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MECHANISM OF DEGRADATION OF THE QUALITY OF NATURAL WATER IN THE LAKES REGION OF THE ETHIOPIAN RIFT VALLEY

TESFAYE CHERNET[1†], YVES TRAVI[1]* and VINCENT VALLES[2‡]

[1]Lab. Hydrogéologie, Université d'Avignon, 33 rue Louis Pasteur, F 84000 Avignon, France and
[2]Laboratoire Chimie et Environnement, Casc 29, Université de Provence (Aix-Marseille I),
3 place Victor Hugo, 13331 Marseille Cedex 3, France

Abstract—The natural waters of the Lakes Region in the Main Ethiopian Rift (MER) show serious problems of chemical quality. The high content of fluoride reaches $300 \, mg \, l^{-1}$ and affects the health of the population who live in this area. Furthermore, the alkaline and sodic characteristics ($8 < pH < 10$ and $0.9 \times 10^{-4} < Na < 0.35 \, M \, l^{-1}$) of these waters destroy the soil for agricultural use. This geochemical study is conducted using analytical data issued from literature (UNDP, 1973; Chernet, 1982) and several field sampling and laboratory analyses completed during the last 4 yr. Chemical analyses of 320 samples taken throughout the region have been analysed using the computer software AQUA for geostatistic, statistic, chemical equilibria and simulation of evaporative concentration process. The results show that the waters issuing from volcanic rocks are characterised by a positive alkalinity residual of calcite. When they concentrate due to the effect of climate, the precipitation of calcite causes a decrease in the chemical activity of calcium. This results in an increase in solubility of fluoride, previously controlled by equilibrium with CaF_2, and the element concentrates without being significantly affected by the precipitation of fluorite. As water concentrates, the low concentration of dissolved calcium emphasises the alkaline characteristics. As a consequence, the pH reaches very high values (9–10) which make the waters unsuitable for agriculture. The adverse elements, namely fluoride, sodium, and alkalinity accumulate in the lower zones of the basins. The acquisition of high fluoride content and the alkaline-sodic characteristics depends primarily on the unbalanced initial stage between the carbonate alkalinity and calcium $[(HCO_3) > 2(Ca + Mg)]$, which results from the weathering and dissolution of the volcanic rocks. The predictive qualities of the model AQUA were tested in the context of this region. A simulation of the concentration of the waters by evaporation has shown chemical variations relatively similar to those obtained with field data which include the minor chemical elements such as the fluoride or the dissolved silica. For field data, enrichment is more variable and may represent localised conditions of mineralization. This model is then used to study a method of defluoridation by supplying these waters with calcium in the form of gypsum. This method also allows the reduction of the alkalinizing and sodifying characteristics of the waters without reaching the fluoride standard concentration accepted for drinking waters. For drinking purpose, waters of the Ethiopian rift should undergo another method of defluoridation. © 2001 Elsevier Science Ltd. All rights reserved

Résumé—Les eaux de la région centrale du rift éthiopien posent de sérieux problèmes de qualité chimique. Les fortes teneurs en fluorures atteignent $300 \, mg \, l^{-1}$ et affectent la santé des populations vivant sur ce territoire. Par ailleurs, le caractère alcalin et sodique des eaux ($8 < pH < 10$) provoque une détérioration des propriétés physiques des sols irrigués pouvant aller jusqu'à leur stérilisation. L'étude géochimique a été conduite à partir de données analytiques issues de la littérature mais aussi de plusieurs campagnes de prélèvement réalisées dans le cadre de ce travail. Les analyses chimiques de 320 échantillons d'eau prélevés sur toute la zone ont été traitées avec le logiciel AQUA en termes de géostatistique, statistique, étude des équilibres chimiques et simulation de concentration sous l'effet de l'évaporation. Les résultats montrent que les eaux, issues de l'altération de roches essentiellement éruptives, sont caractérisées par une alcalinité résiduelle calcite positive. Lors de leur concentration sous l'effet du climat, la précipitation de la calcite conduit à une diminution de l'activité chimique du calcium, ce qui induit une forte solubilité du fluorure préalablement contrôlé par l'équilibre avec CaF_2. Cet élément se concentre sans être significativement affecté par la précipitation de fluorine. Lors de leur concentration, le caractère alcalin des eaux s'affirme du fait de la faible teneur en calcium dissous. Le pH atteint alors des valeurs élevées (9 à 10) incompatibles avec un usage agricole. Les éléments néfastes, notamment le fluorure, le sodium et l'alcalinité s'accumulent dans les zones basses du paysage. C'est le déséquilibre initial entre l'alcalinité carbonatée et le calcium, résultat de l'altération des roches volcaniques, qui est responsable à la fois de l'acquisition des fortes

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*Author to whom all correspondence should be addressed. Tel.: +33-4-9014-4488; fax: +33-4-9014-4489; e-mail: yves.travi@univ-avignon.fr

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

‡E-mail: valles@up.univ-mrs.fr

teneurs en fluorures et du caractère alcalin-sodique. Les qualités prédictives du modèle AQUA ont pu être testées dans le contexte de cette région. Une simulation de la concentration des eaux par évaporation montre une évolution similaire à celle observée sur le terrain, y compris pour des espèces chimiques mineures telles que le fluorure ou la silice dissoute. Elle montre aussi l'influence de la signature initiale des eaux, superficielle ou thermale, qui se traduit par une dispersion parfois importante des points sur les graphes. Le modèle a été utilisé pour étudier la méthode de défluoruration par apport de calcium sous forme de gypse. Cet apport permet aussi de réduire le caractère alcalinisant et sodisant des eaux, mais la teneur en fluorure reste toutefois supérieure à la norme de potabilité. Pour la potabilité de l'eau de cette région du rift éthiopien, une autre méthode de défluoruration plus performante devra impérativement être recherchée. © 2001 Elsevier Science Ltd. All rights reserved

Key words—fluoride, alcalinisation, ethiopia, rift, hydrochemical modelling, gypsum treatment

INTRODUCTION

In the rift valley of East Africa, some lakes are known to show very high concentrations of fluoride which can reach $7.9 \, mM \, l^{-1}$ in the Natron lake (Gueddari, 1984) and $36.8 \, mM \, l^{-1}$ in the Magadi lake in Kenya (Jones *et al.*, 1977). In comparison, the average concentration in the ocean lies between 1.6×10^{-3} and $7.1 \times 10^{-2} \, mM \, l^{-1}$ (Gaciri and Davies, 1993), and in continental waters is generally lower than $0.53 \, mM \, l^{-1}$ (Travi, 1993).

In Ethiopia, the lakes Abiyata and Shalla, located on the rift floor, have fluoride concentrations which can reach more than $15.8 \, mM \, l^{-1}$. Such high natural concentrations of fluoride in this region of the African continent is exceptional, and so, the chemical processes involved are of great interest (Chernet and Travi, 1993). The high concentration of fluoride affects the health of the population and the cattle which use the waters for drinking.

As a result of intense evaporation, the region is semi-arid and high salinity occurs in the plain of closed basins. The salts accumulate making the waters unusable for irrigation. Agriculture is important in the rift valley and the adverse physico-chemical properties of the waters are a problem for development.

The aim of this work is to characterise the dynamics of the dissolved elements in the waters and soils of this region. In order to improve understanding of the mechanism of soil water degradation as well as the high fluoride content in drinking waters, fluoride and alkalinity formed the basis of this study. This effort of identifying the geochemical mechanism and its thermodynamic representation constitutes a required prerequisite to determine a solution to control and improve the water and soil quality. The validity of the thermodynamic model of AQUA (Valles and de Cockborne, 1992) will be tested for this purpose and used in an attempt to simulate the possible improvement of the water quality, by adding gypsum. We demonstrate, by modelling, that this method often suggested for defluoridation (Appelo and Postma, 1996), could reduce alkalinity significantly and sodium concentrations but the fluoride concentration remains higher than the standard value for drinking water.

MATERIALS AND METHODS

Theoretical base of the thermodynamic model

The activity of ions in a solution and mineral equilibria are usually calculated using two types of models:

- ion interaction models, which take into account a large number of interactions, from short range to long range, and thus provide accurate estimates of ion activities under strong ionic strengths (five and above). These models require many fitting parameters (Pitzer, 1973, 1975), which are not always available for the type of solution being studied;
- ion pair models, which have the advantage of requiring no other fitting parameters than the stability constants of the complexes are considered. These models are usually built around a Debye–Hückel extension for saline solutions. Indeed the Debye–Hückel law itself deals only with (long-range) electrostatic interactions and gives poor results when applied to brines. Various extensions of it have been suggested. The Scatchard extension (Scatchard, 1968; Scachard *et al.*, 1970) is among the most commonly used. Such an extension was used for calculation with the model called AQUA (Valles and de Cockborne, 1992; Valles *et al.*, 1996). It works well for electrolyte solutions with ionic strengths up to one which is the upper value occurring in the Main Ethiopian Rift (MER). The speciation and mineral equilibria calculations as well as evaporation process modelling, performed by AQUA present the following specifications:

- the program uses continuous fraction iteration and stops when the relative variation is less than 0.1% (δ activity/activity $< 10^{-3}$);
- the files are documented for 90 dissolved species (62 ionic and 28 neutral). Twenty-six relevant mineral thermodynamic data were used in this study for evaluating saturation states ($\log Q/K < 10^{-3}$ for minerals allowed to be dissolved or precipitated). Elements and species can be easily added to these files.

This model was tested for diverse geochemical contexts, the neutral saline soil in Tunisia and Algeria (Valles *et al.*, 1997), the alkaline soils of Sahalian Africa (Barberio, 1994; Barberio *et al.*, 1995; Dosso, 1980; Marlet, 1996; Valles *et al.*, 1989), but not for the minor elements such as the fluoride under the Ethiopian conditions. The model will then be validated for the dynamics of fluoride in the carbonate waters of the Ethiopian rift.

The concept of generalised residual alkalinity

Alkalinity can be defined as the capacity of a solution to neutralise acids. It is the sum of the products of the alkaline compound concentrations by the number of protons each can neutralise, minus the proton concentration (Stumm and

Morgan, 1981; Morel, 1983; Drever, 1988). The alkalinity is mainly due to carbonate species in most soil waters when the proton and hydroxide ion concentrations and non-carbonate alkalinity are negligible.

The residual alkalinity (Beek and Breemen, 1973) which is derived from the residual carbonate concept (Eaton, 1950) is calculated by subtracting the total concentration of divalent cations from the carbonate alkalinity (alk.$_{residual}$ = Alk.$_c$ − 2[Ca^{2+}] − 2[Mg^{2+}]). This concept was later generalised to successive precipitations of several minerals containing calcium or carbonate such as calcite followed by gypsum, Alk.$_{residual}$ = alk.$_c$ − 2[Ca^{2+}] + 2[SO$_4^{2-}$], (Droubi, 1976; Valles et $al.$, 1989), or calcite followed by fluorite, Alk.$_{residual}$ = Alk$_c$ − 2[Ca^{2+}] + [F$^-$] (Barbeiro, 1994). More recently, Ribolzi et $al.$ (1996) have shown that, in the case of carbonate precipitation, the generalised residual alkalinity increases proportionally to the reduction of the solution volume as a conservative tracer.

Two cases may arise when evaporation concentrates a solution in equilibrium with atmospheric pCO$_2$ and calcite at given T and P. If the calcium equivalent is higher than the carbonate alkalinity (alk. residual calcite < 0), then calcite precipitation is limited by alkalinity and due to excess calcium, this element increases during the evaporation process while pH drops. If the calcium equivalent is less than carbonate alkalinity (alk. residual calcite > 0) then molalities change in the opposite direction. After each mineral precipitation the rate of concentration of the elements concerned changes. Residual alkalinity is generally used for understanding the changes affecting the chemical facies of natural solutions undergoing evaporation (Beek and Breemen, 1973; Droubi, 1976). For example, if gypsum saturation is reached when SO$_4$ + alk. > Ca (alk. residual calcite + gypsum > 0), related gypsum precipitation must be limited by Ca content; the latter then begins to decrease as alkalinity and sulphate content increase.

Presentation of the study zone

The study area is located between 135 and 270 km south from Addis Ababa in the rift and includes three closed basins which, from north to south, are the Ziway-Abiyata basin, the Shalla basin, and the Awasa basin (Fig. 1).

In this region, called the Lakes Region, mean annual precipitation ranges from 700 mm on the lowlands to 1000 mm on the highlands. The potential evapotranspiration is about 2500 mm in the lowlands and 1000 mm in the highlands. Within these closed basins the mineralization of the surface waters is considered to be greatly influenced by the high evaporation rate.

The rift valley runs north–south in the area and is rimmed by large fault escarpments. Most of the region is covered by volcanic rocks. These rocks mainly consist of ignimbrites (58%), basalts and rhyolites (14%). On the rift floor, lacustrine sediments derived from the rift escarpments are found around the lakes; in these sediments groundwaters generally present a high fluoride content.

Recent faulting of the Wonji Belt runs in the middle of the area and along this belt stand acidic volcanic complexes such as the Aluto and Corbetti which consist of alkaline and peralkaline rocks. As a consequence of the recent volcano-tectonic activity, geothermal features are well represented in the Ziway-Shalla basins. Hydrothermal activity is present on the western side of the MER and along the shores of the lakes. Thus, the chemical composition of groundwaters is strongly influenced by volcanic rock types and to some extent geothermal effects.

Sampling and analyses

This study relies on a large amount of data taken from literature (UNDP, 1973; Craig et $al.$, 1977; Chernet, 1982) and also on new data carried out during the present work. Two major field trips were conducted in 1994 and 1995 and many water samples were collected and analysed for the parameters: K, Na, Ca, Mg, Cl, SO$_4$, F, H$_4$SiO$_4$, B, and Br. Field measurements of temperature, conductivity, pH, and alkalinity (titration with a precision of 8%) were recorded at each sampling location. For major and trace element analysis, 0.45 µm filtered water samples were collected, acidified with nitric acid for cations and unacidified for anions. Major cations were analysed by atomic absorption spectrometry and most anions by ionic chromatography
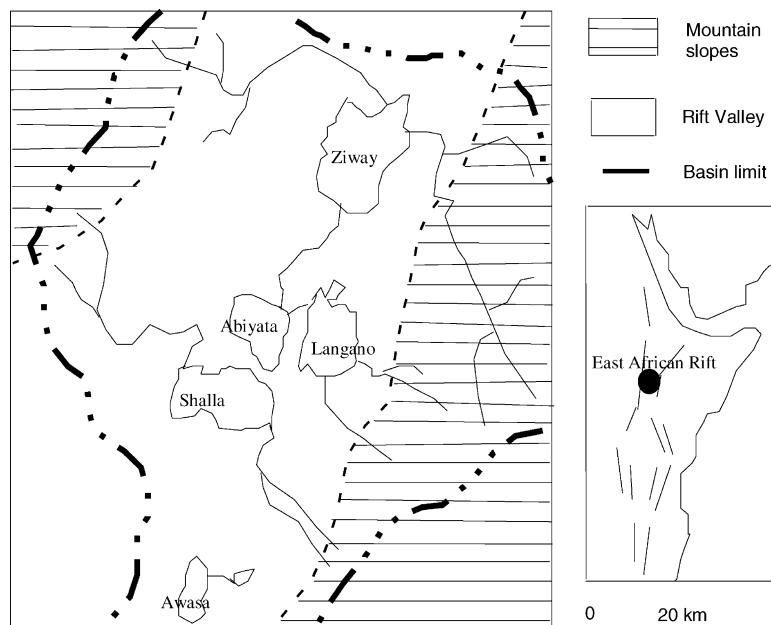

Fig. 1. Location map of the hydrographic system.

with an analytical precision better than 3%. Data taken from literature were evaluated using ionic balance. F^- contents were measured using a sensitive electrode with an analytical precision of 5% and H_4SiO_4 contents by colorimetry with a precision of 5%.

Finally, more than 200 samples were collected from the different hydrogeological units. The location of wells and boreholes sampled is shown in Fig. 2 (Chernet, 1998).

RESULTS

The fluoride content: average and extreme values, comparison with health norms

The data base consists of 320 water analyses which are fairly distributed within the study area. The average concentration of fluoride is $0.928 \times 10^{-3} M l^{-1}$, or $18 mg l^{-1}$ of F (Table 1), which is about ten times greater than the potability standard recommended by the WHO, EEC, or French legislation (Mazounie and Mouchet, 1984). The maximum value, reaching $15.8 \times 10^{-3} M l^{-1}$, is about $300 mg l^{-1}$, in the lower zones of the basins, which means in the terminal lakes (Abiyata and

Shalla). These high values cause health problems to the population exposed who suffer from bone and dental fluorosis (Chernet, 1982). The high standard deviation ($2.21 \times 10^{-3} M l^{-1}$) (Table 2) gives evidence of a strong dispersion and it becomes important to find out if it is related to a spatial variation, or if it can also be related to some geochemical mechanisms.

Statistical approach on the geochemical nature of fluoride

Since most waters are dominated by HCO_3, Cl, Na and K, the electroneutrality is approximately $[Na^+]+[K^+]-[Cl^-]=[HCO_3^-]$. Therefore, there is an evident linear relation between this solutes. As expected, the Principal Componant Analysis carried out, based on the matrix of correlation (Fig. 3; Table 2), shows a clear opposition between two groups of parameters (first factorial plan which represents 59% of variance).

The fluoride values are poorly correlated with Ca and Mg, and to some extent, with an intermediate
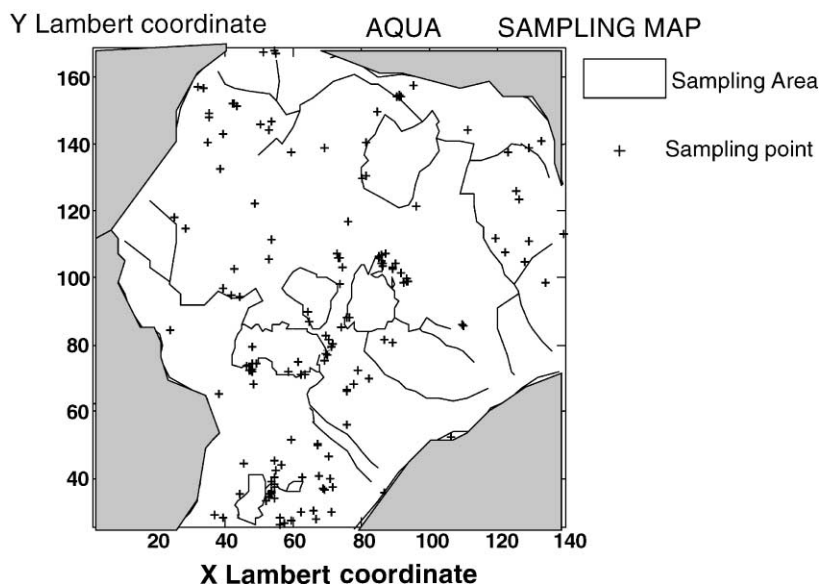

Fig. 2. Location of new sampling points.

Table 1. Averages and variations of different measured chemical parameters (concentrations expressed as M)

Variable	Moyenne	Minimum	Maximum	Std. Deviat.
Alk.Car.	1.88E−02	1.00E−05	4.46E−01	4.74E−02
H	2.29E−08	6.31E−11	3.98E−07	3.80E−08
K	9.91E−04	1.00E−06	2.41E−02	2.47E−03
Na	2.67E−02	9.00E−05	5.87E101	6.98E−02
Ca	3.99E−04	1.00E−06	2.22E−03	3.93E−04
Mg	2.65E−04	1.00E−06	2.30E−03	3.44E−04
Cl	6.82E−03	1.00E−06	1.60E−01	1.99E−02
SO4	4.46E−04	1.00E−06	4.51E−03	8.53E−04
Si	1.44E−03	1.00E−05	5.53E−03	7.88E−04
F	9.28E−04	1.00E−06	1.58E−02	2.21E−03
B	1.15E−034	1.00E−10	2.24E−03	2.81E−04
Br	5.61E−06	1.00E−06	1.44E−04	1.54E−05

Table 2. Correlation matrix for chemical parameters

	Alk.Car.	H	K	Na	Ca	Mg	Cl	SO₄	Si	F	B	Br
Alc.Car	1.00	−0.206	0.829	0.829	−0.236	−0.103	0.888	0.197	0.289	0.863	0.681	0.157
H+	−0.206	1.00	−0.231	−0.210	0.116	0.054	−0.199	−0.142	−0.162	−0.164	−0.130	−0.119
K	0.829	−0.231	1.00	0.748	−0.299	−0.127	0.855	0.301	0.407	0.818	0.654	0.188
Na	0.829	−0.210	0.748	1.00	−0.302	−0.175	0.838	0.211	0.309	0.812	0.645	0.182
Ca	−0.236	0.116	−0.299	−0.302	1.000	0.610	−0.306	−0.211	−0.198	−0.282	−0.224	−0.188
Mg	−0.103	0.054	−0.127	−0.175	0.610	1.00	−0.194	−0.093	−0.114	−0.176	−0.147	−0.102
Cl	0.888	−0.199	0.855	0.838	−0.306	−0.194	1.00	0.259	0.326	0.908	0.766	0.304
SO₄	0.197	−0.142	0.301	0.211	−0.211	−0.093	0.259	1.00	0.438	0.207	0.279	0.151
Si	0.289	−0.162	0.407	0.309	−0.198	−0.114	0.326	0.438	1.00	0.276	0.247	0.205
F	0.863	−0.164	0.818	0.812	−0.282	−0.176	0.908	0.207	0.276	1.00	0.789	0.115
B	0.681	−0.130	0.654	0.645	−0.224	−0.147	0.766	0.279	0.247	0.789	1.00	0.232
Br	0.157	−0.119	0.188	0.182	−0.188	−0.102	0.304	0.151	0.205	0.115	0.232	1.00

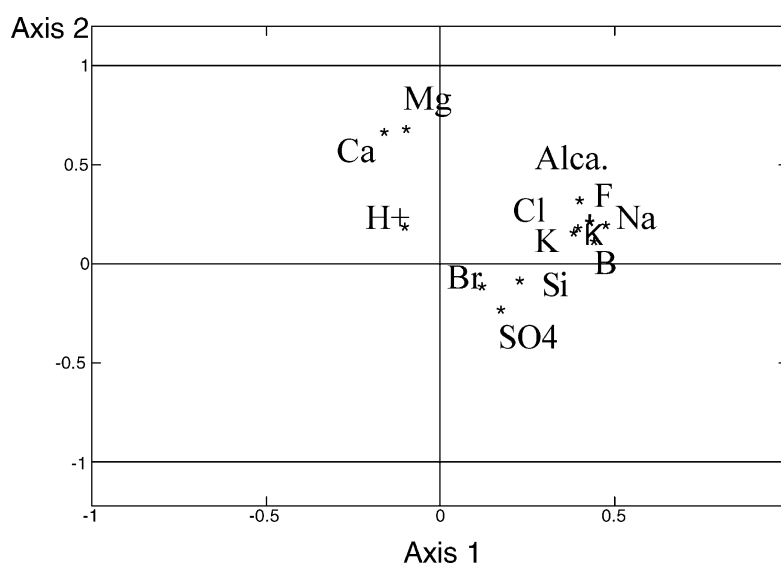Fig. 3. Principal component analyses: physico-chemical parameters in the first plan.

group including Si, Br and SO₄. On the contrary, they are strongly correlated with ionic species such as Cl, alkalinity, K and Na. As high fluoride values are usually controlled by fluorite equilibrium (Travi, 1993), this relation seems to be unusual and may characterise a specific geochemical process in this region of Ethiopia.

Furthermore, a preliminary study of TDS/chemical elements relationships carried out by Chernet (1998) showed that: (1) in most diluted waters, calcium content is increasing up to $3.7\,\mathrm{mM\,l^{-1}}$, then decreases regularly. This change could be attributed to calcite precipitation; (2) the Na enrichment seems to be rather uniform and could correspond to dilution or concentration of a unique salinity source (silicate hydrolysis); (3) chloride and sulphate mainly follows an evaporative pattern, but are locally enhanced. This evolution may reflect a distinct secondary salinity source which involves salt supplies of different origins.

Spatial distribution of the fluoride contents

On a map constructed by means of krigeage method (Chernet, 1998), fluoride shows a spatial distribution which is relatively well structured. Low contents of fluoride, less than $0.5\,\mathrm{mM\,l^{-1}}$, characterise the waters from the high elevation zones, the

escarpments and the plateaus. Around the lakes the concentrations become high; the highest values are observed in Abiyata and Shalla lakes.

The geographical distribution of fluoride looks like that of sodium and alkalinity carbonate which are unlikely to be strongly affected by mineral precipitation. In comparison, calcium and magnesium exhibit a distinct geographical grouping which is consistent with geochemical controls.

In the dilute groundwaters of the highlands, cation enrichment (Na, Ca, Mg) is variable depending on mineral variations within the reservoir and the extent of weathering.

INTERPRETATION AND DISCUSSION

The chemical facies and their characteristics

The ionic composition of the water samples induces relatively variable chemical facies; waters are Ca^{2+}, Mg^{2+}, Na^+ and HCO_3^- dominated for the diluted waters, and become Na^+ and HCO_3^- dominated with a Cl^- increase for most concentrated waters (Fig. 4). A small group of samples provides mixed facies with a sulphate enrichment. This change may be attributed to local mixing with deep thermal waters.

All the chemical facies evolve towards a greater amount of sodium and alkalinity; such a context is particularly unfavourable for the fertility of soils when the waters are used in agriculture (Cheverry, 1974; Rieu, 1978; Valles, 1987). The problems arising are the alkalinization and the sodification of the complex exchange which induce degradation of the physical properties of the soils and a lack of mineral supply to the vegetation (Marlet *et al.*, 1996).

Concentration diagram

The concentration diagrams of solute X is a graph of log[X] as a function of log concentration factor (CF). CF under natural conditions can be estimated by using a reference tracer whose properties have been checked in the context of the study (Gac, 1980; Barbeiro, 1994; Ribolzi *et al.*, 1996). Its values are then estimated as the ratio between the tracer content in sample *i* and the tracer content of the most diluted solution involved, *d*.

Taking into account preliminary data, concentration diagrams were constructed by using Na as a tracer, $CF_i = Na_i/Na_d$ with Na_i and Na_d, the respective values of sodium in the samples.

This estimation of the concentration factor assumes, as will be shown later, that the sodium value is not significantly affected by the phenomenon of precipitation, ionic exchanges or other bio-geochemical processes. The results (Fig. 7) effectively show that no chemical element has an increase in concentration greater than sodium. In this study, we did not use the halide Cl^-, generally considered to be uninfluenced by rock–water interaction (conservative behaviour) for the following reasons: (1) in the highlands, Cl^- contents are very low for a wide range of salinities and (2) in a TDS versus Cl^- diagram the Cl^- enrichment is variable and may represent distinct evolutionary pathways which involve different supplies. Significant amount of chloride is believed to originate from human influence and deep thermal waters near volcanic centres.

In the diagram (Fig. 7), the carbonate alkalinity regularly increases during the process of concentration all along, but less than the concentration factor. The slope of the alkalinity curve is less than that of
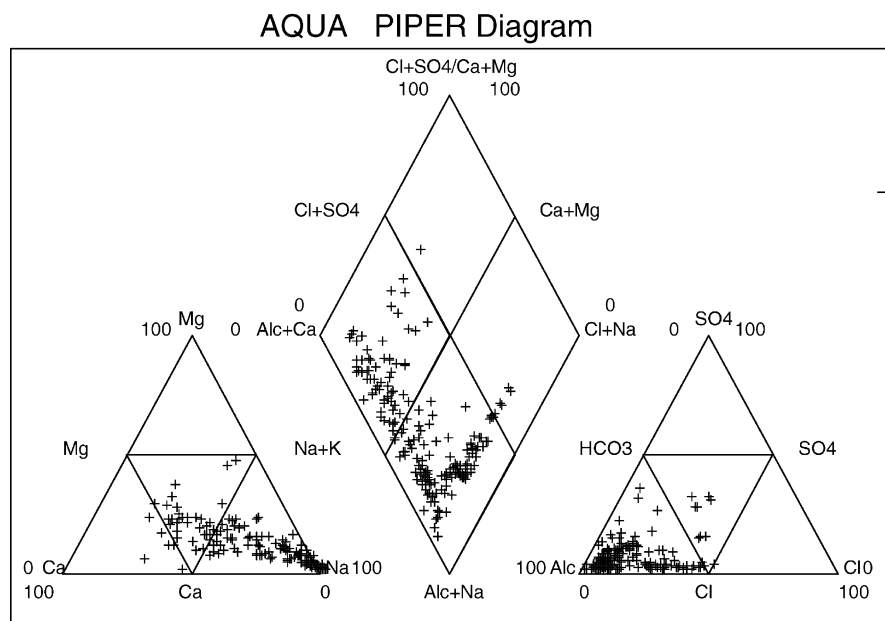

Fig. 4. Piper diagrams applied to all water samples of the study area.

sodium (Fig. 7). This indicates a loss of carbonate alkalinity in the aqueous phase, probably because of calcite precipitation. Such an assumption is supported by calcium values which remain constant or decrease slightly when CF reaches 1. This hypothesis should be confirmed considering the saturation with respect to calcite.

The molality of silica increases proportionately with the concentration factor for the waters with a $\log_{10}(CF) < 0.7$. Starting from this concentration factor, the silica increases, subsides as a consequence of a control mechanism attributed to a silicate precipitation. The behaviour of magnesium, often associated with silica at the time of the neosynthesis of magnesium silicates such as the magnesium clays, confirms this hypothesis. Beyond $\log_{10}(CF) = 2.2$, the molality in silica stabilises at $\log_{10}(CF) = 2.7$ characterising the solubility of amorphous silica.

In this manner, the successive precipitations of calcite, magnesium silicate, amorphous silica, and fluorite seem to be suggested by the concentration diagrams. These hypothesis must also be validated by the study of equilibrium diagrams between solutions and minerals.

The residual alkalinity of calcite in the waters is positive ($Alk_{res}.calcite > 0$). Alkalinity is, in any case, greater than the equivalents of calcium which characterises the chemical weathering of the volcanic rocks in the Main Ethiopian Rift. When these waters concentrate, the alkalinity increases despite the precipitation of the calcite and the molality in calcium decreases and stabilises. The increase of the alkalinity induces an increase of the pH which can reach values up to 10.

The residual alkalinity of calcite-fluorite is also positive $Alk + F > 2[Ca^{2+}]$. As the waters concentrate, the molality of fluoride increases in the same order as alkalinity which explains its very high concentration occurring in this area. All these variations agree with the principle of the generalised residual alkalinity.

Equilibrium diagrams

Activity calculations were carried out with the computer software AQUA which also evaluates the saturation state of the solutions with different minerals (Fig. 5). The waters of the area are generally saturated with respect to calcite (Fig. 5), with the
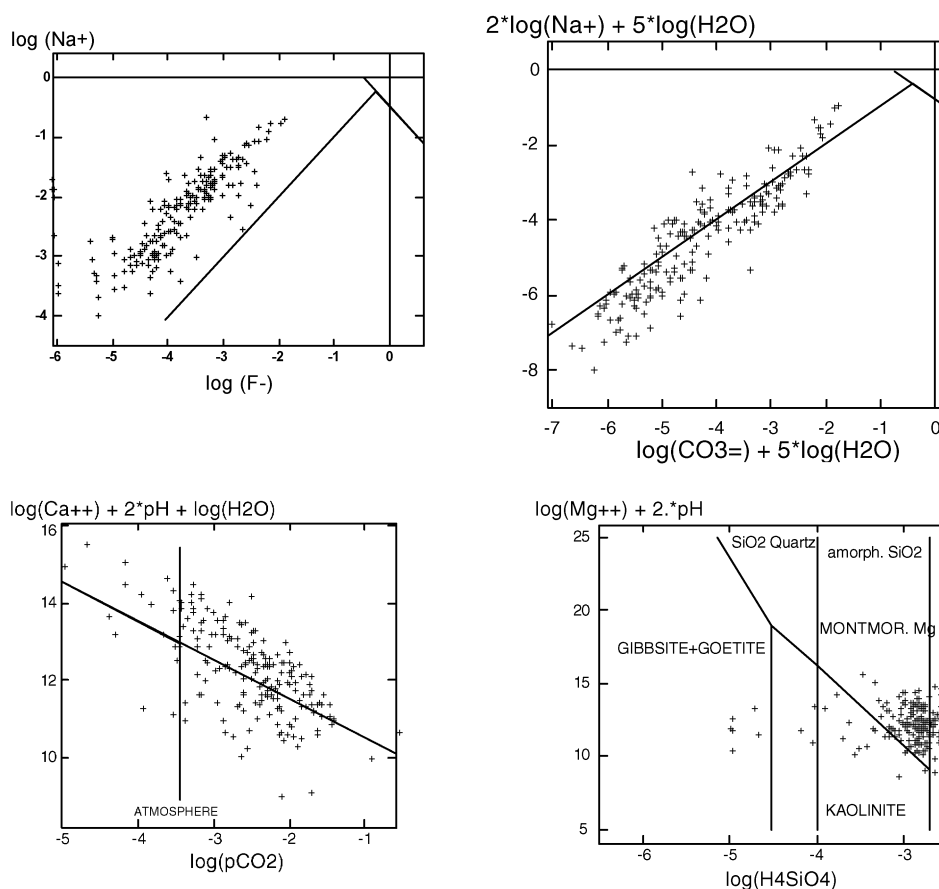

Fig. 5. Equilibrium diagrams between waters and different minerals (villiaumite, natron, calcite, magnesium silicate). Line with slope −1 represents theoretical equilibrium; line with slope 1 represents anion/cation equality.

exception of the most diluted waters in the highland which are slightly under-saturated with respect to this mineral. When equilibrium with calcite is reached, the activity ratio Ca^{2+}/CO_3^{2-} evolves in the branch $CO_3^{2-} > Ca^{2+}$, according to the sign of the alkalinity residual. This result confirms the hypothesis related to the role of calcite precipitation in the evolution of alkalinity and calcium content.

Waters are all under-saturated with respect to sodium bicarbonate and sodium carbonate such as trona, natron, or nacolithe; the same is also regarding sodium chloride (halite), but the diagrams show an evolution towards these minerals. Therefore, it is likely that a more arid environment, responsible for the increase in concentration of solutions could lead to the formation of such minerals.

The equilibrium with fluorite is reached when the waters are concentrated (Fig. 6). Once equilibrium is obtained, the solutions evolve in the branch $F^- > Ca^{2+}$, which fits the law of the generalised alkalinity residual, applied to the successive precipitations of calcite and fluorite. This result does not necessarily imply the formation of fluorite from calcium and fluoride, but simply means that the solutions are controlled at equilibrium. However, fluorite could precipitate when solutions are concentrated and impoverished in calcium; such fluorite deposits, over calcite beds, could result from replacement reactions calcite-fluorite with alkaline, fluoride bearing solutions:

$$CaCO_{3(solid)} + 2F^- \rightarrow CaF_{2(solid)} + CO_3^-.$$
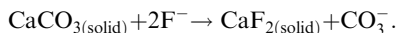
This agrees with the works of Ames (1961) and the observations of Icole *et al.* (1987). Conversely, the solutions are all under-saturated with respect to villiaumite. However, the equilibrium diagram of
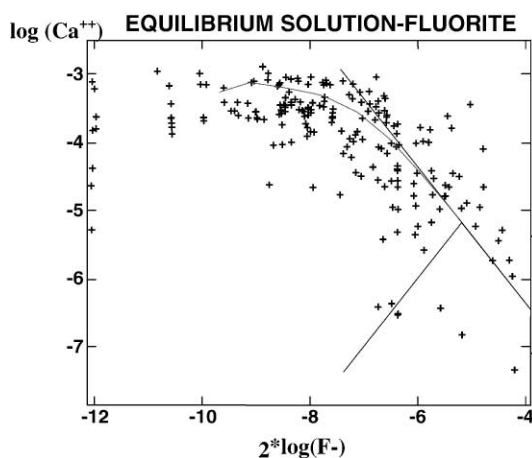
Fig. 6. Comparison between field data and modelling of the variations of fluoride and calcium chemical activity. The points represent the experimental data and the curve line indicates the evolution of the relations Ca^{2+}/F^- during the simulation on the sample TC54. The straight but oblique line represents the theoretical equilibrium between water solutions and fluorite.

sodium fluoride shows a moderate under-saturation for the most concentrated waters. Therefore, close to the shorelines of the most saline lakes, this soluble salt may locally precipitate when the sediments rapidly dry out, and then remain a potential source of fluoride for groundwaters.

As is usually expected in surface conditions, the most diluted solutions are slightly over-saturated with respect to the quartz. The most concentrated solutions, in the zone close to the terminal lakes, reach equilibrium with the magnesium silicates of sepiolite or stevensite type which can be used as analogues of diverse magnesium silicates in alkaline evaporite context. The precipitation of a magnesium silicate, whatever its mineralogical nature, leads to an accumulation in the solid form of an alkaline reserve (Marlet, 1996; Marlet *et al.*, 1996). Finally, the most concentrated waters reach the solubility of amorphous silica and keep this level which leads to a sufficiently strong control to cause the precipitation of this mineral, which is commonly observed in the field.

The main saturation steps identified using the observed variations in concentration diagrams are confirmed by equilibrium diagrams.

Modelling of the variations in fluoride content and other chemical elements

The model AQUA was used to simulate the evolution of chemical characteristics during the evaporative concentration process. The sample taken for simulation is TC54 (hand dug well west of Butajira in weathered ignimbrite), a diluted water showing a small fluoride content sufficient to be measured with a good precision by specific electrode. Its sodium content is 0.52 mM., which is then translated by a concentration factor:

$$CF = 0.52 \times 10^{-3}/0.9 \times 10^{-4} = 5.7778$$

$$\text{or} \quad \log 10(CF) = 0.7618$$

with the most diluted sample TC20 (spring west of Butajira from basaltic aquifer) which contains the lowest amount of sodium ($0.9 \times 10^{-4}\,M\,l^{-1}$) taken as a reference to set up the concentration diagrams.

The simulations were carried out for a fugacity in CO_2, $\log_{10}(fCO_2) = -2.0$, an average value observed in the study zone and in open system with respect to water. Different tests of sensibility were conducted for different parameters and, in order to validate, the results obtained for $\log_{10}(fCO_2) = -2.5$ were plotted on the same figure.

The concentration diagram was adjusted to a relative concentration factor of sample TC20 by dilution of sample TC54 in order to facilitate a comparison between the field data and the simulation. On the diagram, this corresponds to $0 < \log_{10}(CF) < 0.7618$.

The evolution of the molality of major and minor elements dissolved in the waters, such as aqueous
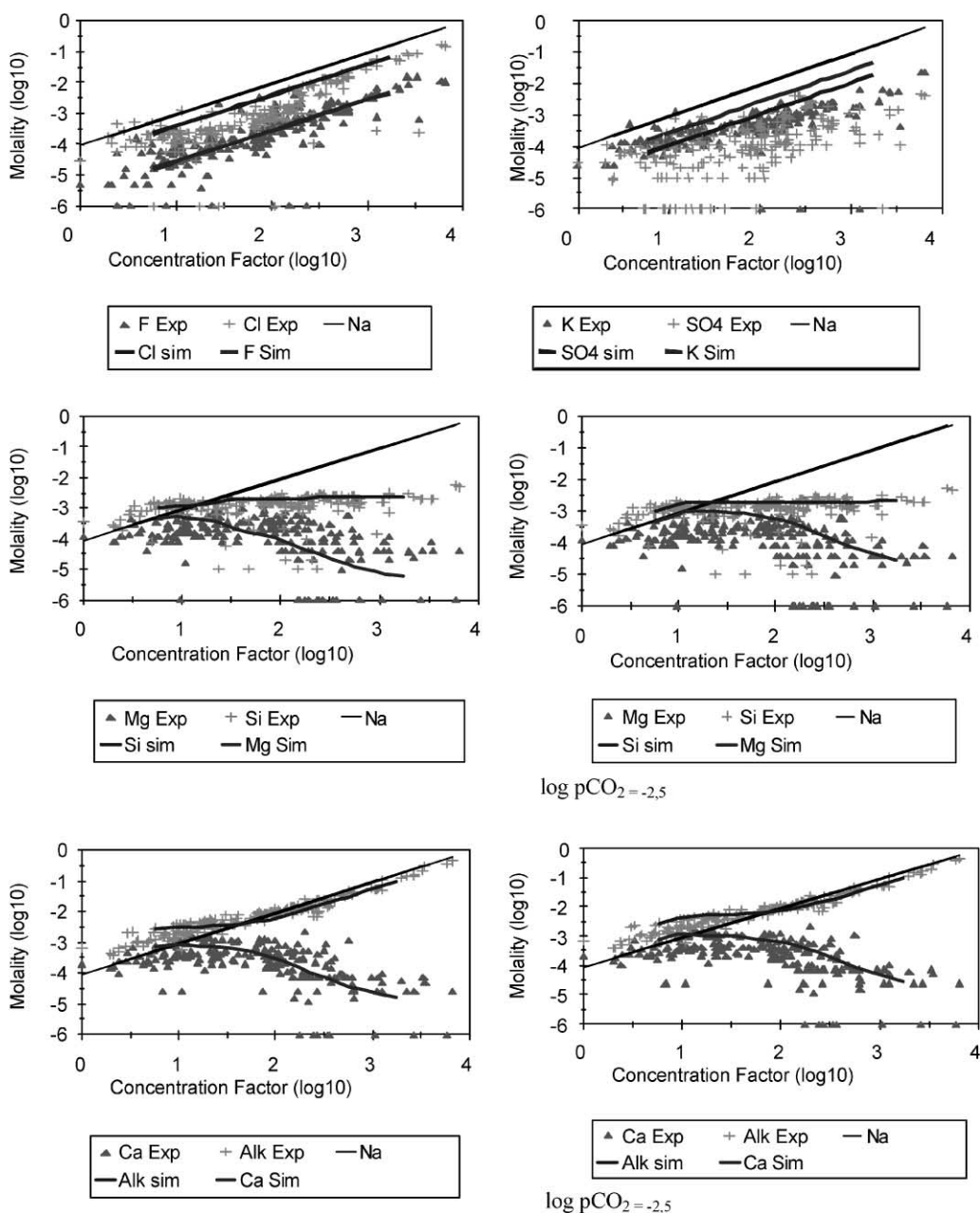
Fig. 7. Compared variations of dissolved elements contents, measured and simulated, during the evaporative concentration process. The sample taken for the simulation is TC54 ($\log pCO_2 = -2$ or -2.5).

silica, calcium, alkalinity and fluoride, is correctly described by the model (Fig. 7). The field variation range is of the same order of magnitude as the estimate variations. This is consistent with an increased mineralisation mainly as a result of the evaporative concentration process of a unique source of elements (silicate hydrolysis). The relative dispersion of the field data around the average tendency emphasises the influence of factor such as the spatial variation of the fugacity in CO_2 which is found between 10^{-1} and $10^{-3.5}$; this may also reflect evaporative signatures partially derived from secondary sources, as thermal waters. Conversely, it

may be noted that the poor agreement observed between measured and calculated data indicates that the chloride and sulphate signatures may have been derived from a variable geographic distribution involving different sources. This may be explained by thermal and anthropogenic influences; thermal springs generate an increase in sodium and bicarbonate alkalinity then the water chemistry remains controlled by Na^+ and HCO_3^-, while the Cl^- and SO_4^- enrichments are more variable.

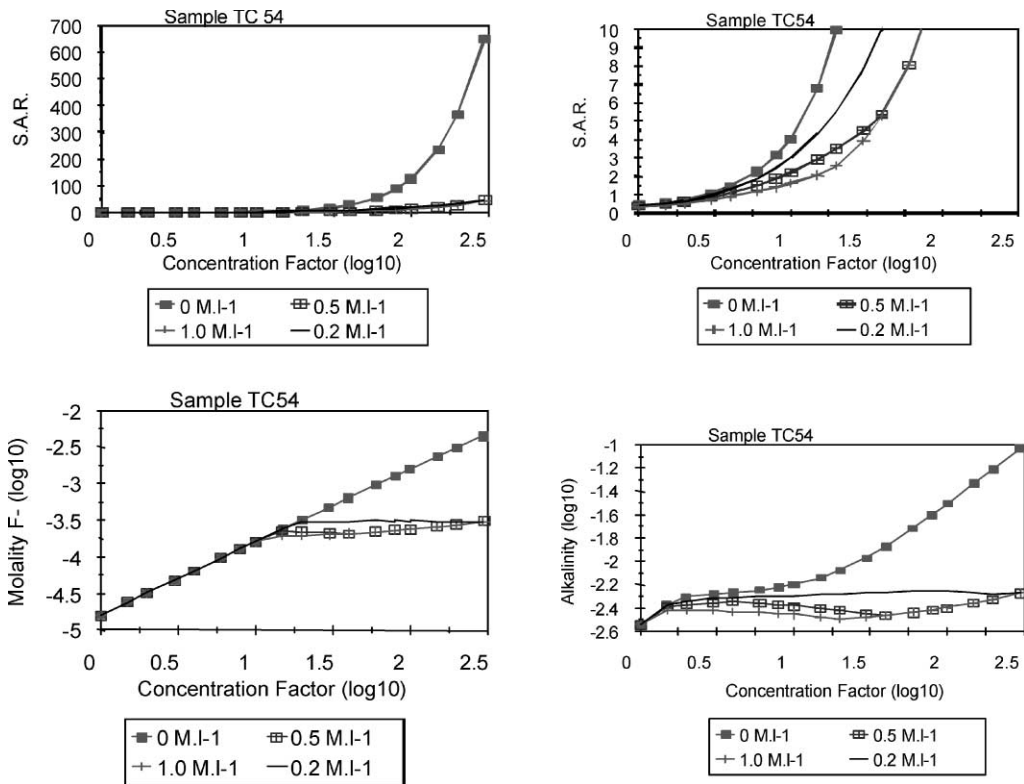Figures 6–8 show that the model satisfactorily confirms the geochemical evolution as calcite pre-

Fig. 8. Simulation of evaporation, after adding gypsum, with the diluted sample TC54, for SAR, pH, F⁻ and alkalinity. The amounts of added gypsum are: 0, 0.5 and 1.0 mmol per initial litre of water.

cipitation, followed by magnesium silicates and finally amorphous silica. These mechanisms affect the concentrations of calcium and magnesium, and to a lesser extent the carbonate alkalinity. The decrease in the calcium activity shows the evolution towards the equilibrium with fluorite which is reached after the precipitation of calcite as indicated above. Then, the small amount of calcium which remains in solution does not allow the fluoride concentration to be controlled by calcium; the residual alkalinity of calcite-fluorite indirectly characterises this lack of control.

Geothermal activity is known to occur in the study area and the temperature variation may affect fluorine and other mineral solubility. Therefore, the relatively strong dispersion observed in the concentration diagrams may partially reflect temperature variations between surface water and warm groundwater. The fluorine is particularly concerned because the solubility of CaF_2 increases with temperature, as in the same time the solubility of calcium carbonate decreases. This agrees with several works in this relation (Fritz, 1981; Travi, 1993; Chernet and Travi, 1993).

The simulated evolution of the relation between the activities of calcium and fluoride describe the average position of the field points (Fig. 7).

Calculated variation in calcium and fluoride chemical activity and field data shows that the model is able to reproduce processes affecting fluoride. It can be applied in order to predict the impact of the gypsum-addition on the quality of alkaline and sodic waters in the Ethiopian rift valley.

MODELLING TEST OF GYPSUM TREATMENT FOR REHABILITATION OF WATER AND SOIL QUALITY

Water quality criteria and the usual methods of improvement

Sodification and alkalinization. When the alkalinity residual of calcite concentrates, the calcium activity decreases while the sodium activity increases. As a result, during irrigation process, the complex of adsorption may be loaded with sodium which enters the clay and makes the physical properties of the soils to be unsuitable for agriculture (Barbeiro, 1994; Marlet *et al.*, 1996). In agriculture, the SAR (Sodium Adsorption Ratio) (Richards, 1954) values are most likely to evaluate the risk of sodic soils.

$$SAR = Na/\sqrt{(Ca + Mg)} \quad \text{with Na, Ca and Mg}$$

expressed in meq l⁻¹

The higher the SAR, the larger the risk is.

The increase in alkalinity and pH induce problems of insolubility and deficiency of mineral-nutrients for
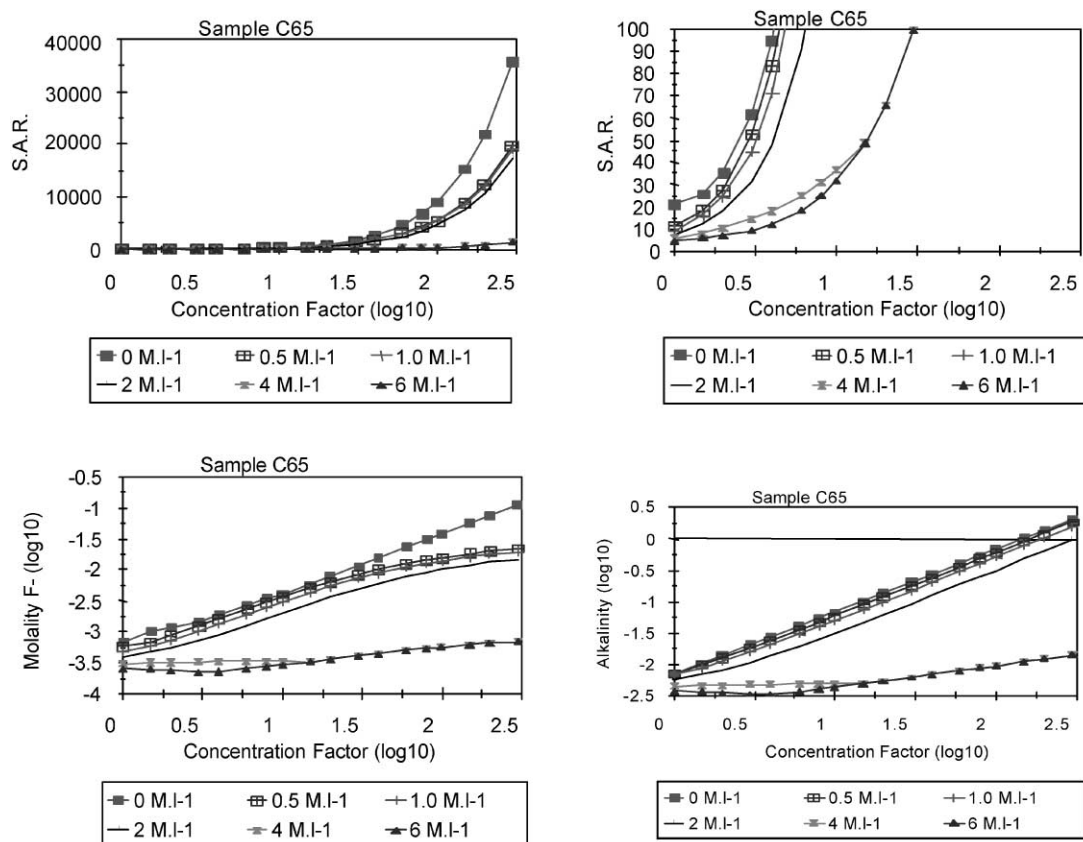
Fig. 9. Simulation of evaporation after adding gypsum with sample C65, for SAR, pH, F⁻ and alkalinity.
The amounts of added gypsum are: 0, 0.5, 1.0, 2.0, 4.0 and 6.0 mmol per initial litre of water.

plant, such as phosphorus and zinc, as well as phenomena of toxicity of sodium (Valles, 1987). The risk of alkalinization is usually estimated by checking the alkalinity of solutions and soil extracts.

The problems of sodification and alkalinization are difficult to solve technically. The classic methods which are the most recommended in agronomy for alkaline and sodic soils and water improvement are the addition of gypsum (Valles and Bourgeat, 1988), phospho-gypsum or sulphuric acid.

Fluoride. Human health problems from consumption of water with fluoride high contents starts from about $1\,mg\,l^{-1}$ or $0.53 \times 10^{-4}\,M\,l^{-1}$ and affects bones and teeth calcification.

Mazounie and Mouchet (1984) have discussed some methods of defluoridation by using floculation with aluminium sulphate, softening with lime, filtration through phosphorus substances or activated alumina, ion exchange and reverse osmosis. Several authors who have worked on the problem of fluoride treatment in Africa include Lagaude *et al.* (1988); N'dao *et al.* (1992), and Travi and Kergall (1991). Moges *et al.* (1996) has done an experiment on the treatment of water using pottery clay to absorb fluoride.

Considering the deficiency of calcium in the rift waters and the fluorite equilibrium control on F⁻ concentration, it would be of interest to test the effect of calcium issued from an addition of gypsum. Such a treatment has often been proposed to remove F⁻ (Appelo and Postma, 1996).

In this way, the criteria adopted in this work in order to appreciate the amendments caused by the gypsum are: pH, alkalinity and SAR related to alkalinization and sodification, while fluoride concentrations are used to access the drinking water toxicity.

Two series of simulation were carried out: the first concerns diluted waters represented by sample TC54, and the second a more mineralised water represented by sample C65. Sample C65 is from a borehole southwest of Shalla lake and considered as an average in account of its position in the equilibrium diagram of the waters with respect to fluorite (Fig. 6).

Simulation of the addition of gypsum in diluted waters

The simulation consists of adding a variable quantity of gypsum (0, 0.2, 0.5, and 1 mmol of

gypsum to 1 l of water TC54) and evaporation up to a concentration factor ranging between $\log_{10}(CF) = 0$ (waters not concentrated) and $\log_{10}(CF) = 2.5$ (waters most concentrated).

The results show that alkalinization and sodification of the water do take place during the evaporative concentration process (Fig. 8). SAR reaches 100 rapidly; pH becomes strongly alkaline with values higher than 8.5, the alkalinity is measured in tens of milliequivalents per liter and the concentration of fluoride reaches approximately 100 times more than the limit of potability.

Addition of even a small quantity of gypsum allows to stop the process of alkalinization and limits sodification. The effect on fluoride content however occurs only later, when the waters are more concentrated. The fluoride content is limited to some tens of millimols, which is largely above the limit of potability.

Simulation of the addition of gypsum in a moderately mineralized water

The selected sample, moderately concentrated, is saturated with respect to fluorite and lies in an average position on the equilibrium diagram. Its initial content of Na^+ is $0.913 \times 10^{-2} M l^{-1}$, which corresponds to a concentration factor of 101.44 relative to TC20, and 17.56 relative to TC54 ($\log_{10}(CF) = 2.0$ and $\log_{10}(CF) = 1.2$).

During the amendment by gypsum, the evolution of water quality is well marked (Fig. 9).

The pH increases rapidly and exceeds nine, then the alkalinity counts in milliequivalents and even in equivalents. SAR reaches and exceeds 100, and fluoride molality reaches tens, then hundreds of millimols per litre.

This dramatic evolution is related to the initial characteristic of the solution C65, already very degraded as compared to sample TC54.

For the small additions, the amendment by gypsum changes the unfavourable characteristic very little as described above. Additions in large quantity, more than 3 mmol of gypsum per litre of water, are needed to significantly improve the water quality. pH and the alkalinity will adjust to an acceptable value in the same way as SAR. An important addition of gypsum will also act on the molality in fluoride, but would not reach the standard for potability.

CONCLUSION

The initial aims of this work were to study and simulate the dynamics of fluoride and other dissolved chemical elements responsible for soil and water quality in this region of the Ethiopian rift valley. Both, analyses carried out in this study, and previous data taken from literature indicate that the waters leaching volcanic rocks have a positive residual alkalinity. When they concentrate, due to climate, the precipitation of calcite leads to a decrease in the chemical activity of calcium, which leads to an enhancement of fluoride solubility; this element concentration increases without being significantly affected by the precipitation of fluorite. As they concentrate, the alkaline trend of the waters result in a reduction of dissolved calcium. The pH then reaches high values which are incompatible with agricultural utilisation. The associated adverse elements, namely fluoride, sodium, and alkalinity accumulate downstream.

In this manner, the acquisition of both the high fluoride contents and the alkaline-sodic characteristic is a consequence of the unbalanced initial conditions between the alkalinity and the calcium, derived from the weathering of alkaline volcanic rocks. A simulation of evaporative effects from representative waters show chemical variation relatively similar to those observed on field data. For sodium, calcium alkalinity, silica and fluoride, the evolution of concentration is correctly described by the model and the field variation range is of the same order of magnitude as the estimated variation. The relative dispersion may be attributed to the field variability for PCO_2 and temperature. This suggests that the mineralisation is strongly influenced by the evaporative concentration process in all the hydrological systems.

Chloride and sulphate also follow an evaporitic trend but with enrichments more variable involving salt supplies of different origin which appears to characterise thermal waters or anthropogenic influences.

The predictive qualities of the model AQUA were tested in the context of this region and the modelling work showed that it was able to reproduce the processes affecting fluoride. As an application, it was possible to test methods of defluoridation and alkaline and sodic reduction using the thermodynamic model AQUA. The addition of gypsum is an amendment often used in the struggle against alkalinization and sodification. In the studied case, the simulations carried out show that this amendment can indirectly (carbonate precipitation and rise in SO_4^{2-}) neutralise an important part of alkalinity; it lowers the pH and the effect on the deterioration of the chemical fertility of the soil. This action of adding gypsum will also allow the reduction of the sodic character of the waters.

However, this method does not give a satisfactory solution to overcome the high fluoride content. This treatment allows the reduction of fluoride content by precipitation with calcium, but the calculation shows that the correction involved by gypsum is not convenient to reach the level of potability for drinking waters. Therefore, one has to consider other techniques of defluoridation to be applied together with or independent of this method.

APPENDIX: CHEMICAL ANALYSIS DATA ON TC54 AND C65

TC54—Hand dug well west of Butajira, on the plateau in the northwest of the region, in weathered ignimbrites.

C65—Borehole, west of Lake Shalla and north of Aje, in acidic pyroclastics

	TC 54 (mmol l^{-1})	C65 (mmol l^{-1})
Na	0.522	9.130
K	0.154	0.436
Ca	0.775	0.150
Mg	0.494	0.041
Cl	0.225	1.210
SO$_4$	0.062	0.542
HCO$_3$	2.85	7.070
CO$_3$	0	0.684
F	0.016	0.017
SiO$_2$	1.00	1.430
HBO$_2$	0.030	0.050

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