Geochemical Monitoring of the Lakes District Area

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ABSTRACT
The study focuses mainly on the Geochemical monitoring of the Langano, Shalla and Wondo Genet areas that are all located in the Lakes District areas, Ethiopian Rift Valley. The main objective of the work is to monitor the changes of concentration of chemical constituents of hot springs present in the Lakes District area, through time, and to assess the stability condition of the geothermal system in the Lakes District area.

Evaluation of change of concentrations of elements (various cations and anions including silica) through time have demonstrated the state of stable condition of the thermal system in the Lakes District area (Langano and Shalla) for the last thirty years. A plot of Cl-HCO₃-SO₄ has indicated that water samples collected from Langano, Shalla and Wondo Genet hot springs are all characterized by near neutral bicarbonate waters. However, water samples from the Bole spring belong to the water type of near neutral chloride sulfate water.

Evaluation of water-rock equilibria based on the Na-K-Mg content of thermal fluid indicates that the waters from Langano, Shalla and Belle spring of Wondo-Genet area get plotted in the partial-equilibrium regions along the dilution line indicating that the waters are the result of mixing of the meteoric and/or shallow ground water and deep reservoir fluid that is in equilibrium with the reservoir rock at a Na-K temperature range of 180-220 ºC. The water from Giorgis spring of Wondo Genet area falls in the region of immature water, indicating that this water can not be used for cation geothermometers.

Evaluation of solution-mineral equilibria based on saturation indices has demonstrated that most of the thermal waters from Langano area are over-saturated with respect to calcite, quartz and fluorite within the various range of temperatures. With the exception of thermal water of Bole spring, all waters from the lakes District area are under-saturated with respect to anhydrite. In Shalla area, there is a tendency of precipitation of travertine associated with hot springs. The super-saturation condition of Calcite in Wondo Genet hot springs is also confirmed by the occurrence of significant hydrothermal deposits of travertine associated with the hot springs.

Application of various cation empirical geothermometers to the waters of the Langano thermal system and Belle spring of Wondo Genet area has documented a sub-surface temperature ranging from 128-221ºC. The Na-K-Mg diagram is also supports this evidence where the Langano waters are plotted in the partially-equilibrated region along the dilution line as a result of mixing of the shallow groundwater and the deep reservoir fluid which is in equilibrium with the reservoir rock at a temperature range of 160-200 ºC. This range of temperature is also supported by the equilibrium temperature (140-200ºC) of Na-K minerals (Albite & Adularia) with respect to the deep fluid of the Langano, thermal system. The range of estimated sub-surface temperatures of Langano thermal system using the silica geothermometers (139-193ºC) is in close agreement with the range of equilibration temperatures of quartz with respect to the deep thermal water of the Langano area (100-200ºC). Na-K geothermometers failed to work for the Shalla hot springs due to mixing of the Na rich Lake Shalla water with the thermal water of the hot springs discharged at the eastern and southwestern shore of the lake.

1. REGIONAL GEOLOGICAL SETTING
The Ethiopia Rift extends over 1000 km in a general NNE direction from the Kenyan boarder and covers about 150,000 km² (see index map of figure 1). The Ethiopian Rift comprises two broad units: (i) the Main Ethiopian Rift (MER); and (ii) the Afar region. In the MER system, the distance separating two parallel faults that determine the width of rift, varies between 35 and 80 km averaging about 50 km. The relative displacement of the rift floor below the edges of the uplifted plateau extends as much 2000m (Mohr, 1966).

The central and southern part of the MER is occupied by a chain of lakes where its elevation extends from 1230m (Lake Chamo) in the south to about 1800 m at the Awash River watershed in the North. This part of the MER is known as the Lakes District Rift. The Lakes District Rift is structurally a
Consequently, the main objective of the present work is to see the changes of concentration of chemical constituents of hot springs present in the Lakes District area (Langano-Shalla-Wondo Genet), through time and to assess the stability condition of the geothermal system in the Lakes District area. In order to achieve this objective, special emphasis was given to: (i) integration of previous representative samples (1973-2001) and current (2003) chemical data; (ii) evaluation of changes of concentration of elements through time; (iii) identification of subsurface temperatures by application of various calibrated empirical geothermometers; and (iv) study of solution–mineral equilibria by processing of chemical data using various geochemical software’s (WATCH93; SOLMIEQ88 etc.).

3. REVIEW OF PREVIOUS WORKS

Geochemical studies in the Lakes District area were conducted in the following stages: (i) during the reconnaissance study (UNDP, 1973); (ii) detailed investigations; (iii) during drilling of the Aluto-Langano Geothermal Field (Abebe, 1983); (iv) after drilling, during the production-test of the wells and feasibility study (ELC, 1987; Mekuria et al., 1987; Mahon, 1987; Teklemariam, 1996); (v) during the utilization of the geothermal resource of the Aluto-Langano field (Teclu and Gizaw, 1999; Teklemariam and Beyene, 2001). Furthermore, a rather comprehensive picture of the Lakes District area has been documented by geological, geochemical and geophysical survey since 1969.

In order to monitor the changes of concentration of chemical constituents of the geothermal systems in the Lakes District area, a number of water samples were collected from the hot and cold springs, temperature gradient wells and boreholes of the whole District. These samples were analyzed for major cations and anions at the Central Geological Laboratory of the GSE.

4. DESCRIPTIONS OF THE AREAS STUDIED: LANGANO, SHALLA AND (WONDO GENET)

4.1 Langano Area

In the Langano area, the hot springs are mainly located in the South and South East of Aluto whereas the steam vents (fumaroles) are widely distributed within the Aluto Volcanic complex. A number of hot springs, with relatively higher discharge, are mainly confined along the northern bay of the Lake Langano area that include springs that occur on the rhyolitic geyser island in the north bay of Lake Langano. Hot springs found along the Bole fault emerge high above the lake and their discharge rate is relatively lesser.

For the present study, representative water samples were collected from the Langano area including: (i) hot springs (SP-84 and SP-2) that are located along the northern bay of the Lake Langano; (ii) Bole hot springs located along the Bole graben; and (iii) temperature gradient wells (TG-31 and TG-32; See Figure 2). Water samples were also collected from lakes, boreholes and dug wells of the surrounding areas.

The most common hydrothermal deposits associated with the hot springs are mainly silica sinters. Intensive alteration of red and white clays was observed in the Bole Graben in association with abundant silica sinters.

Hot springs located along the northern bay of Lake Langano (SP-84 & SP-2) have moderate temperature (61-62°C). They have alkaline to near neutral pH (7.64 -8.19). Waters collected from the temperature gradient wells have temperatures (61-64°C) comparable to those measured in the springs (SP-2 and SP-84). The pH is near neutral (7.7-7.8). Waters collected from the Bole springs have higher temperature (84-90°C) and near neutral to alkaline pH (8.38 - 8.80), waters samples were collected from the hot springs (SP-84 and SP-2) and temperature gradient wells (TG-31 and TG-32).

4.2 Shalla Area

Lake Shalla (1550m a.s.l) is a separate terminal lake that possesses the distinction of being one of the deepest lakes (266m) in the Eastern Africa Rift system. A major hydrothermal field about 3 km long occurs on the Eastern shoreline of Lake Shalla. In shalla area, hot springs emerge along eastern, southern and western shore of the lake. For the study, water samples were collected from: (i) the eastern, and (ii) south western shores of the lake.

Lake Chitu, 1 km in diameter is located 1.5 km south of the southern shore of Lake Shalla. A hot spring located along the eastern shore of Lake Chitu was sampled.

In Lake Shalla area, no significant sinter deposits were recognized. Instead, significant salt deposits were identified associated with the hot springs located along the eastern shore of the lake. Most of the hot springs located on the eastern part of Lake Shalla are boiling springs with temperature ranging from 91-95°C. The waters have pH ranging from 8.3-8.9. Hot spring located along the southern part of Lake Shalla has almost similar temperature (55°C) to the Chitu spring (57°C).

4.3 Wondo Genet Area

Wondo Genet area is located east of Awassa that is very close to Lake Shalla. There are a number of cold and hot springs in this area. Hot springs found in the Wondo Genet area are the source of Belle stream (UNDP, 1973). The springs are collectively known as Wondo Genet springs.

For the present study, water samples collected from the Wondo Genet area are mainly from (i) Belle hot spring located along the way to Wondo Genet bath; and (ii) Giorgis Tsebel located high on the scarp south of Kenteri. Water sample was also collected from the cold spring of Kenteri.
5. MATERIALS AND METHODS USED
For chemical and isotope determinations, a total of 36 water samples (24-chemical and 12 isotopes) were collected from hot springs, boreholes, temperature gradient wells, dug wells, surface waters (lakes and rivers), and of the Lakes District Area, Ethiopian Rift Valley.

The determination carried out both at the field site and field laboratory were temperature, pH, Eh, conductivity, TDS, Cl, CO$_3$ and HCO$_3$. Water samples were chemically analyzed at the Central Geological laboratory of the GSE. Water samples collected for isotope determinations (O$^{18}$, Deuterium and Tritium) were analysed at the Isotope Hydrology Laboratory of the IAEA, Vienna Austria Table 1.

6. DATA ORGANIZATION OF PROCESSING
Representative chemical data from the Lakes District area (UNDP, 1973; Glover, 1976; Craig, 1977; Teclu and Gizaw, 1999) were used together with the present data for data processing and interpretation (see Table 1). All these data were computed and processed using the geochemical software such as Watch93 (Arnorsson et al., 1982) and Somineq 88 (Kharaka et al., 1989).

7. ANALYTICAL RESULTS AND DISCUSSION
In order to evaluate the chemical changes in the Langano, Shalla and Wondo-Genet geothermal areas through time chemical data, from 1973 to 2003, were taken and plotted for each area against time.

7.1 Langano Area
From the Langano area, SP-2, SP-84, Bole spring and temperature gradient well (TG-32) were selected for time-series analysis.

A plot of Na, SiO$_2$ and K concentrations versus time for samples Bole Spring and SP-84 are shown in Figures 2A and 3A respectively. A plot of anions versus time for major anions of Bole and SP-84 Springs (Figures 2B and 3B) indicated insignificant change for the last 30 years. The plotted figures for the Langano area indicated that the Langano geothermal system is reasonably in a stable condition.
7.2 Shalla Area
From the Shalla area two samples were taken; one from the Eastern and the other from SW shore of Lake Shalla, for time analysis.

A plot of cations, anions and silica against time for these springs (e.g. Figures 4A and 4B) indicate no significant change of constituents of elements in the thermal waters of Shalla area.

7.3 Wondo Genet Area
Two samples, one from Belle hot spring and other from Giorgis Tsebel hot spring, were selected for time-series analysis. For cations, Na and K were taken in addition to Silica (SiO₂), and Cl, F, HBO₂ and HCO₃.

The plot of cations and silica against time indicated the absence of significant change in both springs (Figure 5A). The HCO₃ and Cl for Giorgis springs show the same trend (Figures 5B).

8. WATER CLASSIFICATION
The chemical data of the present work (2003) are plotted in the Cl-HCO₃-SO₄ triangular plot for Langano, Shalla and Wondo Genet geothermal areas (Figure 6). In the figure, water samples from Wondo Genet area (Belle and Giorgis hot springs) are plotted very close to the bicarbonate corner (about 80% of bi-carbonate) whereas samples from the Eastern shoreline of Lake Shalla plotted relatively far from the bicarbonate corner than all the other samples (about 65 % of bicarbonate). Other samples from the Langano, South western shoreline of Lake Shalla and Chitu plotted between Wondo Genet and Eastern shore line of Lake Shalla samples.

Sample from Bole fault is plotted exceptionally at a point where SO₄ is 40%, bicarbonate 40% and chloride is 20%. This is due to the presence of relatively high concentration of SO₄ in the Bole spring than any other samples collected during the present study. The source of high SO₄ for the Bole spring needs to be further investigated in conjunction with the surface alteration mineralogy. Previous studies (Mekuria et al., 1987) have suggested the occurrence of magmatic input to the system (steam heated water). But as sulfide is negatively correlated with bicarbonate, in this case, it seems to be unlikely due to the low concentration of bicarbonate.
9. EVALUATION OF WATER-ROCK EQUILIBRIA

9.1 Na-K-Mg content of geothermal fluids

The chemical data of Langano, Shalla and Wondo Genet hot springs generated during the present study (2003) are plotted in Figure 7. The figure reveals that chemical data from Belle hot spring (Wondo Genet area) and Chitu hot spring (Shalla area) fall on the boundary line between the immature water and partially equilibrated waters. The rest of the samples from all areas are plotted in the partially equilibrated region; along the dilution line indicating that the waters are in partial equilibrium with the reservoir rock.

They are found to be the result of mixing between the shallow ground water (immature water) and the deep reservoir fluid, which is in equilibrium with the reservoir rock at a temperature range of 160 – 220°C.

9.2 Based on Saturation Indices

The alteration minerals that are assumed to occur in the Langano (including the Aluto-Volcanic complex), Shalla and Wondo Genet areas are considered here. The state of saturation of hot spring waters, from these areas with respect to Quartz, Calcite, fluorite and anhydrite are calculated. For the hot springs from Langano area, the state of saturation indices for albite and adularia hydrothermal minerals were calculated with a view of using some cation geothermometers such as Na-K; in order to calculate the subsurface temperature of the system. This is mostly on the assumption that application of chemical geothermometers is based on the attainment of solution-mineral equilibria in geothermal systems. Discussion of solution-mineral equilibria is presented below, area-wise.

9.2.1 Langano Area

Figures 8 and 9 depict a plot of “Saturation index” (Log Q/K) vs. “temperature” for hot springs of Bole and SP-84 respectively. For this area, alteration minerals were selected based on the information obtained from the core samples recovered from the deep exploratory wells of the Aluto-Langano geothermal field.

The thermal water from Bole spring is under-saturated with respect to fluorite and anhydrite. The water is near to equilibrium with respect to anhydrite at the higher temperature range of 250-300°C, and with quartz and adularia at a temperature of about 100°C, and with albite at a temperature of about 130-140°C. The Bole hot spring water is over-saturated with respect to calcite throughout the temperature range (Figure 8).

On the other hand, the thermal water from SP-84 is under-saturated with respect to anhydrite and over-saturated with respect to fluorite through out the temperature range (100-300°C; Figures9). This water from SP-84 is nearly in equilibrium condition with respect to quartz, calcite and adularia at a temperature of about 150°C.

In general, the thermal waters from Langano area are over-saturated with respect to calcite, quartz and fluorite within the various range of temperatures. This means that there is a tendency of precipitation/deposition of sinters, travertine and minerals enriched with fluorite associated with hot springs of Langano area. With the exception of thermal water of Bole spring, all waters are under-saturated with respect to anhydrite.
9.2.2 Shalla Area

Figures 10 shows a plot of “saturation index” vs. “temperature” for the hot spring found along the eastern shore line of Lake Shalla. Na-K minerals such as albite and adularia were not considered here since there is a possibility of mixing of Na-rich lake water with the deep reservoir fluid. As a result, deposition of salt was observed in association of hot springs of the Shalla area.

In the figure, anhydrite, quartz and fluorite are found to be under-saturated with respect to the geothermal water of Shalla hot spring throughout the temperature range. This thermal water is over-saturated with respect to calcite throughout the temperature range (100-300º C).

9.2.3 Wondo Genet Area

Figures 11 depicts a plot of “saturation index” vs. “temperature”. Thermal water from Giorgis spring is in equilibrium with quartz and calcite at a temperature of about 100 ºC. In this water, Calcite is over-saturated at a temperature of >100 ºC whereas quartz remain in solution at a temperature >100 ºC. The super- saturation condition of calcite in these springs is also confirmed by the occurrence of significant hydrothermal deposits of travertine associated with the springs.

10. CHEMICAL GEOTHERMOMETERS

The study focuses on the application of various empirical geothermometers of Na/K, Na-K-Ca and Silica geothermometers to the hot spring waters of the Lakes District area (Langano, Shalla and Wondo Genet) with a view to estimate the deep reservoir temperature of the hot springs considered by this study (Table 2). The chemical data of 2003 were used for the calculation.

10.1 Langano Area

The calculated sub-surface temperature (144ºC) of Bole hot spring using the Na/K empirical geothermometers of Nieva and Nieva (1987) is in close agreement with the equilibrium temperatures of albite (140ºC) with respect to the Bole hot spring thermal water. Other cation geothermometers are found to be far from the equilibrium temperature of albite with respect to the Bole hot spring thermal water. The estimated subsurface temperature using one of the silica geothermometers (146ºC) is found to be higher than the equilibrium temperature of quartz (100ºC) with respect to the thermal water (Table 2).

The estimated sub-surface temperature of Spring 84 (192ºC) using the Na/K geothermometer of Nieva and Nieva (1987) is in very good agreement with the equilibrium temperature of albite (190ºC) with respect to the thermal water of Spring 84. However, the equilibrium temperature of adularia, calcite and quartz with respect to the water of spring 84 is found to be about 150º C (Figure 8). The equilibrium temperature of quartz...
(150°C) is in line with the calculated sub-surface temperature of this spring using silica geothermometer (148 °C; Table 2).

10.2 Shalla Area
Na-K geothermometers failed to work for the Shalla hot springs due to mixing of the Na rich Lake Shalla water with the thermal water of the hot springs discharged at the eastern and southwestern shore of the lake. The estimated sub-surface temperature of Shalla hot springs using the silica geothermometer is in the range of 116-146°C. However, quartz is found to be under-saturated with respect to the thermal water of Shalla hot springs throughout the temperature range (100-30°C).

10.3 Won do Genet Area
The silica temperature (TQA) for the thermal fluid in the Wondo Genet area yielded a value in the range of 140-148°C, which is much lower than the equilibration temperature of quartz (200°C) with respect to the thermal water of Belle hot spring. This could possibly be explained due to mixing of the deep reservoir fluid with the meteoric or less mineralized water. Another explanation could be precipitation of silica during up-flow of the deep fluid to the surface. On the other hand, the estimated sub-surface temperature of Belle spring (200°C) using Giggenbach (1988) is in close agreement with the equilibrium temperature of adularia (190-200°C) with respect to the deep thermal water of Belle hot spring. Na/K geothermometer is not calculated for Giorgis hot spring as it falls in the field of immature water in the triangular diagram of Giggenbach (1988) and gives erroneous results of equilibrium temperature.

11. SUMMARY OF RESULTS
Evaluations of change of concentrations of elements (various cations and anions including silica) through time have demonstrated the state of stable condition of the thermal system in the Lakes District area (Langano and Shalla) for the last thirty years.

A plot of Cl-HCO₃-SO₄ has indicated that water samples collected from Langano, Shalla and Wondo Genet hot springs are all characterized by near neutral bicarbonate waters. However, water samples from the Bole spring belong to the water type of near neutral chloride sulfate water.

Evaluation of water-rock equilibria based on the Na-K-Mg content of thermal fluid (Giggenbach, 1988) indicates that the waters from Langano, Shalla and Belle spring of Wondo Genet area get plotted in the partial-equilibrium regions along the dilution line indicating that the waters are the result of mixing of the meteoric and/or shallow ground water and deep reservoir fluid that is in equilibrium with the reservoir rock at a Na-K temperature range of 180-220 °C.

Evaluation of solution-mineral equilibria based on saturation indices has demonstrated that most of the thermal waters from Langano area are over-saturated with respect to calcite, quartz and fluorite within the various ranges of temperatures. With the exception of thermal water of Bole spring, all waters from the lakes District area are under-saturated with respect to anhydrite. In Shalla area, there is a tendency of precipitation of travertine associated with hot springs. Besides, the super-saturation condition of calcite in Wondo Genet hot springs is also confirmed by the occurrence of significant hydrothermal deposits of travertine associated with the hot springs.

Application of various cation empirical geothermometers to the waters of the Langano thermal system and Belle spring of Wondo Genet area has documented a sub-surface temperature ranging from 128-221°C. The Na-K-Mg diagram is also supports this evidence where the Langano waters are plotted in the partially-equilibrated region along the dilution line as a result of mixing of the shallow groundwater and the deep reservoir fluid which is in equilibrium with the reservoir rock at a temperature range of 160-200 °C. This range of temperature is also supported by the equilibrium temperature (140-200°C) of Na-K minerals (Albite & Adularia) with respect to the deep fluid of the Langano, thermal system. The range of estimated sub-surface temperatures of Langano thermal system using the silica geothermometers (139-193°C) is in close agreement with the range of equilibration temperatures of quartz with respect to the deep thermal water of the Langano area (100-200°C).

REFERENCES
Abebe, M: Geochemistry of the deep wells drilled at the Aluto-Langano Geothermal field. Internal report. Geothermal Exploration Project. (1983), C/83/1


Table 1. Chemical data (2003) from the hot springs of the Lakes District areas (Langano, Shalla & Wondo Genet). Concentrations are in PPM, ND= Not determined; TG= Temperature Gradient wells.

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TABLE 2. Estimated Temperatures from various Solute Geothermometers for Langano, Shalla and Wondo Genet Areas.

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TQC= Quartz Conductive; TQA= Quartz Adiabatic; TCH= Chalcedony (Fournier, 1977); F= Fournier (1973); F&T= Fournier & Truesdell, 1973; A1= (Arnorsson et al. 1983a; 25-250ºC); A2= (Arnorsson et al., 1983a; 250-350ºC); N= (Nieva & Nieva, 1987); G= Giggenbach (1988).