GEOCHEMICAL AND ISOTOPIC COMPOSITION OF NATURAL WATERS IN THE CENTRAL MAIN ETHIOPAN RIFT: EMPHASIS ON THE STUDY OF THE SOURCE AND GENESIS OF FLUORIDE

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GENERAL INTRODUCTION

In the Main Ethiopian rift (MER) system, groundwater resources from wells and springs as well as from rivers are a very important supply of drinking water for millions of people living in the area. The MER is characterized by semi-arid to arid climate conditions where water scarcity is often associated with water quality problems (Fig. 1).

The natural waters of this region are characterized by geochemical anomalies of high fluoride concentration (Kilham & Hecky, 1973; Gizaw, 1996) often exceeding the 1.5 mg/l tolerance limit for drinking water (WHO, 2006). The local population is affected by diseases such as mottled teeth and skeletal fluorosis (Tekle-Haimanot *et al.*, 1987).

Many geochemical studies have addressed the fluoride problem in order to elucidate its origin (Gizaw, 1996; Yirgu *et al.*, 1999; Chernet *et al.*, 2001; Rango *et al.*, 2009) and to investigate the associated health problems (Tekle-Haimanot *et al.*, 1987; Kloos & Tekle-Haimanot, 1999). Although the health related impact of fluorine is well known, the hydrogeochemistry of fluorine, with respect to the controlling phases (minerals and/or amorphous), and the processes that induce its enrichment are not extensively studied in the Ethiopian rift system. Similarly, geochemical studies on trace elements are also not yet well investigated in the region.

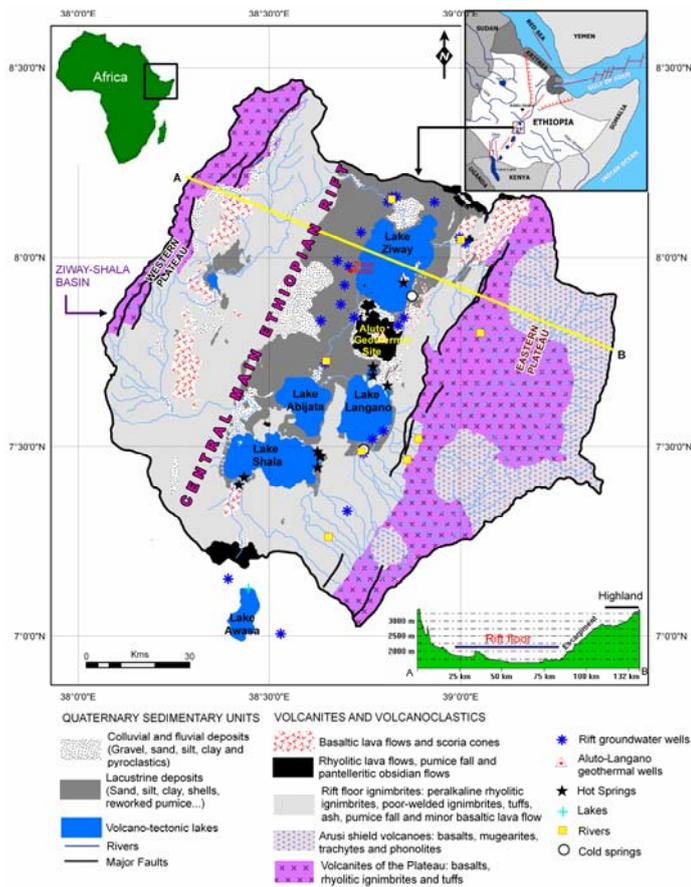Such kind of studies are extremely important especially in

Fig. 1 - Simplified geologic map of Ziway-Shala lakes basin with water sampling points.

active volcanic areas which are characterized by extremely reactive lithotypes (that can release their chemical budget into the interacting water) and by persisting geothermal manifestations (possibly including juvenile fluids) that can pollute the shallow aquifers. This is the case of the Main Ethiopian rift (MER), where the presence of felsic-volcanic rocks (ashes, tuffs, rhyolitic ignimbrites) and their weathered and re-deposited fluvio-volcano lacustrine sediments, as well as the presence of active geothermal activities, could contribute to the existence of multiple geochemical anomalies with detrimental effects on human health.

This study mainly deals with the natural occurrence of these trace elements, particularly fluoride and arsenic. The other aspect addressed in this study is the isotopic composition of natural waters δD, $\delta^{18}O$ and strontium isotope ($^{87}Sr/^{86}Sr$) in order to understand surface water and groundwater circulation and their interactions, and water-rock interactions in the region.

Therefore, the objectives of this study can be summarized into three parts:

- To gain a better knowledge and understanding of fluoride problem with respect to its sources, genesis and distribution in order to support water quality management issues in the region;

- To perform a more general water quality assessment, and identifying other potentially toxic trace elements;

- To investigate the origin of waters, water/rock interactions and mixing processes in the basin using stable isotopes δD, $\delta^{18}O$ and radiogenic isotopes ($^{87}Sr/^{86}Sr$) in waters and lithotypes.

GEOCHEMISTRY OF ROCKS AND SEDIMENTS IN CENTRAL MAIN ETHIOPIAN RIFT

The results of bulk rock XRF analyses of the aquifer solid matrixes were reported in an alkali-silica classification diagram, indicating that the prevalent volcanic rocks are rhyolites, and that the fluvio-volcano lacustrine sediments simply represent the weathered - redeposited products of the above mentioned volcanic rocks. The petrographic investigation of representative thin sections shows that they are characterized by a few crystals of quartz, alkali-feldspar, orthopyroxene and amphibole within a prevalent glassy groundmass.

The microprobe analysis on ignimbrites revealed that the concentration of F is as high as 180 ppm in the glassy groundmass and up to 260 ppm in accessory phases such as alkali amphibole (riebeckite composition). Therefore, considering the modal proportions of the investigated rocks (hydrous mineral phases are extremely rare), we assume that most of the fluorine budget is concentrated in the glassy matrix.

Representative samples were subsequently selected for leaching experiments. In these experiments, powdered samples were mixed with distilled water having a *p*H of about 5.5, at a ratio of 1 to 5 (10 g / 50 ml; room temperature), and shaken for 12 months at a frequency of 100 rev/min. The test simulates the potential leachability of soluble components during water-rock/sediment interactions.

GEOCHEMISTRY OF MER WATERS

The major ions analyses of the different MER water types show extremely variable composition, ranging from low TDS (and *e.g.* low F⁻) in rivers to very high TDS (and *e.g.* high F⁻) in the rift groundwater wells, hot springs and lakes (sampling points on Fig. 1).

The average TDS values in the groundwater wells and hot springs (39-96°C) are 1050 and 3610 mg/l respectively. TDS is even more variable in lake waters, with values which vary from the fresh

water Ziway lake (379 mg/l), brackish water Langano lake (1377 mg/l) to the saline Shala, Abijata and Chitu lakes (11563, 52725 and 64267 mg/l respectively). *p*H ranges between 6.8-9.1 in groundwater wells, thermal springs and rivers whereas the lakes have pH range of 8.6-10, with the highest value recorded in the alkaline lake Chitu.

Hydrochemical facies of different water types, *i.e.* groundwater wells (in the rift and highlands), geothermal wells, hot springs, rivers and lakes were identified based on the Piper classification diagram. Groundwater from the highlands (Ayenew, 2005) typically show a $Ca^{2+}(Mg^{2+})$- HCO_3^- hydrochemical facies similar to that of rivers and cold springs where the sum of Ca^{2+} and Mg^{2+} exceeds Na^+ and K^+. On the contrary hot springs and most groundwater in the rift display a Na^+-HCO_3^- fingerprint, with Na^+ and HCO_3^- proportions constituting more than 80% of all the ionic species in the solution.

Fluoride concentration increases along the groundwater flow path displaying low values in Ca^{2+}-Mg^{2+}/HCO_3^- waters from the highlands and higher values in the Na^+-HCO_3^- waters from the rift. The average concentration of fluoride is 0.8 mg/l in rivers, 32 mg/l in thermal springs, 27 mg/l in deep (> 2 kms) geothermal wells, 6 mg/l in groundwater wells, and 121 mg/l in lakes. 38% of rivers, 87% of the groundwater wells and 100% of lakes, thermal and geothermal waters have fluoride value beyond 1.5 mg/l.
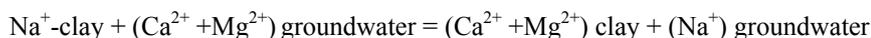
High F^- is associated with high pH, Na^+, and HCO_3^- values, whereas F^- is inversely related to Ca^{2+} and Mg^{2+} in the groundwater wells, hot springs and geothermal wells of the MER (Fig. 2). Accordingly, high fluoride concentration is found in leachates characterized by high pH, Na^+ and HCO_3^-.

Fluoride enrichment mechanism

Fluorine occurrence is associated with the presence of silicic rocks and their weathering products. The fluoride activity in the solution is controlled by the solubility product, $K_{fluorite}$ as expressed below:

$$CaF_2 = Ca^{2+} + 2 F^-$$
$$K_{fluorite}: (Ca^{2+})(F^-)^2 = 10^{-10.57} \text{ at } 25°C$$
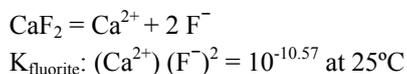
This suggests that the fluoride concentration in natural waters is inversely related to Ca^{2+}. This permits free mobility of the fluoride ion into the solution at lower Ca^{2+} content. This effect (Ca^{2+} deficiency) is magnified in the rift (MER) where cation exchange took place within the sediments (fluvio-lacustrine, volcano-lacustrine) causing the removal of ions from the solution (mainly Ca^{2+}) by replacement with Na^+ ions from the clay exchange sites (Rango *et al.*, 2009).

$$Na^+\text{-clay} + (Ca^{2+} + Mg^{2+}) \text{ groundwater} = (Ca^{2+} + Mg^{2+}) \text{ clay} + (Na^+) \text{ groundwater}$$

Such hydrogeochemical processes are responsible for the evolution of Ca^{2+}-Mg^{2+}/HCO_3^- to Na^+/HCO_3^- types of groundwater and thermal water with a parallel enrichment of fluoride.

In order to sort out other potentially hazardous geochemical anomalies, the measured concentrations of trace elements (and major ions) in MER natural waters were compared with existing drinking water standards recommended by the authorities (WHO 2006; EU directives, 1998; USEPA, 2003).

The result showed that major ions (F^-, Na^+, Cl^-, SO_4^{2-} and NO_3^-) and trace elements such as As, B, Mo, U, Fe, Al, and Mn often exceed the tolerance limit of drinking water fixed by the authorities.

Among trace elements, arsenic represents another geochemical anomaly that potentially induce serious health problem. The average concentration of arsenic is 0.9 μg/l in rivers, 39 μg/l in thermal springs, 236 μg/l in deep geothermal wells, 21.4 μg/l in groundwater wells and 77 μg/l in lakes, with maximum values of 3 μg/l, 156 μg/l, 278 μg/l, 157 μg/l and 405 μg/l respectively. It has to be noted that 35% of the MER groundwater wells (the main source of potable water) contain more than the safe limit 10 μg/l (WHO, 2006).

Fig. 2: Relationship between pH, F^-, Na^+, HCO_3^-, Ca^{2+} and Mg^{2+} in waters of the central MER.

F^- in MER groundwater wells positively correlated with Na^+ ($R^2 = 0.7$), HCO_3^- ($R^2 = 0.5$), TDS ($R^2 = 0.64$) and EC ($R^2 = 0.73$) and similarly arsenic shows a positive correlation with Na^+ ($R^2 = 0.63$), HCO_3^- ($R^2 = 0.7$), TDS ($R^2 = 0.6$) and EC ($R^2 = 0.67$). Arsenic also correlates with some trace elements such as Mo ($R^2 = 0.79$), V ($R^2 = 0.68$), and U ($R^2 = 0.70$), whereas no correlation with Fe and Mn were observed.

LEACHING EXPERIMENTS

The comparison with the tolerance limits indicated by international guidelines has been extended to the experimental leachates, showing that the concentration of elements potentially affecting human health such as F, As, Fe, Al, Mo, and U are often beyond the admissible limits. These comparisons simply define the higher relative vulnerability of natural waters to the above mentioned elements in the region.

For instance, fluoride concentrations exceeded the drinking water standard of 1.5 mg/l in 10 out of 11 leachates, arsenic concentrations exceeded the standard of 10 μg/l in 3 out of 11 leachates, iron concentrations exceeded the standard of 200 μg/l in 4 out of 11 leachates and aluminium concentrations exceeded the standard of 200 μg/l in 3 out of 11 leachates. It is also very interesting to note that leachates from sediments display higher concentration of toxic elements with respect to those obtained from volcanic rocks. This indicates that the sediments are the major reservoir and source of toxic elements. High arsenic and fluoride concentration is found in leachates characterized by high pH, Na^+, and HCO_3^-.
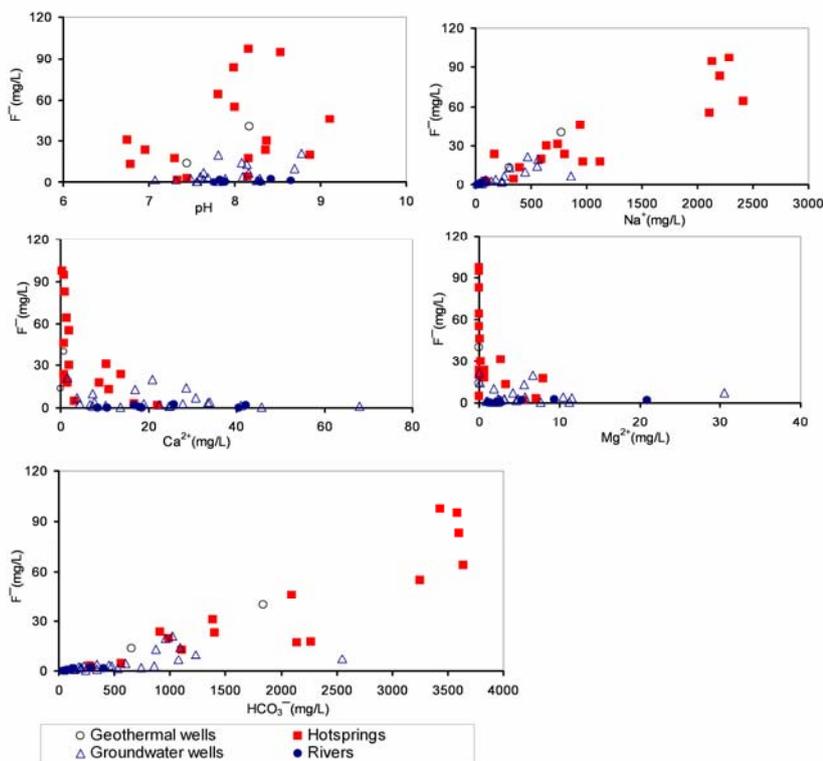
Column laboratory experiments were also employed to asses the leaching behavior of pyroclastic ash deposits so as to elucidate its source and simulate the water-rock interaction processes, and to quantify the distribution of F⁻ within different grain sizes. The pyroclastic ash was separated into coarse and fine fractions. Then, three columns were respectively filled with raw (unsieved), coarse and fine fraction and flushed with synthetic rain water in saturated conditions (Fig. 3).

Very fast F⁻ leaching was observed on the fine fraction column at the start of the experiment while in the other two columns F⁻ was slowly released; additionally, a strong accumulation of F⁻ was found in the fine fraction. The effect was more pronounced in the fine column due to the available effective adsorbing surface area in the fine grained fractions. Subsequent to elution experiments, the columns were characterized via moment analysis of tracer test. Finally, flow and transport modeling was employed to compute the amount of F⁻ adsorbed onto solid phase, comparing the calculated conservative transport of F⁻ and the observed concentrations. The results gained in this study confirm the sources of leachable F⁻, is principally constituted by F⁻ adsorbed on to the silicate glass surfaces of pyroclastic particles.
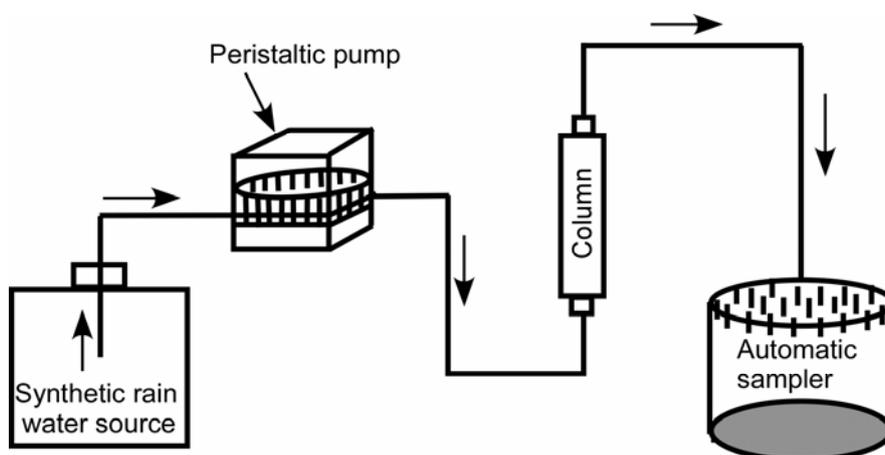

Fig. 3 - Schematic diagram of the column experimental set-up.

ISOTOPE GEOCHEMISTRY OF MER WATERS AND ROCKS

Defining the local meteoric water line (LMWL)

In the study area the local meteoric water line (LMWL; $\delta D = 7.02$, $\delta^{18}O + 9.1$) is defined based on the interpretation of isotopic data ($\delta^{18}O$, δD) of rain in the basin (at Asela, Ziway, Silte, Butagera, and Awasa towns) that were collected by (Chernet, 1998) in the period of June-August 1994 and 1995 with precipitation varying from 2.5 to 75 mm.

Samples from groundwater and geothermal wells, hot springs, lakes and rivers were analyzed for δD, $\delta^{18}O$, $^{87}Sr/^{86}Sr$ isotopes, and trace (Li, B, Sr, and Rb) elements in order to investigate groundwater and lake water interactions, water-rock interactions, and to evaluate groundwater flow path.

The principal groundwater recharge in the region, particularly east of Lake Ziway, are meteoric waters coming from highlands, mainly recharged by the NNE/SSW faults bounding the rift floor. Different ranges of isotopic values are recorded for different water types: hot springs $\delta^{18}O$ (-3.36–3.69)

and δD (-15.85–24.23), groundwater wells δ^{18}O (-3.99–5.14) and δD (-19.69–32.27) in contrast to the Lake δ^{18}O (3.98–7.92) and δD (26.19–45.71) (‰ V-SMOW). δD and δ^{18}O of the water types compared with LMWL and GMWL (δ^{2}H = 8 δ^{18}O + 10).

Dissolved strontium isotopic ratios range from 0.7045 to 0.7076 in the hot springs, and the two deep geothermal wells situated along the fault at the up flow part of Aluto-Langano geothermal field, have 0.7043 and 0.7054 values, respectively. These ratios lie in the range of Sr isotopic signature of MER basalts and rhyolites, which showed overlapping signatures. The diversity in strontium isotopic ratios in waters is probably caused by complex mixings, interactions with multiple lithotypes, and different degree of water-rock/sediment interaction.

CONCLUSIONS AND RECOMMENDATIONS

The geochemical composition on natural waters of the central MER in Ziway-Shala basin has been investigated in order to understand the source, genesis and distribution of chemical elements with particular emphases to fluoride.

In this framework we performed an integrated study of both waters and coexisting representative solid aquifer matrixes, in order to unravel the water-rock/sediment interactions that ultimately lead to the peculiar geochemical features of the Ethiopian rift waters. Therefore, the hydrochemical investigation was coupled with the mineralogical/geochemical characterization of the lithologies outcropping in the area. Moreover, laboratory leaching tests (batch and column) were also carried out to evaluate the potential release of fluoride from the various rock/sediment types. These approaches serve to understand the lithologic sources and the enrichment mechanisms controlling the anomalous fluoride content in the water.

The geochemical anomalies in the studied natural waters are predominantly linked to the mode of emplacement of volcanism in the Ethiopian Rift system. The general hydrochemical evolution, in which Ca^{2+}(Mg^{2+})-HCO$_3^-$ waters, typical of the highlands, are transformed along the flow path into alkaline *p*H and Na$^+$-HCO$_3^-$ waters (typical of the rift area), is clearly related to water-rock/sediment interactions, is probably triggered/favoured by the high geothermal gradient and the high activity of CO$_2$ that characterize the rift valley. In these interactions, the matrixes are mainly rhyolites consisting of volcanic glass (usually more than 95% in proportion). This glassy material is extremely reactive, and its weathering products (*i.e.* the fluvio-volcano lacustrine sediments) can further concentrate geochemical elements. Therefore, the interaction of these "reworked" volcanic products with water and carbon dioxide (juvenile?) progressively lead to a "secondary" clay-bearing mineral assemblage that and under high *p*H conditions can release some chemical species (*e.g.*, F$^-$, As) into the interacting water.

A comparison of major and trace element concentrations of MER natural waters with standards set by three authorities (WHO, EU directives, USEPA), indicated significant quality problems (in all water groups at different percent proportions).

Together with the renowned F$^-$ problem, the possible presence of geochemical anomalies in As, B, Mo, U, Al, Fe, and Mn have to be taken into consideration in water quality issues. Furthermore, future work has to be done to investigate their possible health impact on the population of MER and other sectors of the east African rift.

Column experiments were also conducted on volcanic ash (vitric ash) materials after separating into different grain size fractions (fine ash, coarse ash and raw ash) to characterize the behaviour of fluoride under flushing of synthetic rain water. The result showed that high concentrations of fluoride

were leached out particularly from the fine ash fraction which in turn suggests pyroclastic materials are the ultimate reservoir of fluoride.

Understanding the distribution and geochemistry of fluorine, arsenic and related elements along with their tolerance thresholds is essential in identifying high-risk areas and for the development of adequate remediation technologies, particularly where people live in scattered villages across the basin. However, considering that water treatments are expensive and barely efficient, we suggest avoiding (as far as possible) the drilling of new wells especially a) in those areas characterized by the presence of fluvio-lacustrine sediments b) close to the outpouring of hot springs. In any case activation of new wells should be preceded by chemical analysis including the above mentioned critical elements.

Moreover, we suggest starting to plan new strategies for water exploitation in the highlands (where elemental concentrations (such as F$^-$ and As are typically low). This is mainly important for water supply of towns. These aqueduct infrastructures would imply an initial investment, but would be cost-effective in the long-term.

The stable δ^{18}O, δD and radiogenic (^{87}Sr/^{86}Sr) isotopic composition indicate different ranges of stable isotopic values were recorded for different water groups. The Sr isotope signatures are typical of water that interacted with the main lithotypes covering the study area. Generally, the result shows that there exists a complex surface water and groundwater interactions that is reflected on a diversity of the stable and Sr isotopic signature in waters.

The general geochemical evolution of rift waters begins from eastern and western highlands following the regional groundwater flow direction; the pristine waters coming from the highlands should display isotopic compositions characterized by less radiogenic ^{87}Sr/^{86}Sr (and more depleted δD, δ^{18}O). This isotopic signature subsequently evolves toward higher ^{87}Sr/^{86}Sr for an interaction with the more radiogenic rhyolites of the rift and their weathered and redeposited products.

The preliminary results of this study has showed that there is a need for future extended works on the geochemistry of solid samples (rocks, sediments and soils) as well as in waters. These studies should investigate a wide spectrum of chemical elements including all the components (trace/rare earth elements) that are potentially detrimental to human health and environment, in order to establish baseline geochemical atlases of the region.

Furthermore, from a water resource point of view, the following work must focus on a comprehensive study of various isotopes and geochemical data to constrain groundwater age dating, water-rock interaction and flow path and thus help to model and systematize the hydrologic cycles in the basin.

REFERENCES

Ayenew, T. (2005): Major ions composition of the groundwater and surface water systems and their geological and geochemical controls in the Ethiopian volcanic terrain. *Ethiopian J. Sci.*, **28**, 171-188.

Chernet, T. (1998): Etude des mécanismes de minéralisation en fluorure et éléments associés de la région des lacs du rift Ethiopien, Thèse Doctorat, Université d'Avignon, 210 p.

Chernet, T., Travi, Y., Valles, V. (2001): Mechanism of degradation of the quality of natural water in the lakes region of the Ethiopian rift valley. *Water Res.*, **35**, 2819-2832.

European Union (1998): Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. *Offic. J. Europ. Comm.*, L330/32-L330/54.

Gizaw, B. (1996): The origin of high bicarbonate and fluoride concentrations in waters of the Main Ethiopian Rift Valley, East African Rift System. *J. African Earth Sci.*, **22**, 391-402.

Kilham, P. & Hecky, R.E. (1973): Fluoride: geochemical and ecological significance in East African waters and sediments. *Limin. Oceanog.*, **18**, 932-945.

Kloos, H. & Tekle-Haimanot, R. (1999): Distribution of fluoride and fluorosis in Ethiopia and prospects for control. *Tropic. Medic. Intern. Health*, **4**, 355-364.

Rango, T., Bianchini, G., Beccaluva, L., Ayenew, T., Colombani, N. (2009): Hydrogeochemical study in the main Ethiopian rift: new insights to source and enrichment mechanism of fluoride. *Environ. Geol.*, **58**, 109-118.

Tekle-Haimanot, R,. Fekadu, A,. Bushra, B. (1987): Endemic fluorosis in the Ethiopian Rift Valley. *Trop. Geogr. Med.*, **39**, 209-217.

USEPA (2003): National primary drinking water regulations. EPA 816-F-03-016, United States Environmental Protection Agency.

WHO (2006): Guidelines for drinking-water quality. 1st Addendum to vol. 1. Recommendations, 3rd ed. Geneva, World Health Organisation, 595 p.

Yirgu, G., Ayalew, D., Peccerillo, M.R., Barberio, C., Donati, C., Donato, P. (1999): Fluorine and chlorine distribution in the volcanics rocks from the Gedemsa volcano, Ethiopian Rift Valley. *Acta Vulcanol.*, **11**, 169-176.