions taking place in the volcanic aquifer. Plagioclase and biotite were taken as a phase in the model and the corresponding elements Ca, Mg, Na, K and Si as constraints. The dissolution of fluorite likely provides input of F⁻ to the groundwater and therefore it was added in the model as a phase and the elements F⁻ as the corresponding constraints. In addition, Ca–Na exchange was included in the model to simulate the high Na⁺ and F⁻ concentration of groundwater in the discharge area. The chemical composition of the waters of cold spring B30 was assumed to represent a pristine recharge area groundwater and its composition was therefore used as initial water in the inverse modeling. The results of the inverse geochemical modeling show that the hydrolysis of plagioclase and biotite is the major geochemical process. Moreover, as can be seen in Table 2, the hydrochemical composition was also affected by the input of calcite and fluorite dissolution. Dissolution of gaseous CO₂ and cation

![Figure 10](image_url). (a) Plot of Ca²⁺ vs. F⁻, (b) saturation index of calcite versus saturation index of fluorite and (c) the relationship between the log activities of Ca and log activities of F⁻.
exchange (Ca-X/Na-X) was required in all cases. The results of the inverse geochemical modeling suggested that the interactions between groundwater and fluoride-rich minerals in the aquifers are responsible for the increase of F$^{-}$ concentration in groundwater along the flow path. It is also observed that the calcium activity is mainly controlled by cation exchange rather than by calcite precipitation, since calcite is mainly dissolved during groundwater interaction. Considering the relationship between F, Na and HCO$_3^-$ in the fluoride enriched groundwater and inverse geochemical modeling results, a path was suggested that can possibly define the evolution of groundwater chemistry that drains the volcanic aquifer (Figure 10b).

### Table 2. Results of mass transfer along the groundwater flow from highland to the rift part of the basin (All mineral and gas mass transfers are in mmol/kg H$_2$O).

| Phase | Plagioclase | Biotite | Calcite | Fluorite | Ca-Na | CO$_2$ (g) |
|-------|-------------|---------|---------|----------|-------|------------|
| B30–B25 | 0.14721 | 0.05082 | 1.60339 | 0.04117 | 1.1576 | 2.75896 |
| B30–B20 | 0.10979 | 0.07604 | 1.39587 | 0.03485 | 1.02302 | 2.32185 |
| B30–B35 | 0.19637 | 0.0184 | 2.44832 | 0.13105 | 2.3787 | 3.01156 |
| B30–B28 | 0.25325 | −0.02664 | 2.04245 | 0.06825 | 2.00979 | 1.96745 |

### 6.4. Implication for Fluoride Geochemistry in Volcanic Aquifers

The results of this study have implications for the evaluation of variations in groundwater chemical composition and concentrations of specific solutes during water-rock interactions in volcanic aquifers. For example, it is showed that deep groundwater from basaltic aquifer of northern Ethiopia is significantly enriched in DIC and major cations due to silicate weathering enhanced by magmatic CO$_2$ [70]. On the volcanic island of Azores archipelago, Cordeiro, Coutinho and Cruz [15] suggested that the composition of groundwater modified by silicate hydrolysis where F concentrations up to 2 mg/L were recorded. This study contributes to understanding the controlling mechanism for the mineralization of groundwater and mobilization of solute including fluoride in environments closely linked to groundwater systems. It also provides insight on the evaluation of element fluxes from groundwater in volcanic aquifers to streams and lake water which can affect ecosystem and biogeochemistry of those hydrologic systems. This study may also contribute to understanding and providing important information on the geologic and geochemical aspect on the finding of the favored site and depth of groundwater development. Better recognition of spatial distribution and the enrichment processes of fluoride will be helpful in the development of strategies that minimize the health risk of exposure to fluoride and identify the hotspot of fluorosis. Even though detailed understanding of the spatial distribution of fluoride with the depth and identification of the potential contribution of litho-type to the release of fluorine will require depth specific sampling and leachate experiment, our study demonstrates that hydrochemical and stable isotopes are useful to provide the full picture of spatial distribution and comprehensive understanding in fluoride enrichment processes in volcanic aquifers.

### 7. Conclusions

Groundwater is the most important source of drinking water in south Ethiopia. The concentration of fluoride in deep aquifers was well above the permissible limit. The mechanisms of F$^{-}$ enrichment were investigated based on the hydrochemistry and stable isotope of groundwater in the Bilate river basin of the Southern Main Ethiopian rift. High fluoride (up to 5.61 mg/L) groundwater mainly occurred in deep wells and low F$^{-}$ concentration (0.5–1.29 mg/L) recorded in water from shallow wells. Spatially, high F$^{-}$ groundwater is concentrated in the rift floor and low F$^{-}$ groundwater in the highland. The high F$^{-}$ groundwater is distinctive in its low concentration of Ca$^{2+}$ but high concentrations of Na$^+$ and HCO$_3^-$ with moderate alkaline pH and is classified as Na-HCO$_3$ type. Such characteristics of groundwater chemistry are closely related to processes of silicate hydrolysis and cation exchange in the aquifer systems. High fluoride groundwater showed significant positive correlations with pH,
Na\(^+\) and HCO\(_3^-\), indicating that the geochemical process that controls overall groundwater chemistry also promotes high fluoride concentration in groundwater. The groundwater with high-fluoride concentrations showed a strong negative correlation with \(\delta^{18}O\), showing that the high-fluoride concentrations were the result of water–rock reactions over a longer period. The insignificant correlation of fluoride with nitrate ruled out the anthropogenic input into fluoride enrichment in groundwater. The thermodynamic relationship between the activities of Ca\(^{2+}\) and F\(^-\) showed two stages of hydrochemical evolving paths of the dissolution (trend I) and ion exchange equilibrium with Ca\(^{2+}\) and Na\(^+\) (trend II) that can explain F enrichment in deep aquifers. The results of the inverse geochemical modeling using NETPATH-WIN also indicate that the interactions between groundwater and fluoride-rich minerals in the aquifers are responsible for the increase of F\(^-\) concentration in groundwater along the flow path. Integration of stable isotopes and major ions in groundwater and volcanic stratigraphy revealed the complicated patterns of fluoride distribution and the enrichment of groundwater with fluoride in the volcanic aquifer of the Bilate river basin. This study has implications for understanding the genesis of high fluoride in water as well as groundwater flow dynamics in volcanic aquifers that are major sources of drinking water in many parts of the world.

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