

Article

# Origin of Fluoride and Arsenic in the Main Ethiopian Rift Waters

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**Abstract:** In the Main Ethiopian Rift (MER) area, rural populations often use water that exceeds the World Health Organization thresholds for fluoride (F<sup>-</sup>) and arsenic (As), two elements that are hazardous for human health. In this study, twenty-nine water samples were collected from lakes and hot and cold springs in southern MER to investigate source(s) and health-risk of the F<sup>-</sup> and As contamination. According to major ion and trace element analyses, only cold spring water is safe for consumption, whereas hot spring water is the most contaminated. Leaching tests performed with the MER rhyolitic volcanic rocks and their weathered products (fluvio-lacustrine sediments) demonstrate that the main cause of the F<sup>-</sup> and As release is geogenic, i.e., not related to anthropogenic activities. The weathering of volcanic glass and minerals (apatites, clays, hydroxides) by CO<sub>2</sub>-bearing alkaline water induces the mobilisation of F<sup>-</sup> and As from solid to liquid phase. This process is particularly fast, when fluvio-lacustrine sediments are involved, and can be further enhanced by hot groundwater leaching. This study, investigating the distribution, sources, and mechanisms of F<sup>-</sup> and As release in MER water, could be of interest also for other sectors of the East African Rift and other similar volcano-tectonic settings.

**Keywords:** fluoride and arsenic; Main Ethiopian Rift; water–rock interaction; weathering; tolerance limit; geogenic contamination

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## 1. Introduction

Groundwater is the major source of drinking water for over half of the global population [1]; however, its quality can be compromised by natural geogenic contaminants such as fluoride (F<sup>-</sup>) and arsenic (As). In some cases, groundwater interacts with F<sup>-</sup> and As-enriched host aquifers, which releases these elements in levels that are hazardous for the human health [2]. The guideline values established by the World Health Organization (WHO) for F<sup>-</sup> and As in drinking water are 1.5 mg/L and 10 µg/L, respectively [3]. Prolonged ingestion of drinking water containing concentrations of F<sup>-</sup> exceeding the tolerance limit can cause dental and skeletal fluorosis, and excess of As exposure can cause skin disorders, respiratory problems, and cancer [2,4]. Therefore, F<sup>-</sup> and As contamination represents a serious health issue, especially in rural communities that receive water from

groundwater wells without testing for the presence of toxic contaminants (e.g., Bangladesh and India [5–7]).

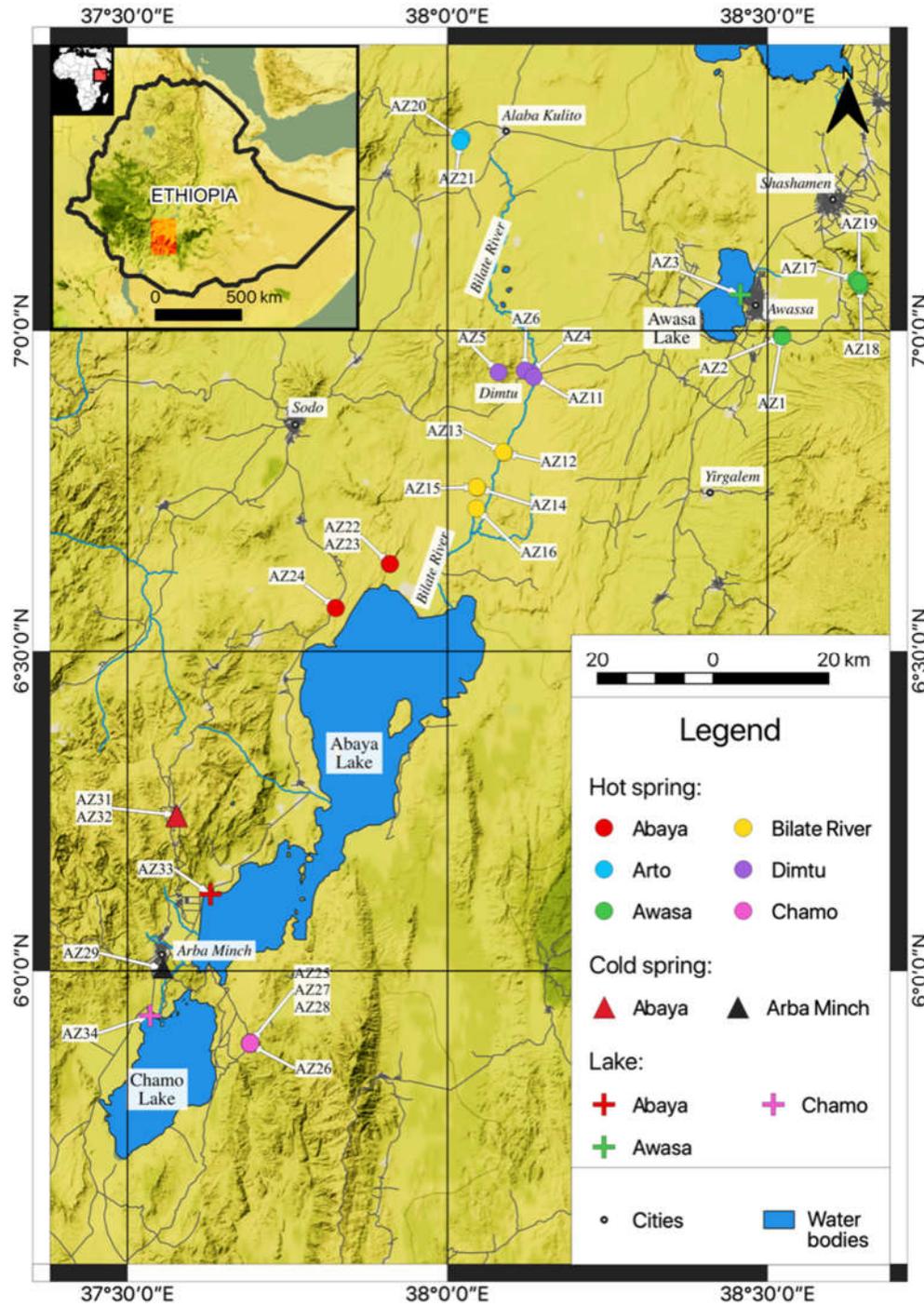
While anthropogenic sources (such as pesticides, fertilizers, and soil amendments) may introduce F<sup>-</sup> and As into the environment [8,9], the most common sources of F<sup>-</sup> and As in groundwater are geogenic processes. The co-occurrence of F and As in groundwater is generally associated with volcanic rocks [10–12], and these elements are ubiquitous in high-temperature geothermal settings [10,11,13]. They are commonly found in geothermal fluids, fumarolic gases, and volcanic emissions, which affect the adjacent environments (aquifers, surface water bodies, and soils [14]). Fluoride- and As-enriched groundwater is associated with geothermal activity along convergent plate boundaries (e.g., the Andes and Himalayas [15]), as well as in intraplate areas characterised by extensional tectonic activity [16–19], especially where a continental rifting phase follows the upraising of a mantle plume (e.g., the Main Ethiopian Rift [16–24]). The concentration and mobilisation of F<sup>-</sup>, As, and other elements associated with geothermal fluids are dependent on chemical and physical processes that occur between groundwater and its geological environment [8,10–13]. In particular, F<sup>-</sup> and As behave as incompatible elements during magmatic processes, as they do not easily fit into the crystal structure of minerals and are preferentially partitioned into melt, remaining in the residual magma until its crystallisation. Therefore, F<sup>-</sup> and As are more concentrated in evolved sialic rocks (e.g., rhyolites) rather than in primitive basic rocks (e.g., basalts) [13]. Accordingly, the concentrations of F<sup>-</sup> and As are higher in waters that leach sialic rocks (e.g., water in Mexico [10,11]) as compared to water leaching basic rocks (e.g., water in Iceland [25]). In fact, various primary mineral phases commonly recorded in sialic rocks, such as fluorite, apatite, amphibole, biotite, and volcanic glass contain F<sup>-</sup> and As [8,10–12,26–30]. Moreover, F<sup>-</sup> and As are adsorbed by secondary minerals, such as Fe-, Al-, and Mn-oxides and hydroxides, and clay [10,11,16–19,31]. Other geochemical factors, such as pH and temperature, strongly affect silica dissolution and adsorption–desorption reactions in secondary minerals during rock weathering [12]. The processes are enhanced in alkaline conditions, especially in arid/semi-arid dry climates that favour F<sup>-</sup> and As mobilisation and release into groundwater [10,11,16–19,31]. In several studies, similar geological, geochemical, and environmental conditions have been identified as key source of F<sup>-</sup> and As co-contamination in aquifers (e.g., Mexico and Argentina [10,11,32]). In rift zones (e.g., in Namibia and Madagascar [33,34]) the release of F<sup>-</sup> and As in circulating groundwater is also enhanced by the presence of active faults promoting the influx of endogenic CO<sub>2</sub> from the mantle source, which facilitates the dissolution of silicates and oxides and hydroxides.

Elevated F<sup>-</sup> and As concentrations were found also in another rift system, the Main Ethiopian Rift (MER), which is part of the East African Rift valley system [19,35]. The MER is the most populated area of Ethiopia (density of population: 250–350 people km<sup>-2</sup>), and the majority of people (84%) lives in rural zones practicing agriculture. In MER, the water supplies are mainly represented by groundwater wells. However, several works have emphasised that up to 8 million people living in the MER are at risk from exposure to high levels of F<sup>-</sup> and As in the groundwater [16–19,36–40]. Considering that anthropogenic contamination is very low in MER water (as demonstrated by the very low contents of nitrate and sulphate), it is plausible to assume that the co-occurrence of F<sup>-</sup> and As is also not related to human activities and has to be considered geogenic [40]. Unfortunately, despite the awareness of the F<sup>-</sup> and As problem, rural communities have relatively limited alternatives to using wells for drinking, and the use of water treatment to remove contaminants is rare [37]. According to Rango et al. [16–19,37,38], MER water use is causing severe deterioration of teeth and bone quality (e.g., dental and skeletal fluorosis) in the local populations, especially in young people [37–39], whereas effects related to As exposure are still not manifested in the MER region. However, in other study cases, such as in Latin America regions, the co-occurrence of F<sup>-</sup> and As in groundwater is currently being monitored as it could be responsible for both dental and skeletal fluorosis and Endemic Regional Chronic Hydroarsenicism (skin lesions [4]), as well as for reducing IQ levels and decreasing intellectual functionality in children [10].

The present work investigates the quality of groundwater in the southern MER sector (i.e., the Awasa, Abaya, and Chamo lakes area; Figure 1), which was not investigated thoroughly in previous studies. In particular, this work presents new geochemical analyses of:

- (1) Lake and hot and cold spring waters (preliminarily studied by Belete et al. [26]);
- (2) Bulk rocks and constituent minerals of MER aquifer matrices;
- (3) Leachates obtained from water extraction tests with the MER rhyolitic volcanic rocks and fluvio-lacustrine sediments, performed to simulate the water–rock interaction processes in the area.

The new data, integrated with those from previous investigations, allow a comprehensive discussion on the origin and geochemical processes that ultimately lead to the MER water geochemistry.



**Figure 1.** Sampling locations of lakes and hot and cold springs in the Awasa-Abaya-Chamo lakes district in the southern Main Ethiopian Rift (MER).

## 2. Geological Setting

The MER valley is a large tectonic basin that constitutes the northernmost extension of the East African Rift system. The rift is oriented in the NNE–SSW direction and is bounded by eastern and western plateaus with an average altitude of 2500 m above sea level (m.a.s.l), and its axial zone is characterised by an average altitude of 1600 m.a.s.l [17]. The rift valley and the highlands are characterised by very different climatic conditions. In the rift valley, the climate is semi-arid to arid (the mean annual precipitation is ~650 mm/year, the mean annual temperature is over 20 °C, and the

potential evaporation is ~2500 mm/year [17,19,26]), whereas the highlands are humid to sub-humid (the mean annual precipitation is ~1100 mm/year, the mean annual temperature is below 15 °C, and the potential evaporation is ~1000 mm/year [17,19,26]).

The formation of the MER and associated volcanism are related to the Afar mantle plume activity [20–24,41]. During the Oligocene, the region was affected by lithospheric bulging and uplift coupled with extensive continental flood basalt activity [20–24]. Differentiated rhyolite magmas appeared late in the volcano-tectonic evolution of the area, marking the onset of the continental rifting stage [23], which ultimately led to the formation of the East African Rift system [42]. At present, the MER represents an evolved continental rifting basin that is mainly filled by volcanic lithologies, such as sialic tuffs and ignimbrites, and subordinate basaltic lava flows [18,43]. In the MER, the rifting processes have formed various volcano-tectonic depressions, favouring the development of closed lacustrine basins in the rift floor. Rock weathering has also provided clastic particles that were transported and redeposited in fluvio-lacustrine sedimentary facies [18,43]. The MER lakes are subdivided into three groups: (i) Koka, Beseka, Gemeri, and Abe lakes in the northern sector; (ii) Ziway, Langano, Abijata, and Shala lakes in the central sector; and (iii) Awasa, Abaya, and Chamo lakes in the southern sector. The MER lakes are commonly bordered by high-temperature thermal springs, whose occurrence is due to the geothermal circulation of hot fluids, probably due to the persistence of magmatic systems at shallow depths [17].

Because of the high level of evaporation in the rift valley, the water resources in the rift floor (lakes, rivers, and springs) are principally recharged by water derived from the surrounding plateaus [26]. In this framework, the pristine calcium bicarbonate ( $\text{Ca-HCO}_3$ ) water with a low concentration of total dissolved solids (TDS), typical of the basaltic plateau, progressively migrates downhill and reacts with the interacting volcanic lithologies. The weathered rocks release ions to the surface and groundwater, which increases their TDS and pH and drives their evolution toward sodium bicarbonate ( $\text{Na-HCO}_3$ ) hydrochemical facies, typical of the rift valley [16–19,26,44]. Notably, in the rift floor the groundwater is generally in an oxidising condition, with a high potential redox (Eh) and dissolved  $\text{O}_2$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3$  [19].

### 3. Materials and Methods

#### 3.1. Sampling

Twenty-nine water samples from lakes and hot and cold springs were collected from the Awasa-Abaya-Chamo lakes district of the MER in January 2012 (Figure 2). Each sampling location was geo-referenced by a portable global positioning system (GPS) (Table 1; Figure 1). Water samples were mainly collected from hot springs bordering the three lakes and along the Bilate River, which feed Abaya Lake. Hot and cold spring samples were also collected inside and/or in the proximity of the following towns: Dimtu, Alaba Kulito (Arto hot springs), and Arba Minch.



**Figure 2.** Hot and cold spring water sampling sites in the MER collected during field work in January 2012.

Water temperature ( $T$ ), pH, and electrical conductivity (EC) were measured directly in the field using a hand-held multiparameter probe (HI9813-5, Hanna Instruments, Ronchi di Villafranca Padovana, Italy) calibrated before sampling. Each water sample was filtered by 0.45  $\mu\text{m}$  filters (Minisart® NML syringe cellulose acetate filters, Sartorius Stedim Biotech GmbH, Goettingen, Germany) and stored in two 100 mL bottles: one for major anion analysis and one acidified with 0.5 mL of concentrated Suprapur  $\text{HNO}_3$  for major cation and trace element analyses. Chemical analyses were performed at the Department of Physics and Earth Sciences at University of Ferrara (Italy).

**Table 1.** Sampling localities, geographic coordinates, and physico-chemical parameters of Main Ethiopian Rift (MER) water from lakes and hot and cold springs in the Awasa-Abaya-Chamo lakes district.  $T$ : temperature; EC: electrical conductivity; TDS: total dissolved solids.

| Sample                        | Latitude      | Longitude     | Elevation (m) | pH  | $T$ ( $^{\circ}\text{C}$ ) | EC ( $\mu\text{S}/\text{cm}$ ) | TDS (mg/L) |             |
|-------------------------------|---------------|---------------|---------------|-----|----------------------------|--------------------------------|------------|-------------|
| Awasa Lake and surroundings   |               |               |               |     |                            |                                |            |             |
| AZ1                           | 06° 59' 36" N | 38° 31' 19" E | 1706          | 6.2 | 61                         | 1200                           | 671        | Hot spring  |
| AZ2                           | 06° 59' 27" N | 38° 31' 22" E | 1707          | 6.9 | >80                        | 2330                           | 1131       | Hot spring  |
| AZ3                           | 07° 03' 22" N | 38° 27' 27" E | 1687          | 9.9 | 25                         | 810                            | 574        | Lake        |
| AZ17                          | 07° 04' 46" N | 38° 38' 17" E | 1914          | 7.4 | 66                         | 1160                           | 573        | Hot spring  |
| AZ18                          | 07° 04' 14" N | 38° 38' 40" E | 1912          | 7.9 | 59                         | 1120                           | 611        | Hot spring  |
| AZ19                          | 07° 04' 32" N | 38° 38' 33" E | 1936          | 7.7 | 59                         | 1020                           | 692        | Hot spring  |
| Dimtu town                    |               |               |               |     |                            |                                |            |             |
| AZ4                           | 06° 56' 05" N | 38° 07' 46" E | 1489          | 7.2 | 37                         | 1030                           | 692        | Hot spring  |
| AZ5                           | 06° 56' 07" N | 38° 04' 46" E | 1491          | 6.9 | 39                         | 950                            | 666        | Hot spring  |
| AZ6                           | 06° 56' 16" N | 38° 07' 14" E | 1491          | 6.8 | 39                         | 960                            | 656        | Hot spring  |
| AZ11                          | 06° 55' 41" N | 38° 08' 04" E | 1490          | 8.3 | 57                         | 1150                           | 745        | Hot spring  |
| Bilate River and surroundings |               |               |               |     |                            |                                |            |             |
| AZ12                          | 06° 48' 35" N | 38° 05' 17" E | 1346          | 7.8 | 45                         | 1340                           | 852        | Hot spring  |
| AZ13                          | 06° 48' 39" N | 38° 05' 13" E | 1346          | 7.5 | 56                         | 1480                           | 913        | Hot spring  |
| AZ14                          | 06° 45' 18" N | 38° 02' 47" E | 1248          | 7.6 | 67                         | 5530                           | 3667       | Hot spring  |
| AZ15                          | 06° 45' 22" N | 38° 02' 44" E | 1248          | 7.8 | 63                         | 5500                           | 3736       | Hot spring  |
| AZ16                          | 06° 43' 22" N | 38° 02' 42" E | 1243          | 7.9 | > 80                       | 6200                           | 3722       | Hot spring  |
| Abaya Lake and surroundings   |               |               |               |     |                            |                                |            |             |
| AZ22                          | 06° 38' 10" N | 37° 54' 34" E | 1197          | 6.6 | 65                         | 2700                           | 1750       | Hot spring  |
| AZ23                          | 06° 38' 10" N | 37° 54' 35" E | 1199          | 7.3 | 61                         | 2560                           | 1903       | Hot spring  |
| AZ24                          | 06° 34' 03" N | 37° 49' 30" E | 1259          | 6.4 | 36                         | 420                            | 280        | Hot spring  |
| AZ31                          | 06° 14' 35" N | 37° 34' 35" E | 2682          | 6.0 | 17                         | 60                             | 67         | Cold spring |
| AZ32                          | 06° 14' 29" N | 37° 34' 37" E | 2681          | 5.3 | 18                         | 10                             | 26         | Cold spring |
| AZ33                          | 06° 07' 10" N | 37° 37' 46" E | 1192          | 9.1 | 26                         | 970                            | 799        | Lake        |

| Chamo Lake and surroundings |               |               |      |     |    |      |      |             |
|-----------------------------|---------------|---------------|------|-----|----|------|------|-------------|
| AZ25                        | 05° 53' 14" N | 37° 41' 29" E | 1116 | 7.9 | 40 | 2270 | 1770 | Hot spring  |
| AZ26                        | 05° 53' 04" N | 37° 41' 26" E | 1136 | 8.0 | 46 | 2400 | 1734 | Hot spring  |
| AZ27                        | 05° 53' 11" N | 37° 41' 30" E | 1126 | 7.5 | 45 | 2450 | 1779 | Hot spring  |
| AZ28                        | 05° 53' 11" N | 37° 41' 30" E | 1125 | 7.7 | 56 | 2600 | 1757 | Hot spring  |
| AZ34                        | 05° 55' 44" N | 37° 32' 07" E | 1121 | 9.3 | 29 | 1640 | 1225 | Lake        |
| Arto (near Alba Kulito)     |               |               |      |     |    |      |      |             |
| AZ20                        | 07° 18' 02" N | 38° 01' 19" E | 1797 | 9.3 | 74 | 1930 | 909  | Hot spring  |
| AZ21                        | 07° 17' 43" N | 38° 01' 11" E | 1777 | 8.9 | 70 | 1800 | 1009 | Hot spring  |
| Arba Minch                  |               |               |      |     |    |      |      |             |
| AZ29                        | 06° 00' 13" N | 37° 33' 20" E | 1199 | 7.3 | 24 | 300  | 222  | Cold spring |

### 3.2. Analytical Methods

Major anions ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ; in mg/L) were analysed by ion chromatography using an ICS-1000 system (Dionex, Waltham, MA USA) calibrated using Dionex "7-ion standard" solutions obtained by different dilutions. Accuracy and precision, based on the repeated analyses of samples and standards, were better than 10% for all the considered parameters. Total alkalinity was determined in water samples using the HI 3811-0 alkalinity test titration kit (Hanna Instruments).

Major cation ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ; in mg/L) and trace element (Li, Rb, Sr, Ba, As, Mo, Cd, Sb, Hg; in  $\mu g/L$ ) analyses were carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an X Series instrument (Thermo-Scientific, Bremen, Germany) on samples previously diluted 1:10 by deionized Milli-Q water (resistivity of ca.  $18.2 M\Omega \times cm$ ), and known amounts of Re and Rh were introduced as internal standards. During ICP-MS analysis, the potential contribution of isobaric compounds (e.g.,  $^{40}Ar^{35}Cl$ ) formed during the measurement of As (mass 75) was minimised by operating in kinetic energy discrimination (KED) mode, with the collision cell fluxed by a mixture of He–H gas. In each analytical session, the analysis of samples was verified with that of the reference materials EU-L-1 and ES-L1 provided by SCP-Science ([www.scpscience.com](http://www.scpscience.com)). Notable, the analyses presented in this work were performed in the same analytical session as other river water samples in which the As concentration was below the detection limit [45], indicating that the significant concentration of As measured in the MER water was not related to systematic analytical interference. Accuracy and precision were determined using several international reference standards and were shown to be lower than 10% of the measured value, with detection limits in the order of 2  $\mu g/L$ .

Major anions, major cations, and trace elements were also measured on leachates, performed to demonstrate the reactivity of the MER lithologies to natural water. This was done by implementing and refining the approach provided by Rango et al. [16]. Extraction tests were performed by leaching 10 g of volcanic rocks or fluvio-lacustrine sediments with 50 mL of deionized water or  $Ca-HCO_3$  water ( $Ca^{2+}$ : 12 mg/L,  $Mg^{2+}$ : 4.4 mg/L,  $Na^+$ : 5 mg/L,  $K^+$ : 5.1 mg/L,  $HCO_3^-$ : 97.6 mg/L,  $Cl^-$ : 5.9 mg/L,  $F^-$ : 0.1 mg/L,  $SO_4^{2-}$ : 1.4 mg/L); the latter has a composition that simulate the recharge water conveyed from the highlands. The leaching experiments were carried out for 15, 30, and 90 days, and the final leachate solutions were centrifuged at 3000 rpm for 10 min and filtered at 0.45  $\mu m$  (Minisart® NML syringe cellulose acetate filters) before the analyses.

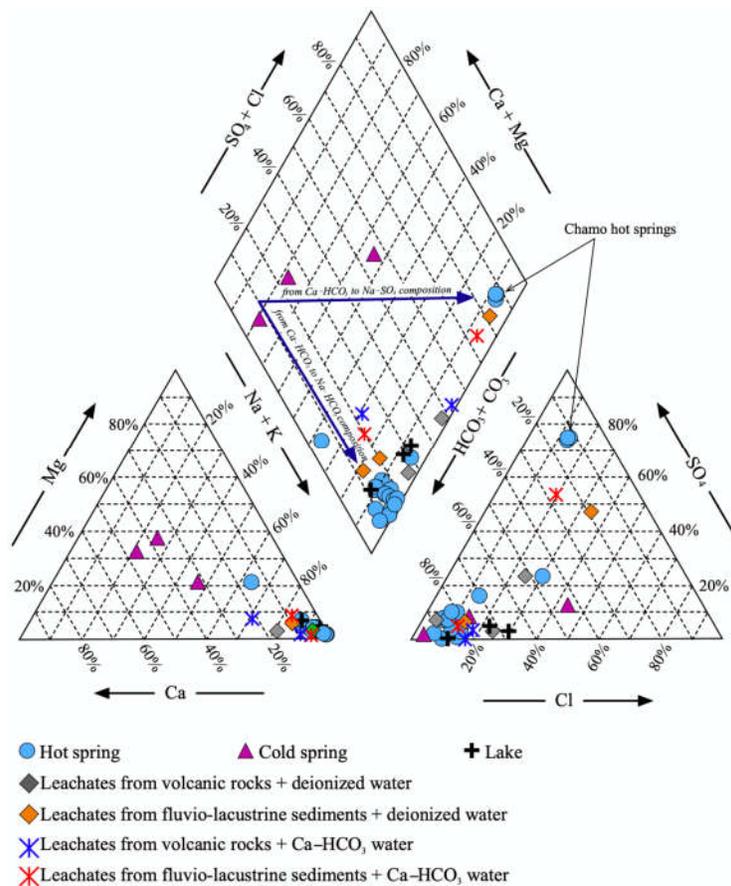
In particular, the leaching tests were performed on three volcanic rock samples and on two fluvio-lacustrine sediments that were originally investigated by Rango et al. [16,19] through X-Ray fluorescence (XRF) for major and trace elements. The same samples were analysed in this new study to obtain their  $F^-$  concentrations on powdered samples digested by alkaline fusion following a protocol by [46] (Table S1). Within platinum crucibles, 0.34 g of sample powders were mixed with 0.3 g of  $KNO_3$  and 2 g of  $Na_2CO_3$  and then heated at 1000 °C, thus transforming the contained material in glass. After cooling, crucibles were soaked in beakers containing deionized water, and put in an ultrasonic bath. Solutions were filtered with Whatman 42 filter papers and decanted in 100 mL flasks. Fluoride analyses were done by an Ion Selective Electrode WQ-FL (NexSens, Denver, CO, USA) calibrated with a series of standard solutions of certified  $F^-$  content buffered by ionic strength adjuster (ISA) solution, which is used to simulate the pH and ionic content of real samples. Insight into the mineral compositions was obtained with an EVO 50 scanning electron microscope (Zeiss, Jena,

Germany) in conjunction with an INCA microanalysis suite (Oxford Instruments, High Wycombe Bucks, UK) (Table S2).

## 4. Results

### 4.1. Geochemistry of the MER Natural Water

The physico-chemical characteristics of the MER waters from lakes and hot and cold springs in the Awasa-Abaya-Chamo lakes district are reported in Table 1. Hot spring water samples showed high temperatures varying from 36 °C to more than 80 °C (average: 56 °C). The pH values ranged from near neutral to alkaline (range: 6.2–9.3; average: 7.5). The EC varied from 420  $\mu\text{S}/\text{cm}$  to 6200  $\mu\text{S}/\text{cm}$  (average: 2178  $\mu\text{S}/\text{cm}$ ) and the TDS concentration ranged from 280 to 3736 mg/L (average: 1400 mg/L). Cold spring water samples exhibited lower temperatures (range: 17–24 °C; average: 20°C), lower pH values (range: 5.3–7.3; average: 6.2), and lower salinity levels (EC range: 10–300  $\mu\text{S}/\text{cm}$ ; average: 123  $\mu\text{S}/\text{cm}$ ; TDS range: 26–222 mg/L; average: 105 mg/L) than hot spring waters. Lake water samples exhibited medium temperatures (range: 25–29°C; average: 26°C), alkaline pH values (range: 9.1–9.9; average: 9.4), and medium salinity levels ( $\text{EC}_{\text{Awasa L.}}$ : 810  $\mu\text{S}/\text{cm}$ ;  $\text{EC}_{\text{Abaya L.}}$ : 970  $\mu\text{S}/\text{cm}$ ;  $\text{TDS}_{\text{Awasa L.}}$ : 574 mg/L;  $\text{TDS}_{\text{Abaya L.}}$ : 799 mg/L), with the exception of Chamo Lake water, which had the highest level of salinity (EC: 1640  $\mu\text{S}/\text{cm}$ ; TDS: 1225 mg/L). The major ion and trace element compositions of the investigated water are reported in Table 2. On the basis of the relative ion abundance (Table 2), each water sample could be assigned to a hydrochemical facies (Figure 3).



**Figure 3.** Piper diagram showing the hydrochemical composition of the MER waters from lakes and hot and cold springs in the Awasa-Abaya-Chamo lakes district. The compositions of leachates that simulate water–rock interactions are also reported. Arrows show the water evolution from the highlands (where the Ca–HCO<sub>3</sub> composition dominates) to the rift floor (where the Na–HCO<sub>3</sub> composition prevails).

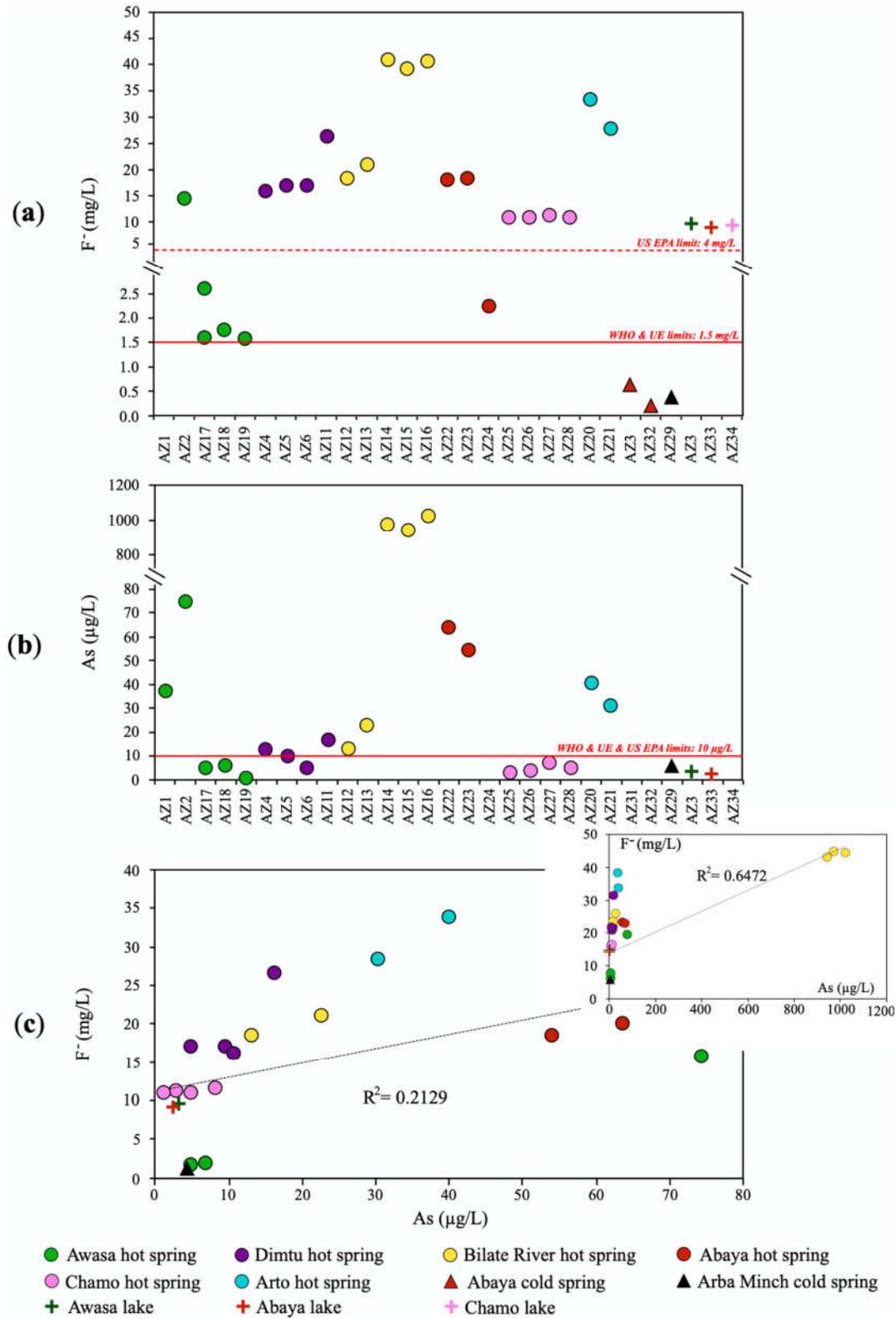
**Table 2.** Major ion and trace element compositions of the MER waters from lakes and hot and cold springs in the Awasa-Abaya-Chamo lakes district. Major anions were analysed by Ion Chromatography, whereas major cations and trace elements were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). n.g.: not given; n.m.: not mentioned.

| Sample                        | Major Ions (mg/L) |                 |                              |                               |                               |                  |                  |                 |                | Trace Elements (µg/L) |      |      |      |      |      |    |    |      |
|-------------------------------|-------------------|-----------------|------------------------------|-------------------------------|-------------------------------|------------------|------------------|-----------------|----------------|-----------------------|------|------|------|------|------|----|----|------|
|                               | F <sup>-</sup>    | Cl <sup>-</sup> | NO <sub>3</sub> <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> | HCO <sub>3</sub> <sup>-</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Na <sup>+</sup> | K <sup>+</sup> | Li                    | Rb   | Sr   | Ba   | As   | Mo   | Cd | Sb | Hg   |
| WHO *                         | 1.5               | n.g.            | 50                           | n.g.                          | n.m.                          | n.g.             | n.g.             | n.g.            | n.g.           | n.g.                  | n.m. | n.m. | 700  | 10   | n.g. | 3  | 20 | 6    |
| EU **                         | 1.5               | 0.25            | 50                           | 250                           | n.m.                          | n.m.             | n.m.             | 200             | n.m.           | n.m.                  | n.m. | n.m. | n.m. | 10   | n.m. | 5  | 5  | n.m. |
| EPA ***                       | 4                 | n.m.            | 10                           | n.m.                          | n.m.                          | n.m.             | n.m.             | n.m.            | n.m.           | n.m.                  | n.m. | n.g. | 2000 | 10   | n.g. | 50 | 6  | 2    |
| Awasa Lake and surroundings   |                   |                 |                              |                               |                               |                  |                  |                 |                |                       |      |      |      |      |      |    |    |      |
| AZ1                           |                   | 36.3            |                              |                               | 444                           | 12.3             | 5.64             | 203             | 15.0           | 142                   | 75   | 183  | 13   | 37   | 18   | 4  | <6 | <2   |
| AZ2                           | 14.6              | 73.2            |                              | 118                           | 600                           | 9.44             | 3.80             | 380             | 25.3           | 277                   | 130  | 304  | 22   | 74   | 20   | 5  | 7  | 3    |
| AZ3                           | 9.56              | 31.1            | 0.52                         | 1.55                          | 372                           | 8.74             | 6.38             | 167             | 25.2           | 79                    | 33   | 100  | 7    | 3    | 12   | 4  | <6 | <2   |
| AZ17                          | 1.58              | 24.7            | 0.22                         | 0.25                          | 393                           | 5.05             | 3.92             | 169             | 36.1           | 36                    | 51   | 96   | 58   | 5    | 14   | 5  | 0  | <2   |
| AZ18                          | 1.76              | 27.0            | 0.12                         | 0.25                          | 429                           | 5.34             | 3.93             | 178             | 38.0           | 39                    | 50   | 99   | 56   | 7    | 11   | 4  | <6 | <2   |
| AZ19                          | 1.54              | 24.9            | 0.14                         | 0.27                          | 426                           | 5.35             | 4.45             | 188             | 41.6           | 41                    | 54   | 109  | 68   | <4   | 12   | 4  | <6 | <2   |
| Dimtu town                    |                   |                 |                              |                               |                               |                  |                  |                 |                |                       |      |      |      |      |      |    |    |      |
| AZ4                           | 15.9              | 20.2            | 4.08                         | 26.5                          | 390                           | 4.66             | 3.52             | 211             | 16.4           | 64                    | 30   | 47   | <5   | 11   | 29   | <4 | <6 | <2   |
| AZ5                           | 16.9              | 17.4            | 3.66                         | 25.0                          | 387                           | 8.38             | 3.17             | 190             | 14.9           | 63                    | 34   | 44   | <5   | 10   | 32   | 5  | <6 | <2   |
| AZ6                           | 17.0              | 17.7            | 2.91                         | 25.2                          | 372                           | 6.53             | 3.50             | 197             | 15.1           | 66                    | 34   | 43   | <5   | 5    | 28   | <4 | <6 | <2   |
| AZ11                          | 26.5              | 36.5            | 0.33                         | 15.5                          | 420                           | 1.52             | 0.53             | 230             | 14.6           | 98                    | 19   | 17   | <5   | 17   | 36   | <4 | <6 | 2    |
| Bilate River and surroundings |                   |                 |                              |                               |                               |                  |                  |                 |                |                       |      |      |      |      |      |    |    |      |
| AZ12                          | 18.4              | 51.0            | 0.30                         | 13.3                          | 462                           | 5.49             | 3.77             | 282             | 15.9           | 99                    | 52   | 63   | 20   | 13   | 28   | <4 | <6 | 2    |
| AZ13                          | 21.0              | 52.4            | 0.35                         | 13.7                          | 516                           | 3.11             | 2.14             | 291             | 13.9           | 131                   | 56   | 59   | 45   | 23   | 27   | <4 | <6 | <2   |
| AZ14                          | 45.2              | 147             | 0.63                         | 73.1                          | 2181                          | 0.46             | 0.60             | 1158            | 60.7           | 1069                  | 481  | 283  | 26   | 970  | 13   | 4  | 76 | 27   |
| AZ15                          | 43.5              | 162             |                              | 75.2                          | 2241                          | 0.16             | 0.69             | 1146            | 67.6           | 1024                  | 501  | 126  | 14   | 940  | 17   | 6  | 80 | 29   |
| AZ16                          | 44.9              | 144             | 1.09                         | 72.9                          | 2193                          | 3.34             | 0.76             | 1195            | 67.2           | 1085                  | 522  | 289  | 43   | 1019 | 22   | 8  | 75 | 30   |
| Abaya Lake                    |                   |                 |                              |                               |                               |                  |                  |                 |                |                       |      |      |      |      |      |    |    |      |
| AZ22                          | 18.1              | 65.5            |                              | 14.9                          | 1347                          | 6.15             | 5.70             | 505             | 26.9           | 390                   | 94   | 108  | 14   | 64   | 17   | <4 | <6 | <2   |
| AZ23                          | 18.3              | 70.4            | 0.19                         | 15.9                          | 1542                          | 5.18             | 6.06             | 531             | 28.2           | 408                   | 94   | 111  | 9    | 54   | 18   | <4 | <6 | <2   |
| AZ24                          | 2.26              | 4.43            | 0.98                         | 0.97                          | 189                           | 11.3             | 9.04             | 52.5            | 9.70           | 20                    | 18   | 102  | <5   | <4   | <10  | <4 | <6 | <2   |
| AZ31                          | 0.61              | 8.56            | 15.45                        | 3.24                          | 600                           | 4.96             | 1.90             | 8.07            | 9.21           | 2                     | 6    | 54   | 53   | <4   | <10  | <4 | <6 | <2   |
| AZ32                          | 0.13              | 1.39            | 2.64                         | 0.91                          | 0.20                          | 2.99             | 1.85             | 2.32            | 2.26           | 1                     | <2   | 42   | 20   | <4   | <10  | <4 | <6 | <2   |
| AZ33                          | 8.97              | 76.1            | 0.33                         | 21.3                          | 6.89                          | 12.7             | 3.58             | 243             | 13.4           | 2                     | 4    | 130  | 11   | <4   | 28   | <4 | <6 | <2   |
| Chamo Lake and surroundings   |                   |                 |                              |                               |                               |                  |                  |                 |                |                       |      |      |      |      |      |    |    |      |
| AZ25                          | 10.9              | 116             |                              | 954                           | 225                           | 21.1             | 5.97             | 430             | 22.5           | 494                   | 154  | 956  | 4    | <4   | 15   | 0  | <6 | <2   |
| AZ26                          | 11.1              | 115             |                              | 938                           | 210                           | 14.3             | 6.22             | 419             | 20.2           | 478                   | 157  | 961  | <5   | <4   | 26   | 4  | <6 | <2   |

|                         |      |      |      |      |     |      |      |      |      |     |     |      |    |    |     |   |    |    |
|-------------------------|------|------|------|------|-----|------|------|------|------|-----|-----|------|----|----|-----|---|----|----|
| AZ27                    | 11.4 | 118  |      | 981  | 195 | 25.4 | 6.43 | 450  | 22.4 | 502 | 167 | 1002 | <5 | 8  | 26  | 5 | <6 | <2 |
| AZ28                    | 10.9 | 115  | 0.15 | 930  | 195 | 25.4 | 6.67 | 441  | 33.3 | 491 | 172 | 966  | 11 | 5  | 19  | 4 | <6 | <2 |
| AZ34                    | 9.33 | 156  | 0.13 | 16.6 | 600 | 8.30 | 9.71 | 411  | 15.0 | 1   | 3   | 133  | 21 | <4 | 29  | 6 | <6 | <2 |
| Arto (near Alba Kulito) |      |      |      |      |     |      |      |      |      |     |     |      |    |    |     |   |    |    |
| AZ20                    | 33.4 | 37.3 | 0.10 | 57.5 | 585 | 0.00 | 0.50 | 309  | 16.7 | 177 | 81  | 44   | <5 | 41 | 26  | 6 | 2  | 2  |
| AZ21                    | 27.8 | 37.1 | 0.16 | 57.4 | 669 | 0.69 | 0.64 | 295  | 15.5 | 175 | 79  | 104  | <5 | 31 | 23  | 2 | 3  | 3  |
| Arba Minch              |      |      |      |      |     |      |      |      |      |     |     |      |    |    |     |   |    |    |
| AZ29                    | 0.37 | 3.74 | 6.39 | 2.05 | 138 | 33.7 | 14.1 | 16.8 | 9.02 | 1   | 12  | 221  | <5 | 5  | <10 | 6 | 1  | <2 |

WHO \* (2011). Guidelines for drinking-water quality [3]. EU \*\* (1998). Council Directive 98/83/EC of 3rd November 1998 on the quality of water intended for human consumption [47]. EPA \*\*\* (2018). National primary drinking water regulations [48].

The majority of the MER water sampled in hot springs belongs to Na–HCO<sub>3</sub> hydrochemical facies with concentrations of Na<sup>+</sup> ranging from 53 to 1195 mg/L and HCO<sub>3</sub><sup>-</sup> concentrations from 189 to 2241 mg/L. Only the water collected from Chamo hot spring shows sodium sulphate (Na–SO<sub>4</sub>) facies composition, having higher concentrations of SO<sub>4</sub><sup>2-</sup> (930–980 mg/L) with respect to the rest of the investigated hot springs (0–117 mg/L). The water samples collected from the Awasa, Abaya, and Chamo lakes belong to Na–HCO<sub>3</sub> hydrochemical facies with ranges of Na<sup>+</sup> (167–411 mg/L), HCO<sub>3</sub><sup>-</sup> (372–600 mg/L), and SO<sub>4</sub><sup>2-</sup> (2–21 mg/L) similar to those of the majority of hot springs. The water sample from the Arba Minch cold spring and one out of two water samples from the Abaya cold springs displayed Ca–HCO<sub>3</sub> hydrochemical facies (Ca<sup>2+</sup>: 3–34 mg/L; HCO<sub>3</sub><sup>-</sup>: 12–138 mg/L). The other sample from Abaya cold spring had a mixed Ca–Na–HCO<sub>3</sub> composition (Ca<sup>2+</sup>: 5 mg/L; Na<sup>+</sup>: 8 mg/L; HCO<sub>3</sub><sup>-</sup>: 15 mg/L). In general, these compositions are in agreement with those identified in a recent study of MER groundwater sampled along the Bilate River by Haji et al. [40]. In order to assess the risk to human health in relation to the use of the investigated water as drinking water, the relative ion and trace element concentrations were compared with the drinking water quality standards recommended by the authorities: (i) WHO (2011) [3], (ii) European Union (EU–directive 1998/98/EC) [47], and (iii) United States Environmental Protection Agency (US EPA–2018 National primary drinking water regulations) [48]. According to the above-mentioned legislation, some investigated water samples displayed SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Cd, and Hg concentrations exceeding the respective tolerance thresholds (Table 2). However, the most worrying elements are undoubtedly F<sup>-</sup> and As, as the majority of the collected samples were found to have high concentrations of both elements (Table 2; Figures 4a–c and 5a,b). In particular, all water samples from hot springs and lakes had F<sup>-</sup> concentrations ranging from 1.5 to 45.2 mg/L, i.e., always higher than the WHO and EU guideline values (F<sup>-</sup>: 1.5 mg/L [3,47]), and in many cases, even higher than the EPA tolerance limit, which is less restrictive (F<sup>-</sup>: 4 mg/L [48]). Comparably high F<sup>-</sup> concentrations were also recorded in the study of Haji et al. [40]. Some water samples from F<sup>-</sup>-contaminated hot springs also had As concentrations exceeding the tolerance limit adopted by all of the legislation considered in this study (As: 10 µg/L [3,47,48]). The hot springs along the Bilate River were found to have the most extreme F<sup>-</sup> and As concentrations, and in particular, those collected in the proximity of the Abaya lake (AZ14, AZ15, AZ16) exhibited severe F<sup>-</sup> and As contamination (F<sup>-</sup>: > 40 mg/L and As: > 900 µg/L; Table 2; Figures 4a–c and 5a,b). Very high F<sup>-</sup> and As concentrations were also recorded in other hot springs near the Awasa and Abaya lakes (F<sup>-</sup>: 1.5–18.3 mg/L and As: 37–74 µg/L; Table 2; Figures 4a–c and 5a,b) and in the Arto hot springs (F<sup>-</sup>: 27.8–33.4 mg/L and As: 31–41 µg/L; Table 2; Figures 4a–c and 5a,b). The hot springs near Chamo Lake exhibited high F<sup>-</sup> concentrations (10.9–11.4 mg/L; Table 2; Figures 4a–c and 5a,b), not correlated with As (<4–8 µg/L; Table 2; Figures 4a–c and 5a,b). Only the water samples from the cold springs had F<sup>-</sup> concentrations acceptable for safe drinking-water (F<sup>-</sup>: 0.1–0.6 mg/L; Table 2; Figures 4a–c and 5a,b). Only one out of the three cold spring water samples had enough dissolved As to be measured with our instrument; however, its concentration was well below the tolerance limit (i.e., Arba Minch cold spring: 5 µg/L; Table 2; Figures 4a–c and 5a,b).

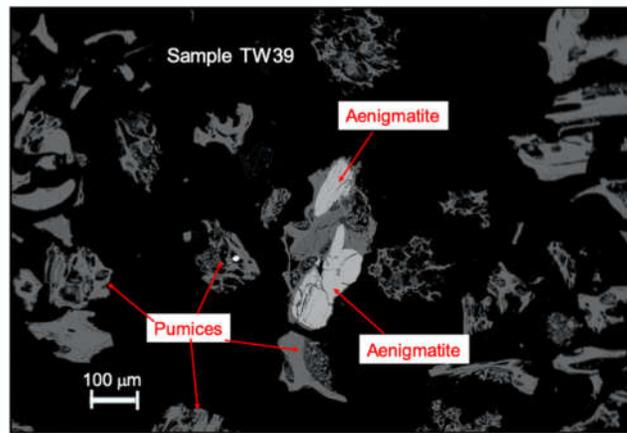


**Figure 4.** Concentrations of (a) F<sup>-</sup> and (b) As in the MER lakes and hot and cold springs in the Awasa-Abaya-Chamo lakes district compared with the WHO (2011) [3], EU (1998) [47], and US EPA (2018) [48] guideline values for drinking water. (c) Correlation of F<sup>-</sup> and As contents in the MER water from lakes and hot and cold springs in the Awasa-Abaya-Chamo lakes district. Note that the correlation lines were calculated using the ordinary least square regression function.

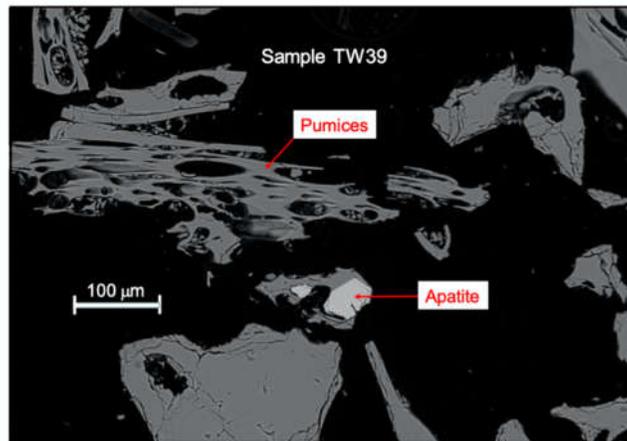


Rift volcanic occurrences [50,51]. The composition of the observed minerals in our samples is listed in Table S2. For the aim of our study, it is important to note that F has been detected in glass (generally 0.2–0.3 wt.%; Table S2), amphibole (up to 2.5 wt.%; Table S2), and fluoro-apatite (up to 6.9 wt.%; Table S2). The F content in glass is consistent with that observed in other East African Rift volcanic occurrences [50,51]. Amphibole in terms of major element classification is intermediate between katophorite and richterite, similar to other East African Rift volcanic mineral assemblages [52–55], and its F content is compatible with what is observed in F-rich sialic rocks [56]. On the other hand, in the MER volcanics, apatite is peculiar as it has a britholite component (Ce-enriched) and an extreme F enrichment, generally only associated with ultra-alkaline/carbonatite melts [57,58], but confirmed by other Ethiopian volcanic occurrences [22].

Arsenic, although below the detection limit, should be present as a trace element in the above-mentioned phases as well as in oxides and hydroxides as demonstrated by several authors [10–12,59–61]. According to Rango et al. [19], As in MER waters is composed of predominantly (over 80%) arsenate (As(V)) rather than arsenite (As(III)) species, suggesting that the groundwater has oxidising conditions.



(a)



(b)

**Figure 6.** Backscattered SEM image of a MER rhyolitic volcanic rock. Vesiculated particles consist of volcanic glass (containing up to 0.4 wt.% of F), whereas the subhedral white crystals are (a) aenigmatite and (b) fluoroapatite (containing up to 6.9 wt.% of F). Analyses of volcanic glass and other F-bearing mineral phases contained in rock matrices are reported in Table S2.

## 5. Discussion

### 5.1. F<sup>-</sup> and As Co-Occurrence in MER Water

Both F<sup>-</sup> and As are positively correlated with Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, Li, Rb, and TDS (Figure S2). The concentrations of these elements coupled with the high salinity of groundwater indicate that they result from water–rock/sediment interaction [10,11,16–19,22]. In the MER, the weathering and leaching processes generate saline groundwater predominantly composed of a Na–HCO<sub>3</sub> hydrochemical facies with an alkaline pH (Table 2; Figure 3). In particular, the water samples from hot springs contain the highest concentrations of major ions and trace elements (Table 2; Figure S2), indicating that the high T enhanced the hydrolysis of aquifer solid matrices, facilitating the mobility of F<sup>-</sup> and As into the MER groundwaters.

Almost all leachates obtained by our extraction tests showed a Na–HCO<sub>3</sub> composition with alkaline pH values comparable with those of natural MER water (Tables 3 and 4; Figure 3), confirming that the water–rock/sediment interaction played a crucial role in the the water's compositional evolution. The only exceptions were the extracts of sample TW22, which exhibited a Na–SO<sub>4</sub> composition (Figure 3).

In comparison with the rhyolitic volcanics, the fluvio-lacustrine sediments released the highest concentrations of most elements, including F<sup>-</sup> and As, only after 15 days (Tables 3 and 4; Figure 7). In particular, TW22 sediments released the highest amounts of F<sup>-</sup> (up to 8.52 mg/L; Table 3) and As (up to 188 µg/L; Table 4). Therefore, the fluvio-lacustrine sediments are not only the main reservoirs of F<sup>-</sup> and As in the MER area but can also easily release F<sup>-</sup> and As into the water system in a few days. This suggests that the weathered sedimentary particles are more prone to elemental transfer (included F<sup>-</sup> and As) to groundwater than rhyolitic volcanic rocks (Figure 7).

Therefore, the weathering of rhyolitic rocks leads to (i) the production of weathered particles (i.e., fluvio-lacustrine sediments), (ii) an increase of pH of natural water, and (iii) the release of F<sup>-</sup> and As, due to the dissolution of volcanic glass hosting these elements (Figure 8). The latter process is facilitated by cation exchange processes that remove Ca<sup>2+</sup> and release Na<sup>+</sup> into the solution [16]. As a consequence, the precipitation of fluorite (CaF<sub>2</sub>) is not favoured, increasing the mobility of F<sup>-</sup> into groundwater [16–19]. Accordingly, the Saturation Index (SI), calculated using the code PHREEQC [62], invariably shows that MER water is undersaturated in fluorite, favouring F<sup>-</sup> mobilisation. However, the weathering of rhyolitic rocks also implies the formation of secondary minerals, such as clay, oxides, and hydroxides, which can further release F<sup>-</sup> and As (Figure 8). Subsequent adsorption-desorption processes are influenced by the pH of the solution. In particular, the desorption rate of As increases in alkaline solutions, especially in arid regions [10–12], like those of the MER area [19]. Therefore, the co-occurrence of F<sup>-</sup> and As in the MER groundwaters is due to a combination of factors: (i) the presence of F<sup>-</sup> and As-bearing rhyolitic lithologies containing a large amount of volcanic glass, (ii) the leaching by alkaline groundwater, and (iii) the arid climate of the area. In addition, the high rate of evaporation, typical of the arid conditions characterising the MER environment [26], further concentrates F<sup>-</sup> and As in the shallower parts of the aquifers [10,11,31], increasing the health-risk for the local population.

**Table 3.** Major ion and trace element compositions of the MER water leachates obtained by the interaction of volcanic rocks and fluvio-lacustrine sediments (10 g of powder) with deionized water (50 mL). Major ions were analysed by Ion Chromatography and trace elements were analysed by ICP-MS after 15, 30, and 90 days. n.a.: not analysed; n.d.: not detected.

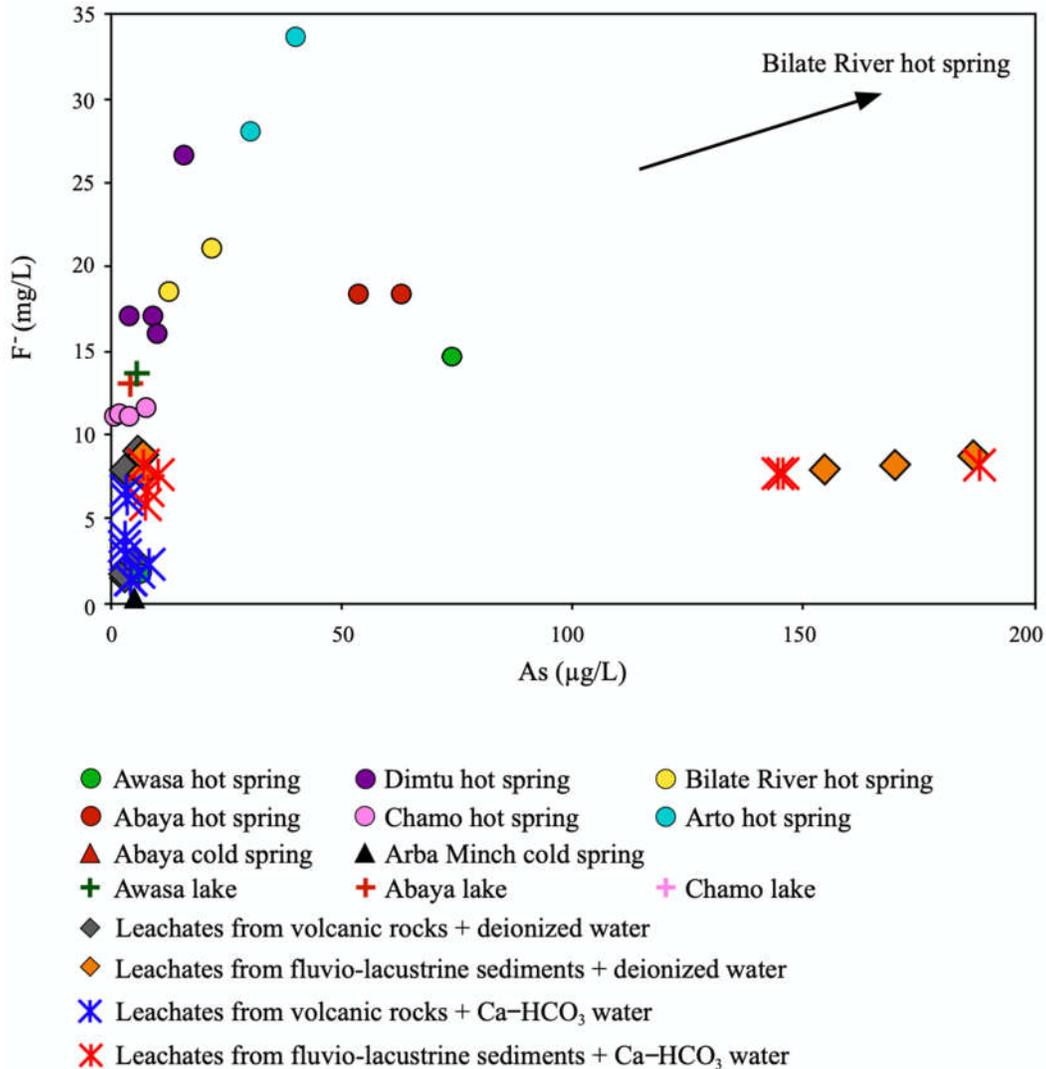
| Sample                          | Ted4                |         |         | TW31                |         |         | TW39                |         |         | TW22                        |         |         | Ted38                       |         |         |
|---------------------------------|---------------------|---------|---------|---------------------|---------|---------|---------------------|---------|---------|-----------------------------|---------|---------|-----------------------------|---------|---------|
|                                 | Pyroclastic Deposit |         |         | Pyroclastic Deposit |         |         | Pyroclastic Deposit |         |         | Fluvio-Lacustrine Sediments |         |         | Fluvio-Lacustrine Sediments |         |         |
|                                 | 15 days             | 30 days | 90 days | 15 days             | 30 days | 90 days | 15 days             | 30 days | 90 days | 15 days                     | 30 days | 90 days | 15 days                     | 30 days | 90 days |
| pH                              | 8.38                | 8.33    | 8.02    | 8.67                | 8.52    | 8.45    | 8.26                | 7.76    | 8.10    | 8.64                        | 7.80    | 8.33    | 8.06                        | 8.10    | n.a.    |
| EC ( $\mu\text{S}/\text{cm}$ )  | 460                 | 401     | 437     | 143                 | 170     | 209     | 199                 | 219     | 191     | 1210                        | 1280    | 1350    | 416                         | 455     | n.a.    |
| F <sup>-</sup> (mg/L)           | 7.73                | 7.48    | 8.93    | 3.16                | 3.66    | 3.66    | 1.62                | 1.82    | 2.35    | 8.00                        | 8.01    | 8.52    | 8.73                        | 7.64    | n.a.    |
| Cl <sup>-</sup>                 | 25.5                | 24.5    | 26.7    | 1.67                | 7.75    | 17.7    | 10.0                | 23.3    | 11.9    | 70.6                        | 70.6    | 160     | 17.1                        | 1       | n.a.    |
| NO <sub>3</sub> <sup>-</sup>    | 35.4                | 35.2    | 35.6    | n.d.                | 0.08    | 0.05    | 4.78                | 6.44    | 19.9    | 0.45                        | 0.46    | 0.94    | 15.0                        | 16.1    | n.d.    |
| SO <sub>4</sub> <sup>2-</sup>   | 33.0                | 32.3    | 34.2    | 0.85                | 2.80    | 0.69    | 4.21                | 4.25    | 4.65    | 300                         | 300     | 310     | 12.1                        | 12.4    | n.a.    |
| * HCO <sub>3</sub> <sup>-</sup> | 96                  | 72      | 27      | 65                  | 71      | 96      | 72                  | 63      | 55      | 120                         | 154     | 46      | 139                         | 176     | n.a.    |
| Ca <sup>2+</sup>                | <0.3                | <0.3    | <0.3    | <0.3                | <0.3    | 2.80    | 4.79                | 5.93    | 4.35    | 7.18                        | 9.64    | 10.8    | 7.61                        | 9.51    | 4.10    |
| Mg <sup>2+</sup>                | <0.4                | <0.4    | <0.4    | <0.4                | <0.4    | <0.4    | <0.4                | 0.50    | <0.4    | 1.26                        | 1.65    | 2.69    | 1.54                        | 2.12    | 3.80    |
| Na <sup>+</sup>                 | 84.3                | 64.9    | 74.3    | 27.0                | 34.1    | 44.9    | 29.8                | 34.0    | 31.5    | 217                         | 225     | 243     | 61.9                        | 68.9    | 108     |
| K <sup>+</sup>                  | 11.0                | 16.7    | 8.71    | 2.92                | 4.01    | 6.00    | 7.47                | 8.02    | 6.32    | 28.3                        | 30.6    | 36.7    | 20.6                        | 24.1    | 26.9    |
| Li ( $\mu\text{g}/\text{L}$ )   | 7                   | 7       | 16      | 8                   | 13      | 22      | 6                   | 6       | 9       | 152                         | 159     | 218     | 52                          | 63      | 70      |
| Rb                              | 18                  | 13      | 20      | 3                   | 3       | 6       | 11                  | 12      | 8       | 18                          | 20      | 25      | 12                          | 14      | 12      |
| Sr                              | <2                  | <2      | <2      | <2                  | <2      | 4       | 12                  | 17      | 8       | 61                          | 73      | 97      | 83                          | 123     | 156     |
| Ba                              | <5                  | <5      | 5       | 6                   | <5      | 8       | <5                  | 10      | 5       | 17                          | 14      | 15      | 6                           | 16      | 5       |
| As                              | <4                  | 5       | 7       | <4                  | 4       | 4       | <4                  | <4      | 5       | 155                         | 170     | 187     | 7                           | 7       | <4      |
| Mo                              | <1                  | <10     | <10     | <10                 | <10     | <10     | <10                 | <10     | <10     | 416                         | 419     | 468     | <10                         | <10     | <10     |
| Cd                              | <4                  | <4      | <4      | 4                   | <4      | <4      | <4                  | <4      | <4      | 4                           | <4      | <4      | <4                          | <4      | <4      |
| Sb                              | <6                  | <6      | 6       | <6                  | <6      | <6      | <6                  | 7       | <6      | 12                          | 9       | 7       | <6                          | 14      | <6      |
| Hg                              | <2                  | <2      | <2      | <2                  | 3       | 4       | <2                  | <2      | <2      | 17                          | <2      | 16      | <2                          | <2      | <2      |

\* HCO<sub>3</sub><sup>-</sup> was not measured but was calculated to reach electro-neutrality.

**Table 4.** Major ion and trace element compositions of the MER water leachates obtained by the interaction of volcanic rocks and fluvio-lacustrine sediments (10 g of powder) with calcium bicarbonate (Ca–HCO<sub>3</sub>) water (50 mL). Major ions were analysed by Ion Chromatography and trace elements were analysed by ICP-MS after 15, 30, and 90 days. n.a.: not analysed; n.d.: not detected.

| Sample                          | Ted4                |         |         | TW31                |         |         | TW39                |         |         | TW22                        |         |         | Ted38                       |         |         |
|---------------------------------|---------------------|---------|---------|---------------------|---------|---------|---------------------|---------|---------|-----------------------------|---------|---------|-----------------------------|---------|---------|
|                                 | Pyroclastic Deposit |         |         | Pyroclastic Deposit |         |         | Pyroclastic Deposit |         |         | Fluvio-Lacustrine Sediments |         |         | Fluvio-Lacustrine Sediments |         |         |
|                                 | 15 days             | 30 days | 90 days | 15 days             | 30 days | 90 days | 15 days             | 30 days | 90 days | 15 days                     | 30 days | 90 days | 15 days                     | 30 days | 90 days |
| pH                              | 8.35                | 8.55    | 8.30    | 8.21                | 8.00    | 8.18    | 7.70                | 7.76    | 7.68    | 8.15                        | 7.86    | 8.30    | 8.00                        | 8.10    | 7.81    |
| EC (µS/cm)                      | 588                 | 483     | 700     | 302                 | 323     | 306     | 312                 | 308     | 278     | 1300                        | 1200    | 1350    | 540                         | 565     | 533     |
| F <sup>-</sup> (mg/L)           | 6.42                | 6.79    | 7.79    | 2.94                | 3.22    | 3.53    | 1.77                | 1.98    | 2.41    | 7.80                        | 7.76    | 8.24    | 5.97                        | 6.68    | 8.26    |
| Cl <sup>-</sup>                 | 32.3                | 33.5    | 36.2    | 7.33                | 17.1    | 8.10    | 17.4                | 17.2    | 18.5    | 7.97                        | 80.3    | 78.5    | 23.8                        | 24.7    | 23.6    |
| NO <sub>3</sub> <sup>-</sup>    | 34.2                | 31.1    | 37.6    | 0.26                | n.d.    | 0.2     | 4.60                | 5.76    | 20.4    | n.d.                        | n.d.    | 1.21    | 15.1                        | 18.0    | 16.7    |
| SO <sub>4</sub> <sup>2-</sup>   | 34.0                | 35.1    | 38.0    | 2.46                | 1.96    | 2.30    | 6.06                | 6.24    | 6.30    | 290                         | 310     | 300     | 14.1                        | 14.8    | 13.7    |
| * HCO <sub>3</sub> <sup>-</sup> | 48                  | 63      | 93      | 144                 | 161     | 166     | 139                 | 127     | 113     | 146                         | 201     | 201     | 216                         | 242     | 233     |
| Ca <sup>2+</sup>                | <0.3                | <0.3    | <0.3    | 1.19                | 4.51    | 4.12    | 11.9                | 10.6    | 11.7    | 9.10                        | 11.3    | 12.5    | 14.3                        | 14.1    | 15.9    |
| Mg <sup>2+</sup>                | <0.4                | <0.4    | <0.4    | <0.4                | 0.66    | <0.4    | 2.69                | 2.01    | 1.56    | 2.29                        | 2.86    | 3.03    | 3.40                        | 4.65    | 4.52    |
| Na <sup>+</sup>                 | 70.4                | 59.2    | 86.3    | 56.7                | 64.5    | 62.5    | 45.1                | 43.8    | 44.6    | 221                         | 246     | 238     | 77.3                        | 85.6    | 81.4    |
| K <sup>+</sup>                  | 17.9                | 13.0    | 21.9    | 8.68                | 9.72    | 9.11    | 13.5                | 11.7    | 12.1    | 35.8                        | 34.5    | 38.9    | 28.8                        | 31.2    | 30.3    |
| Li (µg/L)                       | 11                  | 14      | 21      | 15                  | 17      | 15      | 8                   | 7       | 6       | 191                         | 191     | 217     | 70                          | 95      | 81      |
| Rb                              | 24                  | 26      | 32      | 9                   | 9       | 9       | 20                  | 18      | 16      | 23                          | 22      | 27      | 17                          | 20      | 18      |
| Sr                              | 2                   | 3       | 4       | 5                   | 10      | 7       | 47                  | 40      | 29      | 90                          | 98      | 107     | 178                         | 193     | 210     |
| Ba                              | <5                  | <5      | <5      | 54                  | <5      | 5       | <5                  | <5      | <5      | 11                          | 20      | 13      | 10                          | 6       | 8       |
| As                              | <4                  | <4      | 62      | <4                  | <4      | <4      | 4                   | 6       | 9       | 145                         | 144     | 188     | 8                           | 8       | 6       |
| Mo                              | <10                 | <10     | 11      | <10                 | <10     | <10     | <10                 | <10     | <10     | 454                         | 432     | 477     | <10                         | 10      | <10     |
| Cd                              | <4                  | <4      | <4      | <4                  | <4      | <4      | <4                  | <4      | <4      | <4                          | <4      | <4      | <4                          | <4      | <4      |
| Sb                              | <6                  | <6      | <6      | <6                  | <6      | <6      | <6                  | <6      | <6      | <6                          | 10      | <6      | <6                          | <6      | <6      |
| Hg                              | <2                  | <2      | <2      | <2                  | <2      | <2      | <2                  | <2      | <2      | <2                          | <2      | <2      | <2                          | <2      | <2      |

\* HCO<sub>3</sub><sup>-</sup> was not measured but was calculated to reach electro-neutrality.

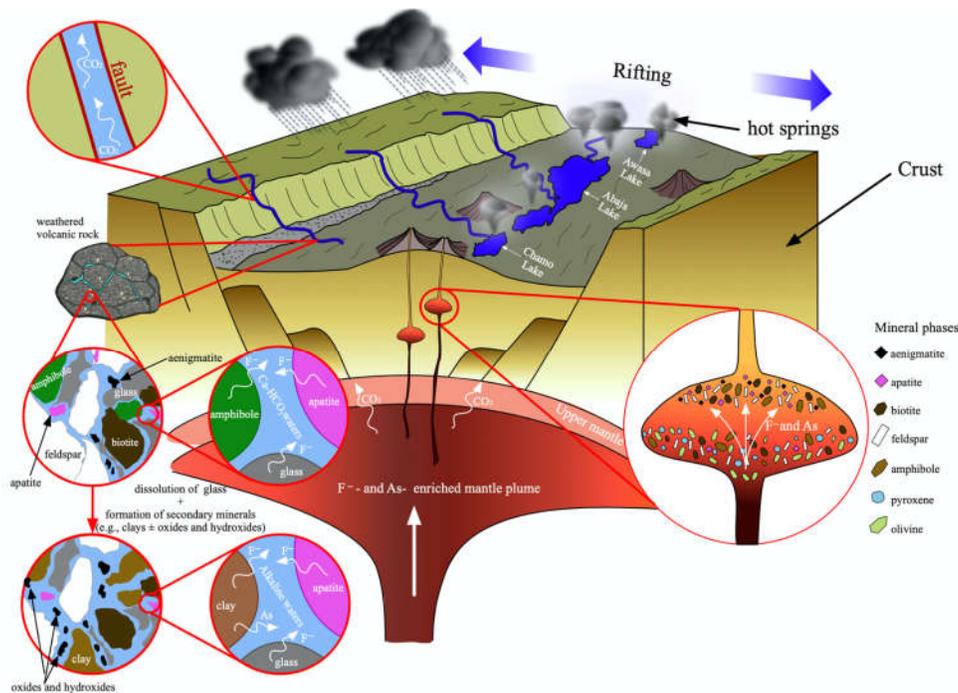


**Figure 7.** F<sup>-</sup> vs. As contents of the MER water compared to leachates that simulate the water-rock/sediment interactions with aquifer matrices. Leachates were obtained by the interaction of the MER lithologies with both deionized and calcium bicarbonate (Ca-HCO<sub>3</sub>) water.

### 5.2. Geological Origin of F<sup>-</sup> and As Co-Occurrence in the MER Water

In order to understand the behaviour of F<sup>-</sup> in geological cycles, the concentration of F has been studied in the main Earth Reservoirs and compared to the concentration of Cl. Fluorine is ten times more depleted with respect to Cl in the most undifferentiated Earth materials provided by chondrites (Ch; F<sub>Ch</sub>: 64 mg/kg; Cl<sub>Ch</sub>: 678 mg/kg [63]). It becomes comparatively enriched in the primitive mantle (PM; F<sub>PM</sub>: 25 mg/kg; Cl<sub>PM</sub>: 17 mg/kg [63]), and especially enriched in the Upper Crust (UCC; F<sub>UCC</sub>: 565 mg/kg; Cl<sub>UCC</sub>: 370 mg/kg [49]). This means that, among halogens, F has a greater affinity to be sequestered by minerals, whereas Cl more likely escapes into fluid phases, ultimately becoming one of the most prevalent ions in the hydrosphere. In magmatic processes during crystal fractionation, F behaves as an incompatible element, as its concentration progressively increases from primitive magma of mantle origin (e.g., basaltic in composition) to residual magma (e.g., rhyolitic in composition), where F concentrates in late stage accessory phases (e.g., apatite, amphibole, biotite, aenigmatite [64,65]). Tectonic settings also play a role in the concentration of this element, and generally, halogens are expected to have higher concentrations in magma from convergent plate settings (i.e., subduction-related) or in magma generated by the melting of very deep mantle sources

activated by uprising plumes [66]. The latter seems to be the case for the MER, as the anomalous F concentration in sialic rocks characterises the whole East African Rift, where magma is plausibly related to plume-related mantle sources enriched in halogens (Figure 8). In the studied volcanic rock, although high F<sup>-</sup> contents have been recorded in amphibole and fluoro-apatite, the main F<sup>-</sup> repository is the volcanic glass that often constitutes up to 90% of the studied matrices. Glassy particles are highly reactive, and during weathering, they are replaced by clay minerals and amorphous and cryptocrystalline compounds (allophane, imogolite, halloysite), having a remarkable capacity to retain F until the leaching of alkaline groundwaters induces its subsequent release (Figure 8) [10,11,67,68]. A similar consideration can be made for As, whose enrichment in the hydrosphere often mirrors that of F<sup>-</sup> [10,11]. In fact, the cycling of this element is strongly constrained by the tectonic setting: As is classically associated with subduction-related magmas; however, it is also concentrated in volcanic areas related to uprising plumes, as recorded throughout the whole East African Rift [15] (Figure 8).



**Figure 8.** Conceptual model of the geological, geochemical, and environmental processes responsible for the F<sup>-</sup> and As-enrichment in the MER waters. The processes started with (1) the uprising of a mantle plume enriched in F<sup>-</sup> and As, which caused the (2) rifting of the area and (3) the eruptions of basic and sialic magmas, which filled the rift valley. (4) During the magmatic differentiation process, F<sup>-</sup> and As behave as incompatible elements, concentrating in volcanic glass and accessory minerals (e.g., amphibole, biotite, apatite) of differentiated volcanic rocks (i.e., rhyolites). (5) The weathering of sialic lithologies by Ca–HCO<sub>3</sub> water, typical of the MER highlands, induces (6) the dissolution of silica glass, i.e., the main repository of F<sup>-</sup> and As, and (7) the formation of secondary phases, such as clay, oxides, and hydroxides, which retain F<sup>-</sup> and As. (8) Subsequently, interactions between rocks and sediments with alkaline water (rich in dissolved CO<sub>2</sub>) further release F<sup>-</sup> and As, inducing the contamination of groundwaters and lakes.

Like F<sup>-</sup>, during magmatic processes and crystal fractionation, As has incompatible behaviour, being finally trapped in residual sialic rocks [13] (Figure 8). In these rocks, As is contained in the same F-repositories, i.e., volcanic glass [10–13,27–30,69], amphibole, and apatite [70]. Coherently arsenate-phosphate hydroxyapatite solid solution [Ca<sub>5</sub>(P<sub>x</sub>As<sub>1-x</sub>O<sub>4</sub>)<sub>3</sub>(OH)] is well known in the literature [71–73]. Moreover, As can be contained in solid solution, e.g., in aenigmatite [74,75], magnetite [76], and sulphides, which are other typical minerals of the MER rhyolitic volcanics. As indicated for F<sup>-</sup>, the

weathering transforms the above-mentioned magmatic minerals in a series of amorphous and cryptocrystalline secondary minerals, especially oxides and hydroxides, which have a notable As adsorption capacity [10,19], until alkaline groundwater undergoes active desorption reactions, which release As into the aquifers (Figure 8). For the thorough understanding of the processes, it is also important to consider the MER geological setting, where groundwater circulates in fault zones that convey mantle-derived CO<sub>2</sub> (Figure 8). This is important as endogenic CO<sub>2</sub> enhances the hydrolysis of silicic minerals, oxides, and hydroxides, which release F<sup>-</sup> and As, as suggested for other rift zones (e.g., in Namibia and Madagascar), where water anomalies have been recorded [33,34].

## 6. Conclusions

In many parts of Ethiopia, including the Main Ethiopian Rift (MER), groundwater is the major source of drinking water. Understanding the occurrence, distribution, and sources of potential contaminants in groundwater is therefore important to protect the health of the local populations. In the Awasa-Abaya-Chamo lakes area (southern MER), groundwater contains elevated levels of F<sup>-</sup> and As, especially in the hot springs. Hot water rich in dissolved CO<sub>2</sub> leaches the rhyolitic volcanic rocks and their weathered products (i.e., fluvio-lacustrine sediments) more efficiently and, subsequently, can contaminate the groundwater aquifers used for drinking in the region. The weathering of rhyolitic volcanic glass, primary mineral phases (i.e., apatites, amphiboles, and aenigmatites), and secondary phases (i.e., clays, oxides, and hydroxides) by the MER alkaline Na–HCO<sub>3</sub> groundwater induces the mobilisation of F<sup>-</sup> and As into aquifers, which reaches concentrations that are hazardous to human health. The potential risk is even more serious considering that the fluvio-lacustrine sediments, the main reservoirs of F<sup>-</sup> and As in the MER area, can release high amounts of these contaminants into the water system in short periods of time (i.e., a few days), as demonstrated in the leaching experiment. This work also revealed that the only safe drinking water with acceptable concentrations of F<sup>-</sup> and As is provided by cold springs far from geothermal systems, as cold water is less effective at leaching the host aquifers. From a practical point of view, the presented data are useful for mapping the quality and geochemistry of water in lakes and hot and cold springs in the MER. In fact, it is necessary to discriminate contaminated water sources that have to be avoided from good-quality water supplies that the locals can access for drinking purposes with the minimal risk to health.

**Supplementary Materials:** The following are available online at [www.mdpi.com/2075-163X/10/5/453/s1](http://www.mdpi.com/2075-163X/10/5/453/s1), Figure S1: (a) Total Alkali Silica (TAS [77]) diagram showing the MER volcanic rock and the fluvio-lacustrine sediment composition investigated in this study. Average compositions of rocks studied by Rango et al. [19] are also reported. (b) Al<sub>2</sub>O<sub>3</sub> vs. FeO diagram proposed by Macdonald [78] showing the MER volcanic rock and fluvio-lacustrine sediment compositions investigated in this study. Average compositions of rocks and fluvio-lacustrine sediments studied by Rango et al. [19] are also reported. (c) Upper Continental Crust-normalised incompatible trace element patterns of the MER volcanic rocks and fluvio-lacustrine sediments investigated in this study. Average compositions of rocks and fluvio-lacustrine sediment studied by Rango et al. [19]; Figure S2: F<sup>-</sup> and As contents of the MER water correlated with Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, Li, and Rb contents and electrical conductivity (EC), total dissolved solids (TDS), and temperature (*T*) parameters; Table S1: Major and trace element compositions of MER rocks and fluvio-lacustrine sediments determined by X-Ray Fluorescence (XRF); Table S2: Compositions of volcanic glass and mineral phases hosting F of MER volcanic rocks and fluvio-lacustrine sediments were carried out through a scanning electron microscope (SEM) fitted with an energy dispersive X-ray (EDX) detector routinely calibrated for analysis of major elements in silicates. An additional wavelength dispersive X-ray (WDX) detector was specifically used for analysis of F.

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