Addis Ababa University
School of Earth and Planetary Science
Department Of Earth Sciences

Carbon dioxide-water-rock interaction and hydrogeochemical evolution of thermal and cold ground waters in Wonchi Crater Lake and Ambo-Woliso area.

By:

HASSEN SHUBE

A Thesis Submitted to the School of Graduate Studies of Addis Ababa University in Partial Fulfillment of the Requirements for the Degree of Master of Science in Hydrogeology

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Declaration

This thesis is my original work and has not been presented for a degree in any other university, and that all sources of material used for the thesis have been duly acknowledged.

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ABSTRACT

Isotopic and geochemical data are used to study the hydrogeochemical evolution of thermal and hypothermal ground waters and CO2-water-rock interaction of ground waters around Wonchi, Woliso and Ambo area. Geochemical data are classified by Q-mode hierarchical cluster analysis in to objective groups in order to identify ground waters that have the same hydrogeological and chemical nature so that to conduct inverse geochemical modeling. HCA classified the water in to two major groups of high and low TDS and six sub-groups. The waters in the classified subgroups are similar in chemical composition, geology and the depth in to shallow and deep aquifer.

Hydrogeochemical evolution of ground waters of the study area is highly influenced by two regional structures like YTVL and Ambo-Wonchi-Butajira faults that cut across this region. Thermal and gaseous ground waters of the study area are particularly aligned along these structures. The CO2 influx to ground waters of the area is due to the deep seated faults that bring this gas from deep source of metamorphic decarbonation or mantle gas origin. The source of CO2 gas is suggested by using $\delta^{13}C$ isotope indicates high values are in thermal and gaseous mineral waters of the region. High TDS thermal and gaseous ground waters are characterized by NaHCO3 in Wonchi and Woliso area while Ambo area is characterized by NaCaHCO3 type waters. Low TDS ground waters are suggested as shallow and cold ground waters of recharge area that undergone less water-rock interaction and characterized by $\delta^{18}O$ enrichment and CaHCO3 and CaMgHCO3 water types except in some mixed ground waters. Stable isotope data indicates that thermal and gaseous ground waters are depleted in $\delta^{18}O$ except in Wonchi area ground waters that shows $\delta^{18}O$ enrichment due to hydraulic connection with Lake Wonchi.

The effect of the influx of CO2 to ground waters of this region plays a major role in CO2-water-rock interaction to be significant and silicate hydrolysis like dissolution and precipitation of silicate minerals during ground water chemical evolution. Trace element mobility is observed in high TDS thermal and gaseous ground waters due to strong CO2-water-rock interaction. Heavy metals that are harmful to the human and environment like Sr, Ba, Mn,Fe and Al are observed in some thermal and mineral waters of the study area above the permissible concentration of WHO drinking water standard.

Key words: hydrogeochemical evolution, thermal, gaseous, CO2-water-rock interaction, trace element mobility, Ambo, Woliso, Wonchi Crater Lake

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First of all I would like to praise almighty Allah for the strength he bestows on me to start and finish this work successfully.

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List of Acronyms

ABL= Ambo-Butajira-Lineament

BH= Bore holes

DL= Dedesa Lineament

ENWRA= Ethiopian Wet Land and Natural Resource Association

EPA= Environmental Protection Authority Of Federal Republic Of Ethiopia

EVP= Ethiopian Volcanic Plateau

GMWL= Global Meteoric Water Line

HCA= Hierarchical Cluster Analysis

HDW= Hand Dug Wells

IAEA= International Atomic Energy Agency

ICPMS= inductively coupled Plasma Mass Spectroscopy

ITCZ= Inter-Tropical Convergence Zone

LMWL= Local Meteoric Water Line

NWP= North Western Plateau

SEP= South Eastern Plateau

PDB= Pee Dee Belemnite

VSMOW= Vienna Standard Mean Oceanic Water

CHAPTER ONE

INTRODUCTION

1.1. Back ground

There are a number of processes by which naturally occurring CO_2 can be emitted in to the atmosphere, however, the most important is through degassing of magma(molten rock i.e. the melting of carbonate rocks(lime stones` ,dolomites, chalks) will lead to the production of gaseous CO_2). The degassing of magma is commonly associated with volcanic activity. The heating and metamorphism of carbonate rocks, such as lime stones, most commonly by magmatic intrusions, also produces co_2.

CO_2 may also form in the geosphere by thermal maturation of coal and other organic material. Most of this co_2 is thought to dissolve in water and eventually precipitate as carbonate cements in the pore spaces of nearby reservoir rocks.CO_2 may also originate from the biodegradation of oil and gas.

When magma rises towards the earth's surface, the pressure on it is lowered. This enables dissolved CO_2 and other gases to come out of solution in the molten rock and accumulate as free gas. Most of the CO_2 originating from the magma degassing is emitted through volcanoes and associated fissures, or hydrothermal sites. However, a proportion may travel up deep seated faults rooted in the lower crust and make its way into sedimentary basins.

The Migration of CO_2 in the geosphere shows that CO_2 is buoyant compared to both rock and the water that is found in the pore spaces of sedimentary rocks. Consequently naturally occurring CO_2 originating at depth in the geosphere tends to migrate upwards towards the earth`s surface.

As it migrates, it travels freely along permeable pathways within the rock succession.

There are examples of natural disasters in volcanic areas caused by sudden emission of large volumes of CO_2. However, the two worst recorded disasters were both associated with sudden emissions of CO_2 from volcanic crater lakes and are linked to a specific set of geographical features and geological processes that are highly unlikely to occur at or near engineered CO_2 storage sites. Crater lakes are perched at the top of volcanoes and are commonly almost surrounded by high crater walls. The lakes overflow down a spillway leading to a valley system. In tropical areas such lakes may be deep and still and the water column within them can become stratified as there is little seasonal mixing of the lake waters. CO_2 percolating through Crater

Lake floors can dissolve into the lower to CO_2. Once saturated, any disturbance that causes part of the lower lake waters to rise could cause CO_2 to come out of solution.

Dormant or extinct volcanoes can also contain crater lakes. Although they are not common, worldwide there are less than 20 such examples in North and South America, Europe, Africa, Indonesia, Australia and Japan(a few like those at Lake Nyos and Lake Monoun in Cameroon) have become saturated with CO_2.

The impacts of natural CO_2 emissions from underground on the biosphere are highly variable. They depend ultimately on the concentration of CO_2 that builds up in the soil and sub soils, atmosphere, sea bed or sea water. In many cases emissions at the ground surface are not a significant hazard to man because they are dispersed by the wind. However, CO_2 is heavier than air and , if not dispersed, it can be a significant hazard because it is an asphyxiant. Thus the main threat to man from CO_2 emissions from underground is where CO_2 is emitted in situations where it can build up to high concentrations, for example in buildings or in hollows in the ground.

These naturally occurring CO_2 emission sites of the world are used as a laboratory in order to select the geological CO_2 sequestration field. The significant reductions in anthropogenic carbon dioxide (CO_2) emissions which is green house gas that cause global warming, requires several parallel approaches, including more efficient energy use, reduction of reliance on fossil fuels, removal of CO_2 from the atmosphere (e.g. through cultivating biomass), and geological storage of co_2. Geological storage of CO_2 together with energy conservation and non-fossil fuel energy sources is thought to be the only way to stem the ongoing buildup of atmospheric CO_2 (IPCC, 2005; Broecker, 2007; 2008). Possible storage places for CO_2 are, among others, saline aquifers in deep onshore and offshore sedimentary formations, the deep oceans and in basalts, granitic and ultramafic rocks.

Thermal and non-thermal waters rich in carbonate are widespread on a global scale. They are particularly common in areas of volcanic activity, but are also found in seismically active zones devoid of volcanic activity. Further, CO_2-waters occur at the boundaries of volcanic geothermal systems and around active volcanoes. Carbon-dioxide emissions from active geothermal systems and active volcanoes are largely diffuse and not confined to fumaroles and hot spring emissions. Some CO_2-waters form by mixing of mantle-derived, magmatic or metamorphic CO_2 with ground or surface waters. In volcanic geothermal systems, CO_2-waters may form by condensation of CO2-containing vapor in perched aquifers or by mixing of downward percolating CO2-rich condensate with the deep primary geothermal fluid. Finally, CO2-waters may form by mixing of high temperature geothermal fluid that has not undergone fluid phase separation with cool ground water.

Wonchi system is one of the natural analogues which diffuses CO2 to the atmosphere; that can intern increase the green house gases in the global warming. The flux of CO2 to the atmosphere through different volcano tectonic structures are significant in this area; especially the Yerer tullu Welel volcano tectonic system which have different major faults cut across the study area. This major E-W trending regional structure contains several local faults such as Ambo-Wonchi-Butajira fault and Dedessa lineaments. Some local faults are also found in this area such as the NW-SE Ameya and Dariyan fault that cut across the crater Wonchi Crater Lake. So these structures are one of the major causes for the co2 flux in the area. There are different thermal and hypothermal springs which are associated to these structures.

The purpose of this study is to evaluate and develop the hydrogeochemical evolution of ground water and carbon dioxide-water-rock interaction. To identify the effect of co2 diffusion to the atmosphere one of the major green house gas that causes the global warming. To characterize the trace element mobility along the reaction flow path. The lithological significance on the source of co2 and hydrogeochemical evolution and the ground water quality of the study area

1.2. Statement of the problem

Now a day the increasing demand of using ground water for domestic purpose and other economic activities is the interest of the global Millennium Development Goal. In Ethiopia the need of bottling high land ground water is appreciably increasing. There fore the Natural sparkling and Mineral waters are commonly found in the Ambo, Wonchi and Woliso area. Many researches were conducted on hydrogeochemical evolution of ground waters of the study area. Thermal and cold ground waters distributed in the study area are highly gaseous and mineralized. Understanding the source of CO2 gas in this ground water is the point of interest of the present study. However, CO2-water-rock interaction in the study area was not understood deeply.

In the context of the present study the effect of CO2 influx to on the hydrogeochemical evolution of ground waters of this region studied by different parameters like raw isotope data, trace element data and conducting geochemical inverse modeling on the selected ground water samples classifies by HCA. The effect of these highly gaseous ground waters in terms of human health and environmental impact is presented in this study.

1.3. Objective

1.3.1. General objective

The general objective of this work is to assess the carbon dioxide-water-rock interaction and hydrogeochemical evolution of thermal and cold ground waters and the impact of co2 diffusion to the environment.

1.3.2. Specific objectives

- To identify the sources of carbon-dioxide and CO2-water-rock interaction**.**
- To determine the dominant hydrogeochemical evolution of thermal and cold ground waters
- To characterize the $\delta^{18}O$, δD, $\delta^{13}C$ isotopic composition of ground waters.
- To distinguish the effect of structures and lithology on the source of co2 and their control on geochemical evolution.
- To identify the major ions and trace element mobilization in ground water along flow path and
- To asses environmental and health impact of CO2 diffusion and trace element mobility from the area.
- To determine the dominant geochemical processes that influence ground water chemical composition.

1.4. Previous works

- Some previous studies were conducted on the study area on the hydrological, hydrogeoogical, hydrogeochemical, geological and structural evolution of the study area. While regarding the carbon dioxide- water-rock interaction of the study area little works were conducted.
- Among some review of existing previous work includes: **Tamiru Alemayehu (2006)** emphasizes thermal springs occurrences in Ambo as a result of cooling igneous chamber that formed Dandi and Wonchi crater lakes.

- Major ion composition of the ground water and surface water system and their geological and geochemical controls in the Ethiopian volcanic terrain addressed by **Tenalem Ayenew(2005),** his paper stresses the chemical composition of natural waters and the amount of species depends on several factors : geology , soil type, solubility of minerals of the rocks, land use land cover condition , residence time of water and chemical composition of the media in which the water passes reserved.
- **Lemmessa mekonta (2001)** has described hydrogeological controls in sand stone of Ambo area. He suggested that the major source of travertine is the dissolution of lime stone which overlain by the upper sand stone. Wonchi shield volcano top part is covered by ashy and tuff deposits and the base is marked by trachy- rhyolite he also indicated that there is good ground water resources at aresonable depth(Kassahun Beyene,2005),besides thermal spring around Wonchi is characterized by total dissolved solids.
- **Tamiu alemayehu and Seifu kebede(2006)** indicated that continuous supply of co2 is linked with degassing of the magma and decarbonation of deep Mesozoic sediments.more over the shallow magma chamber of Dandi and wonchi is responsible for the high temperature which induces fault controlled thermal springs, located along the structure that runs from Ambo to Woliso.
- **Ferdinand Herick (1983)** suggests that Adigrat sand stone is affected by tertiary tectonic activity and E-W running fractures take control of of the mineral water available between Ambo and Sankale being trapped in Adigrat sand stone. Travertine out crop is frequent in Ambo swimming pool and sankale with average thickness of 10-15 and 17m in those respective places. Co2 comes from deep following structural control and mixes with fresh water in Ambo sand stone aquifer its concentration is 4976mg/l before degasification. He concluded that co2 rich water of sodium bicarbonate type water in the sand stone is associated with tertiary or quaternary volcanic activity.
- **Seifu kebede,Tamiru Alamayehu,Tenalem Ayanew,Yves ,T., (2005**),the paper addresses ground water recharge,circulation and geochemical evolution in the source region of blue Nile river, Ethiopia. According to these researchers two major structurally deformed regions with distinct ground water circulation and evolution history were defined. One of which is the Yerer Tulu welel volcanic lineament zones (YTVL).they

indicated also co2 influx from deeper sources plays major role In controlling ground water chemical evolution of the high TDS NaHco3 in thermal ground water.

- **WWDSE(2004)** has conducted a study in thermal ground water resources potential asses ment of Negash Lodge compound. They emphasized on the geological, hydrogeological, and geophysical (vertical electrical sounding) investigation to determine depth to thermal ground water of the compound.
- **Kassahun Beyene(2005);**studied ground water resource evaluation of Walga river basin; showed ground water recharge and hydrochemistry of the basin; fluoride is one of the abundantly occurring anion found both in the cold and thermal ground water systems of the area, for example, Chitu cold springs has 19.6mg/l.
- **Abenezer Kefeni(2007)** has worked on hydrogeochemical evolution in the Ambo-Woliso area, He identified the hydrogeochemical evolution towards west and along the flow path there are at least two water types, high TDS NaHCO3 and fresh(low TDS) CaHCO3 water. Low PH and high electrical conductivity water is limited to Ambo thermal springs emerging sites, Wonchi and Woliso which are connected by NNW and SSE structures. The low PH is attributed to high co2 supply from Mesozoic decabonation and Dandi-Wonchi related magma chamber degassing. Travertine and silica sinter deposits are encountered in the area where thermal springs are outpoured, the deposits occur owing to drop in temperature, pressure and mixing of thermal springs with fresh water coming from the high attitude ridges. Generally ionic evolution is highly affected by geological condition and deep seating structures.
- **Berhanu Gizaw(1996).** The origin of the high bicarbonate and fluoride concentrations in waters of the main rift valley, East African Rift system. In this paper it was mentioned that NaHCO3 and F are high and the PH is near neutral. The high HCO3 is attributed to co2 out gassing; high fluoride is attributed to the acid volcanic, low Ca and geothermal heat. Evaporative concentration is responsible for the increment of the salinity of the lakes in closed basins.
- **K. Yoshimura; et.al.,(2004)** Deep source CO2 in natural waters and its role in extensive tufa deposition in the Huanglong Ravines,Sichuan, China; they pointed out that The spring water contains high concentrations of CO2 supplied via faults: the resulting high

concentration of dissolved CO2 gives rise to much greater dissolution of carbonate rocks than is usual in karst springs and also to the dissolution of silicate rocks.

- **William C. Evans et al;(2002)** : Tracing and quantifying magmatic carbon discharge in cold ground waters: lessons learned from Mammoth Mountain, USA; The total water flow from all sampled cold springs was v1.8U107 m3/yr draining an area that receives an estimated 2.5U107 m3/yr of recharge, suggesting that sample coverage of the groundwater system was essentially complete. Some of the waters contain magmatic helium with 3He/4He ratios as high as 4.5 times the atmospheric ratio, and a magmatic component in the dissolved inorganic carbon (DIC) can be identified in virtually every feature sampled.
- **Tsegaye Abebe et al.,(1998)**. the Yerer –Tullu Wellel volcano tectonic lineament: a transtensional structure in central Ethiopia and the associated magmatic activity: He mentioned that an east-west trending structure in central Ethiopia, the Yerer Tullu-Welel vocanotectonic lineament, intersects the main Ethiopian Rift and lies between latitudes 8^{0}20`N and $9^{0}$05`N. Along this structures there are several central volcanoes concentrated along the latitude of 8^{0}45`N. the central volcanoes are usually located at the intersections of the above described fracture system.
- **Therese K. Flaathen, et al.,2009**. **Chemical evolution of the Mt. Hekla, Iceland, ground waters; A natural analogue for CO2 sequestration:** The chemical composition of the groundwater surrounding the Mt. Hekla volcano in south Iceland was performed to assess fluid evolution and toxic metal mobility during CO2-rich fluid basalt interaction. These fluids provide a natural analogue for evaluating the consequences of CO2 sequestration in basalt. The concentration of dissolved inorganic carbon in these ground waters decrease from 3.88 to 0.746 mmol/kg with increasing basalt dissolution while the pH increases from 6.9 to 9.2.
- **Y.K. Kharaka et al.,2006;** Gas-water-rock interactions in Frio Formation following CO2 injection: Implications for the storage of greenhouse gases in sedimentary basins: He mentioned that Dissolution of minerals, especially iron oxyhydroxides, could mobilize toxic trace metals and, where residual oil or suitable organics are present, the injected CO2 could also mobilize toxic organic compounds. Environmental impacts could be major if large brine volumes with mobilized toxic metals and organics migrated into potable groundwater.

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- **Omer Izgec et al;2007**: **CO_2 injection into saline carbonate aquifer formations: laboratory investigation;** This study presents the results of computerized tomography (CT) monitored laboratory experiments to analyze permeability and porosity changes as well as to characterize relevant chemical reactions associated with injection and storage of CO_2 in carbonate formations. CT monitored experiments are designed to model fast near well bore flow and slow reservoir flows.
- **Yang Fang et al .,2010: Characteristics of CO_2 sequestration in saline aquifers ;** Storage of CO_2 in saline aquifers is a viable option for reducing the amount of CO_2 released to the atmosphere. This paper provides an overall review of CO_2 sequestration in saline aquifers. First, the principles of CO_2 sequestration are presented; including CO_2 phase behavior, CO_2-water-rock interaction, and CO_2 trapping mechanisms. The storage capacity and CO_2 injectivity are discussed as the main determinants of the storage potential of saline aquifers.
- **Elizabeth H. Keating., et al 2009**. The impact of CO_2 on shallow groundwater chemistry: observations at a natural analog site and implications for carbon sequestration; the paper mentioned that Despite relatively high levels of dissolved CO_2, originating from depth and producing geysering at one well, pH depression and consequent trace element mobility are relatively minor effects due to the buffering capacity of the aquifer. However, local contamination due to influx of brackish waters in a subset of wells is significant. Geochemical modeling of major ion concentrations suggests that high alkalinity and carbonate mineral dissolution buffers pH changes due to CO_2 influx.
- **Martin-Del Pozzo,A.L. et al., 2002**.spring water and co2 interaction at Popocatepetl volcano, Mexico; He reported that the magma provides CO_2-rich fluids into the water system controlled by meteoric recharge. The P_{co2} in equilibrium with the springs is two to four orders of magnitude higher than air saturated water.
- **Nunzia Volatattorni**.,etal. Study of co2 natural emission in different Italian geological Scenarios: a refinement of natural hazard and risk assessment; he mentioned that the solfatara crater is characterized by intense and diffusive fumaroles and hydrothermal activity geochemical surveys in this area, reveal the presence of co2 content in ground water.

- **Pauline Humez et al.,2010**. CO2 leakage up from a geological storage site to shallow fresh groundwater: CO2-water-rock interaction assessment and development of sensitive monitoring; he mentioned that A modeling study of the geochemical impact on fresh ground waters of the ingress of CO2 during geological storage was conducted. The 3D model includes (i) storage saline aquifer, (ii) impacted overlying aquifer containing freshwater and (iii) a leakage path way up through an abandoned well represented as 1D porous medium and corresponding to the cement-rock formation interface. This model was used to simulate the supercritical CO2 migration path and the interaction between the fluid and the host rock.
- **W.J.J. Huijgen & R.N.J. Comans,2003., Carbon dioxide sequestration by mineral carbonation:**they mentioned that the so-called "mineral CO_2 sequestration" route in which CO_2 is chemically stored in solid carbonates by the carbonation of minerals. As mineral feedstock, rocks that are rich in alkaline earth silicates can be used. Examples are olivine ($MgSiO_4$) and wollastonite ($CaSiO_3$).

CHAPTER TWO

SITE CHARACTERIZATION

2.1. Description of the study area

The Wonchi system is located in the adjacent North western Ethiopian plateau. The area is enclosed in three major basins such as Abay, Awash and Gibe basin. There are two major asphalt roads that passes through this study area are Addis Ababa to Jimma and the Addis Ababa to Wollega . Another local gravel roads are Ginchi to Tullu Bolo , Ambo to Wonchi crater lake and to Woliso.

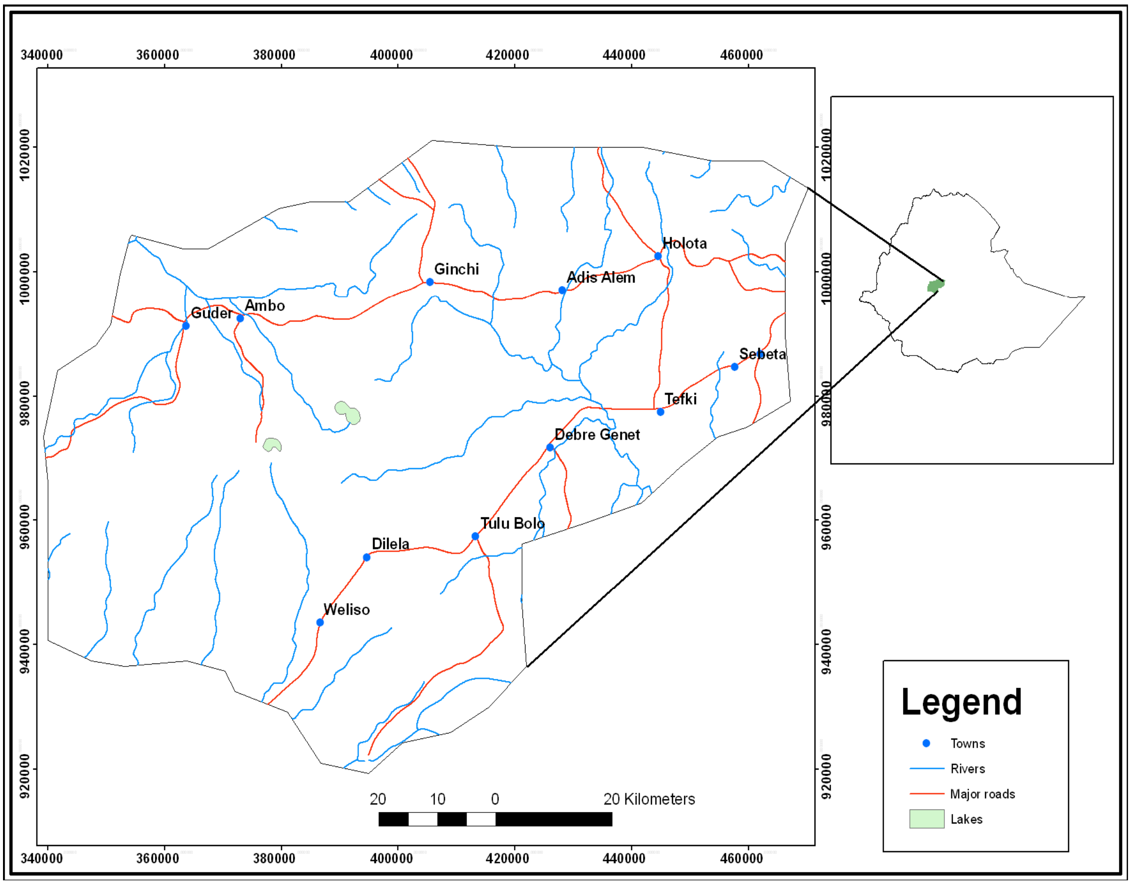

Figure 2-1 location map of the study area

2.2. Physiography

The physiography of the study area consists of various high rugged mountains such as Jibat-Mecha escarpment, Wonchi and Dandi volcanic centers and Gorfo Mountain of basaltic cliff and

Ambo -Gedo escarpments. The well known Becho plain is found in the Awash basin which is enclosed in the system. The areas around Wonchi Crater Lake are highly disturbed by rugged topography especially near Altufa village. The deep gorges, incised river valleys, and rolling plains are a specific feature of the study area.

The prominent Awash River starts from the Ambo lineaments, at the base of Herer Kura ridge near Ginchi town. The major perennial streams are Huluka River emerge as out late from Dandi crater lake and Dabis River source is Gara Ola at the north part of the study area are the tributaries of Guder River which as a sub basin of the Abay basin. Walga river is sub-catchment of gibe basin and Jalewan River its source is Goro Wonchi and Goro Dandi ridge chain, southern ridge of the study area as the tributary of Awash. More over lake Wonchi and Dandi and are one of important drainage element together with numerous fracture controlled cold spring and hot spring of Ambo and Woliso. Dendritic, parallel and radial drainage patterns are attributed to topographic setting which is characterized by abrupt slope change, dissected gullies and gorges in association with various volcanic land forms that are modified by geological events.

The physical conditions in altitude have resulted in a slight diversity of climate, soil, vegetation and impressing scene of topography, shaped by volcanic activity together with recent sedimentary processes.

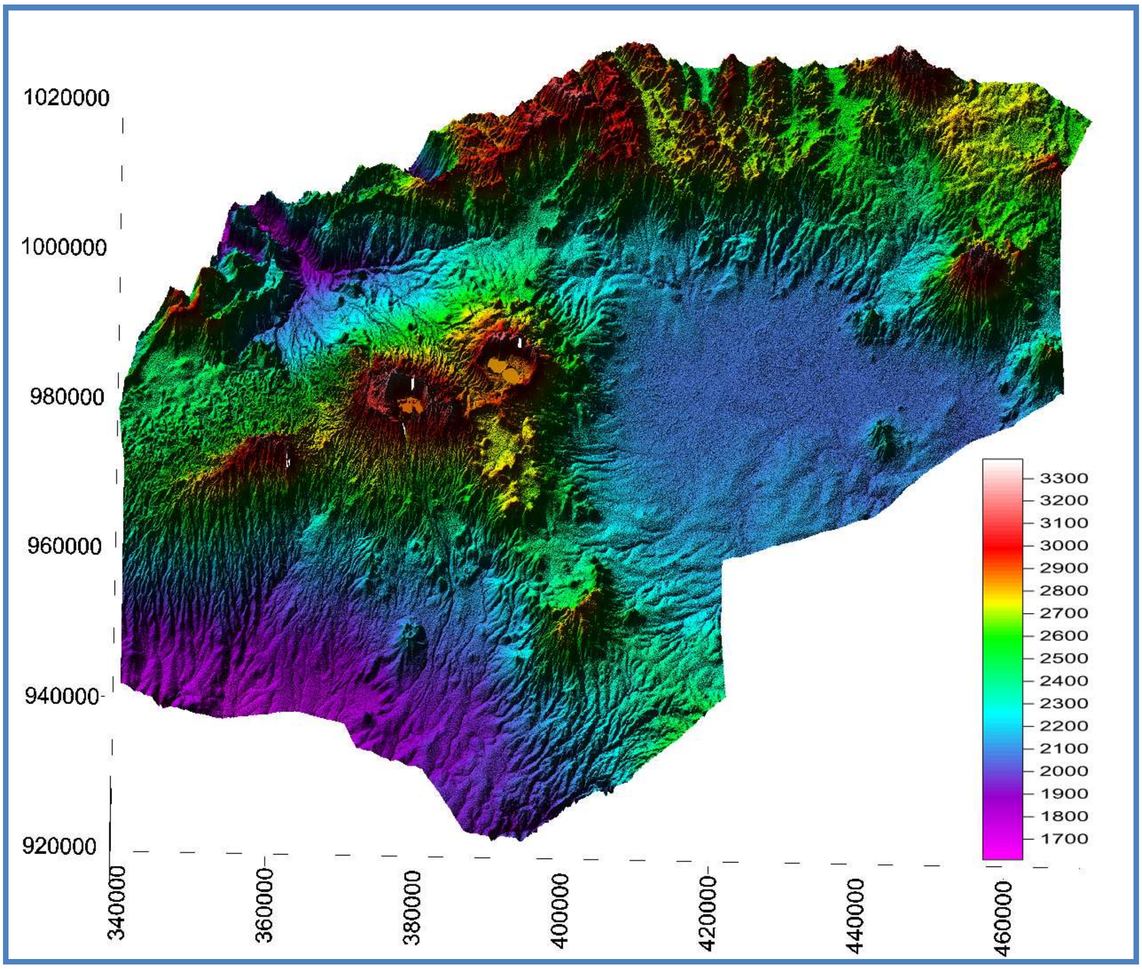

Fig: 2.2. Physiography of the study area.

2.3. Land use land cover

Traditional farming is one of the major activities to generate income among the rural inhabitants; the land s intensively cultivated by the indigenous people for production of subsistence crops like Teff, maize, cheek beans, peas, wheat, corn, barley, ensate, some oil crops ,etc. small scale irrigation is practiced in some areas such as Bukisa, Wodessa from Homi springs Awaro from Chancho spring. The crop produced here is significantly contributed to the demand of the country while stock breeding is another important activity besides crop production.

Because of ever increasing population size traditional farming is advancing at the expense of deforestation; as a result hillsides, mountains and plain land are stripped of their forest and grasses. Taking advantages of this erosion is also washing away most fertile soils out of the area from all direction every year.

Based on conducive climate; bush, shrubs, big trees and grasses used to cover most part of the study area. Unlike past days the vegetation density is too little if there is any spared remnant forest along the hillside of few streams and Chillimo forest (protected by Farm Africa), even these are average of fading due to all round problems such as, replacement by eucalyptus tree which sold for a good amount of money, unlimited farmland expansion, burning of charcoal etc. Generally, unwise natural resource utilization and mismanagement is endangering and complicating the ecosystem.

The towns include Ambo, Ginchi, Meti, Guder, Olenkomi,Menagesha and Asgori are located in the northern part while woliso, Dilella, Tulubolo, Busa and Asgori are the southern periphery in the town people led diversified livelihood.

From infrastructural point of view there is no as such prominent factory except that of Ambo Mineral water factory, Hometcho ammunition and chemical engineering factory, Senkele lime factory and Ambo sand stone quarry that is used for construction purpose.

2.4. Geology

2.4.1. Regional geology

The geologic units of Ethiopia fall into three major lithologic categories. They are Precambrian basement rocks, Mesozoic sedimentary rocks (late Paleozoic to early tertiary) and Cenozoic volcanic rocks.

Regional tectonic activity associated with rifting events in the Red sea, Gulf of Aden and East African rift valley during the late tertiary caused faulting and fracturing together with wide spread volcanism. Vast quantities of basaltic lava were extruded over the western half of Ethiopia. This was accompanied by ash and coarser tephra forming a sequence known as the Trap series.

The basement rocks are relatively impermeable and thus water resources are in general only associated with fracturing and faulting resulting from rift development. For much of the early Paleozoic, Ethiopia was in a state of steady uplift, which caused wide spread erosion in most parts of the country. Subsidence followed in the Mesozoic with a large shallow sea spreading initially over the Ogaden province eventually extending further north and west as the land continued to subside. Generally uplift and drying out of lake beds to leave gypsum followed this sequence and anhydrite precipitates.

Quaternary deposits are mainly confined to those associated with large depression and lakes. Seismic and volcanic activity continues today along the Ethiopian Rift valley system, manifestation of thermal springs are related this events. Mesozoic lime stone, dolomitic and marl deposits in western and northern Ethiopia occur in Tigray, in the Danakil Alps and the Blue Nile (Abay) valley. Equivalent to Addigrat sand stone outcrops of Mesozoic liming materials occur in the central plateau area near Ambo town, in Dedessa valley (Kazmin 1972).

Geologically, Ethiopia lies at the northern of the continental part of the Eastern Rift. Voluminous piles of mainly tertiary volcanic rocks occupy large parts of the country along the Rift valley. Proterozoic rocks occur in western Ethiopia, and Mesozoic and Tertiary rocks underlie most of the eastern part of the country. The floor of the rift valley is filled with relatively young lacustrine sediments and volcanic. Several alkaline plugs are known form Ethiopia, for instance volcanic plugs around Wonchi and Dandi are typical example in the study area.

The regional geological map of Ethiopia recognizes the study area as one unit, early tertiary volcanic. Normally, two major rocks found as outcrops in the study area: sedimentary rocks and igneous rocks. The Mesozoic sedimentary succession boundary is limited to the northwestern part of the study area around Ambo town. The Adigrat equivalent upper Ambo sand stone is one of the major Mesozoic formations exposed as out crops in the area. One can encounter gray colored sand stone on the way from Ambo to Wedessa along the bank of Dabis River and extends beyond towards north it is intercalated with variegated shale. The colorful sand stone is exposed west of the town near the Ambo Agricultural College. These localley exposed sedimentary sequences are due to erosion and faulting effect; Tsegaye Abebe, F, Innocenti (1998).

The north western tip is marginalized by the Adigrat sand stone formations, which belongs to the lower sand stone, formed during Mesozoic as a result of regression and transgression episodes.

Overall, the plateau volcanic exhibits upper Oligocene-Lower Miocene ages, corresponding to the phase of higher effusion rate that has been regionally recognized (Mohr and Zanettin,1988);the age distribution of products of the upper volcanic sequence (Miller and Mohr,1966;Morton et al.,1979;Berhe et al.,1987;woldeggabriel et al.,1990) bimodal volcanic products, basaltic and rhyolitic formed the western central plateau of Ethiopia, Bekele Abebe,Mario Boccaletti, et al(1998). Dandi and Wonchi volcanic canters are shoulder of Ethiopian rift western escarpment having general trend east west in parallel with Ambo fault belt.

2.4.2. Geology of study area

The following units are the local geologic units of the study area.

- Adigrat sand stone
- Amba alaji rhyolite
- Tarmaber scoraceous basalt
- Tertiary trachyte
- Tertiary ignimbrite
- Quaternary basalt

2.4.2.1. Quaternary basalt

This unit is found as a ring surrounding Woliso and Ambo characterized by volcanic plugs that extruded through it forming different volcanic edifices. Weathering effect has played role in disintegrating and breaking in to pieces the upper part which exposed to the atmosphere at stream cuts, road cuts, and quarries and erosion uncover areas. For instance basaltic boulders in Debis stream, Aleltu stream and Huluka stream exhibits denser vesicles in the upper than the lower of the rocks. The exposure of this unit is not limited to those site rather one can see them all around the way Ambo to Ginchi and to Woliso.

It is affected by lineaments that are oriented in different direction such as NW-SE, W-E and NE-SW these in turn shaped the morphology and controlled the streams patterns by interfering with each other. At macroscopic scale two type of texture is observable: aphanitic (fine grained textures) and porphyritic texture (course grained) the latter is dominated by vesicles and phenocryst minerals such as olivine and plagioclase.

2.4.2.2. Alaji Rhyolite

It characterize the north west border of the area around Ambo fault belt being confirmed in between Ambo-Woliso quaternary basalt in the south and blue Nile basalt in the northern margin its west ward extension is interrupted by Adigrat sand stone they pinch out within each other.

This unit has formed steep slope and easily transported being aided by running water and gravity, it is commonly found at the base of Ambo fault belt cliffs in association with others .Weathering effect has induced fragmentation, filling, cracks and slightly developing joints and other growing structures.

2.4.2.3. Tarmaber scoraceous basalt

Tarmaber scoraceous basalt is found in the east part of the area. It also extends towards the east outside the area; it becomes wider as it advances towards the east. The lithology occupies the slope of the Ambo fault belts and most of the plugs created hills adjacent to the lineament swallowed by scoraceous materials. Some scoria cones are also found around northen side of Woliso town near Obi and Kudurus villages. Scoria mounds are part of the Yerer-Tullu-Welel volcano tectonic lineaments (Abebe, 1998).scoria shows dark-brown color and vesicular in texture. Some of the vesicles are filled with quartz minerals, which shows later invasion of hydrothermal activity. In some deep bore holes like Negash lodge ,IIRO-WCV, Lions Club and daughters of Mercy bore holes, pumice and ignimbrite rocks are found which are not exposed on the surface.

2.4.2.4. Tertiary trachyte

The source of this lithology is part of the prominent volcanic centre peaks, Dandi and wonchi volcanic centers. The formation is limited to the central part of the study area, it appears that the flow took place to all direction just making those high points as a centre in all direction bordered by the quaternary basalt. In the north east and south part circled by the quaternary basalt.

Starting from the peak of Dandi and Wonchi Mountains it spread away forming slopping land escapes to all direction, exposed along the streams, roads and geological lineaments. Mostly the outcropped one is subjected to weathering, differentiated by dense fractures through which water easily percolate and enhance more weakness, for instance the numerous springs emerging from the mountains chain take advantage of the well developed openings.

The formation is visible along Qerensa stream and its adjacent ridges such as chefe qerensa, Boda hills, Golja ,Golole are typically sites where this unit can be seen to the extent it has suffered weathering by different means like plant roots intensive and heavy orographic controlled rain fall.

The orientation of this unit is north east southwest around Dandi mountains though this does not mean that it is identical thoroughly because there are various lineaments oriented in different directions.The major traceable structure located in between Wonchi and Dandi lake just parallel to Huluka stream that begins from the Dandi crater lake as an out let.

2.4.2.5. Tertiary ignimbrite

The tertiary ignimbrite covers the almost the whole Becho plain, just located east of Dandi mountain. This lithology is usually not visible rather covered by soil. But many bore holes logs that are dug for water supply and other purpose bear witness that the immediate underlying unit below the top soil is ignimbrite.

2.4.2.6. Adigrat sand stone

Adigrat sand stone of Mesozoic sediment is found in Ambo area. It includes various colored sand stones, the naturally decorated; known by the name Ambo sand stone is classical example which possesses fine to medium grained intact texture, relatively resistant to weathering. In construction it is preferred for its dual purpose; beauty and durability. There is also intercalation of other sedimentary unit in association with the sand stone for instance north of Dabis river variegated cone shaped shale is typical example.

At the southern adjacent of this formation there is noticeable Alkali trachyte and subordinate basalt, at this point the quaternary basalt, tertiary trachyte and sand stone confront and merge to each other; the lithologies are mixed as result of baking, cementing and lithification.

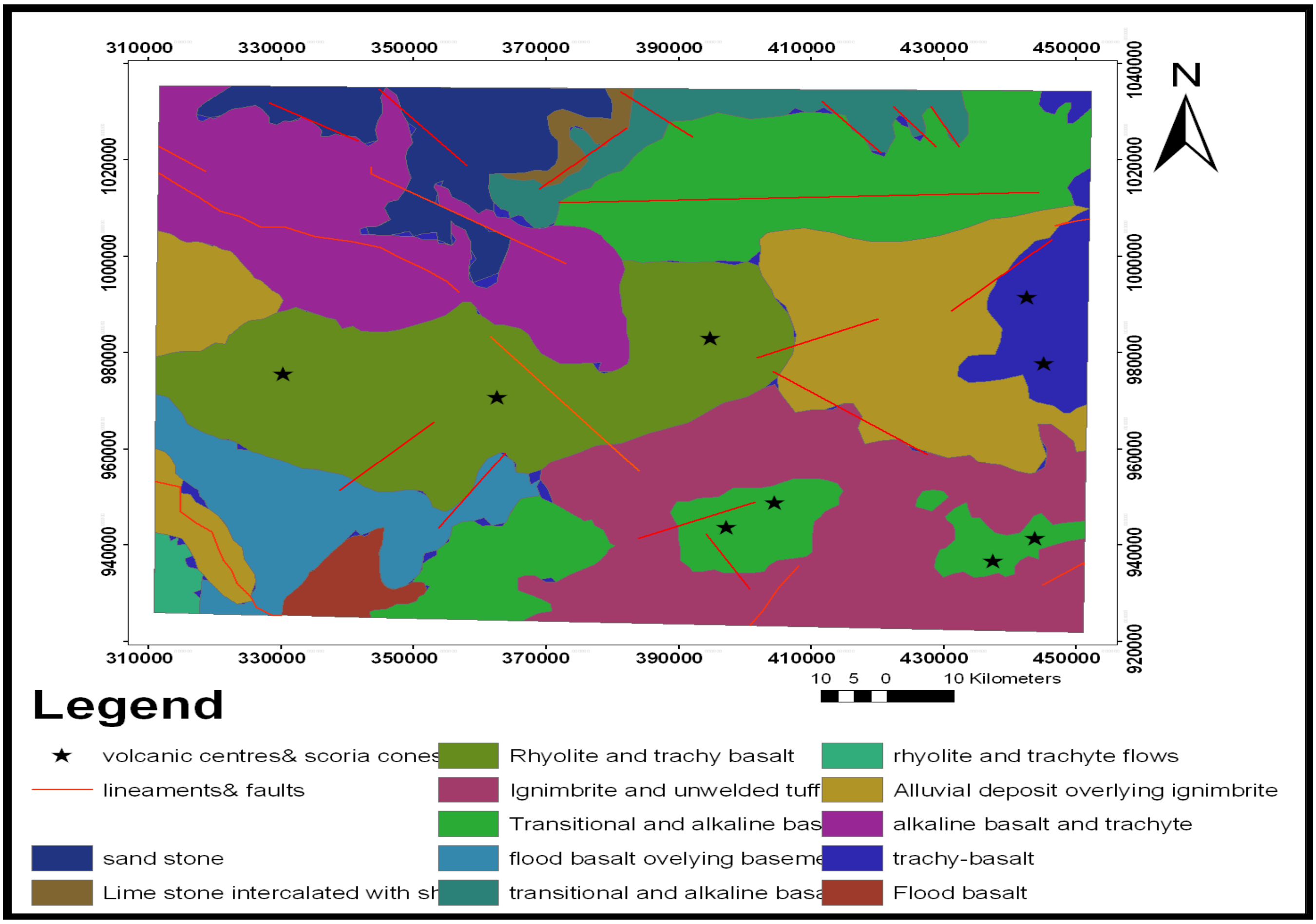

Figure: 2.3. Geology of the study area

2.5. Volcano tectonic lineament

There is the prominent tectonically deformed region that crosses the study area. This is the Yerer Tullu Welel volcanic lineament zone (YTVL) .The YTVL is an east–west trending zone that has a length of 800 km and a diameter of 80 km. The YTVL is a kind of half graben bounded by the Ambo fault from the north (Abebe et al., 1998). The Ambo fault has a throw of about 500 m. The major lineaments in the YTVL zone are the Didesa Lineament (DL) and the Ambo-Butajira Lineament (ABL). These lineaments are deep faults that cut across the YTVL. Along the YTVL, 3 main rock successions crop out: the Precambrian basement, the Mesozoic sedimentary rocks, and the Cenozoic volcanics. The volcanics are predominant whereas the basement and the sedimentary rocks are locally exposed. The sedimentary rocks (sand stones and lime stones) thin out towards the southern part of YTVL. The Quaternary volcanic which cover the YTVL are mainly rhyolites and trachytes with abundant alkali–feldspars, alkali amphiboles and quartz. Faulting in the YTVL (the Ambo fault and associated lineaments) for instance juxtaposes the Mesozoic sediments and the volcanic cover favoring the formation of high discharge, low temperature thermal springs in the region.

Two sequences have been recognized in the volcanic succession. The lower volcanic sequences, exposed mainly in the western and central areas, consist of flood basalts with associated trachyte to phonolite domes and necks. It is strongly eroded and dissected by faulting, and locally it is unconformably covered by the products of the upper sequence. The lower volcanic sequence (Oligocene-lower Miocene; is considered to belong to the uplifted Ethiopian volcanic plateau (EVP), however, its products are down thrown by about 500m with respect the EVP regional erosional surface (2700m), as shown in the north-northeast-south-southwest sectional across the YTVL between Ambo and Addis Ababa.

The upper volcanic sequence, which is late Miocene to recent in age, consists mainly of several central volcanoes and associated small domes and cones, all of which are roughly aligned east-west. A gap in the spatial distribution of volcanic canters is present between the Dedessa River and Tullu Welel. Geothermal springs are roughly aligned NW-SE along the Ambo-Wenchi-Butajira lineament.

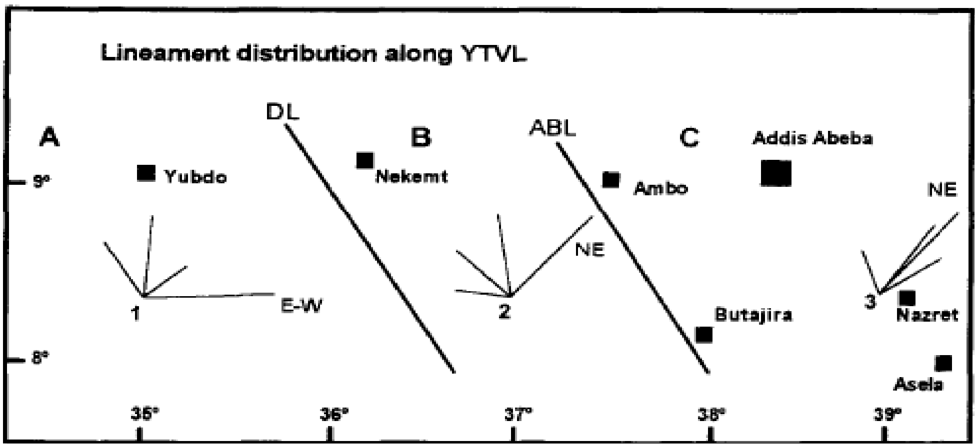

Fig: 2.4. Lineament distribution along the YTVL. Bars represent the azimuthal peaks. The longer the bar the more important the peak; DL Dedesa line, ABL Ambo-Butajira-Line, A, B and C are the labels of areas with different trend assemblages from West- East (modified after Tsegaye Abebe et al., 1998)

2.6. Hydrology

2.6.1. Rainfall

Rainfall in Ethiopia is controlled primarily by monsoon winds either from the Atlantic or from the Indian oceans depending on the season (Griffiths, 1972; Lacaux *et al.*, 1992; figure). Seventy five percent of annual rainfall on the NWP and in the MER occurs during the summer (June-September) when the Inter-Tropical Convergence Zone (ITCZ) is located north of Ethiopia (Nicholson, 1996). During this period, the Indian and the Atlantic Ocean monsoons converge in the ITCZ. The Atlantic monsoon is also believed to rely on moisture advection from the tropical vegetation basin of Congo through the southwesterly low-level moisture flow (Kebede, 1964; Shinoda, 1986). The other 25% of rainfall occurs in spring (March-April) when the ITCZ passes southwards. During this period, the north Indian Ocean is believed to be the main source of moisture. During the rest of the year (October-February), the climate is characterized by prevailing dry and relatively cold weather. The mean annual air temperature of the NWP is 16°C compared to 35°C in the Afar. The annual rainfall in NWP ranges between 1000mm and 2000mm. In Afar rainfall amount is less than 300 mm/year. Rainfall amount in the MER is intermediate between the NWP and the Afar.

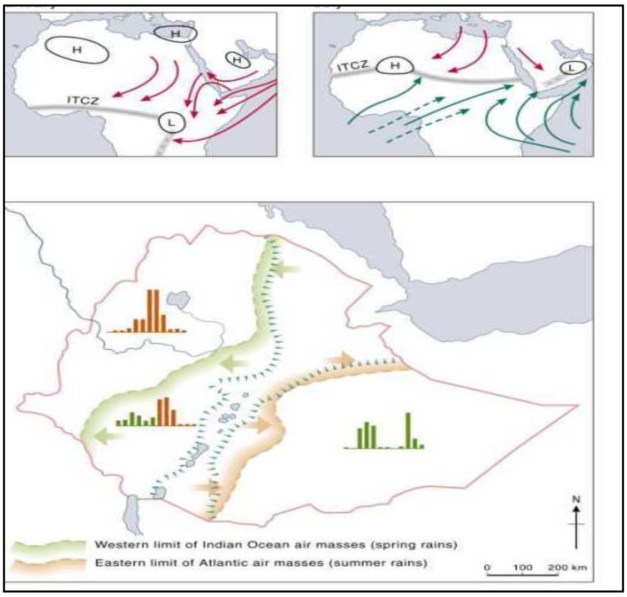

Figure: 2.5. Seasonal drifting of the ITCZ over Africa and its control on the rainfall regime of Ethiopia, modified from Lacaux et al.,1992.

The study area is known as the central plateau, its relief is very essential in controlling the climatological condition. Considerable rainfall is received in the west central part due to High Point Mountains that poses

Two prominent climatical conditions prevail in the study area: wet season (June to September) and dry season October to May with slight Belg rainfall from April and May. precipitation, sunshine duration, relative humidity, evaporation, wind speed and temperature data are obtained from Ethiopian Metrology Service Agency. To characterize the hydrologic property of the area different stations of the study area such as: Ambo, Woliso, Asgori, Ginchi, Tulu Bollo, Busa and Olenkomi are used.

months	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean
Mean catchment temperature	18.1	19.1	19.4	19.6	19.2	18.1	17.2	17.3	17.3	17.2	17.4	17.3	18.1^{0}C
Mean relative humidity (%)	50.4	44.3	50.5	54	56.7	71.7	78	79.4	76.1	57.6	48	47.8	59.57%
Catchment mean wind speed	3.0	3.1	2.6	2.4	1.8	1.2	1.0	0.9	1.1	2.2	2.9	3.3	-
Average sunshine hours	8.6	9.5	7.8	7.0	7.7	5.7	4.6	3.6	4.4	7.3	9.2	9.7	-

Table: 2.1. Mean catchment temperature, relative humidity, mean wind speed and sun shine hours.

Station	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total(mm)
TuluBolo	18.3	18.6	54.2	67.8	78.4	192.9	287.5	277.7	90.6	24.6	7.4	7	1125
Asgori	18.5	32.8	53.6	83.6	67.9	128.1	242.5	239.4	102.2	25.7	6.9	5.3	1006.5
Woliso	23.9	27.4	66.5	84.8	122.8	190.9	271.9	257.3	130.5	40.4	7.6	5.3	1229.3
Busa	21.3	59	55.9	73.7	84.4	179.8	358.2	372.5	164.9	43	10	9.1	1431.8
Wolonkomi	22.8	29.2	66.1	72.4	77.9	154.4	240	234.4	133.7	36	12.2	6.6	1085.7
Ambo	31.87	15.27	52.76	74.65	73.18	149.87	177.2	163.2	87.71	45.83	9.22	11.3	892.09
Ginchi	33.9077	65.93	84.38	105.1	87.46	148.68	238.7	224.3	150.6	32.04	4	16	1191.19
Arthimetic mean	24.37	35.46	61.92	80.3	84.58	163.52	259.4	252.7	122.9	35.37	8.19	8.66	1137.38

Table: 2.2. Arithmetic mean rainfall of the study area annual mean is 1137.38mm

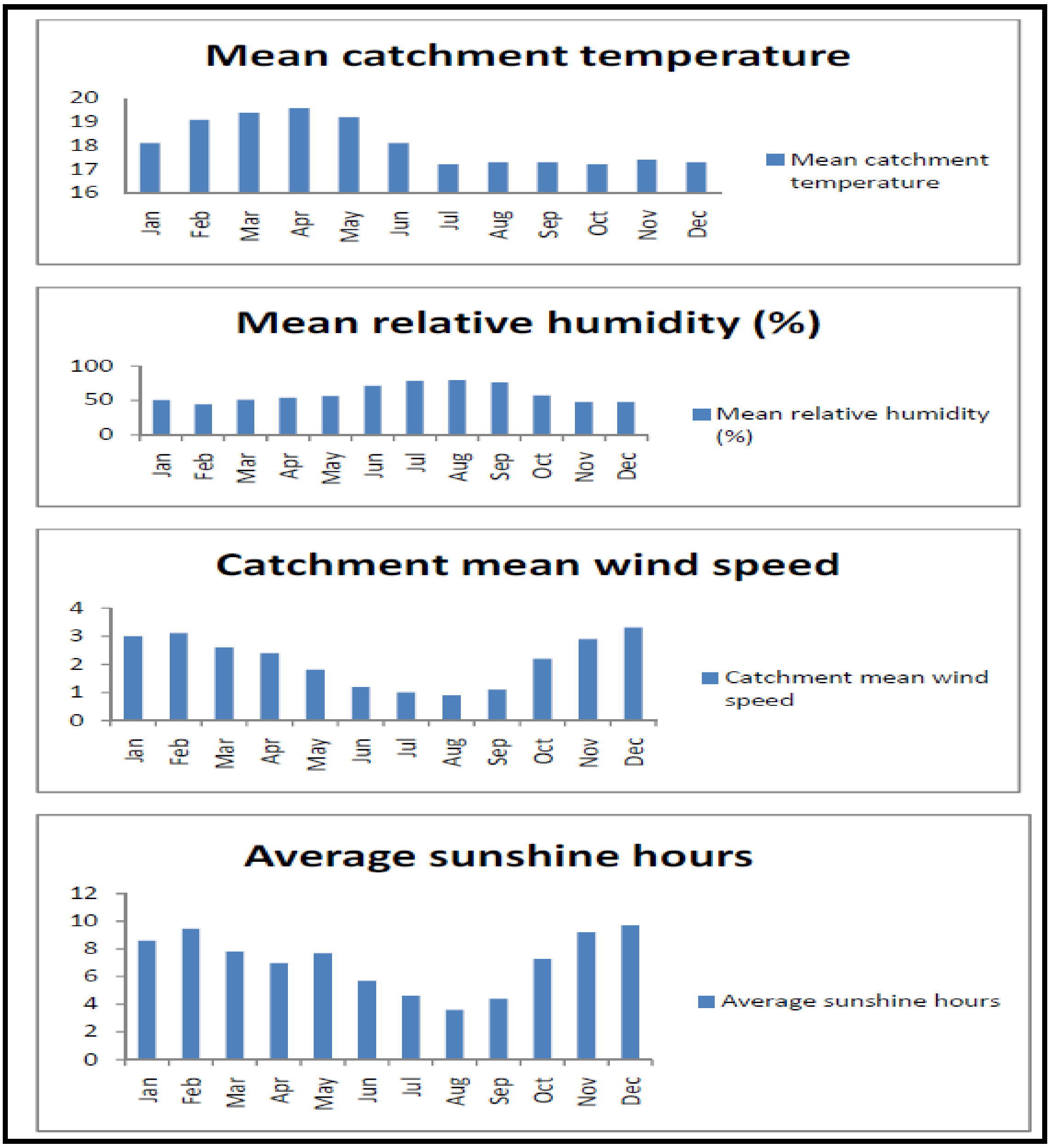

Figure: 2.6. mean catchment temperature, wind speed, relative humidity and sun shine hours

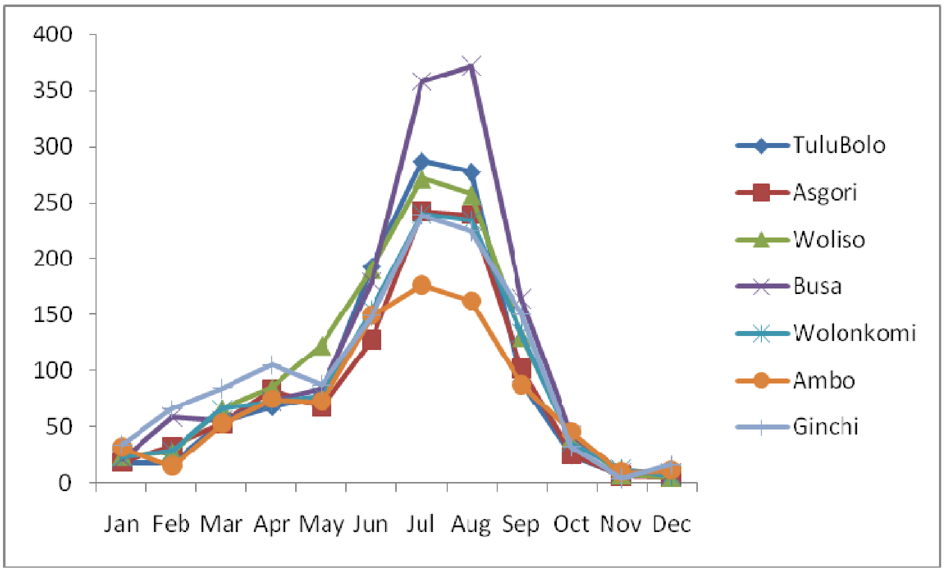

Figure: 2.7. precipitation range of different satations in months of the year

2.6.2. Surface Hydrology

Surface hydrology refers to general surface water bodies that may occur in the form of streams, lakes, ocean, sea, ponds, etc. Generally, surface water can be obtained from precipitation, groundwater out flow, irrigation water and other artificially induced source.

2.6.2.1. Streams

Surface water condition in the study area includes streams and lakes. Several perennial and intermittent streams emerge from ridges located in the north and south just parallel to the regional structure, Ambo fault belt. It is clearly seen that geological structures are the main drainage controlling physical features. Some of major perennial streams in the study area include: Huluqa, Jalewean, Qernsa, Dabis, Aleletu, Awash and Walga. In the rainy season the intermittent streams themselves carry huge volume of water. Presence of intensive faulting contributed for the emergences of numerous cold springs and thermal springs, besides it has enhanced occurrence of groundwater. In east of the Dandi volcanic cones, Becho plain receives storms of run off; Awash and Jelewan Rivers are the main draining system huge water from the upper slopes through the Becho plain.

Both streams Huluka and Debis drain to Abay basin. Huluka is from the Dandi Lake as out let while that of Debis is from the ambo fault belt foot; it share the same surface water divide with that of Awash River, which begins from Herar Kura village. Debis accommodates more discharge than Huluka this can be linked with geology, length, width and morphology of the streams. Geology may affect stream in a way that facilitating infiltration or overland flow structural control may play key role too. For both streams, Debis and Huluka the peak month is attained during August, which implies they experience relatively identical rainy Seasons.

Jemjem makes up the upper Awash together with the initial source of the stream located at west of Ginchi on the Chilimo Herarkura range. It may be responsible in recharging Gaji hills from which foots Berodo spring emerges between Holonkomi and Ginchi. Moreover the streams merge with Awash before it reaches Becho plane, and make up the very upper awash as Perennial River and continues to Somalia drenching Ethiopian rift. The upper Awash is responsible for flooding of Becho plane where many people suffer displacement especially if the season is accompanied by heavy rain.

In rainy time the streams are overloaded with vast sediments that brought by gullies as overland flow washing away from the adjacent slopes, for instance streams joining Awash River leave some of their burden on Becho plane. Huluka and other streams flowing to Abay basin also carry a lot of soil taken from stripped lands, once covered lands by vegetation and grasses become naked and washable at ease. Huluka river is treated and used for the Ambo town water supply.

2.6.2.2. Lake

Dandi and Wonchi crater Lakes are other important surface water resources in the area. The origin of these Lakes is linked with volcanic centers oriented East-West. They are fresh and the only central highland far west rift escarpment lakes located at high point (>300m.a.s). Dandi is an 8 km wide caldera in central Ethiopia, quite close to Wonchi caldera. Dandi's rim is made of poorly consolidated ash deposits. The broad flat floor contains two shallow crater lakes. Wonchi contains a single crater lake about 450 meters below the rim of the volcano. Passage into the caldera floor is via a narrow gash worn through the caldera rim by a small stream. Flooding of the lake at that time may have been due to an underwater eruption that raised the lake level, killing many trees on the previous shore. Wonchi's caldera is as much as 900 meters deep, and lake itself could be as deep as 400 meters.

Now a day Wonchi Lake has got more recognition than Dandi, located east of it. Tourists are visiting; development work is on going around the lake. Population density is ever increasing and put a pressure on existing natural resource including the Lake. However besides any kind of resource utilization proper attention should be given to the ecological balance where by resource sustainability can be ensured. Professional designed plan is essential to prolong the resource from any kind of spoil such as contamination that potentially alters the chemistry and its aesthetic value even disappearance. Obviously, it is our recent memory that Ethiopia rift Lake are retreating and drying as a result of limitless interference and lack of proper management. Such problem is not limited to a given area and society rather poses impact everywhere as long as interaction is there. Hence it is advisable to take wise measures and feel responsibility during resource utilization.

2.6.2.3. Springs

Springs in hydrogeology represents out flowing of groundwater from the saturated zones as a result of hydraulic head difference between recharge zone and discharge zone here the driving force will be gravitational energy this holds true for cold springs. Point of groundwater table intersection with the surface is known as eye of spring or the contact point between the atmosphere and the emerging water.

In case of thermal spring the driving force is association of geothermal gradient and/or cooling igneous chamber. The thermal springs are manifested in response to high energy developed from boiling of water in the crust. Cold water circulating beneath may come in contact with hot magma chamber or gain heat from geothermal gradient increment with depth. Heated water forces its way upward following defined routes such as faults and fractures.

Numerous, springs emerging from the ridges are remarkably fresh water resources of the area. There are several springs, occur taking advantage of structures, contacts and topography. A considerable yield springs flows out of Dandi-Wonchi mountain range. Those springs flowing to the east at the foot of Dandi Crater Lake appear as depression springs, OAO spring at Tulubolo, Bashi springs in between Busa and Boda together with springs in Becho plain are examples of topographical controlled springs.

Most springs are flowing toward North from the volcanic center aligned E-W and to the south from the Ambo lineament oriented parallel to the volcanic centers. Springs merge to each other to form perennial streams, for instance structure controlled Qerensa stream is just a spring which source is below Goro Dandi on the way before it joins upper Awash near Ginchi more springs for example Arbu, Shone, Molche, Koromi, ect flow to it. Shone at central part, Hora Chancho east of Ambo at Awaro, Homi at foot of ambo fault belt in wodesa are cold spring governed by localized and time to time propagating fractures, the mentioned springs clearly seen that their emergence is due to the presence of geological structures that allow the out flowing. Bukisa Spring near Meti town, serves for water supply of Bollo village, comes forward through well defined massive fractured (with considerable spacing and density) basalt.

Generally, springs in the study are very crucial from water supply point of view. Most high land inhabitants rely on spring water source for drinking purpose sometimes for local small-scale irrigation where the yield is high and topographic setting is conducive to drive water by gravitational force. Distribution of springs is well known by the local people as their lives are highly linked with surface water. Those slope inhabitants' in the north and south part of the study are dependent on springs and streams for water supply. Even the downstream part settlements depend on such water body for themselves and their livestock.

The pathways of these springs are governed by structures, topography, geology and availability of shallow circulating groundwater. The fractured trachaytes in the north and highly weathered basalt in the south are key sources for these springs. Local macro fracture and growing faults are responsible in many cases to facilitate pathways.

Thermal springs manifestation is noticed around Ambo, Wonchi and Woliso town their manifestations are credited to Dandi and Wonchi volcanic center. The residue of cooling magma beneath the volcanic center might have been responsible for the origin of thermal spring, which emerges through structural conduit in Ambo area. Hot springs in Ambo town are located along Huluka River right and left bank just below the main bridge of Huluka near swimming pool, at the swimming pool north side there is hot spring flowing into the pool, Ambo bathing center also caped this hot springs for commercial purpose. The guiding path for these springs is the structure oriented east west north- south, which defines the path followed by Huluka stream.

2.6.2.3. Wet lands

Wet lands are areas of marsh, fen, peat lands or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt including areas of marine water the depth of which at low tide does not exceed six meters (Ramsar, 2004).

The ecological diversity of Ethiopia, characterized by altitude range from 4620m above sea level to 125m below sea level, enables it to have all types of wetlands except marine related ones (Leykun, 2003). Wetlands of Ethiopia are roughly estimated to cover 18,580 km2 (1.5%) of the total surface area of the country (EPA, 2004). The Ethiopian wetlands consist of swamps/marshes, fresh and brackish lakes, riverside flood plains, swamp forests and human made wetlands (EWNRA, 2001; Hughes and Hughes, 1992,). Seasonally inundated flood plains occupy the largest share of the wetlands (47.2 %) followed by freshwater lakes (30.6%), swamps and marshes (12.6%) and the rest is occupied by the other types of wetlands (EPA, 2004).

The Ethiopian wetlands are distributed across all agro- ecological zones of the country from high altitude alpine lakes of Bale mountain (>4000m above sea level) to lakes of Denakil depression (125m below sea level). On the basis of ecological zones, the Ethiopian wetlands are classified into four major categories: Afro-tropical highland wetland systems; Sudano-Guinean wetland systems; Somali-Masai wetland systems; and Sahelian transitional wetland systems (Leykun, 2003).

The freshwater marshes and swamps dominantly found at the valley bottom are widely distributed in South-west highlands of Ethiopia. Swamp forests are small in extent mostly found along Baro river depression in western Ethiopia. Human made wetlands include artificial impoundments, hydropower dams and municipal water supply reservoirs (EPA, 2004; Leykun, 2003; Ethiopian Wetlands and Natural Resource Association EWNRA, 2001).

The major riverside flood plains of Ethiopia include Wabeshebele-Genale flood plains in South-eastern Ethiopia, Awash River flood plain extended from central to North- eastern (Tefki flood plain around Becho plain -upper Awash and Middle Awash floodplain –Dugda Bora), Omo river flood plain in South-west, the permanent swamps and flood plains along Akobo, Baro and Gilo rivers in the west along the border of Sudan (Hughes and Hughes, 1992).

The Afro-tropical highland wetland systems include the wetlands of central plateau and south and north-western highlands that serve as the prime watershed of the major rivers.These wetlands are found at the headwater of the Blue Nile with high ground bogs, valley bottoms and marshy areas including Lake Tana and its surrounding flood plain and Atbara in the north and the Sobat in the South-west (Leykun, 2003; Howard and Abebe, 2002). The Sudano-Guinean wetland systems include the riverside flood plains and swamps at low altitude of western

Ethiopia where the Sobat River spreads out before leaving the border of Ethiopia (Howard and Abebe, 2002). Somali-Masai wetland systems include the wetlands in south and south-eastern parts including the rift valley lakes and riverine floodplains. The Sahelian transitional wetland systems are those found in the north-eastern parts of Ethiopia that includes saline marshes and lakes in the Denakil depression (Leykun, 2003).

The wet lands in the study area are found in the Afro-tropical highland wetland systems include the wetlands of central plateau. These are the Chitu floating wetland at the western side of Woliso town, the wet land near Wonchi crate lakes and the riverside wetlands in the Becho plain near Tefki town.

2.7. Hydrogeology

The hydrogeology of study area is classified based on the lithological, stratigraphical and structural aspects and understanding of the factors that regulate effective infiltration, ground water reserve, the circulation and out flow of the ground water. The study of porosity, degree of fracturing, karstification, alteration of the rocks, verification of the minor and major permeability among the rocks that are outcropped in the study area are used to classify the hydrostratigraphy of the area.

As explained in the local geology of the study area two terrain types are identified: volcanic and sedimentary the later is minor unit, pinches out near Ambo town. The Mesozoic unit that does not extend in the east farther than Ambo town contains:

- Sandstone
- Mudstone-Shale
- Limestone.

The sedimentary unit constitutes Adigrat sandstone, minor intercalation of shale and limestone under the sandstone on the way to Gudar from Ambo. The sandstone is moderate Aquifer and tap mineral water in Ambo Sankale (Ferdinad.H1983) while that of shale is confining bed. The sandstone is relatively intact and cemented by iron oxide and silicon. Unlike the gray colored, outcropped on north of Dabis stream the aforesaid one is characterized by low permeability and shows uniform texture where every grain size grow to each other to fill every voids that can exist as primary porosity. The later posses' secondary porosity fractures and less cemented as compared to the earlier.

Generally, the sandstone is considered as confined aquifer for example Ambo mineral water source formation is designated as this formation ; Lemessa Mekonta (2001) having the confining layer as Mudstone-shale unit and basalts. The shale unit is not continuous confining layer; somewhat it is localized and found as minor intercalation.

Volcanic products over dominate any type of lithology in the area and believed to be as influential groundwater controlling media. In such area hydrolithology heterogeneity with depth and lateral extent is inevitable according to bore hole log data.

The volcanic rock type supposed to govern groundwater system may include:-

- Quaternary basalt,
- Amba Alaji rhyolite
- Tarmabar scoracious basalt,
- Tertiary Trachaytes, and
- Tertiary ignimbrite.

These listed units are the mapable ones; practically there are diversified volcanic products that may determine groundwater occurrence and movement. Such temporal and special heterogeneity of lithology can be characterized by aquifer parameters such as: Hydraulic conductivity, Transmissivity, Storativity, Permeability and Porosity.

2.7.1. Trachaytes

Trachaytes flow from the Dandi -Wonchi volcanic centers mountain range is affected by weathering clearly the rate of weathering is not uniform throughout its distribution. The outcropped trachaytes has undergone alteration due to various factors that may include:- climatological change, biological weathering, ect. Trachaytes exposure on Tulu Boda, Golole, and Cheffe qerensa shows fracturing and high weathering effect. There are also places where slightly weathered and intact trachaytes is observable; this is outcropped along some streams just below the Dandi slope. Exposure of trachaytes in Qerensa stream appears to be very dark in color that is reaction result with iron mineral otherwise lighter when broken. Generally, the fresh part of this unit is impervious as compared to the weathered and fractured parts. Many perennial springs in the central part of study area emerge along the openings of this unit. Normally, in such hard rock terrain fracture and the matrix of the rock is vital in controlling groundwater system.

The springs emerge at Qerensa Stream bank from the fractured trachaytes which evidences the lithology can allow both recharge and discharge. The spring source is could be the eastern Qerensa stream plain of Hubato (Goda Lafen) here the ridge over topped by plain and followed by steep cliff on its rim of west and north part in the direction of the stream that flows in the direction of N-S running structures. Ashane perennial spring is flowing through fracture at Qerensa stream bank.

2.7.2. Tertiary Ignimbrite

The ignimbrite demarks eastern tip of the study area extending all along the Becho plane. Regionally ignimbrite covered area designated as aquiclude, which may not hold true as whole when viewed at local scale though the unit has no appreciable permeability. Drilling work accomplished in the area testifies the presences of other materials like ash, scoracious basalt. In addition structural influence and weathering effect altered the nature of the unit which in turn tends to improve the permeability, commonly secondary porosity faults, fractures, joints, types of contact; etc are more useful than scarce primary porosity in such hard rock terrain.

The artesian well developed in Becho plain confirms that ignimbrite is confining layer, implying low permeability hydrolithology. Based on the boreholes data it shows the ignimbrite is impervious unit below which weathered basalt, scoria, seldom-massive basalt, clay interblended with scoria unit are the prominent formation considered as good aquifer in the area. Recharge probably takes place along the faults located near the conduits of volcanic center and at the base of the slope more over the outcropped basalt unit in between the ignimbrite and the trachaytes also most important site which transfer water toward the formation lying below the ignimbrite.

2.7.3. Basalt

The woliso-Ambo basalt is one of important hydrolithology in the area. It is intensely broken and dissected by small scale growing structure and map able lineaments show also other secondary structures and primary porosity such as vesicles. The presence of those principal geological structures uncovered the unit to further weathering and disintegration on the scale of continues geological processes. Due to the effect the lithology come into good aquifer that serve as recharge and discharge controlling.

Occurrence of plenty of springs also strengthens its suitability media to transfer water in to and out of the system. In southern part of the study Area near Woliso borehole construction in Obi (between Woliso and Tulubolo) peasant association indicates that basalt is major aquifer.

Basalt is the major hydrolithologic unit around Ambo, Meti, Asgori, Awaro. As log data demonstrate basalt occurs being fractured, weathered and as intercalation with travertine, soil, etc. Geological formation obtained from Awaro and Meti (about 5km and 10 km East of Ambo on the way to Addis Ababa)

The Awaro area potential aquifer is weathered basalt and fractured basalt overlain by confining layer of ash and clay, therefore here the basalt is confined aquifer and receive recharge along the major and minor deep setting faults. The subsequent underlying massive fresh basalt probably fractured due to the intensive buried and visible faulting effect.

In general, basaltic formation is encountered as multi layer confined and unconfined aquifers in the study area and it is found to be the best water holding media, which attributed to its being affected by geological processes.

In association with basalt, scoracious materials are crucial formation in transferring and accumulating water. This unit is found to be good aquifer, its exposure is encountered along the ambo fault belt, in the central part of the study area. For example, Tarmabar scoracious basalt along Ambo lineament is believed to serve as recharge inducing components. The red colored scoria show dense vesicles of interconnected primary structures, which is very suitable in maintaining groundwater circulation and storage.

2.7.4. Alluvial

The alluvial deposit is found to be indispensable water tapping aquifer, in eastern part of the area (around Becho plane) hand dug wells are simply developed in the soft unconsolidated river transported aggregates using local digging tools. The reason for this material to be obtainable in some area can be linked with geomorphology and topographic settings. As mentioned in the physiographic part, the north and southern portion is distinguished by parallel volcanic landform that rose to highest point in turn denudated and dissected by regional and local structures. Taking the advantage a lot of perennial and intermittent streams explode to all direction from the summits of mountains and hilltops (volcanic plugs) whereby slope materials are carried away fast to the surrounding flat low lying bottom where the load is leftover.

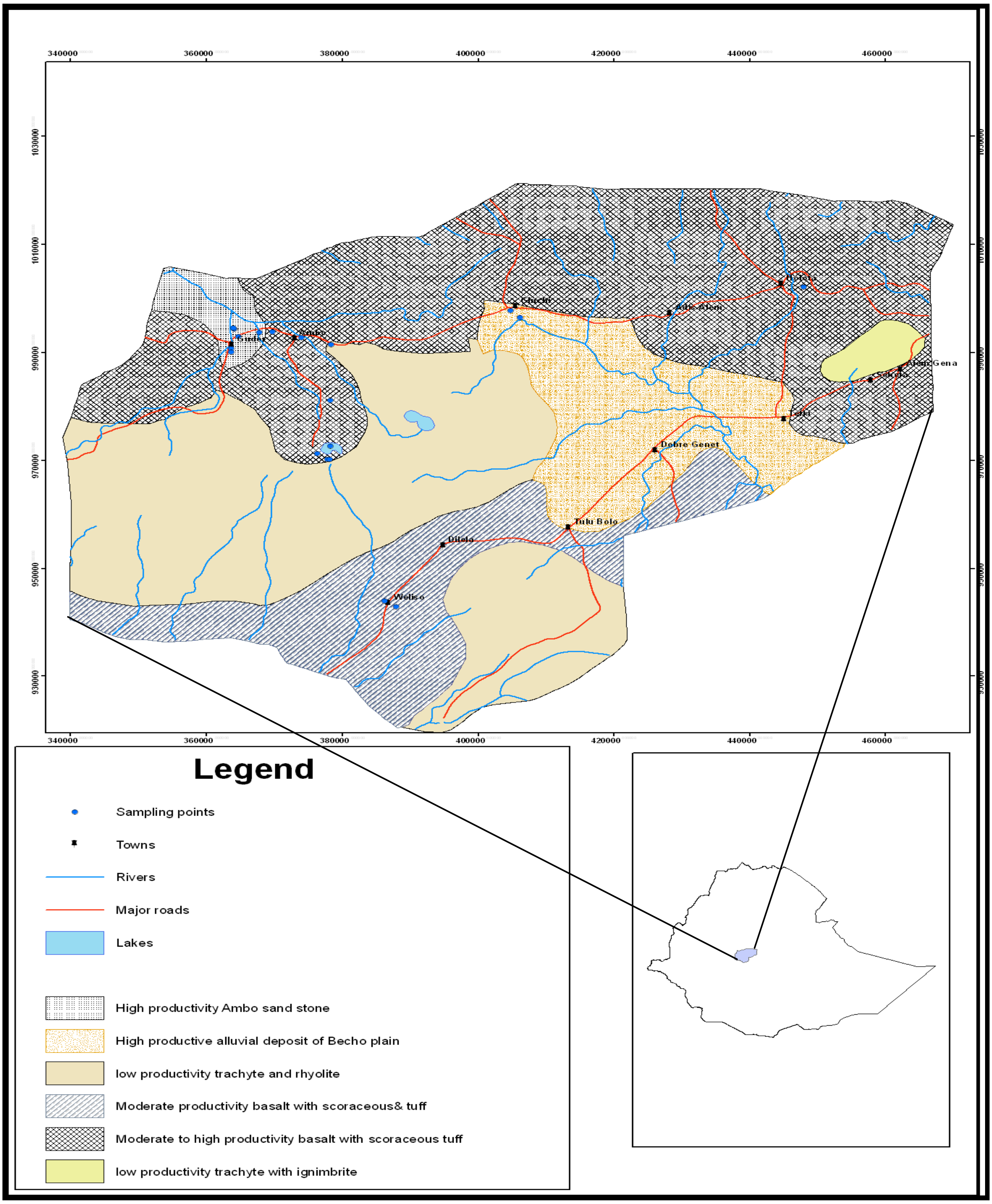

Figure: 2.8. Hydrogeological map of the study area

CHAPTER THREE
METHODOLOGY AND MATERIALS

3.1. Methodology

The methods used to achieve the objectives includes: Secondary data compilation and interpretation of Geological information (bore hole data), Hydrometeorology, Satellite and air photographs, Hydrogeological maps, digital elevation map, Surface water and ground water condition and field data and sample collection for laboratory analysis

Direct analysis of the raw isotope hydrological and geochemical data, heirarcical cluster analysis and, inverse geochemical modelings are used. Furthermore δ13C, pH, TDS, EC and carbonate species compositions of the ground waters were used to gain additional insight on groundwater geochemical evolution. The PH, TDS, EC, Temperature, dissolved oxygen(DO) and alkalinity were measured in the field. For the chemical and environmental isotope data, the majority of the water samples were collected from Wonchi system which is located in the Abay basin,Awash basin and Gibe Omo basin. . A total of 20water samples were collected from groundwater wells, springs, lakes and rivers between December 3, 2010 to December 4,2010. The samples were analyzed for their major ion concentrations as well as for their isotope contents ($\delta^{18}O$, δD). The samples for stable isotope (δ18O and δD) were analyzed at Addis Ababa university isotope laboratory. And some Selected representative groundwater samples were analyzed for δ13C and trace elements at the University of Avignon (France), laboratory of hydrogeology. Chemical analyses were carried out for major ions at laboratory of ministry of water resource, Ethiopia. The δ18O and δD compositions were reported in & notation calibrated against the V-SMOW.

The δ13C is reported in & notation calibrated against PDB. Cation species were analyzed using Atomic Absorption Spectrometry. Anion species were analyzed using a Dionex Ion Chromatograph equipped with automatic sampler. The δ13C is used to identify the source of co2 and the co2-water-rock interaction. Alkalinity , pH, electrical conductivity, total dissolved solids, dissolved oxygen and temperature were measured in situ.

Inverse geochemical modeling has been widely conducted in groundwater chemical evolution studies (Plummer et al., 1983; Kenoyer and Bowser, 1992; Varsanyi and Kovacs, 1997; Hidalgo and Cruz-Sanjulian, 2001; Wang et al., 2001). It is a useful approach to determine the type and amount in moles of minerals that dissolve or precipitate along a groundwater flow path.

PHREEQC computer code(Parkhurst and Appelo, 1999) was used to simulate the geochemical evolution for speciation, reaction-path, and inverse geochemical calculations. Designed to perform a wide variety of aqueous geochemical calculations, PHREEQC is based on an ion-association aqueous model and has capabilities for: (1) speciation and saturation-index calculations; (2) reaction-path and advective-transport calculations involving specified irreversible reactions, mixing of solutions, mineral and gas equilibria, surface-complexation reactions, and ion-exchange reactions, and (3) inverse modeling, which finds sets mineral and gas mole transfers that account for composition differences between waters, within specified compositional uncertainties.

Representative water samples were collected from different bore holes, springs, rivers and lakes to analyze trace element mobility. These trace element samples are analyzed in laboratory of hydrology Vienna, France. This method is used to identify the contaminant mobility during co2-water interaction in the form that may cause damage to human or environmental receptors. To see the impact of an introduced contaminant on geochemical equilibrium and the potential for release of a contaminant by a change to the environment.

Statistical classification of geochemical data by using hierarchical cluster analysis (HCA) has proven to provide a suitable basis for objective classification of water composition into hydrochemical facies and for geochemical modeling (Alberto et al., 2001; Barbieri et al., 2001; Meng and Maynard, 2001; Swanson et al., 2001; Güler et al., 2002; Güler and Thyne, 2004).

Environmental isotopes are natural and anthropogenic isotopes whose wide distribution in the hydrosphere can assist in the solution of hydrogeochemical problems. The Typical uses of environmental isotopes in hydrology include:

- Identification of mechanisms responsible for stream flow generation.
- Testing flow path and water budget models developed using hydrometric data.
- Characterization of flow paths that water follows from the time precipitation hits the ground until discharge at the stream.
- Determination of weathering reactions that mobilize solutes along the flow paths.
- Determination of the role of atmospheric deposition in controlling water chemistry.

- Waters recharged at different times, in different locations, or that followed different flow paths are often isotopically distinct; in other words, they have distinctive **fingerprints**.
- Unlike most chemical tracers, environmental isotopes are relatively conservative in reactions with catchment materials. This is especially true of oxygen and hydrogen isotopes in water; meteoric waters retain their distinctive fingerprints until they mix with waters of different compositions or, in the case of isotopes of dissolved species, there are reactions with minerals or other fluids.
- Both biologically cycling of solutes and water/rock reactions often change isotopic ratios of the solutes in predictable and recognizable directions; these interactions often can be reconstructed from isotopic compositions.
- If water from an isotopically distinctive source(e.g., rain with an unusual isotopic compositions) is found along a flow path, it provides proof for a hydrologic connection, despite any hydraulic measurements or models to the country.
- For the purpose of this study environmental isotopes are used to identify the CO2-water-rock interaction, hydrogeochemical evolution and the trace element mobility along the reaction flow path during ground water evolution.

The isotopic compositions of materials analyzed on mass spectrometers are usually reported relative to some international *reference standard.* Samples are either analyzed at the same time as this reference standard or with some internal laboratory standard that has been calibrated relative to the international standard. Alternatively the absolute ratios of isotopes can be reported. Small quantities of these reference standards are available for calibration purposes from either the national institute of standard and technology (NIST) in the USA, or the International Atomic Energy Agency(IAEA) in Vienna.

The δ values of the standards have been defined as 0‰. δD and δ18O values are normally reported relative to the SMOW standard(Criage,1961) or the equivalent VSMOW(Vienna-SMOW) standard. The δ13C values are reported relative to either the PDB(Pee Dee Belmenite) or the equivalent VPDB(Vienna-PDB) standard.

The sampling method

- The samples for **δ18O**/δ2H are collected in a clean dry glass bottles, which is filled completely almost to the top, and capped tightly. The main objective is to protect the sample from evaporation and exchange with atmospheric water vapor. Sample size is lab dependent; typical volumes range from 10-60ml. The laboratory chosen to analyze the samples normalizes their values according to IAEA guide lines (Coplen,1994). The laboratory method used for these isotopes is LWIA for water stable isotope measurement. These isotopes are analyze at Addis Ababa University Isotope hydrology laboratory, Ethiopia.
- The samples for δ13C isotope analysis are collected from the field in tightly capped dark plastic bottles. The dark plastic bottles are used to avoid the entrance of light into the highly gaseous co2 water that can develop algae. Mass spectrometry is laboratory method used for d13C at University of Avignon, France.
- Samples for trace element analysis are collected in glass bottles. These samples are carefully filtered at the sampling site before filling in to the bottles and then capped tightly. The laboratory method used for this sample analysis is ICPMS for trace element analysis at University of Montpellier, France.
- Field measurements such as PH, TDS, EC, T, DO and alkalinity are measured insitu. Field alkalinity is by measured by titatration method using the 0.1NHCl for 100ml of water to titrate until the color turns in to red when the PH becomes 4.5.
- Sample collected for laboratory analysis of Major cations and anions are analyzed at water chemistry laboratory of Federal Ministry of Water and Energy, Ethiopia.

3.2. Materials used

The materials used to achieve the objective of this research work are listed below.

- software components such as Arc GIS9.2,Surfer 9,Global mapper 11 to analyze the location, physiography, land use land cover and sampling points;
- Aquachem 4, phreeqc 2.8 to analyze the geochemical characteristics, the typical ground water types and inverse geochemical modeling and excel sheet to plot the stable isotope data and their global meteoric water line.
- Statisticaca8, soft ware is used for HCA, to classify the waters in to objective groups.

- Field instruments are used in the field work to measure the insitu condition of water samples; the scientific materials such as: PH meter, DO meter, EC meters, alkalinity measuring instrument, different glass and plastic bottles for sample collection were used.
- GPS and topographic map of the study area were used to identify the location of the study area. Geological and hydrogeological map were used to identify the geological, structural and major litho-units of the study area while hydrogeological map to identify the hydrostratigraphic units of the study area.

CHAPTER FOUR

DATA ANALYSIS

4.1. Field data analysis

4.1.1. PH

Hydrogen ion activity (PH), because of hydrogen ions, its activity or effective concentration in ground water is an especially important parameter. The hydrogen ion activity is a master variable of the ground water system because the hydrogen ion participates in most of the chemical reactions that affect water composition.

Measurement of PH of ground water is essential because many of the solution process (aqueous complexation), water/rock interactions (mineral solubility and adsorption properties), gas solubilities, and biochemical reactions are PH sensitive.

The pH of ground water is commonly buffered by the inorganic carbon constituents in solution; the PH may still change appreciably when the water is exposed to surface conditions and allowed to equilibrate with atmospheric CO2 concentrations.

The PH of the waters of the study area can be classified as high, medium and low. The high PH is above 7.5, medium PH is between7.0 to 7.5 and the low PH is below 7.0. The highest PH is observed in Lake Wonchi, Woliso prison compound BH, Guder river and Indris river have greater than 8. Cold spring on the Wonchi crater Lake Escarpment, Negash Lodge hot spring and Ambo Awaro BH1 have greater than 7.5. The Hot spring of Wonchi crater lake, Ginchi Boda BH, Ginchi BH2, Guder town water supply, and Ambo Awaro BH2 have the medium PH.

Whereas, the Boji spring, Menagesh HDW, Hometcho Factory BH1 and BH2, Ambo mineral water, Yai Chebo Turura HDW, Ambo hot spring of Ethiopia Hotel and gaseous spring of Wonchi have the lowest PH values. The lowest PH values are observed in Gaseous ground waters bore holes and springs of the study area. The lowest PH is measured in Wonchi gaseous spring that has similar taste with Ambo mineral water.

4.1.2. Temperature

The waters of the study area are classified as the temperature above 25, 20-25 and below 20. Based on this the highest temperature is for the thermal springs and mineral waters. Negash Lodge hot spring has the highest temperature up to 39.6^{0}C and Ambo Ethiopia Hotel hot spring, Wonchi thermal hot spring and Ambo mineral water have 36, 32.3 and30^{0}C respectively. Generally ground waters around Ambo and Guder area have relatively high temperature. The Ambo water supply bore holes and Hometcho factory bore holes, boji spring near Senkele lime factory and Woliso prison compound bore holes have the temperature of relatively from 25 to 30^{0}C.

Ginchi water supply bore holes and gaseous spring near Wonchi, Guder river and Menagesh hund dug well have the temperature between 20 to 25^{0}C. While lake Wonchi, spring at the ridge of Wonchi crater lake, Yai Cebo Turura hand dug well and Indris river have the temperature below 20^{0}C.

4.1.3. Electrical conductivity, total dissolved solids and dissolved oxygen

The gaseous and thermal ground waters in the study area have the highest electrical conductivity, total dissolved solids and dissolved oxygen. For instance, the highest TDS is measured in the Ambo hot spring, Ambo mineral water, gaseous spring around Wonchi crater lake which is similar to Ambo mineral water, Hot spring of Wonchi crater lake, Boji spring near senkele lime Factory and Negash Lodge hot spring respectively. While the medium TDS is detected in Ambo Water supply bore hole around Awaro and Ginchi water supply bore holes. The Ground water around Guder town water supply bore hole and Hometcho ammunition factory bore holes have the TDS between 200 to 400.The TDS below 200mg/l is observed in cold spring at the escarpment of Wonchi crater lake, Indris river, lake Wonchi, Guder river, Woliso prison compound bore hole, Yai Chebo Turura and Menagesha hand dug well. The lowest TDS is observed in cold spring on the escarpment of Wonchi Crater Lake.

4.1.4. Alkalinity

Alkalinity is the measure of acid neutralizing capacity of the water. The alkalinity of the water is measured in the field by titrating the water with 0.1N of HCl to an end point PH of about 4.5. Most of the alkalinity in ground water is due to the amount of dissolved inorganic carbon ions present in the solution, therefore, the alkalinity measurement can be used to determine the bicarbonate and carbonate concentration of the ground water. The DIC is composed of CO2(aq), H_2CO3, $HCO3^-$ and $CO3^{2-}$.

The highest alkalinity measurement of the waters in the study area is recorded in gaseous springs and ground waters wells. The spring near Wonchi Crater Lake which has similar test of Ambo mineral water has the highest alkalinity measurement in the study area. The Ambo hot spring, Ambo mineral water, thermal spring around Wonchi Crater Lake, Boji spring near Senkele lime factory, the two bore holes of Awaro area for Ambo water supply and Negash Lodge hot spring are followed respectively with alkalinity measurements from 400 to 1262.7mg/l.

The two Ginchi town water supply bore holes, Hometcho Ammunation factory BH1 and BH2 and Guder town water supply bore holes have the alkalinity measurement between 200 and 400mg/l. while cold spring on the ridge of Wonchi crater lake, lake Wonchi, Menagesha hand dug well, Guder river, Yai Chebo Turura hand dug well and Indris river have the alkalinity measurement of below 200mg/l.

The low PH value waters of the study area have the highest alkalinity value. The highest alkalinity measurement has the lowest value of PH. Except at thermal spring of Wonchi crater lake which shows the high alkalinity value at PH of about 7.25.

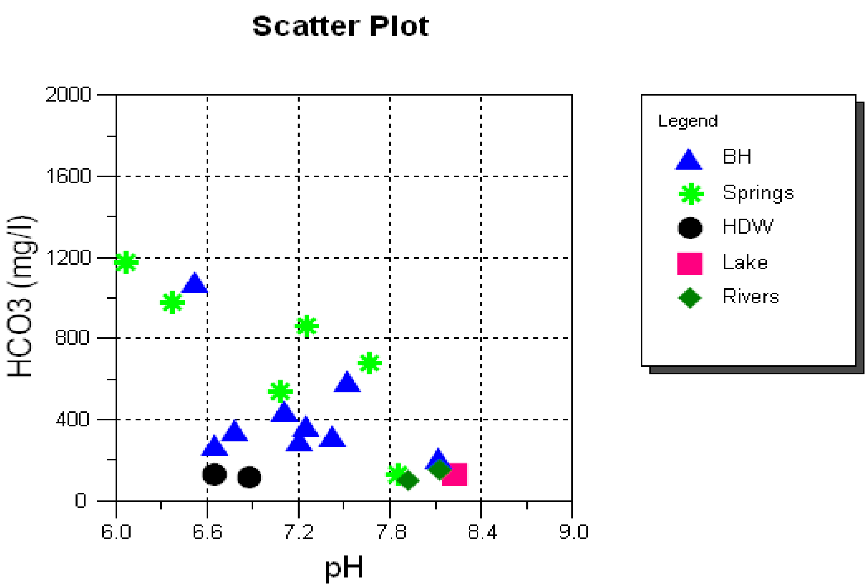

Figure: 4.1. $HCO3^-$ value against PH relation ship

Alkalinity increases with increasing temprature. There is exceptional case on spring near Wonchi crater lake which is highly gaseous and has similar taste to Ambo mineral water shows the highest alkalinity with low temprature of about 20^0C. The Negash Lodge hot spring also shows medium alkalinity with high temprature.

Alkalinity increases with increasing TDS values.The highest alkalinity value is measured in Wonchi gaseous spring, Ambo mineral water, wonchi hot spring and Ambo hot spring.

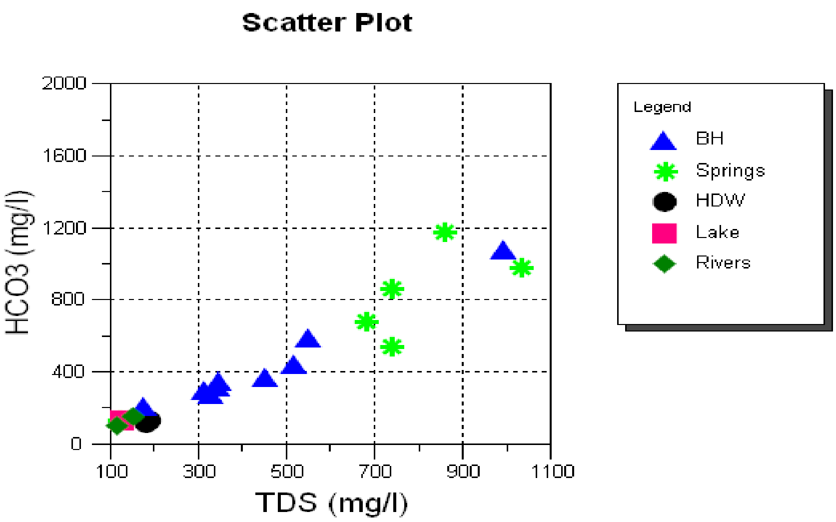

Figure: 4.2. Alkalinity value Vs TDS relation ship

The temprature Vs TDS have no strong relationship. The low PH value waters have high TDS values and the highest PH values have low TDS values. The menagesha HDW,Hometcho Amunition factory BH1&BH2 and Yai Chebo Turura HDW show the low PH values with low TDS values. While Boji spring near Senkele Lime factory, Woliso Negash Lodge hot spring have the neutral PH values with high TDS values. In the medium values there is no strong relationship of the PH values Vs TDS values. There is no good realationship between temprature and TDS values. But in the waters of the study area there is a relative increase of TDS with increasing temprature. But the exception can be observed in cold spring in the escsrpment of Wonchi crater lake which have lowest temprature with low TDS value, Yai chebo turura HDW, Woliso Negash lodge hot spring has the highest temprature of the study area and Wonchi gaseous spring has low temprature with high TDS show out of the normal trend in the graph of Temprature Vs TDS value.

4.2. Geochemistry laboratory data analysis

The samples collected for physico-chemical prametres were analyzed at the laboratory of Minsrty of water and Energy,Ethiopia. This analysis were carried out for major cations and anions and some physical and biological prametres. Among the major cations(Na,K,Ca,Mg) and anions(Cl,SO4,HCO3/CO3) are used to plot the piper plot of the ground water for the analysis of hydrochemical facies and to identfy the dominant types of ground waters.

The chemistry data were used for inverse geochemical modelling and reaction path modelling. From the major cations and anions observed from the laboratory results the highest value of sodium(Na) which is above the maximum standard of WHO is observerved in the water samples of the Wonchi and Woliso area. These are Negash Lodge hot spring, Wonchi thermal spring, Wonchi gaseous spring and Wonchi cold spring. Most of the Ca values observed from the laboratory results are below the standards. The highest value of Ca is observed around Ambo area in Boji spring near Senkele Lime factory, Ambo mineral water and Ambo Awaro bore holes. Whereas, the highest K value is observed in Wonchi gaseous spring and Wonchi thermal spring. The highest value of total iron is measured in Wonchi thermal spring.

Among the major anions the highest chloride value is observed in ground waters around Ambo area. The highest value is observed in Ambo hot spring of Ethiopia hotel and followed by Ambo mineral water, Boji spring and Ambo awaro BH2. The ground waters of Woliso area such as Negash Lodge hot spring, Wonchi thermal spring, wonchi gaseous spring have the highest value of flouride content which is more than WHO standard. Relatively the maximum value of HNO3 among the collected water samples are observed in Yai chebo Turura HDW, Ginchi BH2 and Boji spring. Whereas, the highest value of the sulphate is observed in Boji spring.

The total hardness is also one of the important parametre. The highest value of the total hardness is measured in Ambo mineral water and Ambo hot gaseous spring respectively. The Ambo mineral water has the maximum value of total hardness which is more than the WHO standard.while the Ambo Awaro bore holes, Ginchi water supply BH, Wonchi gaseous spring and Hometcho Ammunition factory BH show relatively higher total hardness values. Turbidty unit is also another parametre that measured in the laboratory. Wonchi gaseous spring, Yai chebo Turura HDW and the Guder river show the highest value of turbidity Unit.

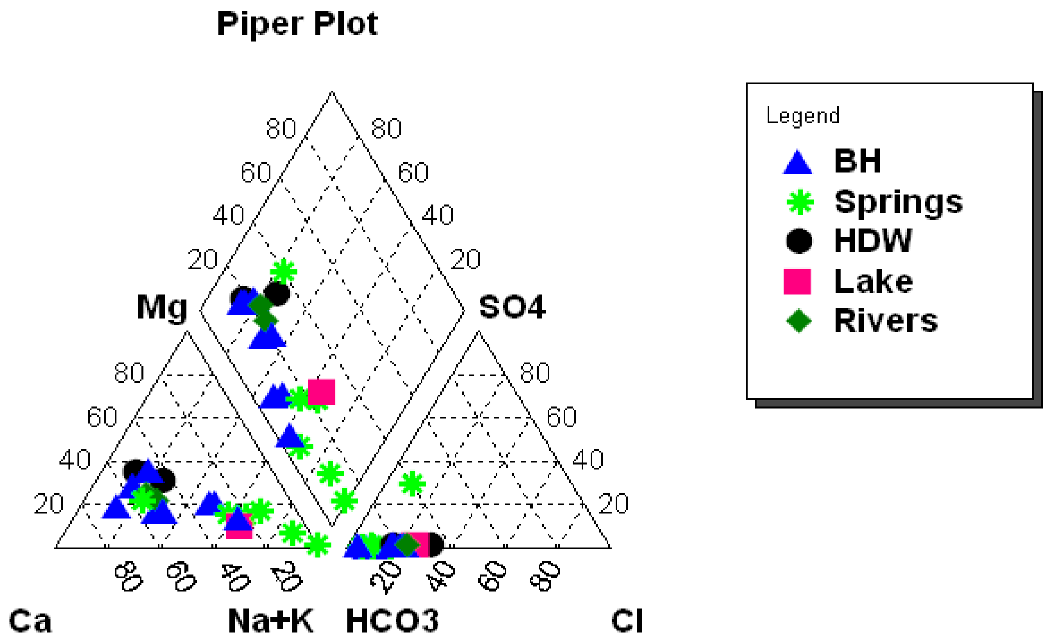

Figure: 4.3. Piper plot diagram of the waters of the study area.

The major ground water types of the study area are plotted on the piper diagram. This diagram is used to analyze many water samples on the same diagram and to show the clustering data points to indicate samples that have similar composition and to identify mixing of different water samples. From the above plot the dominant ground water types of the study area are CaHCO3 and NaHCO3 type. To anayze them separately Ambo mineral water, Ambo Awaro BH1,Ambo hot spring of Ethiopia Hotel and Woliso prison compound bore hole are the Na-Ca-HCO3 water type. while Ambo Awaro BH2 is Ca-Na-HCO3 type ground water.

The ground waters around Wonchi crater lake; such as Wonchi gaseous spring, Wonchi thermal spring and Negash Lodge hot spring are NaHCO3 type ground water. But lake Wonchi and Wonchi cold springs are Na-Ca-HCO3-Cl type ground water. Whereas, Yai chebo Turura HDW and Hometcho BH2 and Guder river are Ca-Mg-HCO3-Cl type ground water and the Menagesha HDW and Hometcho BH1 are Ca-Mg-HCO3 type ground water.

The Ginchi town water supply of Boda site is Mg-Na-HCO3 type, but Ginchi BH2 which is found near Awash river is CaHCO3 ground water. Another mixed type of ground waters of the study area are Indris River(Ca-Mg-Na-HCO3-Cl type), Guder town water supply BH(Ca-Na-HCO3-Cl type) and Boji spring near Senkele Lime Factory which has a very distinct type of ground water with Ca-Na-Mg-HCO3-SO4 type.

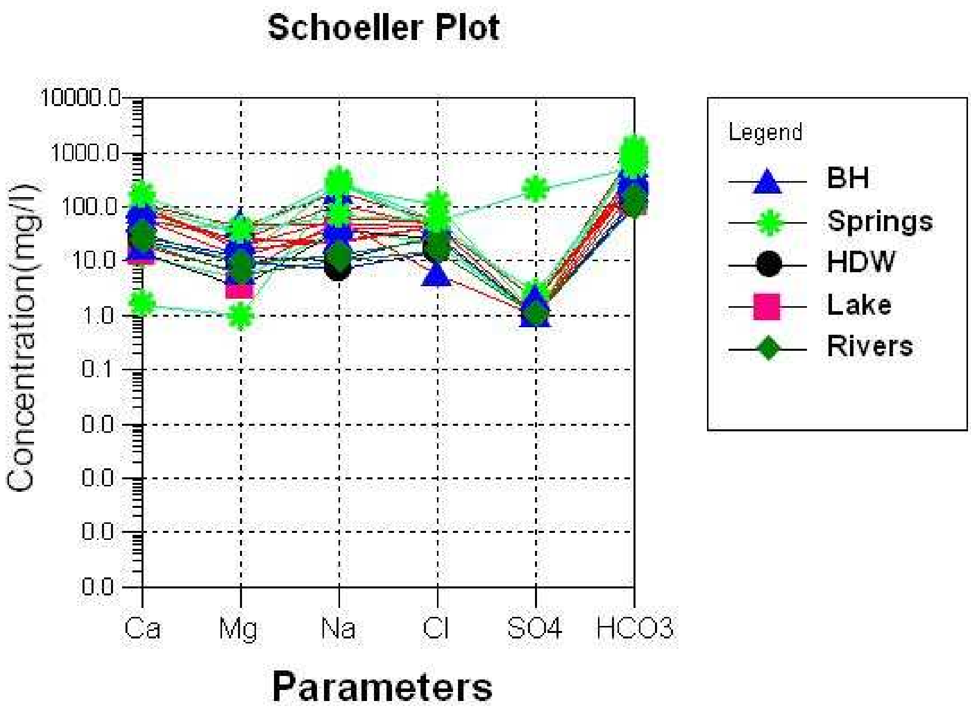

Figure: 4.4. The scholler plot diagram of waters of the study area.

The above schoeller diagram plot is used to reperesent the major ion analysis. In this case the actual sample concentrations are displayed and compared to each other for the the water samples of the study area. From the figure the dominant major cations are sodium and magnesium. While the dominant anion is HCO3- with a little significance of chloride.

The scatter plot diagram is also used for geochemical analysis to see the direct relationship exists between two parametres in the smple records and allows a regression line to be compared. The sactter plot figure to see the relation between Na and Cl shows that only few samples show high value of Na with High Cl value but the others are scttered within high value of Na and low value of chloride ion no strong relation ship. The plot between Na Vs HCO3 for the waters of the study area shows the dirct relation ships.

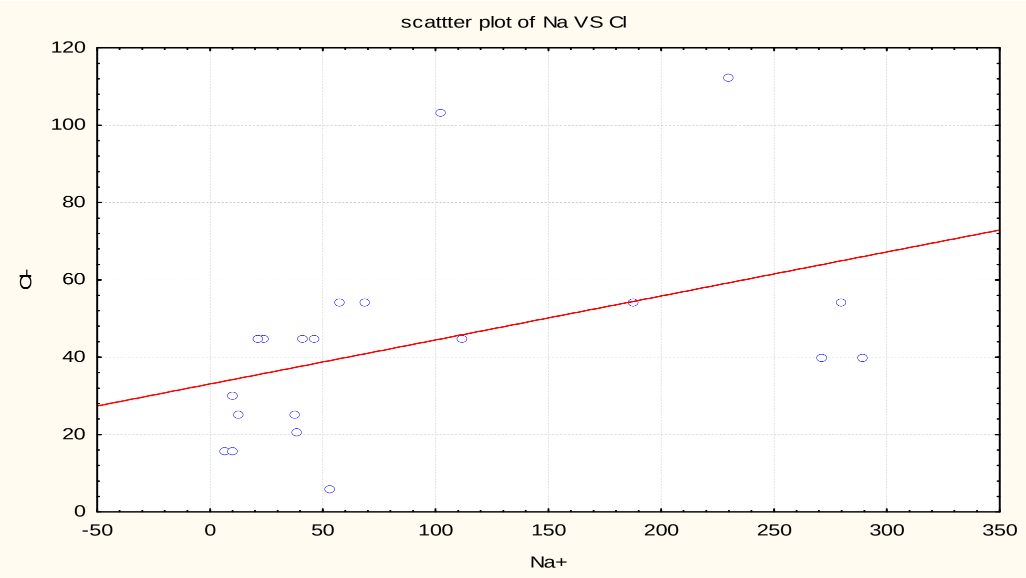

Figure: 4.5. Scatter plot of Na+ against chloride value.

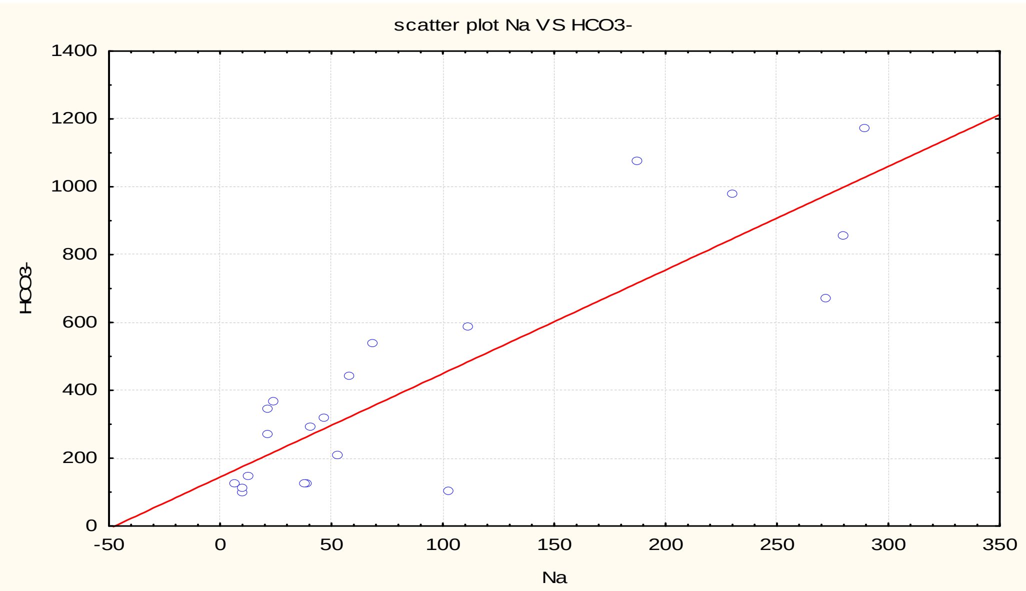

Figure: 4.6. Scatter plot of Na+ against HCO3 value.

SmapleID	Li	B	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Sr	Mo	Cd	Cs	Ba	La	Pb	U
W1-HDW1	0.773	6.750	1.183	0.194	0.282	0.147	0.212	0.882	0.017	2.684	1.860	72.640	0.063	1.029	101.600	0.165	0.058	0.063	24.850	0.010	<LoD	<LoD
W2-BH1	4.942	26.440	0.825	0.277	9.475	0.072	3.905	3.539	0.081	2.662	28.560	54.990	0.476	2.472	109.700	2.256	0.024	0.054	27.800	0.017	0.037	0.761
W3-BH2	0.823	12.130	0.197	0.342	18.280	0.100	1.907	0.020	0.063	1.716	13.230	31.710	0.136	1.560	157.400	0.469	<LoD	0.032	26.750	0.014	<LoD	1.701
W4-R1	0.429	6.839	183.800	6.102	1.311	0.287	19.800	155.800	0.079	0.533	0.922	12.740	0.146	7.264	63.390	0.891	<LoD	0.024	8.376	0.236	0.052	0.217
W5-BH3	4.165	13.230	0.324	0.275	5.165	0.273	0.001	0.006	0.016	2.477	4.364	49.440	2.836	8.039	237.600	1.375	<LoD	0.213	59.360	0.009	<LoD	2.288
W6-BH4	8.217	19.740	0.194	0.311	1.697	0.025	42.410	0.450	5.081	6.973	1.139	40.520	1.231	10.930	264.700	2.972	<LoD	0.433	114.200	0.004	<LoD	0.922
W7-BH5	2.925	16.560	0.229	0.322	6.176	0.245	1.584	0.136	0.099	0.796	0.808	7.758	0.564	9.601	201.500	3.034	<LoD	0.218	69.490	0.006	<LoD	1.797
W8-R2	0.480	7.480	2.369	0.343	2.226	0.156	0.409	5.725	0.067	0.566	0.828	2.464	0.207	4.595	136.300	0.895	<LoD	0.018	15.480	0.020	<LoD	0.428
W9-S1	24.020	75.720	0.772	4.198	13.700	0.212	0.017	0.621	<LoD	0.514	0.147	6.815	0.149	4.182	1292.000	0.580	<LoD	0.033	29.400	0.020	<LoD	2.069
W10-BH6	151.600	193.600	0.422	0.153	0.078	0.014	290.400	5.878	0.029	0.188	0.436	13.630	0.115	60.090	469.000	0.220	<LoD	2.550	1779.000	0.021	0.015	<LoD
W11-BH7	30.640	67.100	0.662	0.358	0.212	0.046	12.480	8.419	<LoD	0.537	0.798	58.570	0.299	11.770	288.300	3.942	<LoD	0.124	33.730	<LoD	0.013	0.571
W12-BH8	40.680	39.510	0.064	0.187	4.301	0.108	1.265	0.177	<LoD	0.370	1.029	7.356	0.279	16.330	358.400	2.024	<LoD	0.100	40.830	<LoD	<LoD	6.317
W13-S2	84.770	122.200	0.269	0.081	0.093	0.028	16.160	176.500	<LoD	0.236	0.358	6.530	0.203	23.330	163.100	0.412	<LoD	0.617	57.360	<LoD	0.018	0.034
W14-HDW2	3.775	12.600	194.700	5.438	0.911	1.009	1.186	124.400	<LoD	0.547	0.713	49.940	0.075	13.650	108.300	0.443	<LoD	0.025	38.950	0.179	0.084	0.084
W15-S2	3.943	8.516	8.465	1.886	0.137	0.039	0.665	36.850	<LoD	0.152	0.320	1.102	0.338	4.746	11.450	3.306	<LoD	0.010	0.992	0.148	<LoD	0.077
W16-L1	3.618	13.250	4.944	0.145	0.120	0.033	1.972	7.178	<LoD	0.226	0.731	0.850	0.274	6.300	18.800	3.158	<LoD	0.015	2.954	0.016	<LoD	0.102
W17-S3	116.500	50.170	1243.000	0.122	0.031	0.031	1256.000	5265.000	0.024	0.380	0.119	13.040	0.066	15.290	61.920	0.429	<LoD	0.020	2.849	0.022	<LoD	<LoD
W18-S4	171.200	118.400	67.460	0.244	0.040	0.056	257.100	1709.000	0.018	0.214	<LoD	3.506	2.312	25.320	9.231	3.095	<LoD	0.048	2.611	0.048	0.070	<LoD
W19-S5	125.800	164.700	8.114	0.438	0.073	0.202	0.980	26.840	<LoD	<LoD	<LoD	0.237	2.398	27.710	10.410	12.050	<LoD	1.125	12.230	0.026	<LoD	<LoD
W20-BH9	4.314	20.640	5.376	0.196	9.470	0.095	0.808	9.873	<LoD	0.117	<LoD	33.620	0.348	8.418	78.780	4.074	<LoD	0.036	7.032	0.021	0.032	0.788
RDS%	2.2	2.2	8.8	7.7	4.3	6.4	3.4	5.3	4.7	5.1	4.5	3.1	4.4	1.9	1.8	3.2	5.3	2.7	1.8	5.2	4.4	2.6

Table: 4.1. laboratory result of Trace element data.

4.3. Trace element data analysis

The representative water samples of ground water wells, rivers, springs and lake were collected to analyze trace element mobility in ground waters of the area. The laboratory result is given in the table for trace elements such as Li, B, Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Ba, La and U

From the trace element laboratory result Li and B are highly measured in Boji spring, Ambo mineral water, the two bore holes of Ambo Awaro well field, Ambo hot spring, gaseous springs around Wonchi lake and Woliso Negash lodge thermal spring. Whereas, appreciable amount of Ti is observed in Boji spring and YaiCHebo Turura HDW and V is high in Ginchi BH of Boda area. The highest amount of Sr is measured in Ambo mineral mineral water, Boji spring and some ground waters wells located around Ambo area. Wonchi gaseous spring and Wonchi thermal spring are highly enriched with Fe, so that this can be observed during field visit around lake Wonchi. Wonchi gaseous and thermal springs, Ambo mineral water and Hometcho BH2 are relatively enriched with Manganese element among the collected water samples.

The highest amount of barium is measured in Ambo mineral water, Hometcho factory BH2 and some amount in Guder town bore hole. While nickel and cobalt are relatively higher in Hometcho Factory bore hole. However, copper is high in Ginchi bore holes and Hometcho factory BH1 and Zinc is highly observed in Menagesha HDW, Ambo Awaro BH1 and Ginchi BH located near Awash river. As can be observed from the figure below Boron, lithium and Barium are higher in gaseous and thermal waters of the study area.

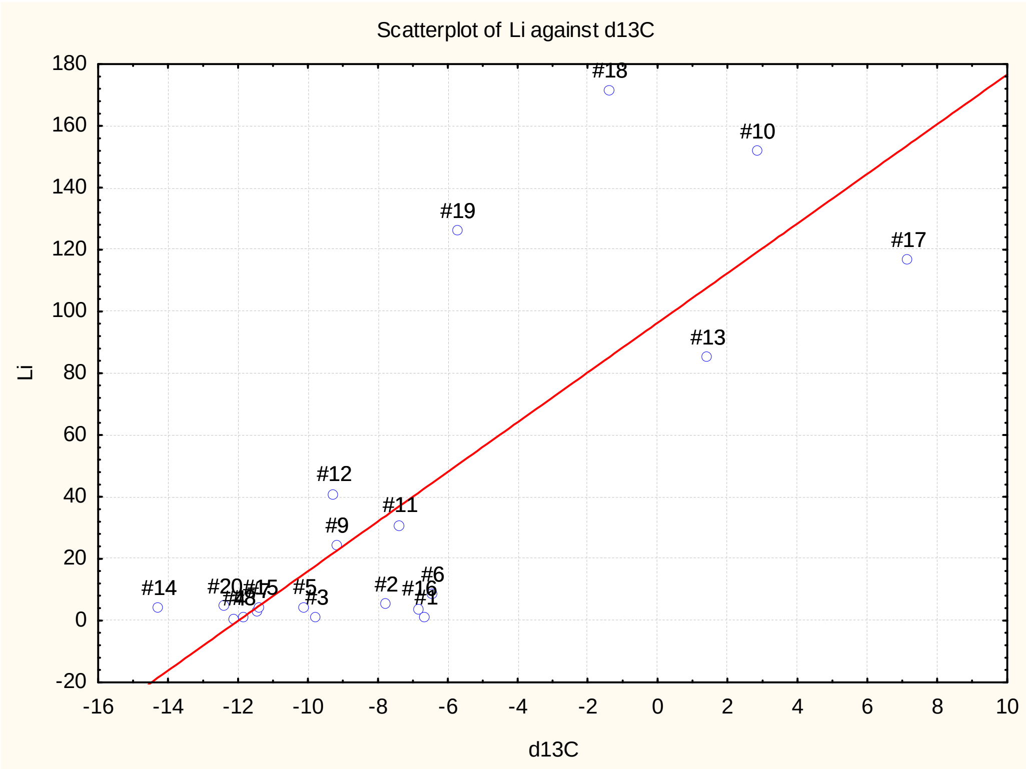

Figure 4-7 scatter plot of Lithium against C-13 value

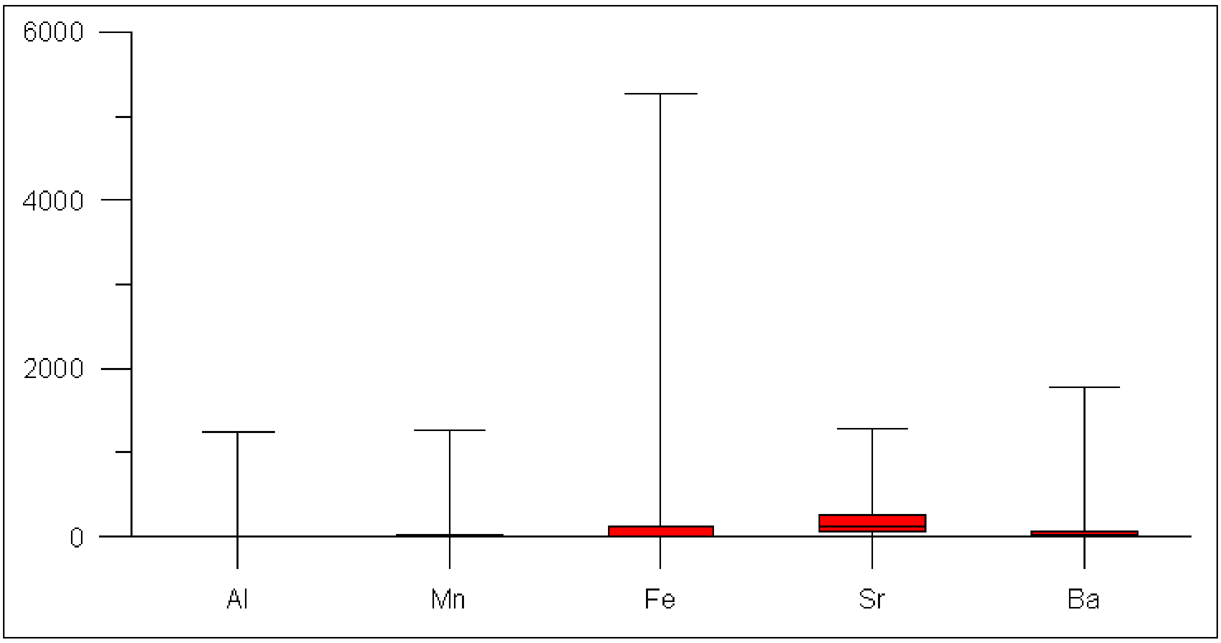

Figure 4-8 Box and Whisker plot of some trace elements

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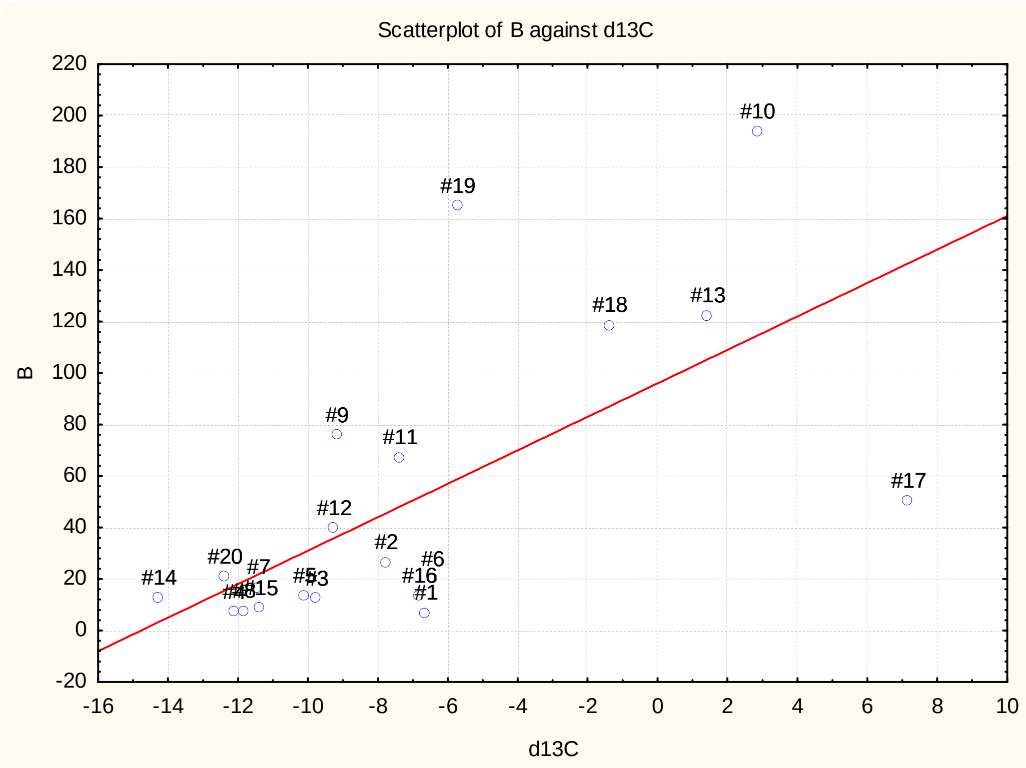

Figure 4-9 scatter plor of Boron against C-13 value.

4.4. Hierarchical cluster analysis (HCA)

Cluster analysis is a collection of statistical methods, which identifies groups of samples that behave similarly or show similar characteristics. In common parlance it is also called look-a-like groups. The simplest mechanism is to partition the samples using measurements that capture similarity or distance between samples. In this way, clusters and groups are interchangeable words. Typically in clustering methods, all the samples with in a cluster is considered to be equally belonging to the cluster (as against belonging with certain probability.

Statistical classification of geochemical data by using hierarchical cluster analysis (HCA) has proven to provide a suitable basis for objective classification of water composition into hydrochemical facies and for geochemical modeling (Alberto et al., 2001; Barbieri et al., 2001; Meng and Maynard, 2001; Swanson et al., 2001; Güler et al., 2002; Güler and Thyne, 2004).

HCA is a statistical technique that can be used to classify the ground water geochemical data in to objective groups in to members of the resulting groups or subgroups are distinct and similar to each other. The characteristics of the groups or sub groups are not pre determined but can be obtained after the classification. The classification of this HCA is useful specially to understand geological controls on water chemistry under a condition where useful geochemical data are available but clear hydrogeologic models have not yet been developed (Swanson et al., 2001). The characteristics of the group or subgroup are not predetermined but can be obtained after the classification. The advantage of HCA is that many variables such as physical, chemical or isotopic composition can be used to classify waters. In order that the variables have equal weight the raw chemical data should first be logtransformed and standardized. This restricts the influence of or the biases caused by the variables that have the greatest or the smallest variances or magnitudes on the clustering results. A detailed description of the advantages and uses of the HCA in hydrogeochemistry and the mathematical formulation behind HCA is thoroughly discussed in Swanson et al. (2001) and in Güler et al .(2002).

The ability of the HCA to classify groundwater chemistry into coherent groups that may be distinguished in terms of aquifer type, subsurface residence time and degree of human impact on water chemistry provides a good opportunity to conduct hydrogeochemical modeling and understand groundwater geochemical evolution among the different groups or subgroups. In this study, HCA is used to classify waters into objective groups and to conduct geochemical modeling among the different hydrochemical facies. A portable STATISTICA 8 Soft ware, is used to conduct HCA.

The HCA is plotted as dendrogram showing the groups and subgroups of ground waters of the study area. The dendrogam plot shows that there are two major groups and six subgroups of waters. The two major groups are classified based on their TDS value. Group 1 waters are observed as high TDS waters. Group II are classified by low TDS compared to group 1 waters. Group 1 waters are sampled from the gaseous and hot springs and bore holes around Ambo and

Wonchi area whereas group 2 waters collected from rivers, cold springs, and hand dug wells and shallow wells that are found around Woliso, Ambo and Wonchi lake.

The six subgroup are: Group I; Menagesha HDW,YaicheboTurura HDW and Woliso prison compound BH, Group II is Indris river, Wonchi cold spring, Lake Wonchi and Guder river. Group III is Ginchi BH1, the two Hometcho Amunition factory bore holes and Guder town water supply BH. Group IV is Ginchi BH2and the Ambo town Bore holes of Awaro area. Group V is Boji spring near Senkele lime factory, Wonchi thermal spring and Woliso Negash lodge hot spring. Group VI is Ambo mineral water BH, Ambo Ethiopia hotel spring and Wonchi gaseous spring.

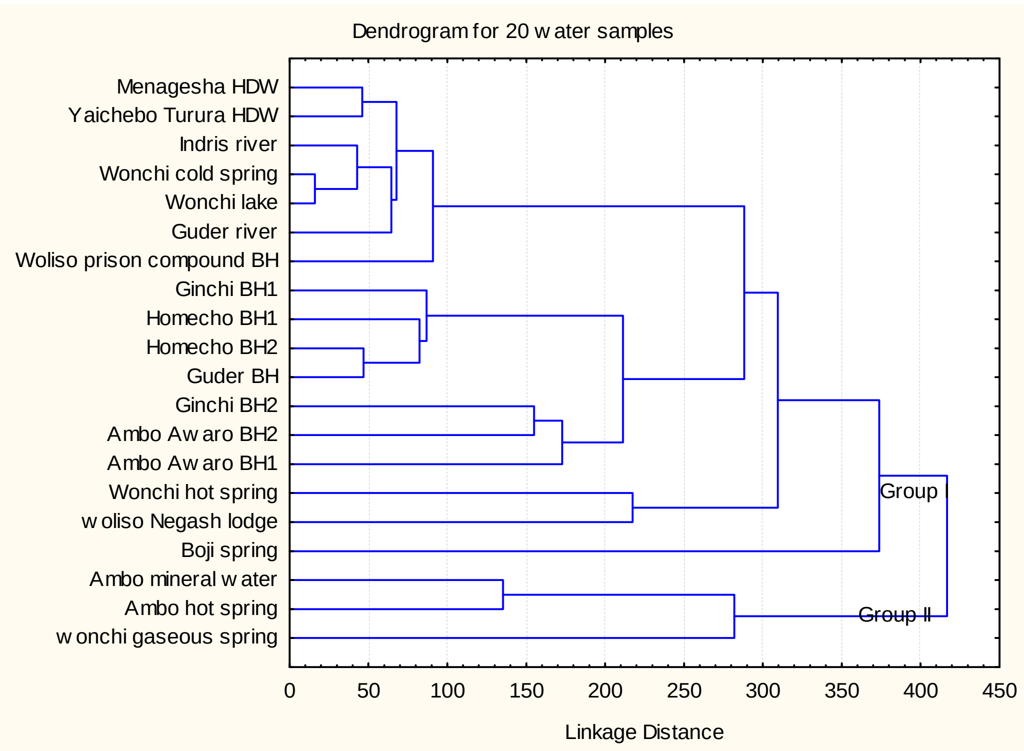

Figure: 4.10. Dendrogram showing Hierarchical cluster Analysis of waters

4.5. Inverse geochemical modeling

Inverse geochemical modeling has widely been conducted in groundwater chemical evolution studies (Plummer et al., 1983; Kenoyer and Bowser, 1992; Varsànyi and Kovàcs, 1997; Hidalgo and Cruz-Sanjuliàn, 2001; Wang et al., 2001). It is a useful approach to determine the type and amount in mole of minerals that dissolve or precipitate along a groundwater flow path. In the cases where information is available on the hydrogeology of the basin, the flow paths can be selected based on the hydrogeological knowledge. The initial and the final member can be chosen by taking into account the location of the point, the hydraulic heads of the aquifer system and observed trends in chemical evolution of the water (Kenoyer and Bowser, 1992; Varsànyi and Kovàcs, 1997; Hidalgo and Cruz-Sanjuliàn, 2001). In areas where information on groundwater flow direction is lacking, the initial and final waters can be selected from the HCA groups. This is based on the logical assumption that waters which fall in a statistical group may have similar residence time, similar recharge history, and identical flow paths or reservoir (Swanson et al., 2001; Güler and Thyne, 2004). PHREEQC computer code (Parkhurst and Appelo, 1999) was used to simulate the geochemical evolution among the average composition of statistical clusters.

4.6. Environmental isotope data analysis

About 20 water samples were collected from groundwater bore holes, springs, lakes and rivers of three major basins:- the Awash basin, Omo-Gibe basin and the Blue Nile basin. These samples were collected during December, 1 to December 3, 2010. The samples were analyzed for their isotopic content of (δ18O, δD) at Addis Ababa university isotope hydrology laboratory. Other samples of thermal gaseous springs, cold springs, ground water wells and rivers and lakes were analyzed for $d^{13}C$ at University of Avignon (France). The $\delta^{18}O$ and δD compositions were reported in & notation calibrated against the V-SMOW. The $d^{13}C$ is reported in & notation calibrated against PDB.

4.6.1. Data analysis for $\delta^{18}O$ and $\delta^{2}H$ isotopes

The representative water samples of ground water wells, rivers, springs and lake were collected to analyze $\delta^{18}O$ and $\delta^{2}H$. Wonchi Crater Lake and hot spring near Wonchi crater lake, gaseous spring near Wonchi crater lake, Yai Chebo Turura HDW and Guder river are the most enriched waters of the study area. While, Indris river which is the tributary of Guder river, Ginchi town Boda site bore hole, Hometcho factory BH1, cold spring of Wonchi on the escarpment of Wonchi crater lake and Menagesh HDW are also have medium enrichment of $\delta^{2}H$.

However Boji spring near Senkele Lime factory, Ginchi town water supply (Boda) bore hole and Hometcho factory BH2 have relatively few enrichment of $\delta^{2}H$. The most depleted ground waters are the gas rich spring and bore holes that are found around Woliso and Ambo area such as Ambo mineral water, Ambo Awaro BH2, Ambo hot spring of Ethiopia Hotel, Negash Lodge hot spring, Guder town water supply bore hole and Woliso prison compound bore hole.

Wonchi Crater Lake, wonchi hot spring, Yai chebo Turura HDW and Boji spring are found below the local meteoric water line. Whereas, Guder river, gaseous spring near Wonchi crater lake, Ginchi town water supply bore holes, cold spring on the escarpment of Wonchi crater lake, Hometcho Factory BH1 and Indris river are found above local meteoric water line. While, Menagesha HDW, Ginchi town BH1 Hometcho factory BH2 and Ambo BH1(Awaro) are found above local meteoric water line with depleted $\delta^{18}O$ value. But the most depleted ground waters that are found below the local meteoric water line are Guder town water supply bore hole, Ambo Hot spring of Ethiopia Hotel, Neagash Lodge hot spring, Ambo Awaro BH2 and Ambo mineral water.
The Wonchi crater lake, Wonchi hot spring, Yai chebo Turura HDW, Wonchi gaseous spring, Guder river and Boji spring are below the global meteoric water line. The depleted gaseous ground waters and springs around Ambo area and the others water samples of the study area are found above the global meteoric water lines. The deuterium excess of the local meteoric water line of the study area is 13.49.

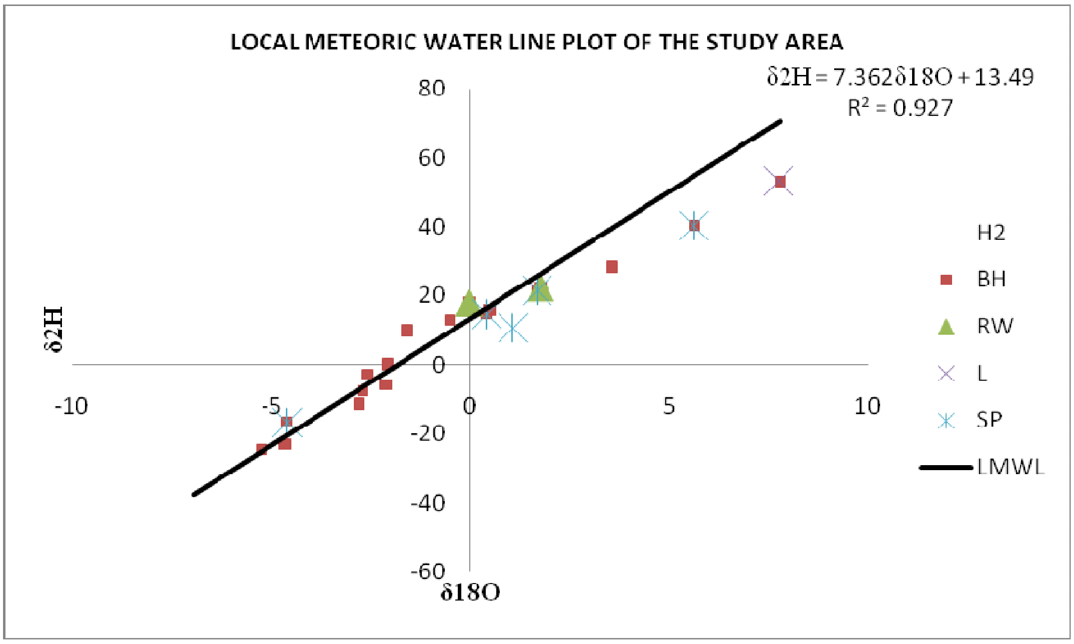

Figure: 4.11. The local meteroric water line and deuteium excess of ground waters of the study are compared with Addis Ababa local meteoric water line.

Sample No.	Sample Code	Sample local name	$d^{18}O$	$d^{2}H$	$d^{13}C$
1	W5-BH3	Hometcho Factory BH1	0.49	15.79	-6.62
2	W6-BH4	Hometcho Factory BH2	-2.06	0.21	-7.76
3	W4-R1	Indris river	-0.01	17.98	-9.75
4	W2-BH1	Ginchi town BH1(Boda)	-1.57	9.96	-12.11
5	W1-HDW1	Menagesha HDW	-0.49	13.11	-10.09
6	W3-BH2	Ginchi town BH2	0.47	15.87	-6.43
7	W20-BH9	Woliso prison compound BH	-2.68	-7.53	-11.41
8	W12-BH8	Ambo town BH2 (Awaro)	-2.56	-2.86	-11.83
9	W13-S2	Ambo hot spring Ethiopia Hotel	-4.61	-16.60	-9.17
10	W10-BH6	Ambo mineral water	-5.22	-24.52	2.86

11	W18-S4	Wonchi thermal spring	5.64	40.55	-7.36
12	W16-L1	Wonchi crater lake	7.80	53.05	-9.25
13	W15-S2	Wonchi cold spring	0.42	14.75	1.44
14	W19-S5	Negash Lodge hot spring	-2.78	-11.44	-14.26
15	W7-BH5	Guder town BH	-2.10	-5.83	-11.36
16	W17-S3	Wonchi gaseous spring	1.70	21.61	-6.81
17	W8-R2	Guder river	1.78	22.24	7.18
18	W11-BH7	Ambo town BH1(Awaro)	-4.64	-23.08	-1.36
19	W14-HDW2	Yai Chebo Turura HDW	3.58	28.36	-5.71
20	W9-S1	Boji spring near Senkele Lime factory	1.07	10.75	-12.37

Table: 4.2. the laboratory result of stable isotopes of $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$

Sample name	GPS location			PH	EC	TDS	Temp	DO	alkalinity
	E	N	El.						
W1-HDW1	0447924	1002120	2411	6.65	334	190	24.4	-	115.9
W2-BH1	0406049	0996479	2219	7.43	577	342	23.8	-	274.5
W3-BH2	0404656	0997734	2233	7.25	755	454	22.8	-	305
W4-R1	0364708	0992962	1977	7.92	187.7	113.2	18.5	0.23	79.3
W5-BH3	0364012	0994386	1933	6.79	575	348	25.2	1.14	268.4
W6-BH4	0363955	0994576	1930	6.66	553	328	25.9	0.93	295.85
W7-BH5	0363642	0990775	2015	7.21	524	314	27.4	1.26	268.4
W8-R2	0363639	0990114	1794	8.12	251	152.1	22.7	1.17	103.7
W9-S1	0367812	0993719	1935	7.07	1235	735	29.4	0.45	488
W10-BH6	0369682	0993850	2016	6.52	1655	994	30.03	1.56	988.2
W11-BH7	0378343	0991473	2188	7.53	920	551	29.3	1.22	481.9
W12-BH8	0378782	099374	2195	7.11	869	519	25	1.06	445.3

W13-S2	0373894	0992816	2195	6.36	1700	1030	36	1.73	1067.5
W14-HDW2	0378209	0981177	2672	6.88	299	179.4	16.9	0.69	95.16
W15-S2	0376303	0971288	2676	7.85	197.9	118.6	11.8	0.71	152
W16-L1	0378141	0972601	2889	8.23	207	128.5	18.1	0.32	152
W17-S3	0377823	0970187	2815	6.06	1463	855	20	1.72	1262.7
W18-S4	0378045	0970164	2817	7.25	1225	736	32.3	0.71	945.5
W19-S5	0387858	0942917	2825	7.66	1127	678	39.6	0.41	427
W20-BH9	0386180	0943990	2039	8.12	294	176.6	26.7	0.04	-

Table: 4.3. The results of field measurements.

4.6.2. The $\delta^{13}C$ data analysis

The $\delta^{13}C$ isotope data is analyzed based on the laboratory analysis done in the Laboratory of University of Avignon. About 20 samples of ground water wells, lake, springs and rivers are analyzed for $\delta^{13}C$ isotope for the CO2-water-rock interaction and hydrogeochemical evolution of ground waters of the study area. The gaseous ground waters of the study area have the highest $\delta^{13}C$ values. The highest value of $\delta^{13}C$ is measured in wonchi gaseous spring, Ambo mineral water, Ambo hot spring, Wonchi thermal spring and Negash Lodge hot spring. The medium value of $\delta^{13}C$ is observed in Menagesha HDW, Hometcho Ammunuation factory BH2, lake Wonchi, Ginchi Boda and Ambo BH1(Awaro). Whereas Boji spring, Ambo town BH2 and Ginchi town water supply BH1 has the medium value of $\delta^{13}C$ value. The Hometcho amunation factory BH1, cold spring in the escarpment of Wonchi crater lake, Guder town water supply BH, Guder river, Indris river and Woliso prison compound BH. The lowest value of $\delta^{13}C$ is analyzed in Yai Chebo Turura HDW.

The results of $\delta^{13}C$ values such as the Wonchi gaseous spring, Ambo mineral water, Ambo hot spring, Wonchi thermal spring and Negash Lodge hot spring show the $\delta^{13}C$ values that indicate the range of dissolved inorganic carbon -5 to 25‰. Menagesha HDW, Hometcho Ammunition factory BH2, Lake Wonchi , Ginchi water supply BH1 and BH2, Boji spring and the two Ambo Awaro water supply BH1 and BH2 are found in the range of atmospheric CO2.

There are some water samples that are found in the range of $\delta^{13}C$ values that indicate the C4 plant and soil CO2 ranges between -10 to -20‰. The Woliso prison compound BH, Yai Chebo turura HDW, Indris and Guder river, Guder town water supply BH, cold spring in the escarpment of Wonchi crater lake and Hometcho Ammunition Factory BH1 are found in the range of the C4 plant -10 to -20‰.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1. Hydrogeochemistry

5.1.1. Introduction

Ground water geochemistry of the waters of the study area is discussed based on the representative water samples collected from the study area. The data of major cations and anions and some field parameters such as PH, TDS, temperature, alkalinity, dissolved oxygen was measured and analyzed. These analyses were done to decipher the hydrogeochemical evolution of thermal and hypothermal ground waters and carbon dioxide-water-rock interaction.

The water samples collected from springs bore holes, lakes and rivers. These water samples include the thermal and cold springs and bore holes from the study area. The pH of ground waters of the study area is measured both in the field and laboratory. The waters of the study area fall in the range of the PH between 6 and 8.23. The highest PH values which are above 7.5 to 8.23 are observed in the samples collected from the Indris and Guder rivers, Lake Wonchi, Woliso prison compound BH, cold spring around Wonchi crater lake, Ambo Awaro BH1 and Woliso Negash lodge hot spring. This is due to the high alkalinity the waters of the area and there cannot be the reactions that lowers the PH.

There are some near neutral PH values in the two bore holes of Ginchi town, Guder town, Boji spring near Senkele and Wonchi thermal spring. The frequent pH value is 7, specify both spring and groundwater are fresh in the area; which is of course, the characteristic of Ethiopian highland water. Its being fresh attributed to the good amount of precipitation received in time of rainy seasons which potentially pose a sort of adjustment in regulating the concentration through supply of huge waters to the aquifers. As result of dilution owing to the foresaid reason when do not find as such exaggerated concentration of groundwater that may induce wide range of pH value.

Low pH waters are concentrated at the area in the gaseous and thermal springs and bore holes around Ambo and Wonchi area. These are the Ambo mineral water, Ambo thermal spring of Ethiopia Hotel and Wonchi gaseous spring are among the low PH ground waters. There are some Hand dug wells such as Menagesha and Yai chebo Turura which show the PH below 7. These are shallow hand dug wells which can have the atmospheric CO2 and vegetation cover, then changed in to H2CO3 to HCO3 that lowers the value of PH. The low PH thermal springs are due to the effect of CO2 injection to charge water so that it becomes violent. Thermal springs with low PH have high values of TDS, EC, DO and alkalinity. The travertine deposits are the common features of these thermal and gaseous springs. While there are some precipitated silica sinters around such springs. According to Abenezer Kefeni et al., 2007, the Huko Korke mineralized spring near Hora Chancho show the typical feature of silica sinter.

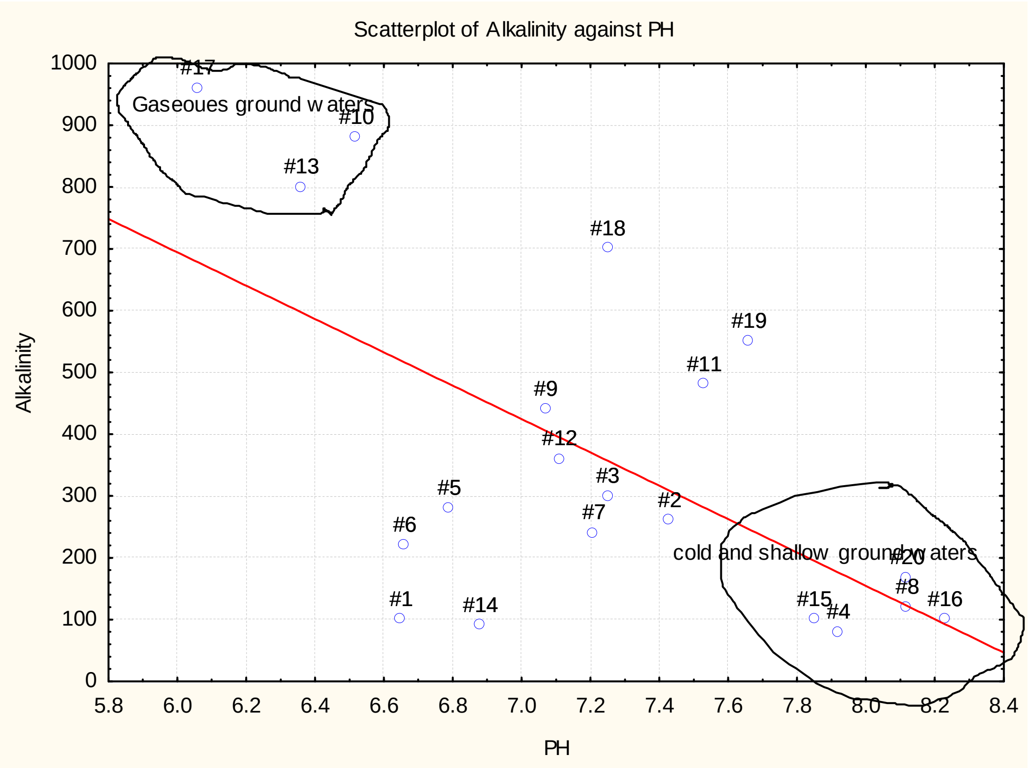

Figure: 5.1. Scatter plot of alkalinity against PH value.

Alkalinity in ground water is due to the amount of inorganic carbon ions present in solution, therefore the alkalinity measurement can be used to determine the $HCO3^{-}$, $CO3^{2-}$ concentration of the ground water. Consequently, as ground water flows through an aquifer, it dissolves more carbonate and silicate minerals thereby increasing the alkalinity and the PH.

The highest alkalinity value among the collected water samples are observed in Wonchi gaseous spring with 1262.7mg/l. The Ambo thermal spring, Ambo mineral water BH and Wonchi thermal spring are followed respectively. This indicates that the long water-rock interaction and the water is energetic enough to leach out minerals from the host rock thereby their chemical concentration increase. In these gaseous ground waters there is a strong CO2-water rock interaction.

The lowest alkalinity values are observed in Menagesha hand dug well, the two river water samples, Yaichebo HDW, cold spring around Wonchi and Wonchi Crater lake. Among the boreholes Hometcho factory bore holes, Guder town bore hole and Ginchi town bore holes have the alkalinity value below 305mg/l, these lowest alkalinity entails very young fresh and shallow ground water that does not make long time interaction with rock in order that the alkalinity is raised.

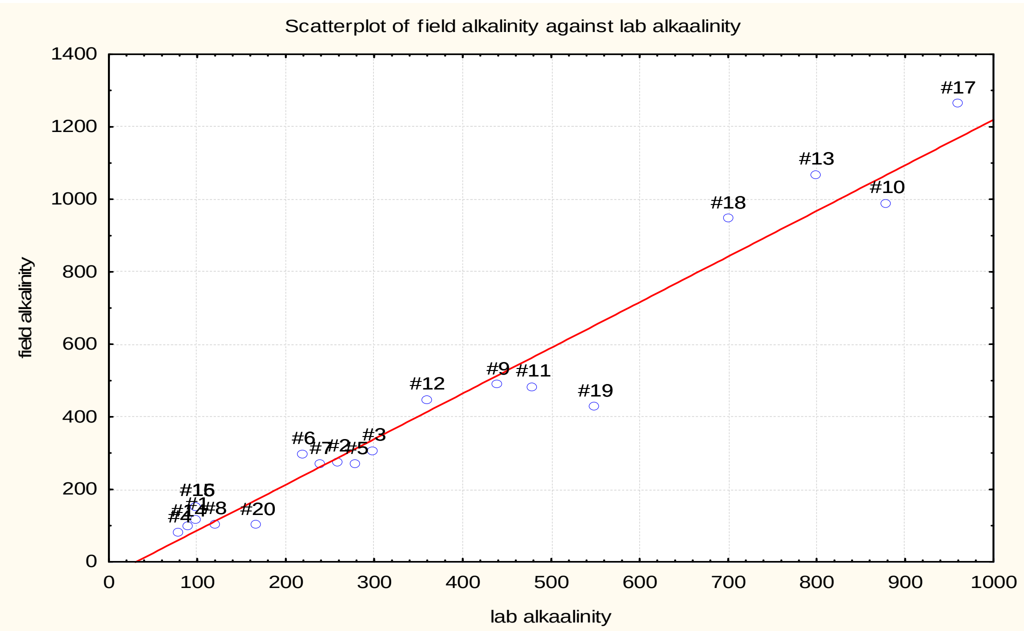

Figure: 5.2. Laboratory alkalinity result against field alkalinity

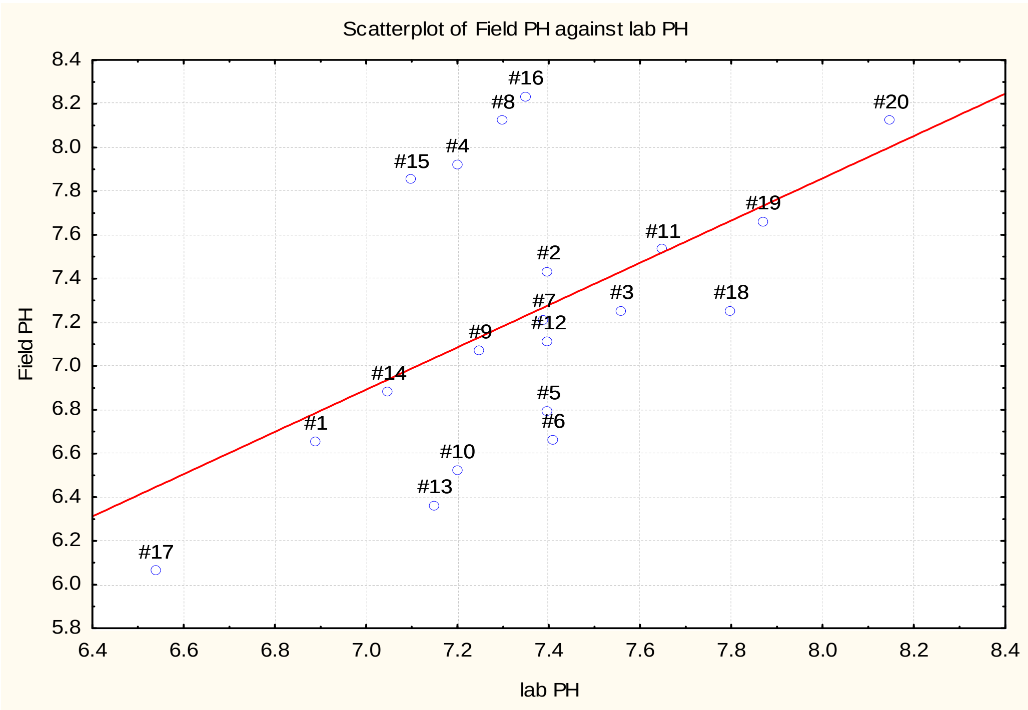

Figure: 5.3. the correlation of field and laboratory results of alkalinity and PH

There is strong relationship of field and laboratory alkalinity but the field PH is not that much correlable with laoratory measurement.

Total dissolved solids of water is an important clue to trace back from which environment or terrain the water is, in addition the extent of solubility of the material through which water makes contact along the flow path. On account of water very nature to react with a lot of substance (rocks) with in its environment of residence or route of journey we can trace dissolved mineral species.

The total dissolved solids of ground waters of the study area from 111.6 to 1030 mg/l. Thermal and gaseous ground waters around Wonchi and Ambo area have high TDS values above 736 Mg/l. The highest TDS value is observed in Ambo swimming pool hot spring. Ambo mineral water and Boji spring around Senkele Lime factory and Wonchi gaseous spring have high TDS vales. This testifies that there is continues CO2 supply which makes the water carbonic acid which is potential fluid to increase dissolved cations and anions species.

Low TDS values are observed in river water samples, lake Wonchi and Wonchi cold spring. This is due the low water rock interaction of the lake and river waters and the spring is also fresh and young ground water that undergoes short time water- rock interaction. The others shallow hand dug wells of Menagesha and Yai chebo Turura and Woliso prison compound bore hole have low TDS values. This indicates that there is shallow subsurface and not significant water rock interaction that can increase TDS value of ground water.

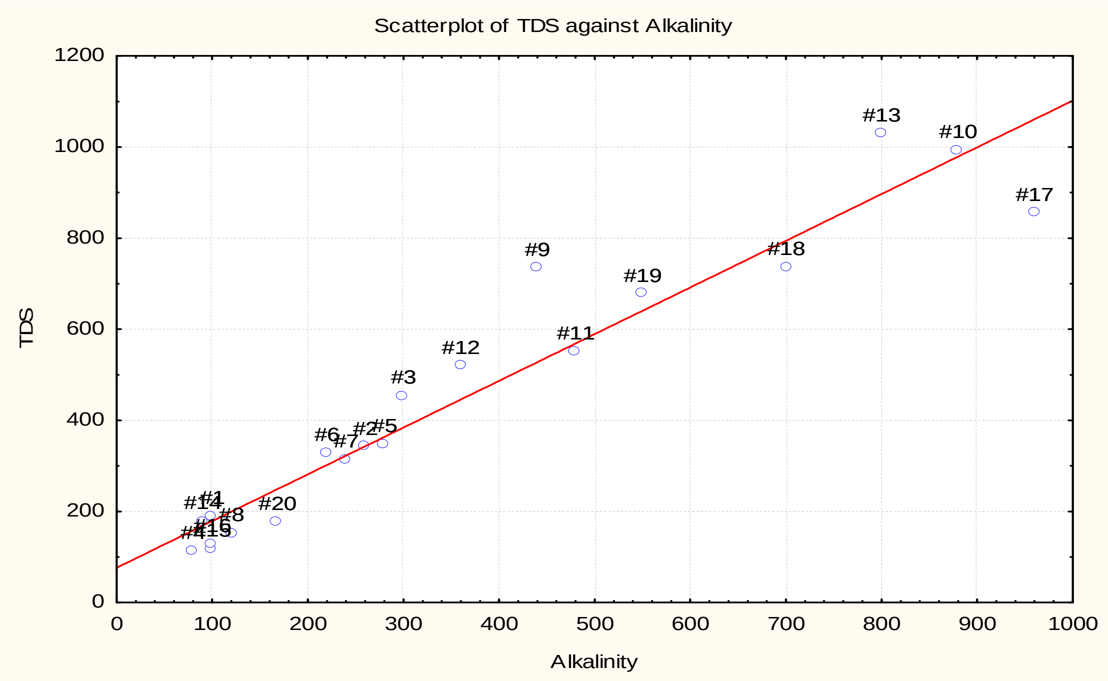

Figure: 5.4. TDS Vs alkalinity

Temperature and other parameters such as color, turbidity, odor, taste, etc represent the physical parameters of water and they are the first hand easiest approach in detecting the quality of water. Most water samples temperature is below25^{0}C except the thermal springs with temperature of 35 to 40^{o}C not irritating when come in contact with the body. From laboratory analysis and field survey color, turbidity, odor and taste of water points do not show objectionable level except limited shallow bore hole and springs which are affected by anthropogenic effect, runoff carried sediments wastes and tree leaves.

In the study area the highest temperature are recorded in Negash lodge hot spring, Ambo swimming pool, wonchi thermal spring and Ambo mineral water. This testifies that the structural effect to bring the water from the deep underground via the fault that crosses along this area. Other parameters like EC and DO increase with increasing alkalinity and TDS.

The hardness of the waters of the study area is measured in areas around Ambo and Guder area. Among the sampled waters, the highest hardness which is above the WHO standard is observed in Boji spring near Senkele Lime Factory. Ambo mineral water, Ambo hot spring, Ambo Awaro BH2, Ginchi BH2, Hometcho BH1 and Wonchi gaseous spring are followed respectively. This indicates that these water samples are rich in calcium which increases the hardness of the waters. This high calcium is imparted by leaching of calcium rich rocks (basic rocks) and from travertine deposit. Ground waters around Woliso area such as Negash Lodge hot spring, Woliso prison compound BH, lake Wonchi and Wonchi cold spring have low hardness. This testifies that acidic rocks like trachyte, rhyolite dominates this area. These rocks release Na to ground water rather than Ca. this seldom decreases the hardness of such ground waters.

5.1.2. **Major ions evolution**

The major cations and anions are presented in the table. The major cations are Ca, Na, Mg and K while the dominant anions are Cl, HCO3 and SO4.

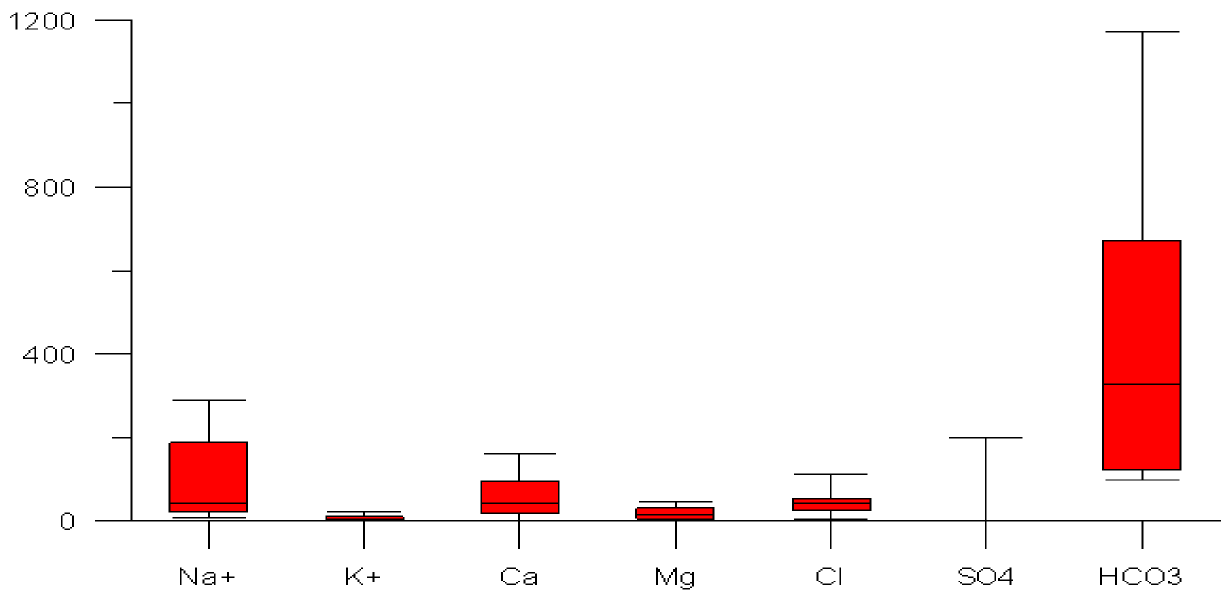

Figure: 5.5. Box and Wisker plot of Major cations and anions

From the major cations observed from the laboratory results, sodium(Na) is the dominant cation. The highest value of Na is measured in the Wonchi and Woliso area. The maximum value which is above the WHO standard is observed in Negash Lodge hot spring, Wonchi thermal spring, Wonchi gaseous spring and Wonchi cold spring. This testifies that the ground waters of the study area drain through the acidic rock such as trachyte, rhyolite which can maximize the value of Na ion. Ambo mineral water and Ambo hot spring of Ethiopia hotel shows high value of Na ion indicates that there is a deep circulation of ground waters of the area and silicate hydrolysis and strong CO2-water-rock interaction. The lowest value of Na ion is observed in Menagesha hand dug well whereas, Guder river and Indris river, lake Wonchi, Wonchi cold spring, Yai chebo Turura HDW and Ginchi BH2 are followed respectively. This shows that there is shallow circulation of ground water and not significant cation exchange to be evolved to Na ion.

Most of the Ca rich water samples were observed around Ambo area in Boji spring near Senkele Lime factory, Ambo mineral water and Ambo Awaro bore holes. Whereas, the highest K value is observed in Wonchi gaseous spring and Wonchi thermal spring. The highest value of total iron is measured in Wonchi thermal spring. The highest Ca which is observed in the area of basic rocks that contain Ca which can be dissolved to the water during hydrolysis of Pyroxene, plagioclase and olivine minerals. In such areas another minerals such as calcite and dolomite can be observed in some sedimentary rocks that out crops in the study area. The travertine lime stone can also found in some hot and gaseous springs can release Ca to ground waters.

In the water samples collected from high lands appericiable values of Mg ion can be observed. The highest value of Mg is observed in Ginchi BH1 which is typical of high land water shallow fresh ground water. This is due to the mineralogy of the rock types of the study area and less water-rock interaction. Where as the highest value of K is mesured in Wonchi gaseous spring and Wonchi thermal spring. This is due to the dissolution of acidic rocks which contains the minerals such as K-feldspars, biotite and secondary minerals such as clay which can release K ion to ground water.

Bicarbonate is the dominant anion in the study area. The highest HCO3 value is observed in Wonchi gaseous spring, ground waters around Ambo area in Ambo hot spring of Ethiopia Hotel, Ambo mineral water, wonchi thermal spring, Boji spring and Ambo awaro BH2. This testifies that these ground waters are rich in CO2. Carbondioxide from magmatic source or metamorphic decarbonation that changed to H2CO3 and then to HCO3.

The ground waters of the Woliso area such as Negash Lodge hot spring, Wonchi thermal spring, wonchi gaseous spring have the highest value of flouride content which is more than the WHO standard. This is due to the dissolution of some secondary minerals of acidic rocks that can release significant amount of flouride to ground waters of Woliso area. The highest value of chloride is observed in Ambo hot spring of Ethiopia Hotel and Wonchi themal spring. This indicates that these ground waters are from deep circulation and there is contact between older ground water. The highest value of chloride can also be due to the low land evaporation and due to precipitation from marine environment.

Relatively the maximum value of HNO3 among the collected water samples are observed in Yai chebo Turura HDW, Ginchi BH2 and Negash lodge hot spring. This value indicates that the pollutant from the Ginchi town and Negash lodge hotel and from the fertilizers of the farm land near Yai chebo Turura HDW. Whereas, the highest value of the sulphate is observed in Boji spring. This is due to evaporative land and or from the sulphate reduction.

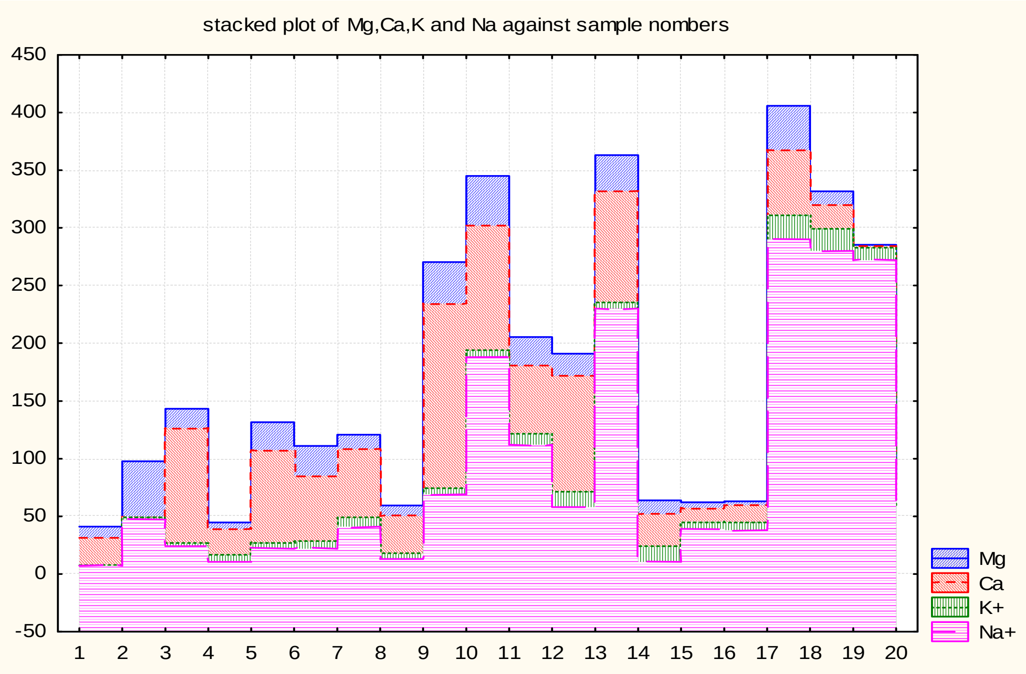

Figure: 5.6. satcked plot of major cations and correlation with sample ID

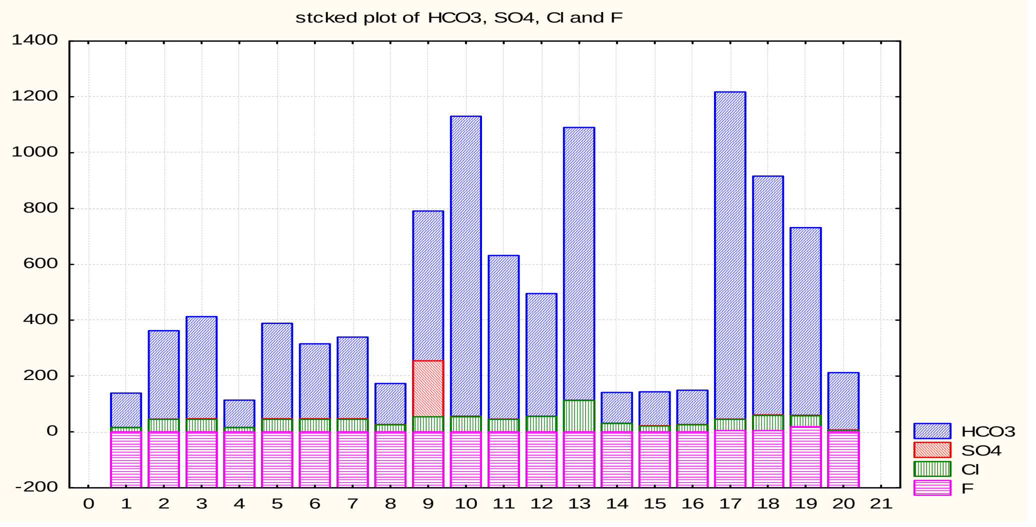

Figure: 5.7. Stacked plot of major anions and correlation with sample ID.

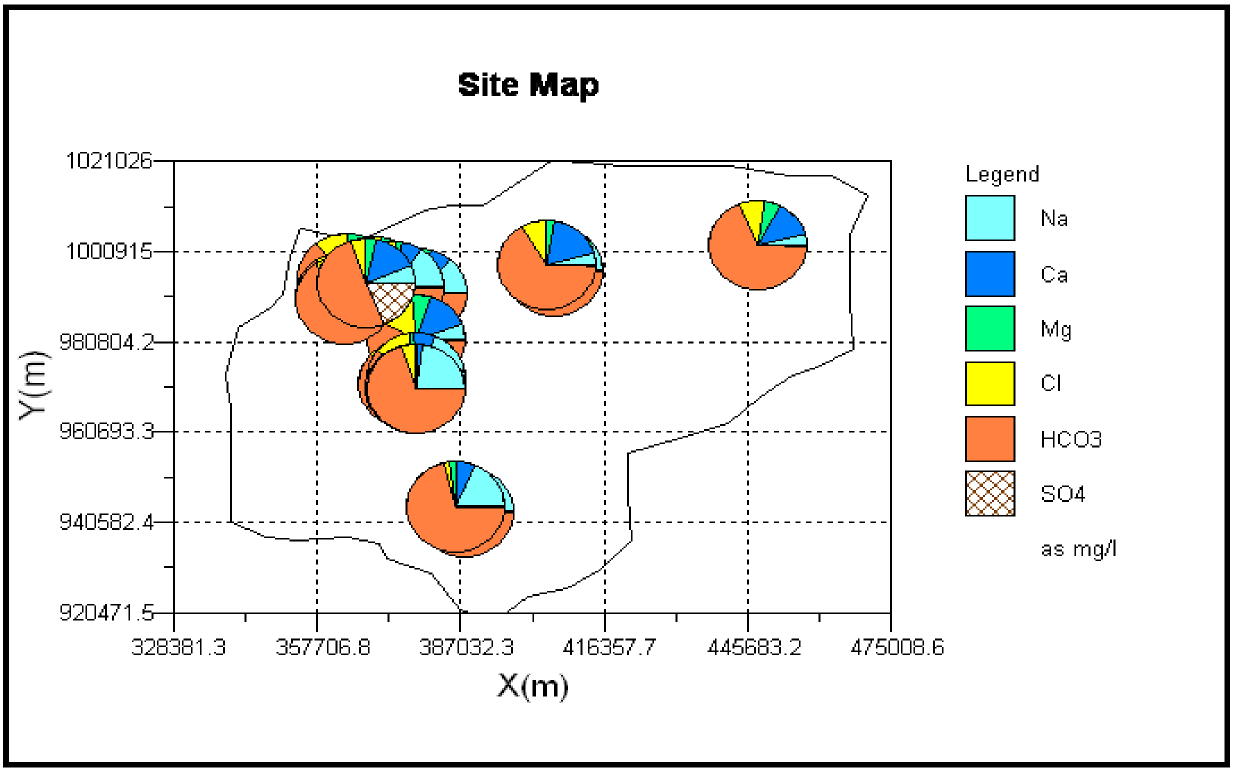

Figure: 5.8. Map showing the Major Ion distribution in the study area

5.2. Hydrogeochemical evolution of ground waters

5.2.1. Hydrogeochemical evolution of thermal and gaseous ground waters

There are two types of ground waters in the regions of thermal and gaseous ground waters of the study area. These are situated in the area around Ambo, Woliso and Wonchi area. In areas around Ambo the water types are Na-Ca-HCO3 while in Wonchi area Na-HCO3. Among the thermal and gaseous ground water Ambo mineral water and Ambo hot spring of Ethiopia hotel are the water types of Na-Ca-HCO3. This suggests that these ground waters show significant water-rock interaction and indicates the long residence time. These ground waters are not completely changed to Na-HCO3, they are balanced ground waters which contains Ca and Na together. This testifies that there is the influence of CO2 influx which can form the divalent ion during the precipitation of calcite with the formation of travertine lime stone. Although sodium and calcium ions are inversely related they can exist together in these ground waters due to the above mentioned reasons.

Whereas, the ground waters in the Wonchi area such as Wonchi gaseous spring, Wonchi thermal spring and Negash Lodge hot spring are completely evolved to NaHCO3 water type. This indicates that these ground waters are deeper fresh ground water which influenced by ion exchange. Silicate hydrolysis such as Albite, NaAlSi3O8 adds the Na ion to ground waters from acidic rocks of rhyolite, pumice and pyroclastic rocks of the area.

Bicarbonate which is the dominant anion in the ground water of the study area indicates that the water has passed through water rock interaction activated by CO2 gas. The source of this CO2 gas from magmatic source and metamorphic decarbonation and in thermal ground water of the study area, silicate hydrolysis is accompanied by influx of CO2 from deeper sources plays a major role for HCO3- enrichment (Kebede, 2005). Due the above reason thermal springs of Wonchi and Woliso area are rich in HCO3- ions. The NaHCO3 ground waters indicate these waters are the deeper circulation and the discharge or outlet area waters.

5.2.2. Hydrogeochemical evolution of cold ground waters

The cold ground waters of the study area are characterized by low TDS, EC and dissolved oxygen. Most of these cold ground waters are the recharge area waters with shallow circulation, short residence time and water-rock interaction. The general trend of ground water evolution of from Western Ethiopian plateau to the rift floor and western low lands is from CaHCO3 to NaHCO3.

Ground water evolution is based on lithology and thermodynamics. The general trend of ground water types of the basaltic aquifer is dominantly CaMgHCO3 while in the acidic rocks such as rhyolite trachyte and Ignimrite the dominant water types are Na-Ca-HCO3. This indicates the influence of lithology on ground water composition.

In the study area the cold ground waters of the study area contains the dominant cations are Ca and Mg while the dominant anions are HCO3 and low concentration of Chloride and sulphate (water sample collected from Boji spring near Senkele Lime factory). Among the water samples of the study area Menagesha HDW and Hometcho factory BH1 are CaMgHCO3 ground water type. This testifies that the typical example of ground waters from high land, shallow, cold and fresh ground water of basaltic aquifer. The source of CaMgHCO3 type water is from recharge area by local precipitation. The ground waters of this type in the study area are characterized by low TDS. Whereas, Ginchi BH2 is CaHCO3 water type. This shows that this ground water is fresh ground water of the recharge area, which is less evolved and there is no significant water-rock interaction. CaHCO3 and CaMgHCO3 have low TDS less than 500mg/l. the low TDS in these bicarbonate-dominated waters is consistent with these ground waters having been recharged relatively recently. The silicate hydrolysis mineral is the dominant process controlling the water chemistry.

The cold ground waters of the study area also contain water types such as CaMgNaHCO3Cl, CaMgHCO3Cl and CaNaHCO3Cl. Such types of waters are found in Indris river, Hometcho BH2, Guder BH, Guder river,Yai chebo Turura HDW, Wonchi cold spring and Wonchi lake respectively. Hometcho BH2,Guder river and Yai chebo turura HDW have the same CaMgHCO3Cl water type. This testifies that Hometcho BH2 and Guder river are nearest to each other and drains in the same lithology. The reason for Cl ion in these ground waters is due to either high evaporation of Guder river due to its low altitude in the deep Gorge that can rise the chloride ion to be high in the river water. When this river water is mixed to the nearest Hometcho BH it can add the chloride in ground water of this water well. While Wonchi cold spring and Wonchi lake are NaCaHCO3Cl water type. The similarity of the two water samples indicates the mixing of lake water and spring due to the hydraulic connection initiated by the structures that disturbed this area. The lithology of the lake area is dominated by acidic rocks that can release the Na and Ca ions. The bicarbonate is due to the silicate hydrolysis. While the chloride ion is from effect of high evaporation of the lake that can precipitate this anion in the water.

Indris river is CaMgNaHCO3Cl water type. This suggests that the river water drains through the basic rocks which can have Ca and Mg ions and the Chloride ion is from the evaporation effect of the river. Bicarbonate is due to the hydrolysis of silicate minerals. Guder BH is CaNaHCO3Cl water type indicates that this ground water is fresh with intermediate water-rock interaction. The source of chloride ion in this ground water is from a clay layer that can be formed as a clay lenses or intercalated in the volcanic aquifer. Boji spring whose water type is CaNaMgHCO3SO4 shows that there is the evaporation effect or H2S reaction in the aquifer.

Ambo Awaro BH1 and Woliso prison compound BH are NaCaHCO3 type of ground water. Whereas Ambo Awaro BH2 is CaNaHCO3 water type. Even if Ca and Na are inversely related in the solution, the Ambo area ground waters are balanced by the two ions. This testifies that the ground waters of such area are influenced by the precipitation of carbonate minerals that that can release the Ca ion to the water and the significant water-rock interaction and ionic exchange can also form Na ion in these ground waters. In Woliso prison compound BH there is a deep ground circulation and long water-rock interaction that can increase the Na ion in this ground water. But the Ca ion in this ground water is from the minerals of basaltic rocks such as hydrolysis of pyroxene.

5.3. Trace element mobility

Twenty representative water samples of the study area are collected to analyze trace element mobility in ground waters. This trace element data is used to conduct the mobilization of trace elements with ground water chemical evolution, for instance in thermal and gaseous ground waters in which significant water rock interaction is commonly expected. The mobility of these elements is used to decipher the role of CO2-water-rock interaction on trace element mobility and the environmental and health impact of ground waters of study area in terms of water quality aspect.

5.3.1. Origin and occurrence of heavy metals

The origin and occurrence of heavy metals in ground water is commonly from acid mine drainage, sulphide minerals and occurrence of nitrate leached from agricultural activities like from fertilizers and manure. Sulphide minerals like pyrite, galena, sphalerite, arsenopyrite and waste materials can heavily pollute ground waters. Acid mine drainage can release low PH and heavy metal loaded water in to the environment (stollenWork1994, Appleyard and Blowes, 1994). The PH has the major influence on the mobility of the heavy metals, but the effect is different for the various metals. Together with sulphate trace components like As, Co, Ni, and Zn are released and reach concentrations many times higher than permissible in drinking water.

The chemical weathering of detrital silicates like amphiboles and biotite and of clay minerals and oxyhydroxides may also release trace metals (Edmundus et al., 1992). Atmospheric input can be important as well. At circum neutral PH, the heavy metals remain fixed by sorption or solid equilibria, but when water turns in to acid they can be mobilized. For example, the water chemistry in shallow aquifer consisting of uncreative siliceous sand has become acidic mainly due to acid rain, and has a PH of 4.5 and increased concentration of heavy metals like Ni, Co and Be (Kjoller et al.,2004). Further down, as the PH increases to around 6.5 and the concentrations of heavy metals are much reduced.

Arsenic may substitute for sulphide in pyrite and the oxidation of pyrite can one of the causes for the high arsenic contents of ground water (Smedley and Kinniburgh, 2002). Subsequent development of anoxic conditions caused the Fe-oxides to become reduced, resulting in the release of the Arsenic to the ground water (Ravenscroft et al., 2001). Recently, Appelo et al. (2002) have proposed that the displacement of adsorbed arsenic by dissolved carbonate could be the cause of the mobilization of arsenic. One of the challenges of hydrogeochemistry is to quantify this sorption behavior, and to assess its influence on the mobility of heavy metals and to predict arrival times of increasing concentrations of these elements. At a given PH, sorption decreases in the order $Cd^{2+} > Zn^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+} > Ba^{2+} > Sr^{2+}$.

Many of the minor and trace elements appear to be useful indicators of lithogenic provenance and ground water chemical evolution. Broadly, Al, Ti, Ba and Rb are indicative of aluminosilicate weathering. For example Rb may be indicative of K-silicate weathering, Ti and Ba of mica weathering. Molybdenum may be indicative of sulphide (MOS_2) or apatite weathering. Indicators of pyrite weathering are less clear because magnetite and ferromagnesian minerals appear to contain and release high concentrations of similar elements, such as Zn, Co and Ni. Lead is present at high concentrations in sulphides (potentially as $PbSO_4$) but no dominant rock or mineral source is obvious for Pb during rock dissolution. While pure calcite dissolution can generate high concentrations of Al, Ti, Zn and As, it is logical to conclude that the concentration of most minor and trace elements will be controlled by silicate dissolution or the oxidation of trace sulphides, because carbonates are proportionally small in catchment bedrock and their minor and trace element concentrations are relatively low.

In ground water samples of the study area the possible source of highest amount of trace elements are probably from the lithogenic source rather than anthropogenic sources like acid mine drainage, agricultural activities such as fertilizers. Elements such as strontium and barium are highly observed in Ambo mineral water, Boji spring and some ground waters around Ambo area. The likely dominant source of Sr is from recrystallization or weathering of silicate minerals and calcite mineral which is common in the area while the source of Ba is from K-Mica or K-feldspars. Elements like Li and B are high in gaseous and thermal ground waters and some water samples such as Boji spring and Ambo Awaro area water wells. The possible source of Li can be aluminosilicate minerals.

Elements such as Mn, Ni and Co are also found in some ground waters. Manganese is highest in Wonchi gaseous and thermal spring, Ambo mineral water and Hometcho bore hole factory. High amount of Ni and Co are observed in Hometcho factory BH2. The possible source of Mn, Ni and CO can be from ferromagnesian minerals. The highest concentration of Fe is measured in Wonchi gaseous, Wonchi thermal springs and Ambo hot spring. The likely dominant source of this element can be from pyrite, ferromagnesian minerals and calcite. However some amount of Cu, Zn and Cr can be seen in shallow ground waters around Ginchi, Menagesha and Yai cheo HDW. The possible source of these elements can be from Magnetite, pyrite, pyroxene and sphalerite.

Figure: 5.9. The photograph of Wonchi gaseous spring highly enriched in Iron.

5.3.2. Environmental and health impact of trace element mobility in ground waters

Heavy metals are strongly poisonous and therefore the highest and admissible concentration for these substances is very low. Enhanced heavy metals concentrations constitute a series problem for water supplies around the world. Once released to ground water the mobility of trace metals is to a large extent controlled by sorption processes which is due to ion exchange. Most sorption is connected with specific binding of heavy metals to the variable charge surfaces of oxides and organic matters.

According to Edmunds and Smedley (1996) the natural geochemistry of groundwaters and surface waters from interaction with rocks, also creates widespread health and acceptability problems in many parts of the world on a regional scale. The case of the arsenic problem in Bangladesh is well known (Smith *et al*., 2000).

Trace metals like Fe, Mn, Cu, Zn, Co, and Ni are micronutrient for living system, their deficiency or excess can lead to a number of disorderness in human body (Jinwal et al., 2009).

Some trace metals like Cd, Pb and Cr can be lethal to human being even at low concentration because of their tendency to accumulate in the body (Domenico and Schwartz, 1998).

The fate of heavy metals, like As, Cd, Hg, Pb and others, in the natural environment is of great concern due to their potential harmful effects (Adriano, 1986 and Alloway, 1995). The deficiencies, excesses or imbalances of chemical elements also have a significant bearing on health. Examples of earth materials include essential and toxic elements are shown in Figure 5.8.

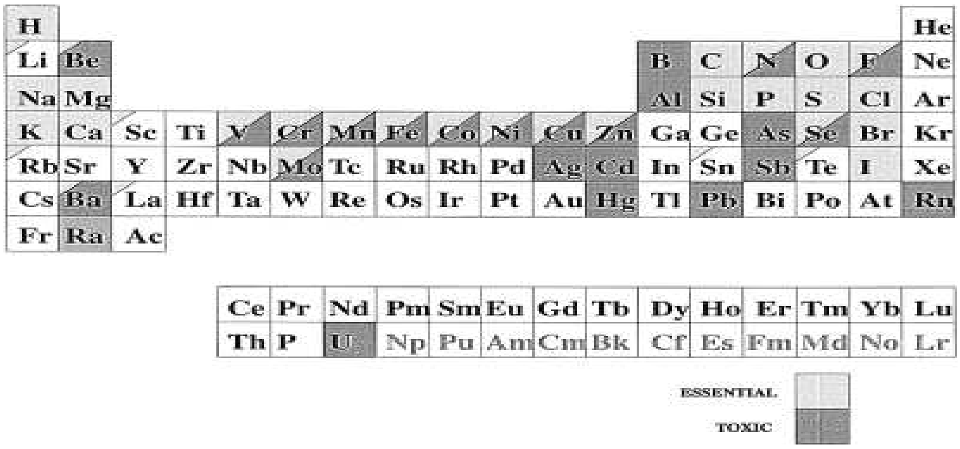

Figure: 5.10. The periodic table showing essential and toxic elements (modified after from Biritish Geological survey).

Trace element mobility in ground waters of the study area interms of health and environmental aspect based on the present data of trace element should be concerned. Trace element data shows that thermal and gaseous ground waters of the study area have the capacity to mobilize trace elements that can be toxic to the human health. High amount of Sr concentration more than WHO standard is observed in 13 ground waters out of twenty water samples. Among the 13 water samples, the maximum concentration of Sr is in Boji spring and Ambo mineral water. Water and soil, which contain much strontium, on consumption often leads to fractures and osteodystrophy. Strontium was also known to have a pronounced rachitic effect (Polyakova et al., 2010). The concentration of Sr was found more than permissible limit of 0.07 mg/L (WHO, 1984). Only Ambo mineral water has higher concentration of Ba more than permissible limit of 0.7 mg/L (WHO, 1984). Barium is not considered to be an essential element for human nutrition (Schroeder et al., 1972). At high concentrations, barium causes vasoconstriction by its direct stimulation of arterial muscle, peristalsis as a result of the violent stimulation of smooth muscles and convulsions and paralysis following stimulation of the central nervous system (Stockinger, 1981). Associations between the barium content of drinking-water and mortality from cardiovascular disease have been observed in several ecological epidemiological studies. Significant negative correlations between barium concentrations in drinking water and mortality from atherosclerotic heart disease (Schroeder & Kramer, 1974) and total cardiovascular disease (Elwood et al., 1974). So that Ambo mineral water Factory due to its high concentration of Barium should have to take remedial measures to avoid such health problems.

Wonchi gaseous spring and Wonchi thermal spring have the concentration of Fe more than WHO standard limit 1.0mg/l. these ground waters have the value of Fe between 5.2 and 1.7mg/l respectively. Whereas Al and Mn are also more than the permissible standard of WHO in Wonchi gaseous spring which are 1.24 and 1.25mg/l respectively. Health wise, there had been a considerable debate on the possible link between Al in drinking water with Alzheimers desease in humans (Craun, 1990; Epstein, 1990; Flaten, 1990). Trace elements like Cu, Zn, Mo, Ni, Co, B and lithium are less than the permissible standard of WHO in ground waters of study area.

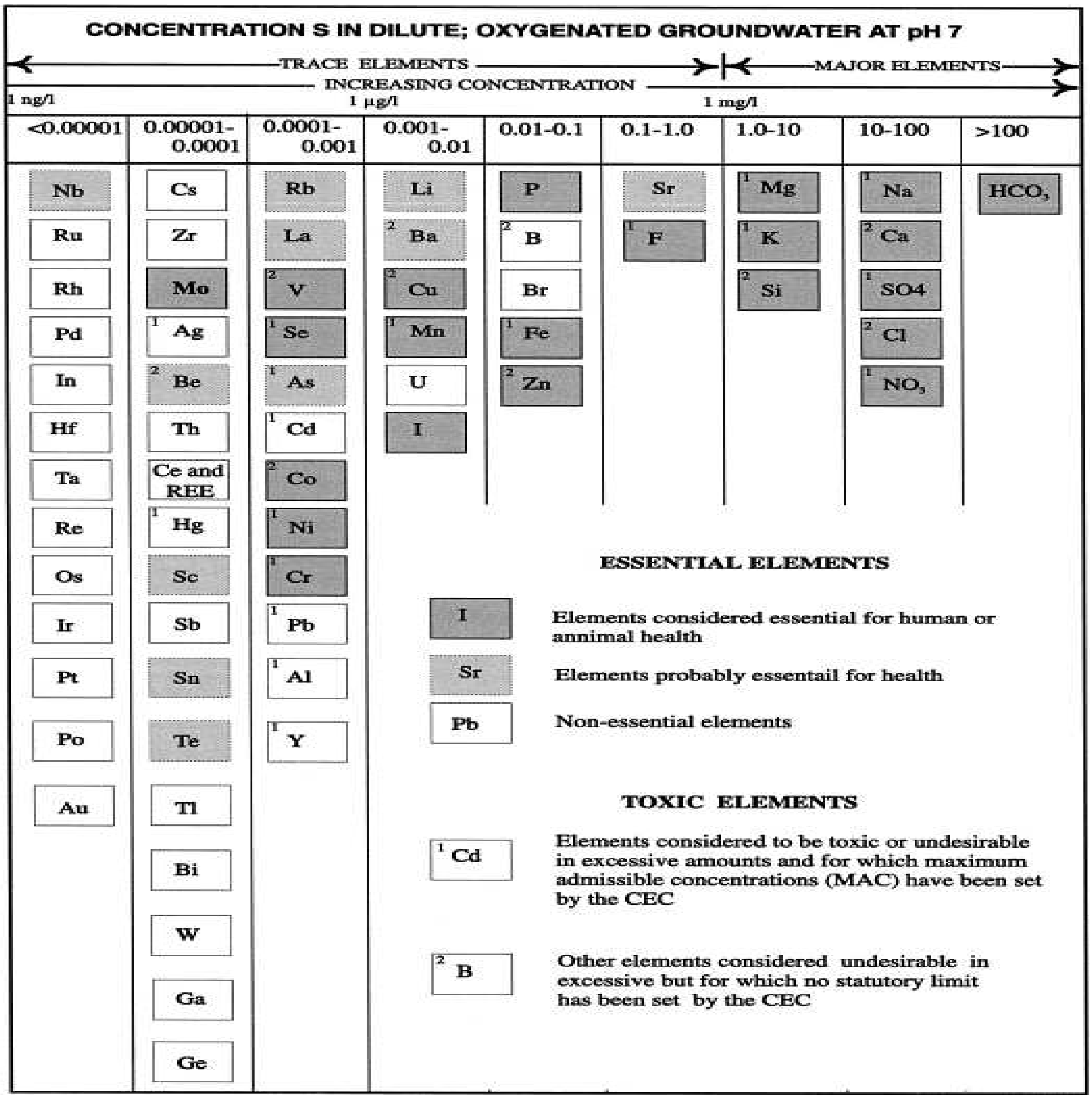

Fig: 5.11. Elements in groundwater and their health significance [after Dissanayake and Chandrajith (1999) and Edmunds and Smedley (1996)]. Some elements are both essential and toxic. Elements that are possibly essential are indicated in a lighter gray shade. (Source: British Geological Survey, UK).

5.4. Isotope hydrology

5.4.1. Isotopic composition of Ethiopian rain fall

Many researches were conducted on identifying the moisture source of the Ethiopian rain fall. The moisture sources of the Ethiopian rainfall come from the Indian and the Atlantic Ocean monsoons (Griffits, 1972, Gemechu, 1977). The flow of the monsoon moisture to the region is controlled by the seasonal migration of the Inter Tropical Convergence Zone (ITCZ).

The seasonal variations control the location of the ITCZ. Hemming et al., 1961; Suzuki et al., 1967; Gemechu et al., 1977; Camberlin et al., 1997; and Nyssen et al., 2004; during summer season (June-July-August) the ITCZ is located in Northern Ethiopia due the influence of the southwesterly and southerly monsoon flows which bring moisture from the Atlantic ocean ,Congo vegetation basin and partly from Equatorial Indian Ocean. Parts of the NWP and the Afar rift get their rain fall during this time. While during October and March the ITCZ is located south of Ethiopia. During this time there will be Northerly flow of dry and cold air of the Arabian continent and the coldest temperature recorded in the high land regions of Ethiopia. Gemechu et al., 1977, the south western plateau produces the rain fall during October-November-December due the moisture source from the Arabian sea and Northern Indian ocean.

The north westerly and south easterly moisture source from the Northern Indian Ocean moving northward brings the spring (March-April) rain at the sectors of south eastern plateau, southern and eastern sectors of the North western Ethiopian plateau. The central parts of the NWP and the lowlands of Ethiopia bordering the Sudan are not influenced by this moisture source. Generally when the ITCZ is located in the North of Ethiopia 75% of the NWP and the MER annual rain falls occurs during the summer season. Whereas, the ITCZ still passing over Ethiopia northwards the 25% of the rain fall occurs during spring season.

There is the local orographic enhancement of rain fall at mountains of Ethiopia (Camberlin, 1997). The African region gets higher rain fall amounts due to orographic enhancement as compared to similar latitude regions of Sahelian Africa. Unlike the Western Sahel which get its moisture from Atlantic Ocean, the Ethiopian highlands also gets their moisture source from Indian ocean and part of its moisture comes from continental sources due to the low-level westerly flows also traverse a vast expanse of vegetated basin in the Congo before they reach the Ethiopian highland.

The isotopic composition of Ethiopian rain fall water shows the seasonal variations. There has been regular measurement of isotopic composition (δ18O, δD and 3H) at an IAEA/WMO station at Addis Ababa since 1965. Although there is a good relation between seasonal variation in isotopic composition of Ethiopian rain falls, the two year rain fall isotopic data of $\delta^{18}O$ and d-exess of Addis Ababa rain falls and the MER show notable seasonal variations.

The isotopic composition of the summer rain fall shows the depletion in $\delta^{18}O$ as compared to spring rain fall. The spring rain fall is enriched and has low d- excess than summer rain falls. The weighted mean composition of the summer rain fall waters at Addis Ababa is -2.5‰ in δ18O and -5‰ in δD and 15 in d-excess while the spring rain fall have weighted mean composition of +1‰ in δ18O, +20‰ in δD in d-excess.

The source of moisture and local meteorological processes controls the depletion and enrichment of the summer and spring rain falls respectively. The summer rain fall (75% of rainfall in Addis Ababa) is derived from the admixture of the Atlantic Ocean and the South/Equatorial Indian Ocean air masses. There is meteorological evidence which states the Congo basin vegetation and Atlantic that are important sources of moisture in summer. Whereas during the most enriched spring rain falls the moisture source comes from the Indian Ocean. This enrichment is controlled by three factors; 1) Joseph et al, 1992 states, the closeness of the Indian ocean to the Ethiopian high lands and the initial stage condensation of the moisture reaches the area without undergoing the major rainout fractionation effect. 2) the low atmospheric humidity, the high temperature and the low amount of rain fall during this time favors the evaporation rain waters leading to enriched rain fall and low d-excess. 3) The high sea surface temperature over North Indian Ocean favors the formation of enriched and low d-excess compositions. The enriched $\delta^{18}O$ and the low d excess compositions of this period reflect evaporation while raining owing to low rainfall during this time. Seasonal variation in deuterium excess is also influenced by the source of moisture and the local conditions. High deuterium excess is recorded in the summer rainfall and in September. The mean weighted d-excess increases continuously from about 10 at the onset of the North Indian Ocean monsoon in March to 16 at the end of the summer monsoon. The continuous increase in d-excess through the summer may indicate the continuous increment in the recycled component of the local moisture. The low d excess in the dry season rains reflect evaporation of rainwater while raining and subsequent evaporative enrichment. The high d-excess in the summer rains also reflect that the rains during this time are less evaporated while raining owing to high rainfall amount and the saturated atmosphere.

There is no direct relation with rain fall and temperature. The rain fall amount and isotopic depletion are not directly related in the NWP, the cold and less humid eastern mountains regions are characterized by the most depleted waters whereas the high rainfall region in western lowlands of the NWP are characterized by enriched meteoric waters. The depleted composition in the eastern highlands of the NWP is therefore the result of rainout effect and low temperature which implies that the 'amount effect' in tropical stations (Rozanski et al., 1993) is suitable to compare inter-annual variation or seasonal variations or rainfall events in δ 18O composition at one particular station than in comparing spatial variations in δ 18O. On monthly time scale also there is no well-defined relation between amount of rainfall and the isotope depletion in Addis Ababa (Gizaw, 2002) and in the west Sahel (Taupin et al., 2002).

There is a good relationship between local temperature and isotopic composition of meteoric waters. This can exist in the NWP as the most depleted meteoric waters are located in the coldest region and the most enriched water in the western warm lowlands. The relation between air temperature and the δ 18O composition has the form: $\delta^{18}O = 0.21\ T\ (°C) - 6.5$.

5.4.2. The $\delta\ ^{18}O$ and $\delta^{2}H$ composition of ground waters of the study area

Isotope techniques are effective tools for obtaining a variety of hydrological information such as origin of groundwater, determination of its age, velocity and direction of flow, Interrelations between surface water and groundwater, possible interconnections between different aquifers, aquifer characteristics, etc. (Aggarwal et al., 2004).

Tracing groundwater by means of environmental isotopes offers unique and supplementary information on the origin and movement of groundwater and its dissolved constituents, as well as allows a quantitative evaluation of mixing and other physical processes such as evaporation and isotopic exchange in geothermal systems (Mook, 2000). They provide important insights into the origin of waters, recharge conditions; water-rock interactions and water flow paths (Clark and Fritz, 1997; Cook and Herczeg, 2000).The isotopic signals vary in water according to history and path way through different hydrological cycles. Based on this features we can use stable isotopes to identify the origin of ground waters.

In this study, $\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$ and some secondary data were used to investigate the hydrogeochemical evolution of thermal and hypothermal and carbon dioxide-water-rock interaction of ground waters of the region. The isotopic compositions of Lake Wonchi, Guder and indris river, thermal and cold springs and the groundwater the ground water bore holes are investigated.

Based on their spatial distribution the isotopic compositions of waters of the study area are categorized into three main groups. The first group comprises groundwater bore holes, springs, two rivers collected from the Ambo and Guder area.The second group comprises the gaseous thermal and hypothermal springs collected from the Upstream and downstream Wonchi Lake. Whereas the third group comprises the water samples collected from the Woliso area. The fourth group comprises the waters collected from Ginchi and Menagehsa area.

5.4.3. The δ ^{18}O and $\delta^{2}H$ composition of thermal ground waters

Most of thermal ground waters of Ethiopia are concentrated in the Rift floor and marginal grabens. This is due to thermal anomalies which are wide spread all along the rift. Whereas the high land thermal springs are associated to regional structures that crosses the area. The thermal springs in the study are associated to the E-W trending transversal fault of Yerer-Tullu-Welel volcano tectonic lineament. The Ambo fault is also the set of this E-W trending regional structure. Ambo-Woliso-Butajira fault is also another structure that channels thermal ground waters in the study area.

The isotopic composition of rain fall and ground waters compared to each other. There is similarity between $\delta^{18}O$ and δD compositions of the ground waters and that of weighted mean summer rainfalls in the rift valley sector (Seifu Kebede 2004). Lack of influence of evaporative concentration of the isotopes in ground waters and the similarity between the isotopic compositions of the ground waters and that of the composition of summer rainfalls indicate that recharge occurs principally from summer rainfall. The spring rainfall oxygen isotopic signature having $\delta^{18}O>0$ ‰ (Seifu Kebede et al., 2003) is not commonly observed in the ground waters. This testifies that recharge to ground waters takes place only from the summer rainfall ruling out the importance of the spring rainfall as a source of recharge.

The isotopic analysis of thermal ground water bore holes and springs of Woliso, Wonchi and Ambo area were conducted for the purpose of this study. According to Seifu Kebede et al.2005, The low temperature thermal waters (hypothermal waters) and the high TDS *Na-HCO3* type waters of the LTG and the YTVL are characterized by relatively highly depleted $\delta^{18}O$ compositions. The highly depleted $\delta^{18}O$ composition of the high TDS *Na-HCO3* springs of the YTVL and the LTG indicate that recharge must have taken place at higher altitude sources. The Wolliso and the Ambo high TDS thermal springs are most likely recharged around the highland midway between the two regions.

In this thermal waters were collected from Ambo hot spring, Ambo mineral water, Wonchi thermal spring and Woliso Negash Lodge hot spring. The $\delta^{18}O$ composition of these samples indicates that they are the most depleted ground waters of the area. Most of these samples are rich in CO2 except the Negash lodge hot spring and Wonchi thermal spring. Exceptional case was observed in Wonchi thermal spring plotted below the LMWL showing signs of $\delta^{18}O$ and δD enrichment. Since this thermal spring emerge near the Wonchi Crater Lake, the heavy $\delta^{18}O$ and δD content is related to mixing of the thermal spring with Wonchi lake water.

The thermal springs in the study area plot above the LMWL. Thermal waters have the δ18O-depleted ground waters and contain higher d-excess. This is related to the negative oxygen shift (displacement of the waters towards the left of the LMWL in a $\delta^{18}O$-δD plot). The Ambo and Woliso thermal waters are rich in CO2 which comes via Ambo-Woliso-Butajira fault (Kebede 2004). Exchange between the ^{18}O of the waters and that of the CO2 can give rise to the negative oxygen shift, a well-known phenomena in CO2 rich thermal waters (D'Amore and Panichi 1987).

As compared to the thermal waters of the study area the relative enrichment of the Rift Valley waters is related to the importance of evaporative fractionation before recharge (Kebede et al., 2003). The geothermal waters of the Rift Valley plot close to the LMWL while thermal waters from three geothermal systems in the axial part of the Afar rift (Allalobad, Tendaho and Dobi) plot below the LMWL following a horizontal line commonly known as the positive oxygen shift. The positive oxygen shift in the Afar geothermal waters, as previously suggested, are the result of 18O exchange between the geothermal waters and the silicate rock matrix of the reservoir (UNDP 1973; Schoell and Faber 1976; Craig et al. 1977) and thermal springs in southern Afar plot close to the LMWL.

There are different mechanisms of isotope exchange between water and minerals. This is restricted to ^{18}O or ^{2}H while some times exchange of other isotope such as ^{13}C can occur between mineral solutes and gases. There must be two phases in contact and be reacting to have isotopic exchange, such as the ^{18}O between water and calcite:

$CaCO2\ ^{18}O + H2O = CaCO3 + H2\ ^{18}O$

Between quartz or chalcedony and water**:**

$SiO\ ^{18}O + H2O = SiO2 + H2\ ^{18}O$

Exchange with feldspar**:**

$CaAl_2Si_2O7^{18}O + H2O = CaAl2Si2O8 + H2\ ^{18}O$

Exchange with clay hydration waters (chlorite in Example

$14(Mg,Fe)5AL_2Si_3O_{10}(OH)7(^{18}OH) + H_2O = 14(Mg,Fe)5Al_2Si_3O_{10}(OH)8 + H_2\ ^{18}O$

Dissolution and precipitation of the mineral is one mechanism by which isotope exchange, where ^{18}O (^{2}H if present in the mineral or gas) is mixed between the two reservoirs. Mineral alteration such as weathering of feldspars to clay minerals, allows the exchange of oxygen and hydrogen exchange with clay hydration waters.

Isotope exchange process is the direct exchange of ^{18}O or ^{2}H between water and mineral crystal lattice. The kinetics of the diffusion controlled reactions are temperature dependent and mineral specific. For example, the loose lattice structure of feldspars allows ^{18}O to exchange, even a temperature below 100C (O`Neil and Taylor, 1967). In a closed system with no significant temperature in and or out, the relative size of the reacting reservoirs become an important consideration.

5.4.4. The $\delta^{18}O$ shift in geothermal waters

Criag, in 1963, first noted that geothermal waters showed positive 18O shifts of varying degrees from the meteoric water line (MWL). He attributed it to high temperature (up to 300C) exchange of ^{18}O between the fluids and reservoir rocks. No effect on the ^{2}H content of thermal waters is evident, due to the low representation of H in most rock-forming minerals. Ground water of meteoric origin are generally far from isotopic equilibrium with the minerals of the host aquifer rocks, given that the water is highly depleted in ^{18}O compared to minerals. Isotopic exchange will slowly move the system towards the equilibrium. In most aquifers the temperature is too low and circulation rates too high for any quantitatively significant alteration of ground water.

At high temperature the equilibrium fractionation for ^{18}O between minerals and water is reduced, thus increasing the initial degree of disequilibrium. The rate of isotope exchange is also increased at elevated temperatures. The ^{18}O reflected in geothermal waters reflects isotopic evolution towards mineral-water equilibrium at reservoir temperatures. The initial isotopic difference between the rocks and the recharge water (^{18}Orock-water), and the water-rock ratio, are also important factors as in any mixing relationship.

In the low temperature water-rock interaction, the geothermal shift observed for 18O in geothermal ground waters is a trend towards isotopic equilibrium between 18O-depleted meteoric waters and 18O-enriched rocks at high temperature. In lower temperature environments, however, the reverse can be observed. Increased fractionation between waters and minerals results in ^{2}H-enriched and 18O-depeleted waters that plot above the meteoric water line. Retrograde exchange between water and primary minerals, and hydration of primary silicates, are the two dominant exchange reactions.

Deuterium enrichment can also arise through exchange with H2S. Hydrocarbon-bearing strata that host formation waters with high sulphate content can produce H2S.

Isotope exchange in gas-water reactions

In most normal ground water systems, dissolved gases have little or no influence on the isotopic composition of ground water. Rather the isotopic composition of a gas phase is generally controlled by exchange with the water.

The ^{18}O exchange between H_2O and CO_2

Another gas-water exchange reaction often implicated in the modification of this isotopic composition of water is that of 18O between CO2 and H2O. In this system with high ratios of CO2 to water, one could expect a negative shift in δ18O-H2O. However, negative oxygen is seldom seen. This may be to the high volumes of CO2 required for a measurable shift in ^{18}O, as well as to the nature of subsurface CO2 sources which are normally enriched in 18O to begin with.

Co2 generated by the high decomposition of lime stone (contact metamorphism) is a principal cause for natural, high Pco2 ground waters. The decarbonation of CaCO3 produces CO2 that is enriched in ^{18}O (Shieh and Taylor, 1969; Valley, 1986).

The thermal and the high TDS ground waters from the YTVL which includes the thermal waters of the Ambo, Wonchi and Woliso contain ^{3}H concentration less than the detection limit. This reflects deeper circulation of groundwater and older ages of the high TDS *Na-HCO3* ground waters. The absence of appreciable amount of tritium in high TDS waters also testifies lack of any modern day meteoric water mixing into them. These waters must have followed deeper circulation pathways before they emerge as low temperature thermal waters.

5.4.5. The $\delta^{18}O$ and $\delta^{2}H$ composition of cold ground waters

The isotopic analysis of $\delta^{18}O$ and $\delta^{2}H$ conducted on cold ground waters from springs, bore holes, hand dug wells, wonchi lake and two river waters of the study area. Most of the cold water samples from the study area are low TDS and high PH waters. Exceptional case was observed in Wonchi gaseous cold spring with highest TDS measurement. Most of these cold ground waters are situated on the high altitudes of the area.

The general trend of isotopic composition of surface waters such as lakes and rivers reflects that of precipitation over the catchment basin. When the rains are more abundant, the river water will be depleted in heavy isotopes as a consequence of the altitude effect. In this case ground water will be depleted with respect to local precipitation. Other isotopic variations in rivers are caused by heavy rains after a relatively dry period. In this case, the different isotopic and chemical compositions of rain and ground water allow the direct contribution of rain water to river discharge to be distinguished from that of ground water.

Lake water is often enriched in heavy isotopes as a consequence of evaporation. Therefore the contribution of lake water to ground water can be identified and under favorable conditions, quantified. The degree of enrichment depends on the lake water balance. The maximum enrichment occurs in closed lakes, where all the inflowing water is removed by evaporation (Gonfiantini, 1986). But in the case of surface waters (rivers and lake Wonchi), the maximum enrichment of $\delta^{18}O$ and $\delta^{2}H$ isotopes can be observed. This is due to the influence of evaporation of lake and river water which can cause the enrichment of heavy isotopes than the adjacent ground water.

Indris river which is the tributary of Guder river which is also the main tributary of Abay basin are sampled for $\delta^{18}O$ and $\delta^{2}H$ analysis show the significant enrichment. These water bodies frequently have isotopic compositions different from that of precipitation over the study area. Rivers often carry water that is derived from precipitation at much higher altitude, and are therefore depleted in heavy isotopes. Sometimes, in arid climates, river water may be enriched in δD and $\delta^{18}O$ through evaporation. Significant heavy isotope enrichment by evaporation is a common feature of lakes and swamps, particularly in semi-arid and arid climates.

According to previous researcher Seifu Kebede et al., 2007, tendency of depletion (- 0.1 ‰/100 m) of $\delta^{18}O$ with altitude is observed in the low TDS cold ground waters. In general, the low TDS cold ground waters in mountainous regions east and northeast of the Blue Nile basin are characterized by relatively depleted $\delta^{18}O$.
The altitudinal variation in $\delta^{18}O$ is consistent with the variations in other tropical regions as reported for mountains in Cameroon (Njitchoua et al. 1999) and Kenya (Rietti-Shati et al. 2000). However the $\delta^{18}O$ of present day highest altitude cold springs are not as depleted as the $\delta^{18}O$ of the high TDS waters. This indicates that recharge of the high TDS waters took place under a probably colder climate than today.

The cold ground waters collected from the study area such as Yai chebo Turura HDW which shows the enrichment of δ18O value up to +3.58‰ with a low temperature of $16.9^{0}C$. This enrichment is due to the evaporative nature of the hand dug well and the nearest swamps surrounding the area. Wonchi cold spring which is found at the escarpment of the Crater Lake indicates the enrichment in δ18O = +0.42‰ with the lowest temperature about 11.8^0C. This indicates that the influence of the evaporation of the lake and the evaporative wet lands above the lake escarpment feeding this spring which is topographically situated downstream.

Wonchi gaseous spring is the exceptional case from other cold ground waters of the area. It indicates the high TDS which is similar to thermal ground waters. But the temperature of the spring is 20^0C. The δ^{18}O of this spring indicates the enrichment up to +1.7‰. The cause of the enrichment of this spring is due to its hydraulic connection with Wonchi Crater Lake and the spring is topographically situated downstream of the lake.

The δ^{18}O value of Guder River shows the enrichment in δ18O= +1.78‰. The cause of this enrichment indicates that Guder River drains through the deep Gorge which can cause the evaporative nature to the river to have the enrichment of heavy isotopes. While the Indris river which is the tributary of Guder River shows the depletion of δ18O = -0.01‰. This depletion indicates that this river drains from high altitude region which cause the depletion in δ18O value.

Ginchi water supply BH2 is enriched in δ^{18}O up to +0.47‰. This enrichment is due the situation of this bore hole near Awash river Which can cause the possibility of evaporative enrichment. While Ginchi BH1 found at Boda area and Menagesha HDW are depleted in δ^{18}O value, which can indicate the recharge source is from the high altitude ground water of the plateau region.
Homecho Factory water supply BH1 and Boji spring near Senkele lime Factory are isotopically enriched in δ^{18}O value up to +0.49 and +1.07‰ respectively. The possible cause of the enrichment of Boji spring is due evaporative nature the spring area. Whereas the enrichment of Homecho factory BH1 is due to the pre evaporative nature the recharge water or due to the mixing of the water with Guder river. Near Hometcho factory BH1 there is the irrigation activity, so that this irrigation water infiltrated to this water well. This can be the cause of enrichment due to evaporation effect. The Homecho Factory BH2 very close about 150m to Homecho BH1 indicates the depletion δ^{18}O value of -2.06‰. The cause for the depletion of this bore hole shows that the

source of recharge is from the high altitude of the area. The difference in isotopic value of these two bore holes indicates that the source of recharge is from different region.

Ground waters of Ambo and Guder area show the depletion in $\delta^{18}O$. The two Ambo Awaro area water supply BH1 and BH2 indicate $\delta^{18}O$ value up of -2.56 and -4.64‰ respectively. While Guder town water supply BH have $\delta^{18}O$ value of -2.10‰. This depletion indicates that the recharge source ground waters Ambo and Guder area is from older and depleted cold ground waters of the high altitude plateau region surrounding the area. Woliso prison compound bore hole which have similar type ground water to Ambo area also depleted in $\delta^{18}O$ = -2.68‰. The recharge source of this ground water is also from the isotopically depleted high altitude region.

According to Seifu Kebede et al., 2005, some representative samples collected from the low TDS ground waters from the basaltic plateau have appreciable amount of tritium unit. This suggests that the recharge of modern ground waters is common to such ground waters.

5.4.6. The $\delta^{18}O$ and $\delta^{2}H$ composition of Wonchi Crater Lake water.

Wonchi Crater Lake is one of the isolated Crater Lake whose hydrology is dominated by ground water inflow with minor contribution of surface inflow from crater walls. The morphometric and chemical characteristics of the lake studied by Seifu Kebede et al., 2009, the volume of the water is 249×10^{6}m, the area of the lake is 4.4km^{2,} the average and maximum depth are 30 and 78m respectively. The dominant water loss is surface water and evaporation while the dominant water gain is by ground water.

According to Seifu Kebede et al., 2009 states that in all the lakes except Lake Tana and crater lakes in the plateau (Wonchi, Zengena and Tirba), evaporation accounts for more than 75% of water loss. Between 50% and 60% of water losses in the closed crater lakes (Wonchi, Zengena, Tirba) is through groundwater seepage.

The $\delta^{18}O$ and $\delta^{2}H$ data show the isotopic enrichment which varies in a wide range. The value of $\delta^{18}O$ changes from ca. +3‰ to +14‰ while δD varies from ca. +25‰ to +80‰. The slope of LEL varies between 5.2 and 6.4 for the majority of the investigated lakes. All other lakes in Eastern

Africa (including lake Victoria, Malawi, Tanganika, Naivasha, Turkana, Chad and several other small lakes) show similar evaporation slope ranging from 5 to 6 (Fontes et al., 1970; Craig, 1974; Gonfiantini et al., 1979; Bergonzini et al., 2001).

The $\delta^{18}O$ and $\delta^{2}H$ composition of Wonchi Crater Lake shows the isotopic enrichment. The value of δ18O and δ2H is 7.8‰ and 53.05‰ respectively. There is hydraulic mixing between the lake water and the surrounding ground water from the upstream and downstream. The lake dominates the springs surrounding its area to be isotopically enriched. This indicates the typical signature of the hydraulic mixing of the lake with ground waters of the area. This mixing of the lake water which caused the isotopic enrichment is due to the NW-SE trending fault which cut across the lake area. The plot for the $\delta^{18}O$ and $\delta^{2}H$ of the study area shows that the lake water is plotted below the local meteoric water line on the evaporation line.

5.4.7. Carbon-13 evidence for the source of CO2

The origin of CO2-rich waters is very controversial and many questions may arise in the appraisal of underground circulation of hot and cold CO2-rich mineral waters of a given study area. The aim of this study is to summarize the available geochemical data on the origin of CO2 in Wonchi system hot and cold CO2-rich mineral waters. The $\delta^{13}C$ values is used in thermal and non-thermal mineral waters to understand groundwater circulation paths and to determine correlations between the thermal and cold CO2-rich mineral waters that discharge in the study area.

Carbon dioxide (or total carbon) is present in mineral water in various forms: CO2 (g), CO2 (aq), $HCO3^{-}$ and $CO3^{2-}$. The proportion of these species is related to the PH and the temperature of the fluid. The carbon dioxide undergoes hydration and ionisation (Hem 1970). The hydration of CO2 forms H2CO3, and the ionisation of H2CO3 produces $HCO3^{-}$ and $CO3^{2-}$.

The carbon bearing materials can have the characteristic $\delta^{13}C$ values. Carbonate rocks typically have $\delta^{13}C$ value of 0±5‰. Hydrothermal carbonate can be outside of this range. Plants convert atmospheric carbon ($\delta^{13}C$= -7‰) to organic compound via photosynthesis. C3 plants have values about -25‰ (range -22 to -33‰). C4 plants have $\delta^{13}C$ values about -12‰(range -10 to -20‰ Bender,1971, Deins, 1980). The $\delta^{13}C$ value of dissolved inorganic carbon (DIC) is generally in the range of -5 to 25‰. More negative values usually indicate the presence of oxidized methane.

The primary reactions that produce DIC are: 1) weathering carbonate minerals by acidic rain or other strong acid. 2) weathering of silicate minerals by carbonic acid produced from the dissolution of biogenic soil CO2 by infiltrating water and 3) weathering of carbonate minerals by carbonic acid.

Previous researchers suggested that the $\delta^{13}C$ is higher in thermal waters, indicating source of CO2 from mantle or from metamorphic decarbonation. The sources of $\delta^{13}C$ in shallow young ground waters from basaltic aquifers show typical soil carbon having its source from C4 plants. This is consistent with the land use pattern and the result of δ13C from plants and soil in the region as reported by Zewdu and Hogberg (2000). Cold ground waters from basaltic aquifers around Addis Ababa (on the southern water divide of the Blue Nile Basin) show $\delta^{13}C$ ranging between -4 and -12‰ (Gizaw,2002) this testify the dominant source of CO2 in shallow ground waters of the basaltic plateau is soil CO2.

The Filwuha thermal springs as noted by Gizaw 2002, the springs are characterized by high TDS, high Na and bicarbonate. Furthermore the springs are enriched in carbon-13. They are the most depleted in $\delta^{18}O$ and δD. The enrichment in carbon-13 is caused by CO2 coming from mantle or fro metamorphic decarbonation of Mesozoic sediment buried at deeper levels. According to some authors indicated that the Filwuha themal spring is similar to Ambo-Wonchi-Woliso in geochemistry, $\delta^{18}O$ and $\delta^{13}C$ characteristics.

The $\delta^{13}C$ value was measured in 20 water samples of the study area. This value ranges from -14.37 to 7.18‰. the ground waters are divided in to two distinct populations, an isotopically depleted $\delta^{13}C$ group from -14.26 to -6.43‰ and isotopically enriched $\delta^{13}C$ group from -5.71 to 7.18‰.The $\delta^{13}C$ content of the high TDS gaseous ground waters varies between +1.44‰ and +7.18‰ PDB. These $\delta^{13}C$ rich waters are Wonchi gaseous spring, Ambo mineral water and Ambo hot spring of Ethiopia Hotel. Thermal spring of Wonchi and Woliso Negash Lodge hot spring have -1.36‰and -5.71‰ respectively.

The gaseous ground waters of the study area are more enriched than the $\delta^{13}C$ value of mantle CO2 which varies between -3‰ and -8‰ (Hoefs, 1997). This is the most plausible mechanism because the $\delta^{13}C$ of CO2 of carbonate rocks ranges between -4‰ and +4‰ (Craig, 1963). The most enriched gaseous ground waters which are in range of +1.44 and 7.18‰ show of the interaction CO2-water-rock from metamorphic decarbonation of carbonate rocks. The carbonate rocks such as lime stone and sand stone occurs around the Ambo area while this carbonate rocks not outcropped on the surface around Woliso and Wonchi area.The $\delta^{13}C$ rich ground waters have high value of HCO3-, TDS,EC and low PH value and depleted in $\delta^{18}O$ and δD composition except the springs around Wonchi crater lake which caused the isotopic composition of the ground waters of the area to be enriched to evaporation effect..

Whereas, Negash lodge hot spring has the value which falls in the range of mantle CO2 between -3 and -8‰. The Woliso Negash lodge hot spring indicates the value of $\delta^{13}C$ in the range of mantle CO2 due to the deep circulation and CO2-water-rock interaction and the structural influence of the NW-SE trending Ambo-Woliso-Butajira fault that brings the mantle CO2 upward and its interaction with the rock and ground water.

The second range of the $\delta^{13}C$ is between -6.62‰ and -14.26‰ which indicates the shallow ground water bore holes and hand dug wells, lake water and river waters of the study area. The water samples collected from Menagesha HDW, Hometcho BH2, Lake Wonchi, Ginchi BH1, Ambo Awaro BH1 show the value of δ13C in the range of -6.43‰ to -7.36‰ indicate the CO2 from the atmosphere. When this diffusion of CO2 enters through the stomata and with enzymatic conversion of CO2 to CH2O in the chloroplast, $\delta^{13}C$ becomes depleted by about 20‰ to give the value of $\delta^{13}C$ for carbon in the C3 plant tissue. When the atmospheric CO2(g) dissolves in water, $\delta^{13}C$ slightly depleted resulting, in a $\delta^{13}C$ up to -8‰ for CO2(aq). There are some water samples that can fall in this range; these are Ginchi BH2, Boji spring and Ambo Awaro BH2.

The water samples collected from the two river waters, Guder town BH, Wonchi cold spring, Woliso prison compound BH, Hometcho BH1 and Yaichebo Turura HDW are in the range of -10.09‰ to -14.26‰. This value indicates the range of C4 plants and soil CO2 gas. Biogenic CO2 is inferred to emanate from plant respiration and soil zone through redox reactions. As this CO2-charged water sinks through the soil zone and moves through the aquifer matrix, it dissolves carbonates if they are present. As the enriched inorganic $\delta^{13}C$ from the carbonate minerals mix with the isotopically depleted biogenic $\delta^{13}C$, the water becomes isotopically enriched, until the CO2 is exhausted, the PH rises, and the dissolution of carbonate minerals stops. Through this process, the isotopic compositions of the groundwaters evolve to a point, which represents a mixture of the $\delta^{13}C$ of the biogenic influx and the $\delta^{13}C$ of the inorganic carbonate influx.

As CO2 gas dissociates into water (CO2 gas–H2CO3–HCO3), there is strong isotopic fractionation (Hendy, 1971; Carothers and Kharaka, 1980; Mook et al., 1974; Salomons and Mook, 1986). Hendy (1971) reports that at 25^0C, there is a +7.7‰ of $\delta^{13}C$ enrichment between CO2 gas and HCO3, Mook et al. (1974) reported the fractionation between CO2 aqueous and CO2 gas at 20^0C as -1.08‰ with the hydration and dissociation of CO2 gas to form HCO3, leading to an isotopic shift of +9.54‰, which combine to give a total fractionation from CO2 aqueous to form HCO3 with a $\delta^{13}C$ shift of +8.46‰. Similarly, Carothers and Kharaka (1980) report a +8.5‰ fractionation between CO2 gas and HCO3 at 20 ^0C. Salomons and Mook (1986) provide similar data but used a standard temperature of 25^0C, stating that the fractionation between CO2 aqueous and CO2 gas is -1.06‰, and further fractionation between CO2 gas and HCO3 produces an isotopic shift of +8.97‰, balancing each other to result in a +7.92‰ increase in the initial isotopic signature ($\delta^{13}C$‰) as HCO3 forms from CO2 gas.

In this open system, where CO2 gas is continuously added, isotopic fractionation between the CO2 and DIC is unlikely to reach isotopic equilibrium, especially at low temperatures. As discussed above, the rate of CO2 influx into the deep cell is controlled by a combination of the rates of CO2 leakage from structural traps and that of groundwater movement. This system is under pressure; this allows more CO2 to be carried in solution than is possible under atmospheric conditions (Ford and Williams, 1992). During groundwater movement through the fracture network of the deep cell, CO2 constantly undergoes hydration to form H2CO3. Some of this carbonic acid is consumed by ongoing silicate weathering reactions, but the residual undergoes dissociation to form HCO3, leading to the observed PH buffering. Boreholes provide a low-pressure conduit for the groundwater stored in this fracture network. This pressure differential draws water from the fractures into the boreholes and towards the surface. As the groundwater moves towards the surface, the P_{CO2} progressively falls to match that of the atmosphere. In this process, CO2 out gassing occurs (carbonates in the water) and provides a gaseous sink for C-12 and results in $\delta^{13}C$ enrichment of the ground waters residual DIC (Salomons and Mook, 1986).

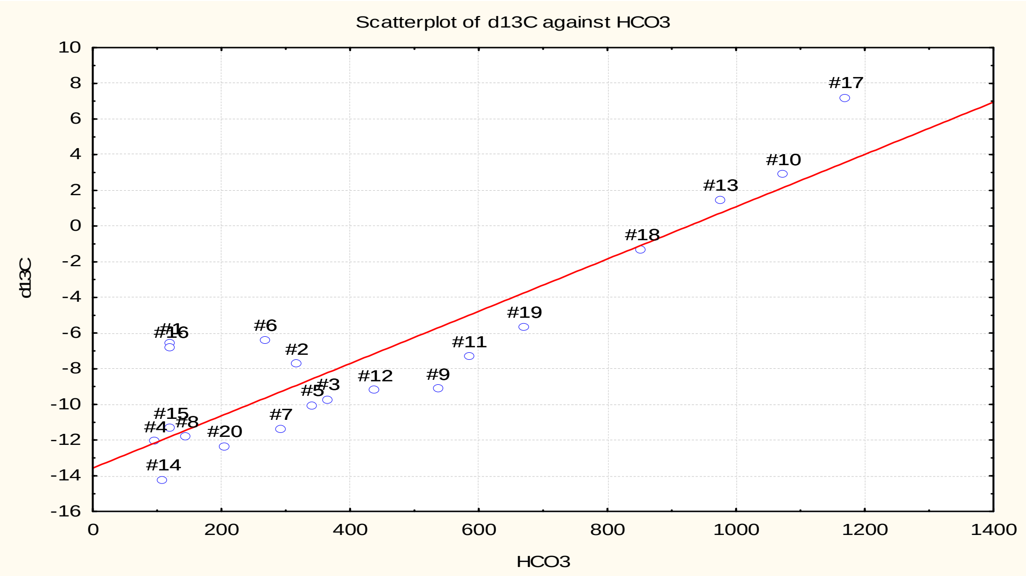

Figure: 5.12. Scatter plot of δ13C Vs HCO3 relationship.

5.5. Hierarchical cluster analysis and its relation to hydrogeochemical Evolution

Hierarchical cluster analysis is used to classify the hydrogeochemical data in to objective water classes. Statistical classification of geochemical data by Q-mode hierarchical cluster analysis (HCA) has been proven to provide a suitable basis for objective classification of water composition into hydrochemical facies (Meng and Maynard, 2001; Güler et al., 2002, Güler and Thyne2003; Kebede et al., 2005). HCA is a multivariate statistical technique intended to classify hydrochemical observations so that the members of the resulting groups or subgroups are similar to each other and distinct from the other groups. The characteristics of the groups or sub-groups are not predetermined but can be obtained after the classification.

HCA is used to classify the ground water samples for the purpose of hyrogeochemical evolution along the flow path and inverse geochemical modelling. Eleven variables (pH, Ca^{2+}, $Mg^{2+,}$ K^{+},

Na^{+}, HCO_3^{-}, Cl^{-}, SO_4^{2-} , EC, TDS and Temperature) were considered to classify the 20 groundwater samples.

From the dendrogram shown in figure (4.10), two major groups and six subgroups were selected visually. The two major groups are classified by their TDS. Group 1 waters are low TDS<850mg/l. Group II are characterised by high TDS >850mg/l compared to group 1 waters. Group 1 waters are collected from the shallow ground waters, rivers hand dug wells and lakes situated around Wonchi, Guder, Ambo and Woliso area. Group II ground waters are collected from thermal and gaseous springs which represent the deep ground water circulation. The two major groups have distinct $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$ values. Group I waters are relatively enriched in $\delta^{18}O$ and $\delta^{2}H$ values and depleted in $\delta^{13}C$ values as compared to group two waters which are highly gaseous enriched in $\delta^{13}C$ and highly depleted in $\delta^{18}O$ and $\delta^{2}H$.

category	Temp	EC	Na+	K+	Ca	Mg	F	Cl	SO4	HCO3	NO3	PH	δ18O	δ13C
Subgroup I	**19.87**	**252.94**	**24.5**	**6.01**	**21.71**	**7.27**	**0.84**	**19.59**	**0.99**	**132.12**	**4.34**	**7.68**	**1.48**	**-10.77**
subgroup II	**19.12**	**237.96**	**38.75**	**5.97**	**16.63**	**5.42**	**1.06**	**17.69**	**0.99**	**145.27**	**1.89**	**7.97**	**-1.31**	**-8.92**
subgroup III	**21.89**	**261.63**	**38.92**	**5.46**	**18.91**	**6.31**	**1.01**	**14.36**	**0.99**	**160.78**	**2.83**	**7.92**	**-2.24**	**-8.79**
Sub groupIV	**29.4**	**1235**	**69**	**5.4**	**160**	**36**	**0.61**	**54.07**	**199.96**	**536.8**	**7.75**	**7.07**	**1.07**	**-9.17**
Sub group V	**20.51**	**249.8**	**38.83**	**5.72**	**17.77**	**5.86**	**1.03**	**16.03**	**0.99**	**153.022**	**2.36**	**7.95**	**1.43**	**-3.54**
subgroup VI	**23.93**	**582.144**	**48.92**	**5.53**	**65.56**	**16.06**	**0.88**	**28.15**	**67.31**	**283.53**	**4.31**	**7.65**	**-2.71**	**3.83**

Table: 5.1. The mean chemical composition of waters resulting in subgroups from HCA

Subgroups	Description
Subgroup 1	**Most of the samples are collected from hand dug wells, rivers, lakes cold springs and shallow bore holes. The water samples of this subgroup are shallow ground waters with low TDS, EC and temperatures. The calcium ion is higher in these water samples specially in cold springs. The dominant anions are HCO3 and slightly less chloride in some surface waters. There are some water samples in which Na is the dominant cation in areas of acidic rocks around Woliso and Wonchi lake. This subgroup indicates the less evolved ground water samples and recharge area waters. Most of these ground waters are CaMgHCO3 and NaCaHCO3 waters with little amount of chloride.**
Subgroup 2	**Several samples of these subgroups are around Guder area except one sample from Ginchi bore hole1. These water samples represent fresh ground waters from recharge area and there is no significant water-rock interaction. The TDS value of these samples show the slight**

	increment as compared to subgroup I. Two samples of this member show the chloride type water involved in this ground water either from the clay layer or the hydraulic connection of these water samples from Guder river. The Ca and HCO3 are the dominant ions in these subgroup.
Subgroup 3	**These samples are collected from Ambo Awaro well field and Ginchi BH2. The two cations Ca and Na occur together in the Ambo Awaro area bore holes which indicate the evolution of ground water with the exchange of the two cations due to the CO2 influx and the calcite dissolution that can release the Ca ion into ground waters. The CaHCO3 Ginchi BH is the fresh ground water from recharge area.**
Subgroup 4	**Boji spring near Senkele lime factory is classified in the dendrogram as one subgroup. Three cations Ca,Na and Mg while HCO3 and SO4 occur together in this water sample. This indicates mixing of ground water and there is a significant evaporation effect which can increase the SO4 in this spring. The evaporation effect can also be traced from isotopic signature which shows the appreciable enrichment. This water sample is mixed ground water from the high land and less evolved water and slight water-rock interaction.**
Subgroup 5	**This subgroup represents the high TDS NaCHO3 thermal springs. These springs are situated along the Ambo-Woliso-Butajira fault. The deep and highly evolved ground water with strong water rock interaction comes along this fault. The probability of high silicate hydrolysis can be observed than another groups. The high TDS and the enrichment of Na therefore testify that the thermal and the high TDS ground waters have undergone a relatively pronounced degree of hydrogeochemical evolution.**
Subgroup 6	**The water samples of this group represent the mineral waters and gaseous springs. These high TDS ground waters are situated around Ambo and Wonchi area. There is the influx of CO2 gas from mantle or metamorphic decarbonation. The water type of this gaseous ground waters is NaCaHCO3 around Ambo and NaHCO3 around Wonchi area. The reason why Na and Ca ion occurs in these water which is highly evolved and significant water-rock interaction is due to the CO2 influx which can precipitate the divalent ions such as Ca during the formation of travertine lime stone.**

Table: 5.2. Description of the chemical composition of the waters in subgroups.

5.6. Inverse geochemical modelling

Inverse geochemical modeling is used to explain the observed groundwater chemical evolution, rather than to predict future compositions (Plummer et al., 1983; Kenoyer and Bowser, 1992; Varsànyi and Kovàcs, 1997; Hidalgo and Cruz-Sanjuliàn, 2001; Wang et al., 2001). The initial and final water compositions and the mineral phases in the system can be used for the modeling. These models calculate how much of each phase must dissolve or precipitate to account for the observed difference in the water compositions. Data required in inverse geochemical modeling include:

1. The compositions of an “initial” water and of a “final” water that are assumed chemically evolutionary,

2. A complete list of the reactions that may be responsible for the observed evolution is needed.

Mineralogical knowledge is needed to make reasonable guesses as to which minerals and gases might be dissolving or precipitating. The models are independent of any assumptions about thermodynamic equilibrium or reaction kinetics and are based solely on mass-transfer considerations. It Contains a routine that speciates the water and calculates saturation indices (SI) for each of the minerals in the data bank.

Inverse geochemical modeling can not account for Mixing, Hydrodynamic dispersion, Solute and Diffusion. Inverse modeling can indicate that the selected waters are not evolutionary. Appropriate reactions have not been included, or too many constraints have been imposed. In inverse geochemical modeling, inability to find an acceptable reaction model indicates inadequate data or an invalid conceptualization of the geochemical and hydrologic system. Usually, a number of plausible conceptual solutions are found for the system of interest, and the user must choose, based knowledge of Mineralogy, Geochemistry, and Hydrology and Conceptual solution that is most realistic.

In areas where there is no knowledge of ground water flow direction, the final and initial waters can be used from HCA groups. This is based on the logical assumption that waters which fall in a statistical group may have similar residence time, similar recharge history, and identical flow paths or reservoir (Swanson et al., 2001; Güler and Thyne, 2004). PHREEQC computer code (Parkhurst and Appelo, 1999) was used to simulate the geochemical evolution among the average composition of statistical clusters.

Inverse geochemical modeling was conducted based on the classification of waters by HCA. The initial and final waters are taken from different subgroups which can represent the logical ground water flow path. The average chemical compositions of the waters are represented in subgroups for waters of the same origin or either recharge or discharge area ground waters.

In the volcanic rocks similar to the lithology of the study area, the dominant mineralogy of the rocks is silicate minerals. Olivine, pyroxene, amphibole, K-feldspar and plagioclase are primary silicate minerals. While crysoltile, kaolinite, montimorilonite, illite (K-mica) are among the secondary silicate minerals which are results of incongruent dissolution. Calcite occurs in volcanic rocks as late crystallization in cavities of lava. Anhydrite and gypsum can occur in amygdaloidal cavities of basalts, in shale or clay material. Halite and sylvite occur in clay, sand or paleosoles due to the pre-burial evaporative processes. Alunite is formed by the reaction of K-feldspar with sulphuric acid in sulphate reducing environment. Fluorite is commonly found associated with acidic volcanic minerals as rare mineral, Dana (1995).

Models	Sample ID	UTME	UTMN	Elevation	TDS	PH	Na	K	Ca	Mg	Cl	NO3	F	HCO3	SO4	Water types
Model A	W11BH7	378343	991473	2188	511	7.53	112	9.9	58.4	24.96	44.42	0.54	1.03	585.6	0.99	NaCaHCO3
	W10BH6	369682	993850	2016	994	6.57	188	5.9	108	43.2	54.07	0.75	0.73	1074	1.97	NaCaHCO3
Model B	W14HDW2	378209	981177	2672	179	6.88	10.5	13.4	28	12	29.93	22.35	0.59	109.8	0.99	CaMgHCO3Cl
	W13S2	373894	992816	2195	1030	6.36	230	5.9	96	31.2	112	0.72	0.84	976	0.99	NaCaHCO3
Model C	W16L1	378141	972601	2889	129	8.23	38	7.2	14.4	3.36	25.11	0.52	1.17	122	0.99	NaCaHCO3Cl
	W17S3	377823	970187	2815	1463	6.06	290	21.5	56	38.4	39.59	0.57	5.85	1171	0.99	NaHCO3
Model D	W16L1	378141	972601	2889	129	8.23	38	7.2	14.4	3.36	25.11	0.52	1.17	122	0.99	NaCaHCO3Cl
	W18S4	378045	970164	2817	736	7.25	280	19.5	20.8	11.52	54.07	0.61	5.71	854	1.97	NaHCO3

Table: 5.3. The chemical composition of the final and initial waters used for inverse geochemical modeling.

In order to conduct inverse geochemical modeling different flow paths are considered in the study area. These flow paths are taken based on the structural, geological and geomorphologic point of view of the study area. The major flow paths in which inverse geochemical modeling is conducted are Ambo-Senkele flow path, Lake Wonchi-Woliso flow path and Wonchi- Ambo flow path. Four inverse geochemical modeling are conducted to characterize these flow paths.

Model A

Inverse geochemical modeling was conducted between Ambo Awaro BH1(W11BH7) which is found east of Ambo town and Ambo mineral water BH(W10BH6) from Senkele area. W11BH7 has TDS value 511mg/l and NaCaHCO3 water type. The chemical components of this bore hole are used as initial solution of the model. W10BH6 is highly gaseous BH for the supply of Ambo mineral water factory. It has TDS value 994mg/l and NaCaHCO3 water type. It is used as a final solution in the modeling.

```
 Phase         mole transfers:
Calcite    -4.444e-003          CaCO3
pyroxene     7.775e-003        Mg0.5Ca0.5SiO3
Halite     3.028e-004           NaCl
   Illite    -1.255e-002          K0.6Mg0.25Al2.3Si3.5O10(OH)2
K-feldspar     4.336e-004        KAlSi3O8
plagioclase     5.175e-003         Na0.62Ca0.38Al1.38Si2.62O8
CO2(g)       2.040e-002        CO2
K-mica       7.096e-003        KAl3Si3O10(OH)2
```

From the result of the model the main reactions are dissolution of pyroxene, K-mica, plagioclase and K-feldspars. These minerals are dissolved from the basic rocks (silicate hydrolysis). Calcite and illite are minerals that precipitate in the solution showing that they are the products of weathering. Illite is a clay mineral that can be formed during the alteration of the rocks while calcite can precipitate due to the travertine formation which is the results of CO2 influx to the ground waters of these areas.

Model B

Inverse geochemical modeling was conducted between Yai Chebo Turura (W14HDW2) near Altufa Villages from subgroup I and Ambo hot spring of Ethiopia hotel (W13S2) used for swimming pool from subgroup II. W14HDW2 has TDS value 179mg/l and CaMgHCO3Cl water type. The chemical components of this bore hole are used as initial solution of the model. W13S2 is hot highly gaseous spring where travertine deposit is common around it. It has TDS value 1030mg/l and NaCaHCO3 water type. It is used as a final solution in the modeling.

```
Phase             mole transfers:
Calcite          -1.116e-002        CaCO3
CO2(g)            3.523e-002        CO2
Halite            2.161e-003        NaCl
Illite           -2.925e-002        K0.6Mg0.25Al2.3Si3.5O10(OH)2
K-feldspar            1.479e-003        KAlSi3O8
Plagioclase           1.274e-002        Na0.62Ca0.38Al1.38Si2.62O8
pyroxene           1.634e-002        Mg0.5Ca0.5SiO3
K-mica            1.607e-002        KAl3Si3O10(OH)2
```

The result of the model shows that most of the reactions are dissolution minerals such as halite, CO_2 gas and trace dissolution of K-feldspars,K-mica,plagioclase and pyroxene along ground water flow path. Clay mineral illite consumed as the result of weathering during silicate hydrolysis. Calcite is precipitated along the ground water flow path due to precipitation of travertine deposits in the study area.

Model C

Inverse geochemical modeling was conducted between Wonchi Crater Lake (W16L1) in the Wonchi volcanic centre and Wochi gaseous spring (W17S2) situated at the downstream of the lake. Lake Wonchi is hydraulically connected to ground waters of its surrounding area.W16L1 has TDS value 129mg/l and NaCaHCO3Cl water type. The chemical components of this lake are used as initial solution of the model. W17S3 is highly gaseous spring whose taste is similar to Ambo mineral water. It has TDS value 1463mg/l and NaHCO3 water type. It is used as a final solution in the modeling.

```
Phase             mole transfers:
Halite     3.770e-004          NaCl
Illite    -4.165e-002          K0.6Mg0.25Al2.3Si3.5O10(OH)2
CO2(g)     6.909e-002          CO2
K-feldspar     1.953e-003       KAlSi3O8
Calcite    -1.764e-002          CaCO3
Plagioclase     1.792e-002      Na0.62Ca0.38Al1.38Si2.62O8
K-mica     2.304e-002          KAl3Si3O10(OH)2
Pyroxene     2.386e-002        Mg0.5Ca0.5SiO3
```

The result of inverse modeling shows that CO2 gas is the major phase of dissolution. Halite, pyroxene, K-mica and K-feldspar also show the trace amount of dissolution along the flow path indicates that there is a silicate hydrolysis and the influx of high amount of CO2 along the flow path. Clay mineral illite indicates the weathering reaction along the flow path while the calcite is precipitated in this ground water probably due to the influx of CO2 in the area which is the source of bicarbonate and the divalent ion is from the silicate hydrolysis.

Model D

Inverse geochemical modeling was conducted between Wonchi Crater Lake (W16L1) and Wonchi thermal spring (W18S4) high discharge spring found downstream of lake Wonchi hydraulically connected to the lake. W16L1 has TDS value 129mg/l and NaCaHCO3Cl water type. The chemical components of this lake are used as initial solution of the model. W18S4 is thermal spring whose TDS value is 1463mg/l and NaHCO3 water type. It is used as a final solution in the modeling.

```
Phase            mole transfers:
Calcite    -1.317e-002           CaCO3
 CO2(g)     1.215e-002           CO2
Dolomite     6.897e-003           CaMg(CO3)2
Halite     7.576e-004           NaCl
Illite    -2.624e-002           K0.6Mg0.25Al2.3Si3.5O10(OH)2
K-mica     1.065e-002           KAl3Si3O10(OH)2
Fluorite     1.196e-004           CaF2
K-feldspar     5.412e-003           KAlSi3O8
Plagioclase     1.667e-002           Na0.62Ca0.38Al1.38Si2.62O8
```

The result of this model shows that halite, dolomite, and K-feldspars are the major dissolution minerals along the flow path. Plagioclase, CO2 gas, K-mica and fluorite also show the minor amount of dissolution. This indicates that silicate hydrolysis is common in the area while fluorite is from acidic rhyolites of that area. Lake water hydraulic connection to ground waters of the study area is the probable source of dolomite mineral along the flow path. CO2 gas source is from the structurally controlled of this thermal water from deep ground waters brought this gas either from mantle or metamorphic decarbonation.

5.7. Carbon dioxide -water-rock interaction

5.7.1. General back ground on CO2-water-rock interaction

Many researches were conducted on CO2-water-rock interaction in order to assess safe geological CO2 sequestration site. Permanent sequestration and storage of CO2 in deep geologic formations is being considered as a means to reduce the concentration of atmospheric CO2 and thus its contribution to global climate change. The types of geologic formations that have been studied for CO2 sequestration include depleted oil and gas fields, deep saline reservoirs, uneconomic coal beds, and basalt formations.

Carbonate minerals are one of the most common groups of non-silicate minerals. Calcite (CaCO3), dolomite [CaMg(CO3)2], and aragonite (CaCO3) are probably the most commonly known of all the carbonate minerals. Calcite and dolomite are the most abundant and constitute more than 90% of the natural rock-forming carbonate minerals (Reeder 1983a). Calcite and aragonite are two of five CaCO3 minerals known to naturally exist. The crystal chemistry and phase relations of carbonate sedimentary rocks and secondary carbonate mineralization in detrital rocks are pertinent to understanding the impact of CO2 injection and sequestration to the carbonate geochemistry of the aquifer host rocks.

Because many carbonate minerals [e.g., calcite (CaCO3), dolomite [CaMg(CO3)2], siderite (FeCO3)] remain stable for geologically significant time frames, mineral trapping is considered as having the greatest potential for long-term, stable geologic CO2 sequestration (Bachu et al. 1994).

Some researches were also conducted on the mineralization of CO2 in to basaltic rocks. How much is environmentally safe and will toxic metals be released during operation of CO2 sequestration. How can we increase the release rate of divalent cations to solution so that the precipitation rate of carbonates can be enhanced? Such questions are useful to understand the CO2-Water-rock interaction in basaltic rocks. The results of some works conducted in such a way shows that the neutralization of CO_2-rich waters by their interactions with subsurface basalt may provide an effective means to fix CO_2 as carbonate minerals. Since this process involves dissolution of the basalt, toxic metals will be released into the solution. In such a case as the pH rises to 9 and higher, toxic metal bearing solids become less soluble and toxic metals adsorb more readily onto mineral surfaces. If CO_2 were injected into less basic rocks (e.g. sandstones) model calculations suggest that

PH would not rise dramatically. In such cases toxic metal mobility could pose an environmental hazard.

Based on the carbon sequestration activities that are common solution of today to reduce the anthropogenic green house gases, natural CO2 analogues like in Wonchi system can be studied in order to understand the CO2- water-rock interaction and trace element mobility during reaction path.

5.7.2. Carbon dioxide water-rock interaction of study area

Evidences from chemical, isotopic data, hierarchical cluster analysis and inverse geochemical modeling are used to discuss carbon dioxide-water-rock interaction in the study area. HCA can be used to discuss the objective subgroups of ground waters. There are a total of six subgroups that can be analyzed to indicate the CO2-water-rock interaction.

Subgroup I

This subgroup contains shallow ground waters such as hand dug wells, cold springs, surface waters (lake and rivers). Most of the ground waters of this subgroup are from recharge areas. The chemical analysis of these waters indicates that low TDS, alkalinity, EC, temperature and major ions and high PH value in most of the water samples. The chemical and isotopic data shows that there is the enrichment of δ^{18}O and δ^{2}H isotope. It is common observation that in these subgroup δ^{13}C is highly depleted. The common water types of this subgroup are CaMgHCO3, CaMgHCO3Cl, NaCaHCO3Cl and NaCaHCO3. The chloride ion in these water types is from evaporative effect of some surface waters such as lakes and rivers which can recharge these shallow ground waters. Ground waters around Wonchi Crater Lake are hydraulically connected to the lake.

These ground waters represent the shallow subsurface residence time and shallow circulation along the flow path. The evidence from δ^{18}O andδ^{2}H indicates that the enrichment of this subgroup waters are due to the evaporative effect of the lake and surface waters. While the δ^{13}C isotopic analysis of these waters indicates the depletion. This testifies that the source of CO2 in these waters is from soil or C3 plants. This subgroup waters are evolved under closed system to external CO2 influx from DIC of either mantle source or metamorphic decarbonation. Silicate hydrolysis and dissolution reactions are common characteristics of this subgroup. The reaction between soil CO2 and infiltrating water will be consumed by silicate reaction to produce the initial H+ ion in CO2-Water-rock interaction. Generally due to the shallow subsurface circulation and short residence time of this recharge area waters and there is no external influx of

CO_2 to these ground waters indicates that there is appreciable CO_2-water-rock interaction in this subgroup.

Subgroup II

The waters in subgroup II except the Ginchi BH1 of Boda site all are from Guder area and the surrounding Hometcho factory bore holes. These ground waters are situated near the Guder river valley representing the intermediate and shallow ground waters. The chemical data of these ground waters indicates that these waters have the TDS value of 314 to 348mg/l and intermediate value of major cations and anions. The alkalinity of this ground water is below 300mg/l while the PH value is below 7 except in Guder bore hole. The $\delta^{18}O$ and $\delta^{2}H$ isotope data of this subgroup indicates that the waters show the depletion except the Hometcho BH1 which is isotopically enriched due the effect of the highly evaporative water from irrigation field nearest to this water well. The water types of this subgroup are $MgNaHCO_3$, $CaMgHCO_3$ and $CaMgHCO_3Cl$. The Hometcho BH2 and Guder BH have similar $CaMgHCO_3Cl$ water type. The origin of this chloride ion is probably from clay layer intercalated in aquifer of these water wells.

The $\delta^{13}C$ isotopic analysis indicates that these waters are depleted $\delta^{13}C$ value. This testifies that the system is closed to the external DIC from either mantle origin or metamorphic decarbonation. The source of CO_2 for this subgroup water is from soil CO_2 or C3 plants. The reactions that are carried out in this system is silicate hydrolysis such as dissolution of silicate minerals. There is no significant CO_2-water-rock interaction in these ground waters due to closeness' of the system to external CO_2 source which can initiate further water-rock interaction.

Subgroup III

The waters in subgroup III are water wells around Ambo Awaro well field and Ginchi BH2. These ground waters relatively represent the deep aquifers. The chemical analysis of these waters indicates that the TDS value of 454 to 550mg/l, alkalinity value from 300 to 480 and the PH value is near neutral. Ground waters of these subgroups are evolved from $CaHCO_3$ to $NaCaHCO_3$ water type. The fresh Ginchi BH has $CaHCO_3$ water type representing the less evolution of ground water from recharge to discharge area but Ambo Awaro bore holes indicates that there is the cation exchange between Ca and Na ions. From the water types of the Ambo Awaro well field one can observe that there is the complete evolution of this ground water to $NaHCO_3$. The calcium ion is not completely replaced by Na^+ ion rather they exist together. This is probably due to the existence of calcite precipitation during water-rock interaction which is the cause to increase the Ca ion in these ground waters.

The $\delta^{18}O$ and $\delta^{2}H$ value of this subgroup water show the depletion except in Ginchi BH2 which is isotopically enriched. Whereas, the stable carbon isotopic data shows the depletion of $\delta^{13}C$ value can be observed in this subgroup waters. The CO2 source for this subgroup is from soil CO2 and they are closed to the mantle or metamorphic decarbonation which can increase the rate of water-rock interaction. In ground waters of this subgroup dissolution of silicate minerals and intermediate water-rock interaction can be expected due to the appreciable ground water evolution and cation exchange reactions.

Subgroup IV

In this subgroup only one ground water sample is classified by hierarchical cluster analysis as an objective group. Boji spring near Senkele lime factory is the typical water sample of the study area. The chemical data shows that the TDS value is 735mg/l, alkalinity is 440mg/l, temperature is 29.4^{0}C and PH is near neutral. This spring has highest amount of sulphate ion and hardness from the study area. The water type of this spring is CaNaMgHCO3SO4. This testifies that it is a mixed type of ground water. While the highest sulphate ion in this water sample is due to the evaporation effect. The source of this ground water is from recharge area whose lithology is dominantly basaltic rocks.

This spring is enriched in $\delta^{18}O$ and depleted in $\delta^{13}C$ isotopic value. The enrichment of this spring in $\delta^{18}O$ indicates that there is the effect of evaporation and the water is undergone shallow subsurface circulation. The source of CO2 is from soil or C3 plants this indicate that there is no influx of external source CO2 from dissolved inorganic carbon or from the mantle origin. From this point of view this spring water is not highly evolved and significant CO2-water- rock interaction is not carried out.

Subgroup V

The waters in this subgroup are thermal waters from Wonchi and woliso area. The chemical data of these waters indicates that the TDS ranges from 678 to 736 mg/l, temperature up to 39.6, alkalinity from 550 to 700mg/l and PH is near neutral. Significant amount of fluoride is measured in this ground waters indicates that there are dissolution of minerals such as fluorite from acidic rocks release appreciable amount of fluoride to the waters. The water type of this subgroup is NaHCO3. This testifies that the origin of these ground waters is from the deep aquifer which is highly evolved along the flow path and undergone significant water-rock interaction.

The isotopic data indicates that wonchi thermal spring is enriched in $\delta^{18}O$ isotope. This is due to the hydraulic connection of the high evaporation effect of lake Wonchi to this spring situated downstream of the lake. While woliso Negash Lodge thermal spring is depleted in $\delta^{18}O$ indicates that the source of recharge to this ground water is from high land. The stable carbon isotopic data of this subgroup water indicates the source of CO2 is from external sources like mantle or metamorphic decarbonation. The influx of CO2 gas to these ground waters is due to the deep seated fault system that cut across the area. Since the system is open to the external source of CO2 the weathering of silicate minerals is significantly influenced by the presence of CO2 gas. Under elevated P_{CO2} conditions, the silicate weathering process accelerates (Stumm and Morgan, 1981, 1996). Through the hydration of the CO2 gas to form H2CO3 and then dissociation to form HCO3, mantle-derived CO2 and metamorphic decarbonation gas undergoes isotopic fraction. The high concentration of CO2 gas influx to the system can promote CO2-water-rock interaction in ground waters of this subgroup.

Subgroup VI

The waters of this subgroup are gaseous mineral waters from Ambo and Wonchi area. These are Ambo mineral water factory bore hole, Ambo hot spring of Ethiopia hotel and Wonchi gaseous spring. Chemical data of these ground waters indicates that highest TDS and alkalinity and low PH value is measured. The temperature is high up to 36^0C in Ambo hot spring and low in wonchi gaseous spring. The water types of this subgroup are NaCaHCO3 in Ambo mineral water and Ambo hot spring while NaHCO3 in Wonchi gaseous spring. The reason why Na and Ca ion occurs together in Ambo area gaseous waters is due to the influence high amount of CO2 gas. The reason why Ca ion exists in these highly evolved waters due the hydration of CO2 that can finally precipitate the minerals such as calcite during travertine lime stone formation. The divalent ions can be taken from silicate hydrolysis during dissolution of silicate minerals.

Wonchi gaseous spring is the highly evolved water that undergone significant water- rock interaction.

The data from isotopic measurement of these ground waters shows that the waters are depleted in $\delta^{18}O$ and highly enriched in $\delta^{13}C$ value. The exceptional case in this subgroup is the $\delta^{18}O$ enrichment of Wonchi gaseous spring. This is due to the hydraulic connection of Wonchi lake to this spring which make it to be isotopically enriched. The δ13C enrichment of these ground waters indicates that the system is open to the influx of external CO2 source from the mantle origin and metamorphic decarbonation. Silicate hydrolysis and ion exchange reactions are elevated by the high influx of CO2 to the region. The influx of CO2 to these ground waters is due to the influence of deep seated Ambo-Wonchi-Butajira fault that brings the gas either from metamorphosed sedimentary rock or from the mantle origin. The ground waters of this subgroup are one of the prominent ground waters in which significant amount of CO2-water-rock interaction is carried out along the flow path.

5.8. General remark on CO2-water-rock interaction of the study area

Wonchi system is one of the natural analogues that diffuse CO2 to the atmosphere. Data from hydrogeochemical evolution of ground water, isotope hydrology, classification of the representative water samples in to objective group by using HCA and inverse geochemical modeling are used together to show the CO2-water-rock interaction of Wonchi system.

- From observed chemical analysis of hydrochemical data, it is clear that the thermal and gaseous ground waters system of the Ambo, Wonchi and Woliso are open to the influx of CO2 gas from a source other than redox reactions. The dominant anion in this region is HCO3 that can be formed through hydration of CO2 gas from H2CO3 and then dissociated to HCO3 and silicate hydrolysis. Alkalinity of gaseous and thermal ground water is high and the PH is low. Whereas the dominant cations are Na and Ca. This in turn testifies that the Na ion is in the highly evolved ground water and the Ca ion is replaced by Na ion in most cases of thermal and gaseous waters of the Wonchi and Woliso area. But in Ambo area gaseous and mineral waters the Ca ion still exists in the waters because of the CO2 gas that forms the travertine lime stone which can release this ion to the ground waters of the area.
- Isotopic data indicates that gaseous and thermal ground waters are depleted in $\delta^{18}O$ and enriched in $\delta^{13}C$ isotopes. There are exceptional cases in which the Wonchi gaseous and

thermal springs are enriched in both $\delta^{18}O$ and $\delta^{13}C$ isotopes. The $\delta^{18}O$ depleted ground waters of Ambo area shows the negative oxygen shift opposite to geothermal ground waters of the Rift valley which have positive oxygen shift. The $\delta^{18}O$ enriched gaseous ground waters of Wonchi area are due to the influence of the hydraulic connection of the lake water to these gaseous ground waters. Due to the influx of CO2, the gaseous and thermal ground waters undergo the significant CO2-water- rock interaction.

- The result of inverse geochemical modeling also indicates that CO2(g) is the major dissolution phase in most of the model results. Silicate hydrolysis and cation exchange reaction are also observed from the geochemical modeling. Silicate minerals such as pyroxene, plagioclase, K-feldspars, K-mica, fluorite are the common minerals of dissolution reaction. Whereas, calcite and some clay minerals are the result of precipitation reactions.

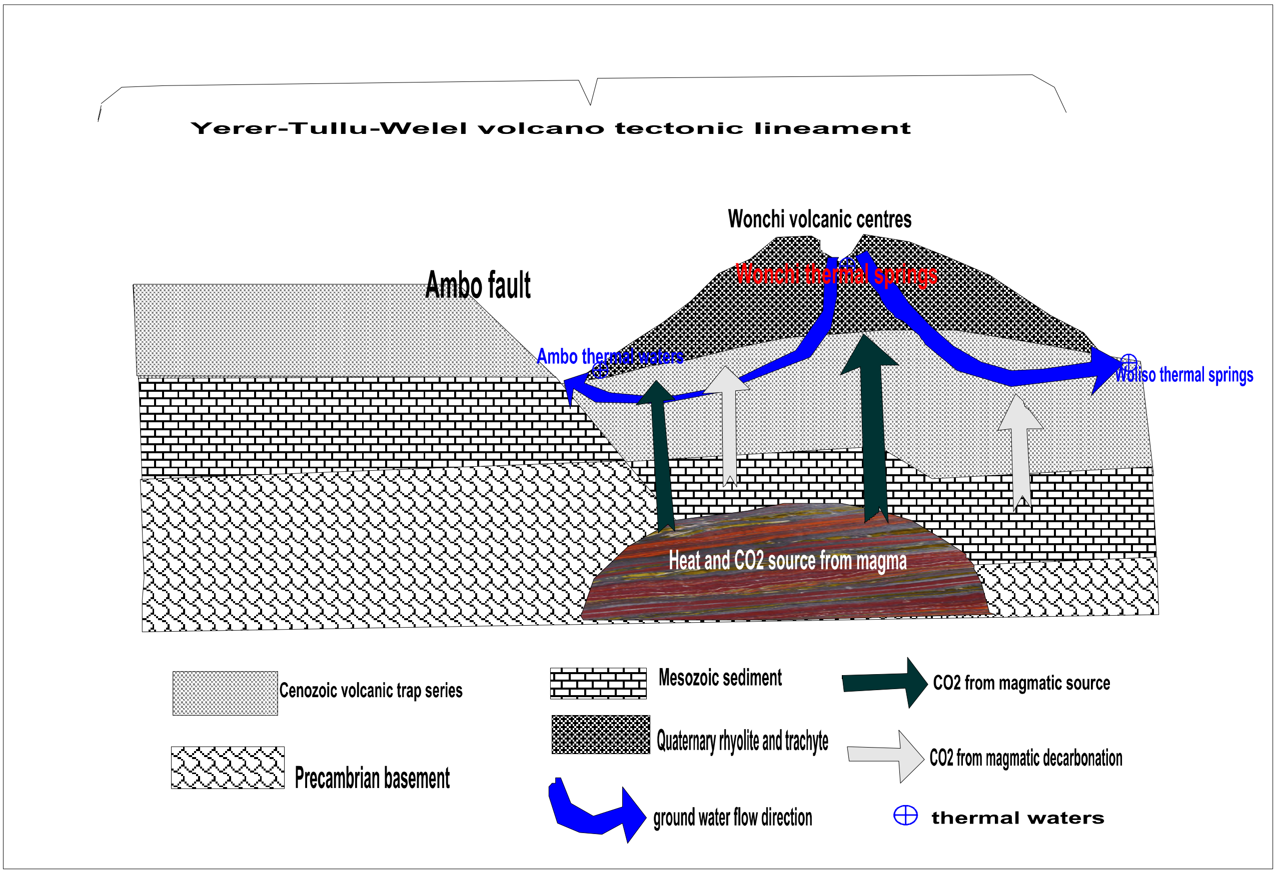

Figure: 5.13. Conceptual schematic diagram of CO2 and thermal ground water source

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1. Conclusion

The ground waters of Wonchi system are classified by hierarchical cluster analysis in to two major groups and six subgroups. The heirararchically similar groups and subgroups show the similarity in geology and hydrogeochemistry. The use of HCA in the elaboration of chemical data of ground waters of the system provide useful information for inverse geochemical modeling to understand the CO2-water-rock interaction in aquifers and the reaction path modeling along the ground water chemical evolution. Since the classified ground waters of each subgroups have its own different characteristics, the inverse modeling has used these subgroups to characterize the ground waters chemical evolution, CO2-water-rock interaction from the waters of the one subgroup to the other due to their distinct difference in hydrogeological and mineralogical nature. This powerful statistical classification can also help to differentiate the deep and shallow ground waters, fresh and saline so that this can be the basic knowledge to use the inverse geochemical modeling and to identify the ground water flow direction.

Geochemical data of the waters of the study area are determined in order to understand hydrogeochemical evolution of thermal and hypothermal ground waters and CO2-water rock interaction. Silicate hydrolysis accompanied by CO2 influx from deeper sources plays a major role in groundwater chemical evolution of the high TDS Na–HCO3 type thermal groundwaters in the region of Yerer Tullu Welel Volcano tectonic lineament (Seifu Kebede , 2005). There are different conclusions from previous researchers that show most of the basaltic plateau ground waters characterized by shallow circulation and low TDS CaHCO3 and Ca-Mg-HCO3 type waters.

The present study shows that the gaseous and thermal ground waters of the region are characterized by two types of ground waters. Thermal ground waters around Wonchi Crater Lake and Woliso area are characterized by high TDS Na-HCO3 type ground waters while gaseous and thermal ground waters of Ambo area show high TDS Na-CaHCO3 type ground waters. Both area gaseous ground waters have low PH value. The woliso and Wonchi area thermal and gaseous ground waters represent the deep and highly evolved ground waters that occur in acidic rocks such as rhyolite and ignimrite. The lithology of this area influenced these area ground waters to have high amount of fluoride content due to the dissolution of silicate minerals that release this ion to ground water. Ambo area thermal waters are not completely evolved to $NaHO_3$ water type. The two cations Na and Ca occurs together in these ground waters due to the influx of CO_2 to the region and the dissolution of travertine lime stone that can release the Ca ion to these thermal waters.

Most of the cold and shallow ground waters of the area are characterized by low TDS and alkalinity and higher PH. $CaHCO_3$, $CaMgHCO_3$ and some chloride and sulphate ions are also common in Surface water samples (rivers and lake) and in mixed ground waters. Cold springs around Wonchi crater lakes show similar water type to the lake water. Cold ground waters around Guder river, springs and Yaichebo HDW nearest few kilimetres to Wonchi volcano shows the ground waters containing the chloride ion. The origin of this chloride ion does not indicate the source of this waters to be from the deep aquifer rather it indicates that aquifer of these ground waters are the clay layer or it can be from the evaporation source. The typical sulphate type water is observed in Boji spring near Senkele lime factory. The possible source of this sulphate can be from the low land evaporation or from the mineral gypsum.

The results of inverse geochemical modeling indicate that there are dissolution reaction and precipitation of silicate minerals along the ground water flow path. The major phases are CO_2(g), plagioclase, pyroxene, K-feldspars, K-mica, dolomite, halite, illite, fluorite, calcite and albite. Minerals like CO_2 (g) pyroxene, plagioclase, halite, K-mica, K-feldspars, fluorite and albite show dissolution reaction in most of the model results. While clay mineral such as illite and carbonate mineral calcite are among the precipitation reactions. Silicate hydrolysis is elevated in most of thermal ground waters of study area due to the influx of CO_2 in to ground waters of the region. This testifies that in thermal ground waters of the study area significant water-rock interaction can be observed due to long residence time of these highly evolved ground waters.

Trace element mobility is observed in some thermal ground waters of the area. This in turn indicates that there is strong waters rock interaction with CO_2 gas that can influence trace element to be mobilized and the cause of low PH value in these waters. In some thermal and gaseous ground waters like Ambo mineral water, Wonchi and Woliso trace elements are higher than the permissible standard of WHO for drinking water. Elements like Sr, Ba, Fe, Mn and Al are observed in some ground waters more than the permissible standard. Although these gaseous and thermal ground waters are used as the natural sparkling waters, the higher mobilization of toxic elements in to these waters can be one way of health impact to the human being. The health problems that can be caused by the excess amount of trace elements in drinking waters are like osteodystrophy and rachitic effect due to higher consumption of Sr(Polyakove et al., 1010), long term exposure of humans to boron compounds cause mild gastrointestinal irritation and high concentration of Aluminium in drinking water can cause Alzhemeir`s disease to humans (Craun, 1990; Epstain, 1990).

The E-W trending Yerer-Tullu-Welel-volcano tectonic lineament and the NW-SE Ambo-Wonchi-Butajira fault (Tsegaye Abebe.,1998) play a major role on the evolution ground waters of the study area. Most of thermal and gaseous ground waters that are characterized by high TDS and alkalinity are situated along these prominent structures. The NW-SE Ambo –Wonchi-Butajira fault that passes along the Wonchi crater lake plays a major role to the influx of CO2 gas from the mantle source or from metamorphic decarbonation. The high TDS NaHCO3 and NaCaHCO3 ground waters of Ambo, wonchi and Woliso area are characterized by long residence time and significant water-rock interaction due to this deep seated fault that initiates the waters to circulate at depth. It is obvious that, Mesozoic sediments are commonly exposed at the surface in Ambo area while at Wonchi and Woliso area this cannot be observed at shallow depth. So that metamorphic decarbonation of this deep Mesozoic sediments at Wonchi and Woliso side which can be the source of CO2 to these ground waters are highly affected by this deep seated structures. On the other hand, the source of these thermal ground waters is also due to the shallow magma chamber that heats the deep circulated ground waters along this fault structures.

Stable isotopic data of $\delta^{18}O$, $\delta^{2}H$ and $\delta^{13}C$ are used in this study to identify the source of recharge, ground water residence time, source of CO2 in ground waters, ground water surface water interaction and CO2-water-rock interaction. The highland areas north and east of the Blue

Nile basin are characterized by relatively depleted $\delta^{18}O$ groundwaters and the meteoric waters of the Blue Nile River basin have higher d-excess compared to the meteoric waters of the Ethiopian Rift(Seifu Kebede, 2005). As far as these study area is found in the Western Ethiopian Plateau the depletion in $\delta^{18}O$ is commonly observed in ground waters around Woliso and Ambo Area indicates that the source of recharge is from the high land. Unlike geothermal waters of the Rift valley which shows the Positive oxygen shift, ground waters of Ambo area have negative oxygen shift. This is due to the influx of CO2 gas to the region that can take place during CO2-water-rock interaction. However, most of the ground water samples collected from Wonchi area is enriched in $\delta^{18}O$ isotope. This testifies that, there is the hydraulic connection of lake water with ground waters around the lake Wonchi. There are some shallow spring and Hand dug wells that show the $\delta^{18}O$ enrichment due to the evaporation effect. The secondary data from ^{3}H isotope according to Seifu Kebede et al., 2005 the low TDS ground waters from basaltic plateau have appreciable amount of tritium unit indicates that this ground waters are young and shallow while the high TDS thermal ground waters have low tritium unit which indicates that these ground waters are from deeper origin and older in age.

The $\delta^{13}C$ isotope is enriched in gaseous and thermal ground waters like Ambo mineral water, Ambo thermal spring and Wonchi gasoues spring. This value indicates that the source of CO2 to these ground waters is from the dissolved inorganic carbon that is from metamorphic decarbonation. Wonchi thermal spring and Woliso Negash Lodge hot spring shows the $\delta^{13}C$ value that show the source of CO2 is from the mantle origin. In these high $\delta^{13}C$ value ground waters significant CO2-water-rock interaction is observed. The $\delta^{13}C$ value in shallow and cold ground waters and surface waters indicates that the source of CO2 is from C3 plants and Soil CO2.

6.2. Recommendation

- The natural sparkling mineral waters in this area especially around Ambo and Wonchi Crater Lake are useful for the mineral water bottling companies and mud pools are recommended to be useful for recreation centre.
- Geophysical investigations are recommended in order to locate the depth of Mesozoic sediments around Wonchi and Woliso area.
- In order to investigate constructive knowledge on CO2-water-rock interaction in this area; laboratory analysis should be conducted on rock samples especially on travertine lime stone deposits.
- Dating of rock samples is recommended in order to understand the age of the travertine lime stone to understand the rate of precipitation of this mineral to be formed so that it can be useful for further understanding about CO2-water-rock interaction.
- The environmental and health aspect of these thermal and gaseous ground waters due to their significant trace element mobility; remedial measures should be conducted.
- Geological CO2 sequestration which is the common activity in the World today to reduce the green house gases that cause global warming is safe in such environments, so that the direction to this activity is highly recommended.
- The effect of natural CO2 influx to the environment in order to increase global warming and the surrounding aquatic environment such as wet lands must have to be further investigated.

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ANNEXES

sample_ID	Sample_date	X	Y	Elevation	Na+	K+	Ca	Mg	NH3	F	Cl	SO4	HCO3	NO3	PO4	DO	Turb	TS	PH	CaCO3	NO2	ground watert type
W1-HDW1	Dec,1,2010	447924	1002120	2411	7	0.3	24	9.6	0.82	0.55	15.45	0.99	122	0.36	0.41	-	0.37	_	6.65	100	0.01	Ca-Mg-HCO3
W2-BH1	Dec,1,2010	406049	996479	2219	47	2.7	0	48	0.71	0.69	44.42	0.99	317.2	7.12	0.74	-	0.37	_	7.43	200	0.01	Mg-Na-HCO3
W3-BH2	Dec,1,2010	404656	997734	2233	24	2.5	100	16.8	0.93	0.69	44.42	1.97	366	18.06	0.66	-	1.46	_	7.25	320	Trace	Ca-HCO3
W4-R1	Dec,2,2010	364708	992962	1977	10.5	6.1	22.4	5.76	0.8	0.73	15.45	0.99	97.6	3.21	0.49	0.23	6.94	_	7.92	80	Trace	Ca-Mg-Na-HCO3-Cl
W5-BH3	Dec,2,2010	364012	994386	1933	22	5.5	80	24	1.2	0.67	44.42	1.97	341.6	7.03	0.41	1.14	0.37	_	6.79	300	0.01	Ca-Mg-HCO3
W6-BH4	Dec,2,2010	363955	994576	1930	22	6.3	56.8	25.92	1.17	0.8	44.42	1.97	268.4	3.8	0.41	0.93	0.73	_	6.66	250	Trace	Ca-Mg-HCO3-Cl
W7-BH5	Dec,2,2010	363642	990775	2015	41	7.6	60	12	0.69	0.74	44.42	1.97	292.8	2.87	0.49	1.26	4.75	_	7.21	200	Trace	Ca-Na-HCO3-Cl
W8-R2	Dec,2,2010	363639	990114	1794	13	4.4	32.8	9.12	0.78	0.64	25.11	0.99	146.4	1.18	0.41	1.17	17.52	_	8.12	120	Trace	Ca-Mg-HCO3-Cl
W9-S1	Dec,2,2010	367812	993719	1935	69	5.4	160	36	1.35	0.61	54.07	200	536.8	7.75	0.33	0.45	4.75	832	7.07	550	0.01	Ca-Na-Mg-HCO3-SO4
W10-BH6	Dec,2,2010	369682	993850	2016	188	5.9	108	43.2	2.08	0.73	54.07	1.97	1074	0.75	0.41	1.56	4.75	1016	6.52	450	Trace	Na-Ca-HCO3
W11-BH7	Dec,2,2010	378343	991473	2188	112	9.9	58.4	24.96	1	1.03	44.42	0.99	585.6	0.54	0.33	1.22	1.83	562	7.53	250	0.01	Na-Ca-HCO3
W12-BH8	Dec,2,2010	378782	99374	2195	58	13.8	100	19.2	1.33	1.14	54.07	1.97	439.2	5.67	0.41	1.06	3.29	522	7.11	330	Trace	Ca-Na-HCO3
W13-S2	Dec,2,2010	373894	992816	2195	230	5.9	96	31.2	2.08	0.84	112.01	0.99	976	0.72	0.66	1.73	3.29	_	6.36	370	Trace	Na-Ca-HCO3
W14-HDW2	Dec,3,2010	378209	981177	2672	10.5	13.4	28	12	0.69	0.59	29.93	0.99	109.8	22.35	0.74	0.69	5.84	_	6.88	120	0.01	Ca-Mg-HCO3-Cl
W15-S2	Dec,3,2010	376303	971288	2676	39	6.3	12	4.8	0.71	1.12	20.3	0.99	122	0.47	1.15	0.71	4.75	_	7.85	50	Trace	Na-Ca-HCO3-Cl
W16-L1	Dec,3,2010	378141	972601	2889	38	7.2	14.4	3.36	0.31	1.17	25.11	0.99	122	0.52	0.74	0.32	1.46	_	8.23	50	Trace	Na-Ca-HCO3-Cl
W17-S3	Dec,3,2010	377823	970187	2815	290	21.5	56	38.4	0.66	5.85	39.59	0.99	1171	0.57	0.98	1.72	31.03	_	6.06	300	0.005	Na-HCO3
W18-S4	Dec,3,2010	378045	970164	2817	280	19.5	20.8	11.52	0.91	5.71	54.07	1.97	854	0.61	0.9	0.71	2.56	_	7.25	100	0.005	Na-HCO3
W19-S5	Dec,3,2010	387858	942917	2825	272	10.7	1.6	0.96	0.15	18.46	39.59	2.56	671	11.82	0.44	0.41	0.37	762	7.66	8	0.29	Na-HCO3
W20-BH9	Dec,3,2010	386180	943990	2039	53.5	4.4	18.4	6.24	0.18	1.11	5.79	0.99	205	2.26	0.17	0.04	0.37	212	8.12	72	0.01	Na-Ca-HCO3

SmapleID	Li	B	Al	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Rb	Sr	Mo	Cd	Cs	Ba	La	Pb	U
W1-HDW1	0.773	6.750	1.183	0.194	0.282	0.147	0.212	0.882	0.017	2.684	1.860	72.640	0.063	1.029	101.600	0.165	0.058	0.063	24.850	0.010	<LoD	<LoD
W2-BH1	4.942	26.440	0.825	0.277	9.475	0.072	3.905	3.539	0.081	2.662	28.560	54.990	0.476	2.472	109.700	2.256	0.024	0.054	27.800	0.017	0.037	0.761
W3-BH2	0.823	12.130	0.197	0.342	18.280	0.100	1.907	0.020	0.063	1.716	13.230	31.710	0.136	1.560	157.400	0.469	<LoD	0.032	26.750	0.014	<LoD	1.701
W4-R1	0.429	6.839	183.800	6.102	1.311	0.287	19.800	155.800	0.079	0.533	0.922	12.740	0.146	7.264	63.390	0.891	<LoD	0.024	8.376	0.236	0.052	0.217
W5-BH3	4.165	13.230	0.324	0.275	5.165	0.273	0.001	0.006	0.016	2.477	4.364	49.440	2.836	8.039	237.600	1.375	<LoD	0.213	59.360	0.009	<LoD	2.288
W6-BH4	8.217	19.740	0.194	0.311	1.697	0.025	42.410	0.450	5.081	6.973	1.139	40.520	1.231	10.930	264.700	2.972	<LoD	0.433	114.200	0.004	<LoD	0.922
W7-BH5	2.925	16.560	0.229	0.322	6.176	0.245	1.584	0.136	0.099	0.796	0.808	7.758	0.564	9.601	201.500	3.034	<LoD	0.218	69.490	0.006	<LoD	1.797
W8-R2	0.480	7.480	2.369	0.343	2.226	0.156	0.409	5.725	0.067	0.566	0.828	2.464	0.207	4.595	136.300	0.895	<LoD	0.018	15.480	0.020	<LoD	0.428
W9-S1	24.020	75.720	0.772	4.198	13.700	0.212	0.017	0.621	<LoD	0.514	0.147	6.815	0.149	4.182	1292.000	0.580	<LoD	0.033	29.400	0.020	<LoD	2.069
W10-BH6	151.600	193.600	0.422	0.153	0.078	0.014	290.400	5.878	0.029	0.188	0.436	13.630	0.115	60.090	469.000	0.220	<LoD	2.550	1779.000	0.021	0.015	<LoD
W11-BH7	30.640	67.100	0.662	0.358	0.212	0.046	12.480	8.419	<LoD	0.537	0.798	58.570	0.299	11.770	288.300	3.942	<LoD	0.124	33.730	<LoD	0.013	0.571
W12-BH8	40.680	39.510	0.064	0.187	4.301	0.108	1.265	0.177	<LoD	0.370	1.029	7.356	0.279	16.330	358.400	2.024	<LoD	0.100	40.830	<LoD	<LoD	6.317
W13-S2	84.770	122.200	0.269	0.081	0.093	0.028	16.160	176.500	<LoD	0.236	0.358	6.530	0.203	23.330	163.100	0.412	<LoD	0.617	57.360	<LoD	0.018	0.034
W14-HDW2	3.775	12.600	194.700	5.438	0.911	1.009	1.186	124.400	<LoD	0.547	0.713	49.940	0.075	13.650	108.300	0.443	<LoD	0.025	38.950	0.179	0.084	0.084
W15-S2	3.943	8.516	8.465	1.886	0.137	0.039	0.665	36.850	<LoD	0.152	0.320	1.102	0.338	4.746	11.450	3.306	<LoD	0.010	0.992	0.148	<LoD	0.077
W16-L1	3.618	13.250	4.944	0.145	0.120	0.033	1.972	7.178	<LoD	0.226	0.731	0.850	0.274	6.300	18.800	3.158	<LoD	0.015	2.954	0.016	<LoD	0.102
W17-S3	116.500	50.170	1243.000	0.122	0.031	0.031	1256.000	5265.000	0.024	0.380	0.119	13.040	0.066	15.290	61.920	0.429	<LoD	0.020	2.849	0.022	<LoD	<LoD
W18-S4	171.200	118.400	67.460	0.244	0.040	0.056	257.100	1709.000	0.018	0.214	<LoD	3.506	2.312	25.320	9.231	3.095	<LoD	0.048	2.611	0.048	0.070	<LoD
W19-S5	125.800	164.700	8.114	0.438	0.073	0.202	0.980	26.840	<LoD	<LoD	<LoD	0.237	2.398	27.710	10.410	12.050	<LoD	1.125	12.230	0.026	<LoD	<LoD
W20-BH9	4.314	20.640	5.376	0.196	9.470	0.095	0.808	9.873	<LoD	0.117	<LoD	33.620	0.348	8.418	78.780	4.074	<LoD	0.036	7.032	0.021	0.032	0.788

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	mean
max average	27.0	28.7	28.2	28.0	28.0	24.6	22.7	22.6	23.9	25.7	26.5	26.5	26.0
min average	11.4	12.4	13.0	13.3	12.2	11.9	12.1	12.2	11.0	10.1	10.8	10.0	11.7
ambo mean	19.2	20.6	20.6	20.6	20.1	18.3	17.4	17.4	17.5	17.9	18.7	18.2	18.9
													0.0
					Woliso station								0.0
max average	26.6	28.0	27.4	27.6	27.3	23.6	21.3	21.6	23.1	25.2	25.6	25.6	25.2
min average	13.2	14.5	14.1	14.0	13.0	12.8	12.8	13.1	12.3	12.4	13.0	13.0	13.2
Woliso mean	19.9	21.2	20.7	20.8	20.2	18.2	17.1	17.4	17.7	18.8	19.3	19.3	19.2
					Tulu bolo station								0.0
max average	24.3	25.0	25.3	25.5	25.7	24.8	23.3	23.5	23.6	23.3	23.9	23.6	24.3
min average	8.6	8.7	9.7	9.9	9.6	9.8	9.8	9.8	9.3	9.0	8.5	8.3	9.2
tulubolo mean	16.4	16.9	17.5	17.7	17.6	17.3	16.6	16.6	16.5	16.2	16.2	15.9	16.8
													0.0
					Asgori station								0.0
max average	27.5	28.5	29.0	28.4	29.0	27.6	25.0	24.8	25.5	25.8	26.5	26.8	27.0
min average	6.1	7.1	8.8	10.0	9.2	9.7	10.5	10.8	9.6	5.8	4.5	4.8	8.1
Asgori mean	16.8	17.8	18.9	19.2	19.1	18.6	17.7	17.8	17.6	15.8	15.5	15.8	17.5

					CATCHMENT'S RELATIVE HUMIDITY							
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Mean RH	50.4	44.3	50.5	54.0	56.7	71.7	78.0	79.4	76.1	57.6	48.3	47.8

				Sunshine duration								
Station	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Woliso Average	8.615	9.54	7.815	7.005	7.745	5.655	4.645	3.6	4.375	7.295	9.18	9.7
Ambo average	8.4	9	7.6	7.1	7.6	4.5	3.675	3.5	4.6	8.85	9.525	9.575
Mean	**8.51**	**9.27**	**7.71**	**7.05**	**7.67**	**5.08**	**4.16**	**3.55**	**4.49**	**8.07**	**9.35**	9.64

Wind speed

					Woliso							
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Total	67.5	65.5	53.2	48.4	32.7	19.7	17.6	16.8	20.7	45.7	65.7	74.9
mean	4.0	3.9	3.1	2.8	1.9	1.2	1.0	1.0	1.2	2.7	3.9	4.4
					Ambo							
Total	17	19.3	17.1	16.4	13.1	10.1	7	6.8	7.7	13	15.7	18.1
mean	2.1	2.4	2.1	2.1	1.6	1.3	0.9	0.9	1.0	1.6	2.0	2.3
					Catchement mean wind speed							
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Catchmeant mean	**3.0**	**3.1**	**2.6**	**2.4**	**1.8**	**1.2**	**1.0**	**0.9**	**1.1**	**2.2**	**2.9**	**3.3**

Rainfall

station	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	Total (mm)
Tulubolo	18.3	18.6	54.2	67.8	78.4	192.9	287.5	277.7	90.6	24.6	7.4	7	1125
Asgori	18.5	32.8	53.6	83.6	67.9	128.1	242.5	239.4	102.2	25.7	6.9	5.3	1006.5
Woliso	23.9	27.4	66.5	84.8	122.8	190.9	271.9	257.3	130.5	40.4	7.6	5.3	1229.3
Busa	21.3	59	55.9	73.7	84.4	179.8	358.2	372.5	164.9	43	10	9.1	1431.8
Wolonkomi	22.8	29.2	66.1	72.4	77.9	154.4	240	234.4	133.7	36	12.2	6.6	1085.7
Ambo	31.87	15.27	52.76	74.65	73.18	149.87	177.2	163.2	87.71	45.83	9.22	11.3	892.09
Ginchi	33.9077	65.93	84.38	105.1	87.46	148.68	238.7	224.3	150.6	32.04	4	16	1191.19
Arithmetic Mean	24.37	35.46	61.92	80.3	84.58	163.52	259.4	252.7	122.9	35.37	8.19	8.66	1137.38

Note: annual total=**1137.37mm/year**