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HYDROGEOCHEMISTRY OF SPRINGS AT AMBO, CENTRAL ETHIOPIA

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ABSTRACT: The Ambo hydrothermal springs are low temperature hydrothermal systems located in central Ethiopia. The area is characterized by CO_2 dominated thermal activity with temperature that varies between 30 and 40°C. The chemical composition of 17 water samples over an area that includes lakes, boreholes, cold and thermal springs were compared. The hydrogeochemical investigation indicates that the most plausible mechanism for the formation of travertine deposit is the release of CO_2 due to pressure relief when the thermal water emerges at the surface. The sources of CO_2 are the degassing of a magma chamber from deeper sources and decarbonation of the Mesozoic sediments. The shallow acidic magma chamber of Dandi and Wanchi could act as a source of temperature and additional CO_2 input. Silica sinters associated with travertine imply the thermal origin of the deposits as well as initial high temperature of the formation. From the positive Saturation Indexes (SI) with respect to carbonate and silica and from the general geology of the region it is expected that the parent bedrocks could be limestones and/or calcareous sandstones that has controlled the hydrochemistry of deep regional groundwater. The hydrolysis of silicates and the chemistry of the outcropping rocks play additional role in controlling the hydrochemical evolution of shallow groundwater.

Key words/phrases: Ambo thermal springs, carbon dioxide, Ethiopia, hydrochemistry, saturation index

INTRODUCTION

The study area, Ambo, is located 125 km west of Addis Ababa, the capital of Ethiopia (Fig. 1). The area is known for its mineral water (Ambo Tebel), and building stone "Ambo Sandstone". The thermal springs are fault-controlled and are aligned along E-W fault line. They tap heat from the underlying magma chamber related to the active Dandi and Wanchi Quaternary volcanic centers (Tsegaye Abebe *et al.*, 1998; Lemessa Mekonta, 2001; Tamiru Alemayehu, 2003). Topographically the area is characterized by elongated ridges and wide plain areas dotted by volcanic hills. The northern part of the area is marked by an east-west oriented regional normal fault. The footwall of this fault forms the water divide between the Awash and Blue Nile river basins. The highest peak in the area is the Dandi and Wanchi volcanic centers (3390 m.a.s.l) located at the southern sector. The Ambo area contains numerous rivers and streams and widely distributed thermal and cold springs. The groundwater geochemical evolution in the area is principally controlled by silicate hydrolysis of the volcanic cover and carbonate mineral dissolution from the Mesozoic sediments. This coupled with high heat source and regional groundwater circulation at the interface between the volcanic cover and the underlying Mesozoic sediment and within in the carbonate sequence has led to the formation of economically viable soda water in the region. High bicarbonate concentration of the spring water is seen to give rise to encrustation of reservoirs and pipelines of the water supply systems.

The central part of the study area is covered with abundant travertine and silica sinter deposits. The objective of this work is to analyze the state of mineral saturation of the waters that gave rise to the travertine and the silica deposits and point out the hydrochemical nature of the groundwater of the area. Three boreholes tap the deep confined aquifer to produce the famous Ambo mineral water for Sankale mineral water factory. On the other hand, the thermal springs are being used by hotels for bathing and for the swimming pools. The authors reviewed most prominent previous works. Except the temperature data of Kondo (1967) and Herrick *et al.* (1980) geological information Mohr (1971) and Tsegaye Abebe *et al* (1998) no further information was available on the thermal condition at depth and the source of CO_2 gas. Processing and interpretation of chemical data focused mainly at defining the geochemical processes that determine the observed water composition and their implication on parent host rock.

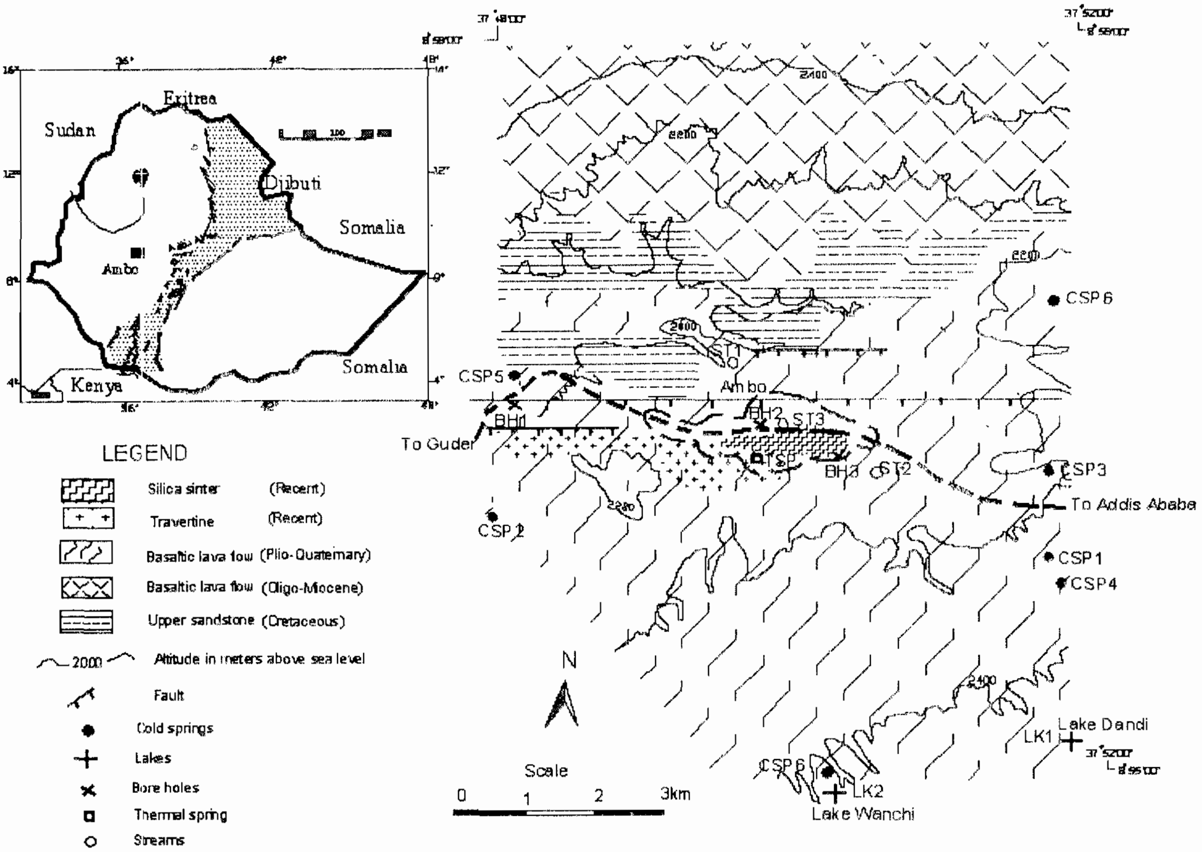

Fig. 1. Simplified geological map of Ambo area and water sampling points.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The area is part of the central Ethiopian plateau comprising Mesozoic sedimentary rocks, particularly sandstone and Tertiary and Quaternary volcanic rocks mainly basaltic and trachytic lava flows and pyroclastic deposits.

The Mesozoic rocks of the Ambo area belong to the sedimentary sequence of central Ethiopia of the Abay basin. The Mesozoic sedimentary rocks sequence in Abay basin according to Kazmin (1975) and later modified by Russo *et al* (1994) is:

Lower sandstone /Adgirat sandstone: mainly comprised by sandstone.
Gypsum and shale containing unit
Limestone
Mudstone
Upper sandstone / Ambaradam formation.

In the Ambo area, the prominent sedimentary rocks are mudstone, gypsum, shale, and upper sandstone. The sandstone sequence overlies the mudstone-gypsum-shale formation. The latter is less resistant to erosion and forms gentle slope while the sandstone forms steep slope.

The sedimentary sequence of the area is covered with Tertiary and Quaternary volcanics. The northern part of the study area is covered by basaltic lava flows of 31-20.6.Ma (Zanettin, 1993) that generated high topography. The basaltic lavas are of transitional alkaline basalt nature (Zanettin and Piccirillo, 1978; Zanettin, 1993). The older basaltic lava flows are separated from the younger Quaternary volcanics of Ambo area by the Addis-Ambo fault escarpment. The southern side of the major fault escarpment including Ambo town is underlain by Quaternary volcanics. The most important structural features of the Ambo region are the Addis-Ambo-Ghedo fault zone, east-west oriented and the NNE-SSW trending Guder lineaments, which cross one another almost at a right angle near Ambo town (Tsegaye Abebe, 1993).

The Quaternary volcanics in the area have resulted in the central type eruptions mainly forming Wanchi and Dandi volcanoes at the southern part of the study area (Kondo, 1967; Mohr, 1971; Herrick *et al.*, 1980; Tsegaye Abebe *et al.*, 1998).

The E-W running Ambo-Ghedo fault has given rise to the exposure of the Mesozoic sediments and the juxtaposition of the sediments with the volcanic cover. A cliff and ridge forming sandstone is exposed at the NW part of the study area. The sandstone is well sorted and intercalated with very thin layers of white-gray to reddish conglomerate. Exposures in some stream valleys show that the sandstone is directly overlain by the Quaternary basaltic lava flows and is also intercalated with a mudstone- gypsum-shale.

Travertine and silica sinters occur as secondary chemical deposits in the area. The exposure follows east-west trending fault line that could be a conduit for the thermal water that is supersaturated with calcium carbonate and silica. They occasionally also occur as precipitates within the rock fractures.

The Ambo area is characterized by unimodal rainfall that is concentrated between April and August with the annual value of 1143 mm and with the mean annual temperature of 17.6°C (Lemessa Mekonta, 2001). Due to favorable climatic condition, rivers such as Huluka and Dabis flow through out the year. The southern highland of the area is occupied by Wanchi and Dandi crater lakes. Numerous cold springs occur in the area as a contact type between different geological formations. The groundwater is being tapped by means of deep boreholes from volcanic and sedimentary aquifers. The main hydrogeological formations in the area fall in three categories:

- The highly fractured and/or weathered lava flow (basalts and trachytes) and the loose pyroclastic deposits:
- The upper sandstone unit
- The mud-shale-gypsum units intercalating the sandstone.

The regional and local tectonic discontinuities play significant role in regional transfer of groundwater into and out of the Ambo basin. The general CO_2 sources within the hydro-geological system are degassing from magma, carbonate dissolution and atmospheric gasses. In open system there is possibility of mixing among different sources.

SAMPLING AND ANALYSIS

After thorough evaluation of the geological setting of the area, water sampling points were identified (Figure 1). Seventeen representative water samples from different water sources have been collected in one-litre polyethylene plastic bottles and these were analyzed for major ions. The analyses were conducted in the Oromiya water quality laboratory and control samples were measured at Addis Ababa Water and Sewerage Authority central laboratory. Anions were measured using UV/VIS spectrophotometer and cations were determined using atomic absorption spectrophotometer. Silica (SiO_2) was analyzed using colorimeteric method. For error control purpose duplicate samples were analyzed and the data were found to be acceptable for interpretation. The obtained data were checked for error that fall below 2.55%.

The raw data were processed using a NETPATH software (Plummer and Back, 1980) to obtain the saturation index and ionic strength of the samples. Aquachem software version 3.6 (Waterloo Hydrologic, 1997) was also used to determine the type of water in the study area.

RESULTS AND DISCUSSION

Analytical results for representative samples are presented in Table 1. The sampling includes cold springs, thermal springs, lakes and boreholes. The main water types of the area are given in Table 2, where Ca and Na are found to be the dominant cations, with HCO_3 as the dominant anion.

The pH of the surface and ground water ranges from 6.2 to 8.2. The high pH water (alkaline water) corresponds to Lake Wanchi. The thermal waters have the lowest pH due to the presence of CO_2, otherwise the shallow springs and cold groundwaters have relatively high pH. The groundwater temperature in some moderately deep wells (in excess of 150 m depth) reaches 38°C, while thermal springs have water temperature of 40°C.

Table 1. Analytical results for water samples in mg/l (CSP: Cold springs, BH: Borehole, TSP: Thermal spring, ST: Stream, Lk: Lake).

Local name	Qeransa	Molche	Buqisa	Chafe	Kilinto	Wachani	Ela	Shamme	Sankale	Hotel	AARI	Ther Spr.	Tiro	Huluka	Huluka	Dandi	Wanchi
Sample Code	CSP1	CSP2	CSP3	CSP4	CSP5	CSP6	CSP7	CSP8	BH1	BH2	BH3	TSP	ST1	ST2	ST3	LK1	LK2
Location (UTM)	N 986850 E 392940	N 986830 E 392924	N 991228 E 389324	N 993389 E 369029	N 996995 E 382762	N 996964 E 382744	N 980185 E 390633	N 994717 E 371506	N 994390 E 369807	N 993248 E 374042	N 991436 E 374012	N 993022 E 373938	N 998507 E 377772	Up stream	Down stream	N 978644 E 389129	N 974014 E 377722
Altitude (masl)	2550	2680	2510	2070	1854	2250	2900	2110	2070	2140	2090	2100	2200	890	900	2850	2890
pH	7.4	6.1	6.44	7.03	7.44	7.1	7.05	6.7	6	6.8	6.34	6.2	8.1	7.91	7.81	7.7	8.2
Eh (mv)	-32	+56	+31	-6.5	-	-17	+0.5	+3	-5.5	+10	+40	+45	-70.1	-	-	-49.2	+76
T(ºC)	17.5	21	19.5	20	16.1	20	18	22.9	30	19.5	38	35	21	16.1	20.2	18	16.5
EC (Mic. S/cm)	162	64	115	651	665	387	65	395	3008	1320	1447	1470	379	141.6	281	120	171
TDS (mg/l)	100	39	69	16	391	242	44	228	1955	793	745	742	238	82	150	66	106
Tot.Alkalinity ($CaCO_3$)	154	46	66	500	400	270	10	480	895	480	1050	970	204	46	139	204	99
NH_4 mg/l	0.026	0.3684	nil	0.503	0.28	nil	0.142	1.88	nil	0.75	1.7	1.72	0.039	2.57	2.406	0.1	nil
Na^+	11.966	15.22	13.88	32.134	5.536	25.134	20.13	25.14	250	182.458	274.997	181.488	50	90.2	115.105	10.126	18.383
K^+	2.013	1.86	2.12	5.407	0.932	4.229	3.21	4.21	38	30.699	29.861	19.707	2	8.2	19.367	5.419	9.839
Ca^{2+}	24.8	20	21.6	112	120	58.4	48	56	75	168	64	180	80	20	11.2	20	11.2
Mg^{2+}	22.08	19.2	15.84	43.2	37.92	17.76	4.8	57.6	50	33.6	62.4	33.6	43.2	21.6	11.52	38.4	2.4
Cu^{2+}	0.02	0.01	nil	0.35	0.92	0.08	nil	0.06	nil	1.68	0.01	nil	0.11	0.06	0.78	0.12	0.02
Fe^{2+}	0.08	0.86	0.12	nil	0.02	nil	0.26	3.75	nil	0.02	0.57	0.44	0.06	2.74	2.13	0.42	0.11
Mn^{2+}	0.2	0.028	0.002	0.014	0.018	nil	nil	5.8	nil	nil	0.2	0.1	0.001	0.13	0.1	0.013	nil
NH_3	0.024	0.3538	nil	0.476	0.27	nil	0.134	1.78	nil	0.71	1.61	1.62	0.037	2.43	2.275	0.098	nil
Cl^-	3	nil	nil	nil	nil	nil	nil	nil	36	220	nil	24	nil	nil	150	nil	8
$NO3^-$	7.48	1.76	19.36	5.72	31.68	9.24	14.08	7.04	nil	157.52	5.28	5.28	4.84	nil	nil	6.6	6.16
$NO2^-$	0.017	0.0033	0.0132	0.023	0.023	0.0264	0.013	0.393	nil	0.0264	0.036	0.003	0.0165	0.073	0.403	0.0132	0.026
HCO_3^-	187.88	56.12	80.52	610	488	329.4	12.2	268.4	1150	585.6	1281	1183.4	248.88	5.61	169.58	248.88	120.78
CO_3^{2-}	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
SO_4^{2-}	nil	1	nil	29	nil	1	1	50	13	77	1	1	7	nil	10	5	nil
PO_4^{3-}	0.17	0.33	0.44	0.78	0.35	0.31	0.13	0.3	0.01	0.53	0.96	0.91	0.58	0.6	0.96	0.58	0.1
SiO_2	-	-	-	20	-	-	-	-	47	30	35	38	-	-	-	-	-
CO_2	-	-	-	-	-	-	-	-	4000	-	-	-	-	-	-	-	-

The comparative survey on ions indicates that deep groundwater is enriched with cations and anions as compared to shallow groundwater. The maximum values lie in deep cold and thermal ground waters. The results in Table 1 indicate that in deep groundwater Na reaches 275 mg/l, Mg reaches 62 mg/l and Ca reaches 180 mg/l. Regarding anions bicarbonate dominates the hydrochemical system in the deep groundwater with the value that reaches 1280 mg/l. While, sulphate and chloride exist at relatively low concentration of 77 mg/l and 220 mg/l, respectively.

Table 2. Water types derived from Aqucahem.

Water point	Water type
Cold springs	Na-Ca-HCO_3, Ca-Mg-Na-HCO_3,
Boreholes	Na-Ca-HCO_3, Na-Mg-HCO_3
Thermal springs	Ca-Na-HCO_3
Lakes	Na-Ca-HCO_3, Mg-Ca-HCO_3

The ion enrichment in the deep groundwater system could be attributed to the high solubility of host rocks, favourable pH and Eh condition for solubility and high degree of water-rock interaction. The most important gas released during hydrochemical reaction is carbon dioxide, which could give clue to its origin. The CO_2 content in artesian borehole measured during the current survey is about 4000 mg/l. The thermal springs and artesian groundwater contains as much as 4497 mg/l of CO_2 (Herrick *et al.*, 1980). The calculated CO_2 content from the artesian borehole water samples is 4980mg/l. Such high CO_2 value at Ambo may not be necessarily related to the release of the gas from carbonate dissociation but also to the additional input through degassing from magmatic activities of Wanchi and Dandi volcanic centres.

Sources of carbonate and silica in the waters

The dissolution of calcium carbonate in the presence of carbonic acid can be written as Langmuir, 1997:

$$CaCO_3 + H_2CO_3 \Leftrightarrow Ca + 2HCO_3^- \text{ .... (1)}$$

In another form the solubility of calcium carbonate in the presence of CO_2 can be represented as:

$$CaCO_3 + CO_{2(g)} + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^- \text{ .... (2)}$$

According to equation 2, addition of more CO_2 to the system favours the forward reaction, i.e. calcite dissolution (or any other carbonate dissolution is favoured by an increase in CO_2 pressure and a decrease in pH). On the other hand, the removal of CO_2 by any means from the system and an increase in pH favours the backward reaction (precipitation of calcium carbonate). The precipitation of calcium carbonate (travertine in the study area) from the solution can occur either due to evaporation process, or decrease in temperature, or release of CO_2 due to decrease in pressure.

Another possibility for the deposition of travertine in the area could be from the dissociation of gypsum ($CaSO_4.2H_2O$) that is intercalated with the sandstone. However, there is a limitation on this possibility as the sulphate content is low in the thermal springs.

The major sources of silica in natural waters are weathering of silicate minerals and quartz rich rocks. The solubility of silica increases with increasing temperature. The strong temperature dependence of its solubility allows silica to be used as a geochemical thermometer (Trainer, 1981). The dissolution and precipitation reaction for silica polymorphs can be described by:

$$H_4SiO_4 \Leftrightarrow SiO_2(s) + 2\,H_2O \text{ .... (3)}$$

The highly soluble form of silica is the amorphous solid variety whereas quartz is the least soluble form. Silica sinter is formed by the precipitation of SiO_2 from silica-saturated solution. As it can only be deposited from thermal waters, it can be used as an evidence for high temperature condition exceeding 180°C, at depth (Trainer, 1981). Other possible sources of silica could be quartz rich sedimentary rocks like sandstone that overly the crystalline basement rocks. Silica sinter can only be deposited from thermal water whereas travertine can be deposited from moderately thermal to non-thermal water (Trainer, 1981).

Since the solubility of silica increases with increasing temperature, large amount of silica exist in solution when the thermal water attains higher temperature at depth. The outpourings of thermal springs that are rich in silica with decreasing temperature automatically reduce solubility of silica facilitating the formation of silica sinter.

The geochemical modelling, using NETPATH, shows that the thermal groundwater and deep and cold ground waters are supersaturated with respect to calcite and quartz (Table 3) that have a potential to precipitate travertine and silica sinters. Up on emergence and the associated release of dissolved carbon dioxide deposition of carbonate minerals could occur.

As it is indicated in Table 4, both for the deep and shallow aquifer system, the presence of carbonate host rocks is always important, as the ratios are very low.

Table 3. The saturation index (SI) values for selected water points.

Samples	Calcite	Chalcedony	Quartz	Dolomite
BH1	+0.7	+0.36	+0.83	-1.16
BH2	+0.11	+0.25	+0.74	-0.43
BH3	+0.31	+0.15	+0.58	
TSP	+0.31	+0.18	+0.61	+0.38

Most of the samples plotted on Figure 2 are closely controlled by CO_2 interaction and involvement of CO_2 is apparent as the samples are clustered together. The chemistry of cold springs is also dominated by HCO_3 ion derived from carbonate aquifer. In this diagram, the real position of water points depends on the concentration of magnesium with respect to calcium that has constrained the percentage values.

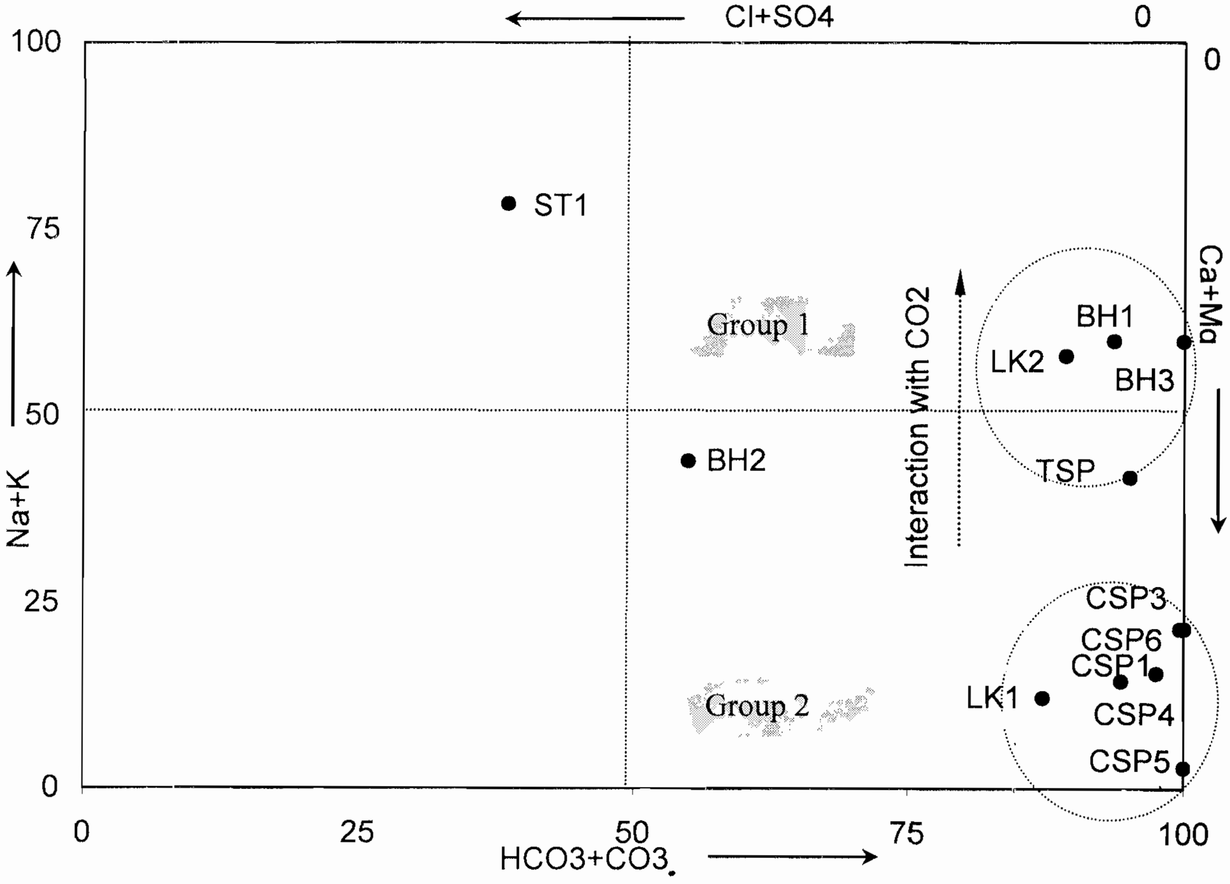

Fig. 2. Langelier-Ludwig diagram (CSP=Cold Springs, BH=Boreholes, LK=Lakes, TSP=Thermal spring, ST: Stream). Codes are as in Table 1.

In Figure 2, the water samples fall in two distinct sectors. The samples from BH1, BH3, TSP and Lake Wanchi are categorized as group one having Na-HCO_3 type water while samples from the thermal springs fall in the transition zone with low Ca, Mg, HCO_3 and high Na, Cl, and SO_4. Cold springs and the Dandi Lake can be categorized as group two having Ca-Mg-HCO_3 type water which is characterized by low Na, HCO_3 and CO_2, and high Ca, Mg concentration. The facies classification indicates that the main process that govern group one members is weathering while group two is controlled by degassing process. Most of the cold springs show enrichment in HCO_3 as compared with the thermal springs derived from dissolution of calcite mineral in the host rocks. Deep boreholes indicate the possibility of CO_2 interaction derived from deep system. In addition to positive saturation indexes (Table 3) and high concentration of CO_2, different enrichment pattern of ions in deep and shallow groundwater could indicate important role played by carbonate dissociation besides silicate solubility and magmatic interaction with the groundwater system.

Chloride and sulphate are important in regulating the chemical quality of cold springs recharged from carbonate materials and volcanic rocks (Table 4). In deep circulation like in BH3 and cold springs (CSP1 and CSP2), the carbonate aquifer play very important role that is confirmed from low $Cl+SO_4/HCO_3$ ratio.

Table 4. Relative importance of anions (Sample code as in Table 1).

$Cl+SO_4/HCO_3$	Samples
0.0008	BH3
0.003	CSP6
0.02	CSP1
0.02	LK1
0.03	TSP
0.04	BH1
0.05	CSP4
0.07	LK2
0.09	ST1
0.27	CSP2
0.51	BH2
1.23	CSP7

Geothermometeres involve consideration of the effects of temperature either on solubility of species (normally in the form of silica) or on the amount of exchange of various cations (the alkali and alkaline earth metals). The drawback of the system is its representativity with respect to the source. In order to estimate the reservoir temperature, the Na/K geothermometer was used considering all its draw backs (Giggenbach, 1986, Celati *et al.*, 1991, Fara *et al.*, 1999). However, as seen below, the calculated values seem to be high in the Ambo area. This method gave more reasonable temperature value in the Aluto geothermal field of lakes region in Ethiopia (Gianelli and Meseret Teklemariam, 1993) as compared to the values obtained for Ambo.

Table 5. Calculated temperature values.

Sample	T °C
BH1	281
BH2	217
BH3	246
TSP	247

The calculated reservoir temperatures for deep groundwater samples is given in Table 5. The closeness of the values could indicate the interconnection or similarity of the aquifer. The comparison with the water temperature at source indicates possible loss of heat on the way to the surface. The experience at Damt thermal springs in Yemen (Fara *et al.*, 1999) indicated that the chemical evolution of the springs is controlled by crustal dissolution process at temperatures below 100°C where the measured spring temperature was 40-45°C. In this regard, the calculated temperature for Ambo thermal springs and borehole waters is exaggerated and is expected to be rather more or less similar to Damt thermal springs.

CONCLUSIONS

The discharge of thermal waters is structurally controlled by the E-W aligned fault lines. The presence of silica sinters along with travertine deposits show their thermal origin as well as the original high temperature of the thermal waters compared to the currently measured temperature on the surface. The maximum reservoir temperature calculated is 281°C and it is expected to be high. The main source of heat supply for the thermal waters could be the magma chamber related to the Wanchi and Dandi volcanic centres.

The thermal waters are currently saturated with silica and calcite where still there is a possibility of precipitation indicated by positive saturation indices. The travertine and silica sinter may indicate the presence of calcite and silica rich rocks that feed the thermal water system, which possibly could be limestone or/and calcareous sandstone.

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