XA9848330

FLUORIDE CONTAMINATION IN THE LAKES REGION OF THE ETHIOPIAN RIFT:
Origin, mechanism and evolution

Y. TRAVI, T. CHERNET*
Laboratoire Hydrogéologie, Université d'Avignon
Avignon, France

Abstract - *The closed lake basins occupying the Main Ethiopian Rift are characterised by unique hydrogeological conditions which have resulted in very high contents of fluoride associated with highly concentrated sodium bicarbonate waters. The origin, mechanism and evolution of fluoride contents have been examined successively by studying, (i) the reservoirs which provide this element in solution, (ii) the hydrochemical context, and (iii) the hydrological evolution which modifies the concentrations. Groundwaters of the ignimbrites present low values compared to those of the lacustrine sediments which can provide contents 5 to 10 times greater. The non equilibrium initial stage between the alkalinity and the calcium, derived from weathering of volcanic rocks, is responsible for the specific chemical evolution and the very high fluoride values. Furthermore, in the thermal waters, the high temperatures (especially those up to 100°C) and the presence of large amounts of* CO_2 *coming from depth increase significantly the fluoride contents. Finally, the fluoride concentrations can change depending on the interrelation of ancient or present surface waters and groundwaters (mixing) and on the hydrological balance (concentration and dilution processes).*

1. INTRODUCTION

The harmful biological effect of the fluoride ion gives this element an important place in the quality of drinking water. Its presence in small quantities prevents tooth decay; however when it is in excess quantity it provokes dental or bone fluorosis. The upper limit for potability is around 1 mg/l. Observations carried out in North and West Africa indicate that this problem is often widespread. It is the case, for example, in Senegal, Niger, Morocco, Algeria and Tunisia. In these countries, harmful concentrations are associated with phosphatic and some igneous rocks. Maximum contents of fluoride are around 10 mg/l and they are controlled by the hydrodynamics of the aquifer and by the fluorite saturation . In some cases, in these non acidic waters, the ion pair MgF^+ is also concerned (Travi,1993).

In Ethiopia, previous studies have shown that extensive areas, with high F- values in natural waters are very frequent, and they are almost exclusively in the Main Ethiopian Rift (MER) (Chernet and Travi, 1993). Furthermore in all the hydrological systems (groundwaters, thermal waters, surface waters) the higher values are localised in the Lakes Region (up to 300 mg/l).

The objective of this paper is to summarise the results of three years' fieldwork, (Chernet, 1998) including previous data, trying to determine the specific conditions of high fluoride removal in the Lakes Region which is located 130-280 km south of Addis Ababa. Considering its very low concentration in rainfall, the fluoride ion originates in the reservoir;

* Present address: P.O. Box 40950 Addis Ababa, Ethiopia.

then it is controlled by hydrochemistry and it changes with hydrological evolution, particularly by mixing between surface waters and groundwaters and according to the hydrological balance (dilution - concentration process)(Chernet and Travi, 1995). These three points will be examined successively after a brief presentation of the hydrogeological setting.

2. HYDROGEOLOGICAL SETTING

The Ethiopian Rift is a part of the East African Rift system and the Lakes Region of closed basins lies in this rift, 150-300 km south of Addis Ababa between latitudes 6° 50' N and 8° 19' N and longitudes 38° 7'E and 39° 24'E. The average width of the rift valley in the region is 70 - 80 km and it runs in a general north - south direction with a total area of about 16000 km^2. In general, the altitude is about 2500 m at the plateau and about 1600 m at the rift floor. The rainfall distribution in the year is typical of the type in the rift valley to the north of the Lakes Region and adjacent to the escarpments with one peak in July-August and another smaller peak in March-May. The average annual rainfall in the region ranges between 600 and 1100 mm, while the potential evapotranspiration ranges between 1000 mm and 2500 mm.

Groundwater lies in volcanic rock aquifers essentially located on the plateau, and lacustrine sediment aquifers in the bottom of the rift. The volcanic rocks are largely ignimbrites (60% of the area), but also alkaline basalts and trachybasalts, recent basalts and acidic complexes (rhyolites, tuffs, pumice and obsidian). They have moderate to high permeability with borehole yields of 0-6 l/s. Lacustrine sediments, the second extensive unit (16% of the area) consist of alternating fine and coarse beds and they are predominantly fine to medium grain. They show low to moderate potential of 1-5 l/s.

The region is a large closed basin of rift valley lakes which are hydrologically interconnected. Each lake has a different level of being closed and of being replenished-discharged-evaporated (Fig.1) which largely accounts for the level of its salinity. Surface and groundwater flows concentrate towards the Shalla Lake, filling up a large caldera in the rift floor, at the lowest elevation. The Lake Region is known to be characterised by geothermal features especially in the areas east and north of Awasa, east and south of Shalla, and north of Langano. Several thermal springs and fumaroles are noted in these localities.

3. ROLE OF THE RESERVOIR

The role of the reservoir has been firstly examined by comparing fluoride contents and the geological nature of the reservoir. On the escarpment sides of the rift, fluoride contents reach no more than 3 mg/l with a gradient downward; most of the cold springs found in the highlands have a fluoride content less than 0.6 mg/l compared to 2.6 mg/l in the lowlands (Buko spring near the Children's Village). Some thermal waters can reach 7 mg/l.

In the groundwater of the lacustrine sediments the amount of fluoride is 5 to 10 times greater than that of the ignimbrites and they generally present a larger range of values. Thus, there is evidence of thermal contribution and hydrological influence due to the proximity of the lakes. As a consequence, in order to determine the specific role of the lacustrine sediments three series of leaching experiments have been carried out.

In order to estimate the fluoride content in the solution when it reaches equilibrium with the sediment, samples have been submerged in distilled water in polyethylene bottles.

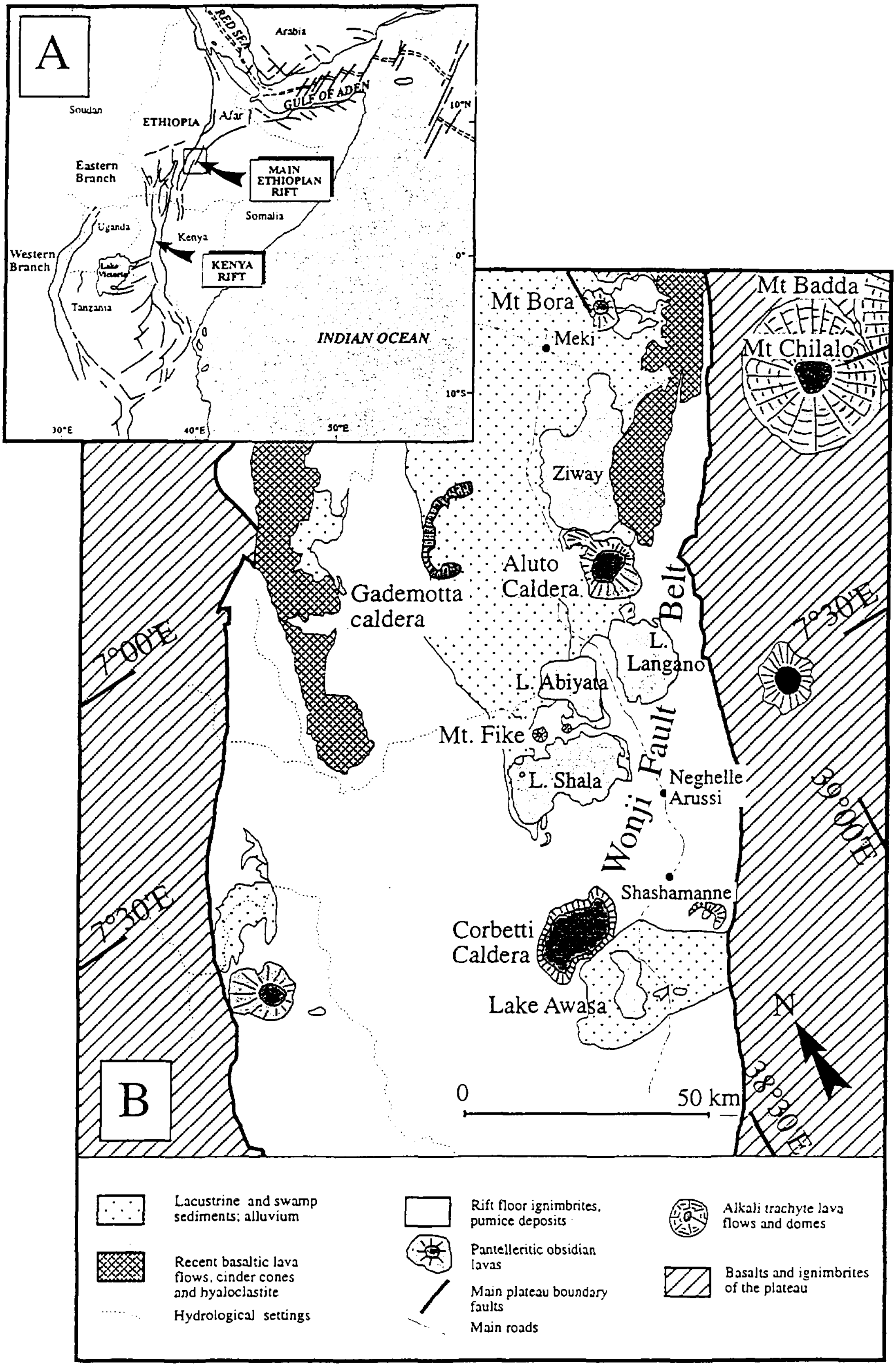

Fig. 1. Location map.

Two kinds of evolution have been reported (Fig 2). The samples which stabilize rapidly for contents of less than 10 mg/l and the others which stabilise for values near 20 mg/l or attain very high values. The results obtained can be related to the geographic position, vertical or lateral, with respect to the lakes.

The influence of CO_2 on the dissolution and equilibrium of $CaCO_3$ and CaF_2 has been studied by comparing the results of the same samples when the bottles are closed or open.

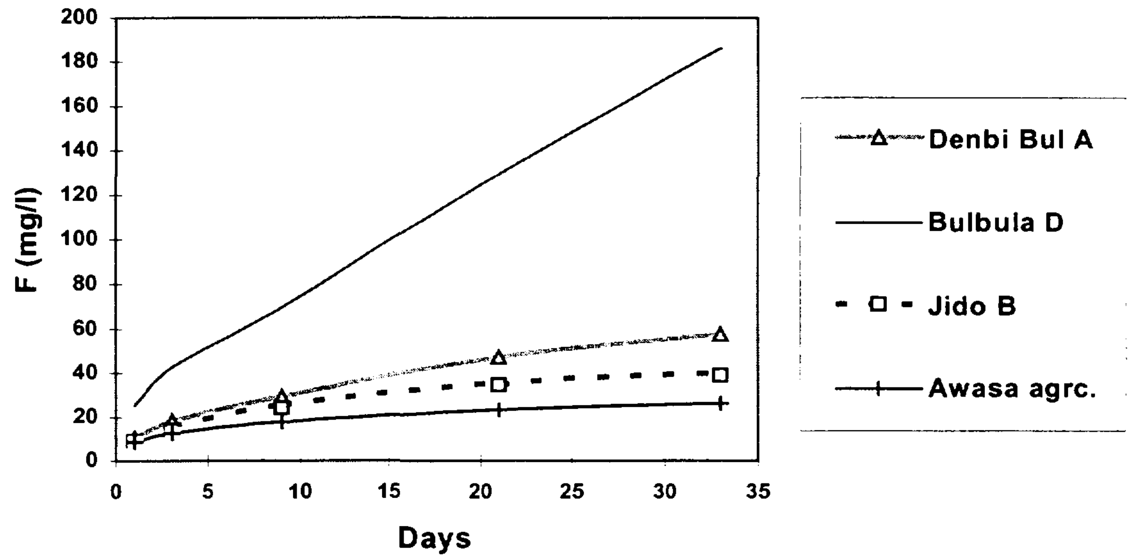

Fig 2. Results of leaching experiments

These experiments have shown the following results:

- rapid dissolution of the fluoride is generally observed in all samples showing probably the presence of free F^- adsorbed to clays;
- for some samples the level of stabilisation is not reached or not reached quickly, which indicates that the control of CaF_2 is noted in certain cases and not in others.
- in some cases, the presence of CO_2 can strongly increase the fluoride content;
- the geographic distribution of these sediments mineralised in fluoride in the zone around the lakes, if examined with a good knowledge of the chemical evolution of the surface waters of the rift, indicate that the fluoride can be used as a paleohydrologic tracer.

4. HYDROCHEMICAL CONTROL ON FLUORIDE

All hydrochemical data of the present and past studies have been plotted on a Piper diagram (Fig. 3). The waters of the region evolve from a calcium bicarbonate type on the highlands to sodium bicarbonate type towards the lakes, and finally to a mixture of bicarbonate, sulphate and chloride type around the lakes, related to thermal features.

All the data have been treated in the computer software AQUA (Valles *et al.*, 1996) in terms of geostatistics, statistics and chemical equilibrium. Concentration diagrams show that sodium, alkalinity and fluoride are relatively conservative and can be used as tracers. The successive precipitation of calcite, magnesium silicate, amorphous silica and sometimes fluoride seems to be suggested.

The waters of the area are generally saturated with calcite. When equilibrium is attained, the ratio of the activity of Ca^{2+} and CO_3^{2-} evolves in the branch CO_3^{--} > Ca, confirming the law of the alkalinity residual. The equilibrium with fluorite is often attained for medium or very concentrated waters (Fig 4).The solutions evolve in the branch F^- > Ca^{2+} which conforms to the generalised law of the alkalinity residual applied to the precipitation of calcite and fluorite (Ribolzi *et al.*, 1996). The decrease in the activity of calcium slows the evolution towards equilibrium with fluorite.

For the most concentrated waters (in lakes) the equilibrium of the sodium fluoride shows moderate under saturation. Therefore, it is possible that at the time of the process of a localised drying up of the sediments this mineral can form and store the fluoride in a form which is rapidly soluble.

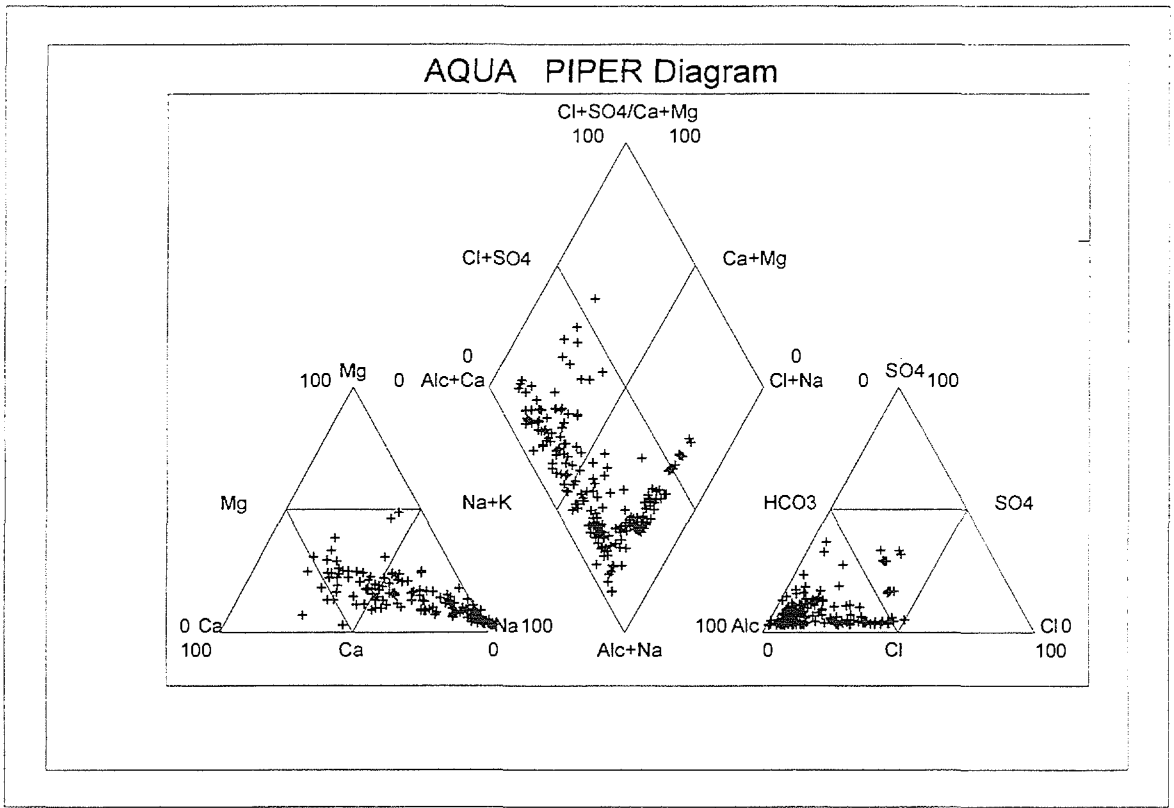

Fig 3. Piper diagram - Chemical characteristics of the natural waters of the area

The influence of the different origins of the waters, superficial groundwater or thermal waters, were able to be observed. Primarily, the acquisition of high fluoride contents and the alkaline-sodic characteristics depend on the non equilibrium initial stage between the alkalinity and the calcium as a result of weathering and dissolution of the volcanic rocks. When the waters concentrate, the precipitation of calcite leads to a decrease in the chemical activity of calcium, which leads to a strong solubility of fluoride; in surface waters the small amount of calcium which remains in solution does not allow direct control of the calcium on the concentration of fluoride. So, by the effect of climate (evaporation), this element concentrates without being significantly affected by the precipitation of fluorite. The fluoride content of thermal waters increases with the temperature up to 100°C. This is related to the fact that the solubility of calcium carbonate decreases without increasing the temperature and at the same time the solubility of fluorite is increasing (Chernet et al., 1997).

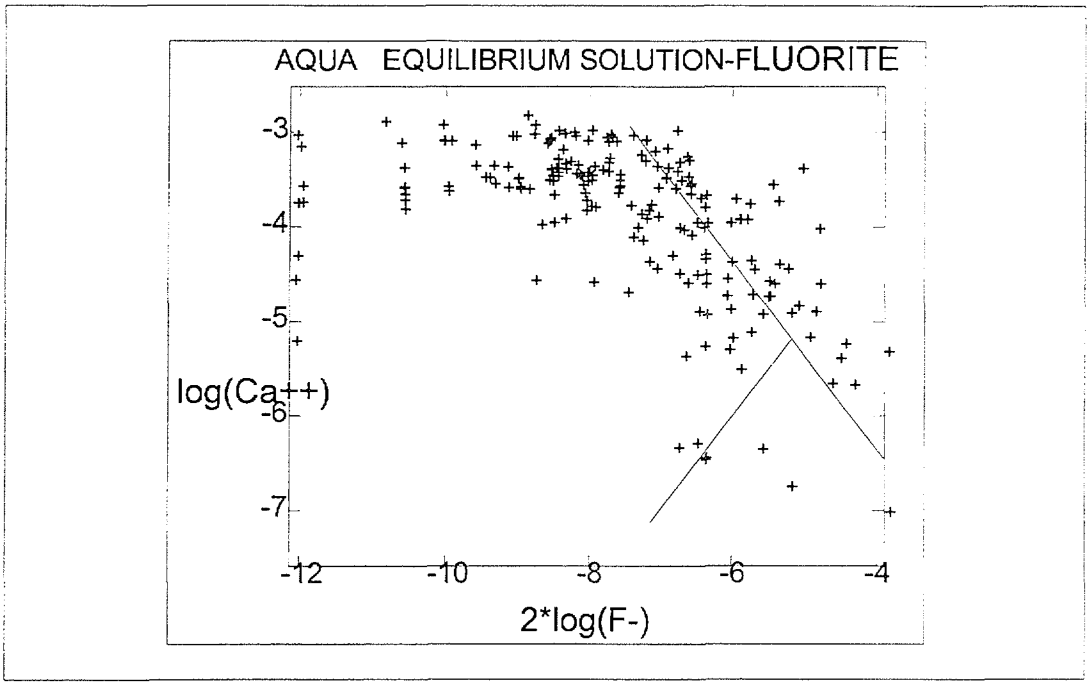

Fig 4 . Equilibrium solution diagram of fluorite concerning the natural waters of the area

5. HYDROLOGICAL EVOLUTION

Hydrometeorologic data from several stations were processed to understand the hydrologic characteristics of the area and to calculate the water balances of the lakes.

Isotope investigations of ^{18}O, ^{2}H, ^{13}C, and ^{14}C were carried out on the rain waters, surface waters, and groundwaters. The input signals were made precise (Fig 5), using the data from Addis Ababa (IAEA network). The rain signals were taken based on 5 stations in the region and Addis Ababa during the main rainy months of June - September of the years 1993-95, and with the surface waters coming from the highlands.

The non-evaporated samples generally lie on a line with deuterium excess of about 15 per mil. The samples coming from the rift show the same distribution as for Addis Ababa, with the same clear difference between the main rainy season and the other seasons which are dry. The global weighted mean is -2.9 $\delta^{18}O$. The weighted mean for the rainy season over the region is 0.30 $\delta^{18}O$.

Waters of rivers coming from the sides of the rift are homogenous (between -1.5 and -2.4‰) and they represent the average values of the rains. Thus the stable isotopes appear to be very useful tracer to study the present and ancient hydrological processes and particularly evaporated surface waters and groundwater interrelations in the low parts of the rift. Some negative values indicate the presence of an altitude effect on the waters of the highlands. Some of these waters can reach directly via the groundwater to the plain (for example north east of the Ziway lake).

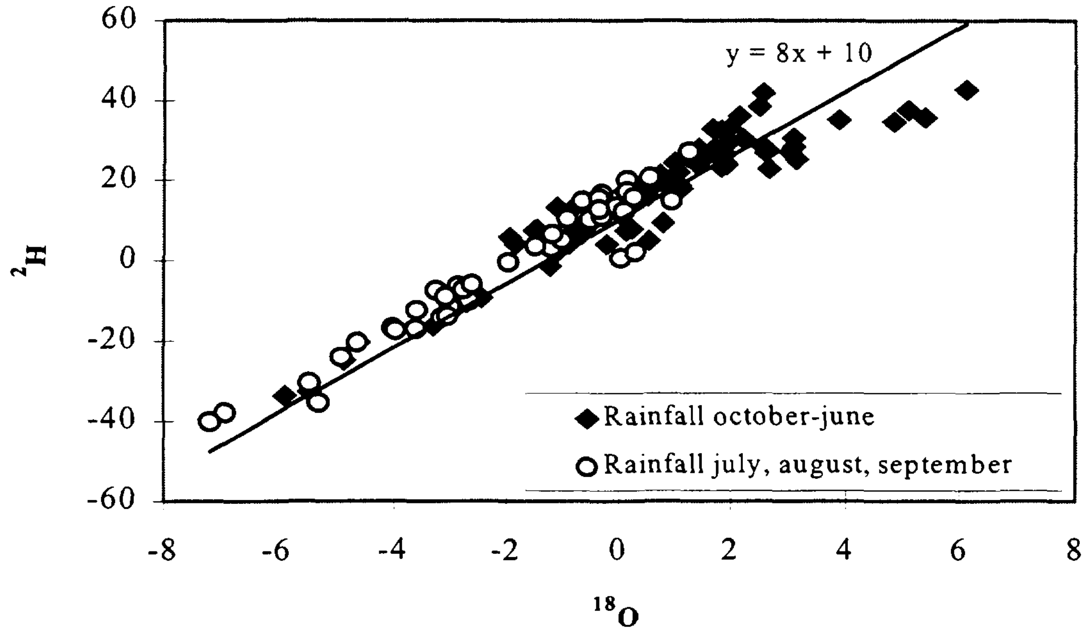

Fig 5 . Relation between ^{18}O and ^{2}H of the rainfall in Addis Ababa and the Lakes Region 94, 95), data for Addis Ababa taken from IAEA, Environmental Isotope Data (61-89)

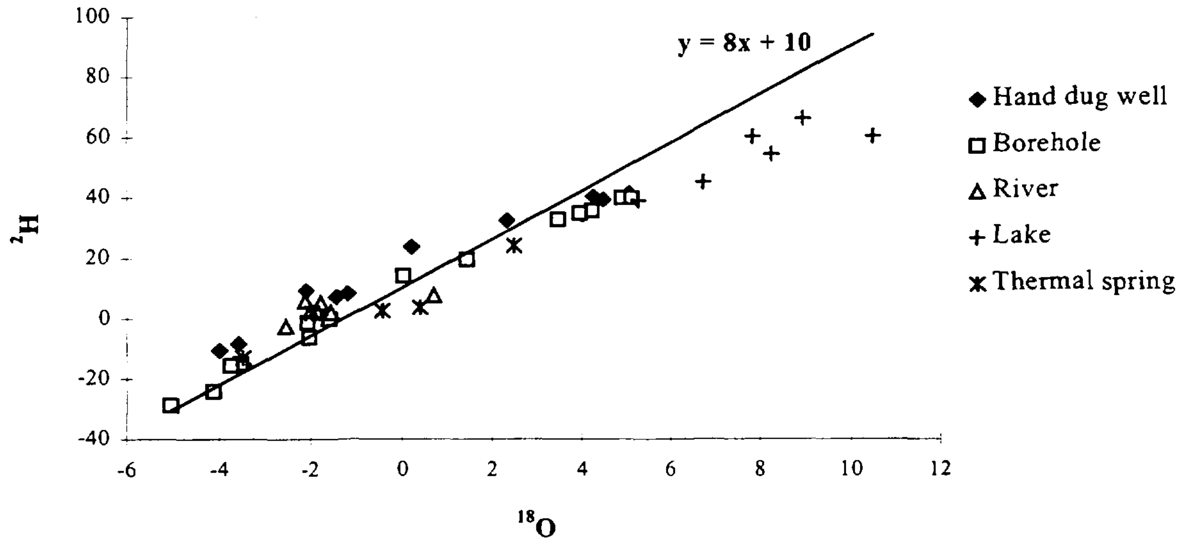

Fig. 6: Relation between 18-O and 2-H in the surface waters and ground waters.

The natural waters of the region can be characterised in a ^{2}H-^{18}O graph (Fig 6). Two categories can be identified: the waters near the input signal and the waters more or less evaporated. The groundwaters show three types of values: the waters near the input signal, waters which have been evaporated, and some samples which are more depleted. Being localised near the west side, they probably characterise local fossil groundwaters. The evaporated waters are located around the lakes, in particular between Ziway and Abiyata (Fig 7), showing clearly the presence of the exchange of water between the lakes and groundwaters (recharge and discharge).

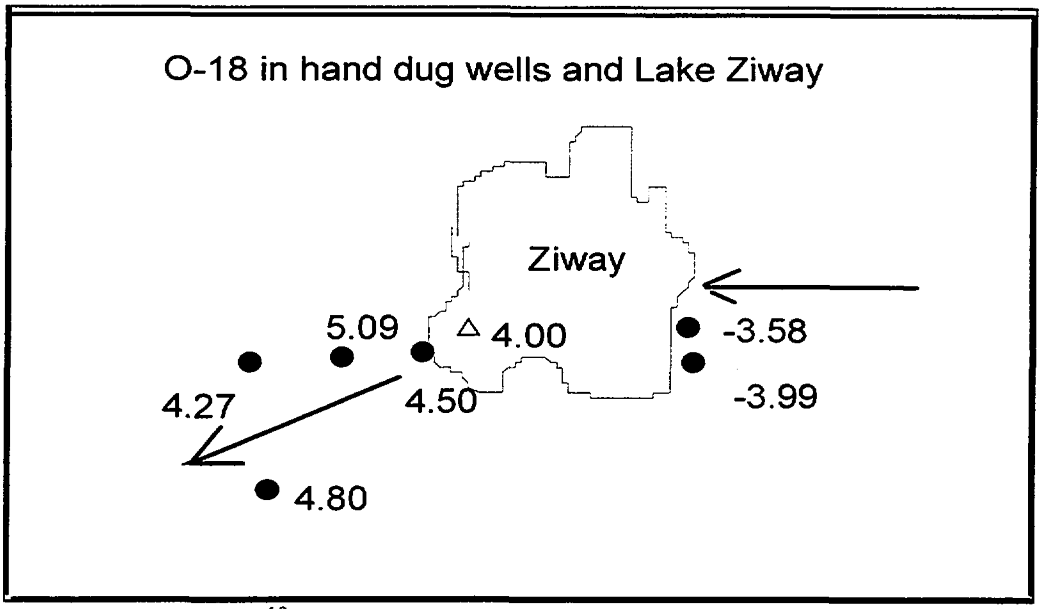

Fig 7. Utilisation of ^{18}O in the estimation of the direction of movement of the ground waters around Lake Ziway

Tritium contents were determined on water in 5 boreholes located in the central part of the plain; very low values are observed (0.8 to 1.7 TU), showing the absence of present day groundwaters, which is in agreement with the low piezometric fluctuations and the large depth of the groundwater.

Table 1 : ^{14}C, ^{13}C, et ^{18}O data for borehole waters

Borehole Site	A% DE 14-C	Estimated Age (years)	$\partial^{13}C$
Arsi Negelle	**89.4 ± 1.1**	**895 ± 95**	**-11.95**
Abiyata usine	**62.2 ± 0.5**	**3810 ± 70**	**-2.54**
Ziway B Mola	**90.0 ± 1.2**	**840 ± 110**	**-1.21**
Langano B Mola	**40.8 ± 0.6**		**-3.60**
Meki	**86.9 ± 0.5**	**1130 ± 50**	**-10.30**
Bulbula	**77.7 ± 0.7**	**2030**	**-3.53**
Source Shalla	**33.5 ± 1.4**		**-2.45**

Some ^{14}C and ^{13}C were measured on total dissolved inorganic carbon (Table 1). Arsi Negelle, Koshe and Meki boreholes, located at the limit of the plain, outside the influence of lake water show isotopic composition between -8‰ and -11,95‰. Taking into account the isotopic fractionation between CO_2 and bicarbonate ion, this corresponds to a CO_2 of C_4 type as it has been measured in soil gases of the region (-14 to -15‰) (Travi *et al.*, 1997). Enriched values (Table 1) represent mixing with evaporated lake waters and in two cases the additional influence of deep CO_2 (Shalla springs and Bekele Mola borehole). In these two last zones, near active faults, ^{13}C values around -1‰ have been measured in soil CO_2 .

The lakes being in equilibrium with the atmosphere, and in the absence of carbonate in the aquifers, the measurements between Ziway lake and Abiyata lake do not necessitate age corrections and the ages of these groundwaters fall between 800 and 3000 years. The high contents of fluoride are found in the same zone and are therefore largely dependent on present and ancient infiltration of lake waters.

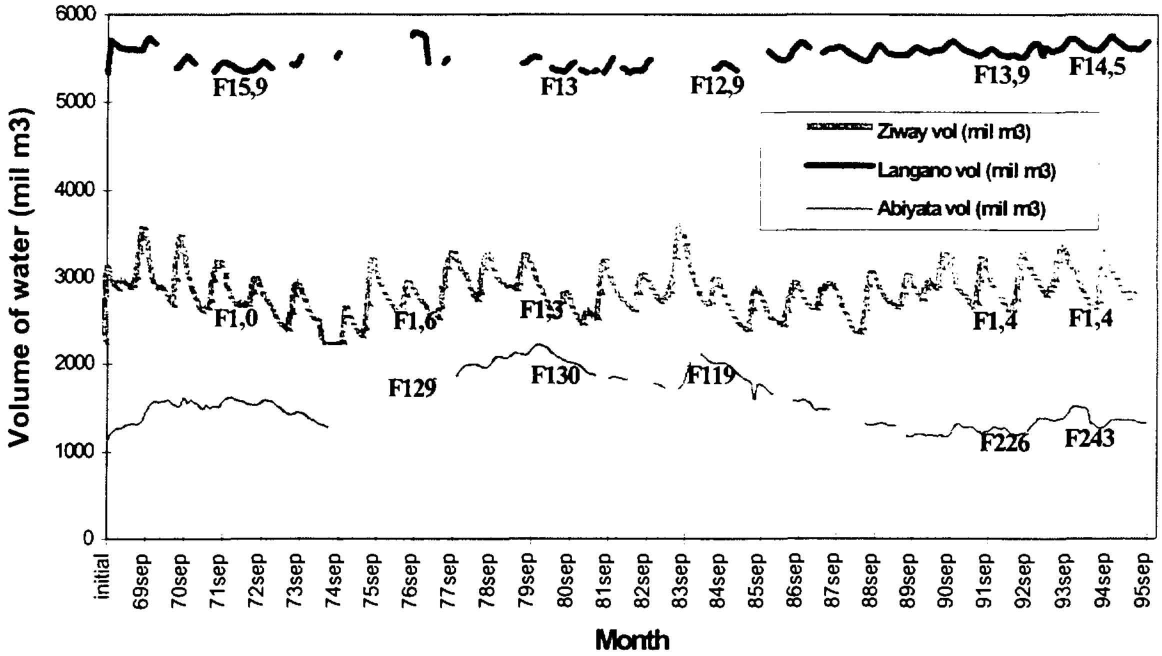

Fig 8 . Variation in volume of water of the lakes during the years 1969-1995 (F129 = Fluoride in mg/l)

A study of the variation in the volume of the lakes in the last 30 years has been carried out (Fig 8). It shows a considerable change in volume of water of Lake Abiyata which became recently closed. This has also resulted in a change in the content of fluoride. In open lakes, low or medium values are observed ; they are directly related to the hydrological balance of the lake (input output, reserve and evaporation volume). The simulated evolution of the chemical characteristics during the process of concentration of waters by evaporation (AQUA model) shows a good agreement with measured data, except in the thermal influence zone. As a result of the specific evolution of alkaline waters (discussed in section 4), the fluoride ion evolves like a conservative tracer with the evaporation and dilution process. Thus, it can be estimated using the hydrological balance.

6. CONCLUSIONS

In the Lakes Region, the origin and the evolution of fluoride content depends on, (i) the nature of the reservoir, essentially ignimbrites and lacustrine sediments, (ii) the hydrochemical processes ; fluorite equilibrium maintains low or medium values in groundwaters or open lakes. In thermal waters, temperature and deep CO_2 allow high values despite a fluorite control. In surface waters evaporation allows very high values, (iii) hydrological features which can change the content by mixing surface and groundwaters and modifying the volume of the lakes.

The main factors implied in the concentration of fluoride can be summarised as in the following table:

Table 2 Factors affecting the concentration of fluoride

ORIGIN	
• **Volcanic rocks** →	**Low levels** (0 - 3 mg/l)
• **Lacustrine sediments** →	**Low or high levels** (5 - 30 mg/l)
HYDROCHEMICAL CONTROL	
(fluorite equilibrium control, alkalinity residual of calcite-fluorite)	
Groundwater and open lakes →	**Medium values**
TWO PROCESSES FOR HIGH FLUORIDE CONTENT	
• **Temperature & CO_2** →	**With fluorite control, thermal springs**
• **Evaporation** →	**Without fluorite control, closed lakes**
HYDROLOGICAL EVOLUTION	
• **Mixing of water, lake and groundwater**	
• **Hydrological balance**	

The leaching experiments indicate that in lacustrine sediments the fluoride content could be used as a paleo-tracer. Furthermore, in relatively concentrated water, the fluoride ion is found to be conservative and it can be used for hydrological tracing.

BIBLIOGRAPHY

Chernet, T. - 1998 - Etude des mécanismes de minéralisation en fluorure et éléments associés de la région du rift éthiopien. Thèse de Doctorat, Université d'Avignon, 210 p.

Chernet, T., and Travi, Y., 1993. Preliminary observations concerning the genesis of high fluoride contents in the Ethiopian rift. Geoscientific Research in Northern Africa. Thonweihe & Schandelmeier (eds), Balkema, Rotterdam, pp 651-655.

Chernet, T. and Travi, Y. - 1995 - Evolution de la contamination fluorurée dans la zone des lacs du rift éthiopien. Approches chimique et isotopique. Isotopes in water ressources management. Proceedings of an IAEA symposium, pp. 457-460.

Chernet, T., Travi, Y. and Gibert, E. - 1997 - The occurrence and hydrogeochemistry of fluoride in natural waters in the Ethiopian rift. International symposium on flood basaltes, rifting and palaeoclimates in the Ethiopian rift and Afar depression, Addis Ababa, February 3 to 14th, 1997, p. 36.

Ribolzi ,O., Valles, V. and ., Bariac, T. - 1996 - Comparison of hydrograph deconvolution using residual alkalinity, chloride and oxygen 18 as hydrochemical tracers. Water Res. Res., 32, 4, pp 1051-1059

Travi, Y., 1993. Hydrogéologie et hydrochimie des aquifères du Sénégal. Hydrogéochimie du fluor dans les eaux souterraines. *Mém. Sci. Géol.* Strasbourg, 155p.

Travi, Y., Gibert E., Chernet T. 1997. Reconstitutions paléohydrologiques dans la zone des lacs du rift éthiopien en liaison avec les teneurs isotopiques de la matière organique. *Isotope techniques in the study of past and current environmental changes in the hydrosphere and the atmosphere*, Proceedings of an IAEA symposium, Vienne, avril 1997..

Valles, V. Ribolzi, O.,de Cockborne, A.M., Cornieles,M. - 1996 - Présentation de AQUA, logiciel de géochimie appliqué aux problèmes environnementaux. GRESSAP, 10 Septembre 1996, ORSTOM, Montpellier.