CO_2- water-rock interaction: Implication for Natural CO_2 Analogue In the Wonchi System; Ethiopia.

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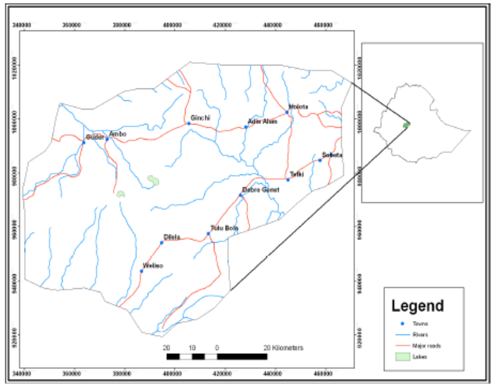
Introduction

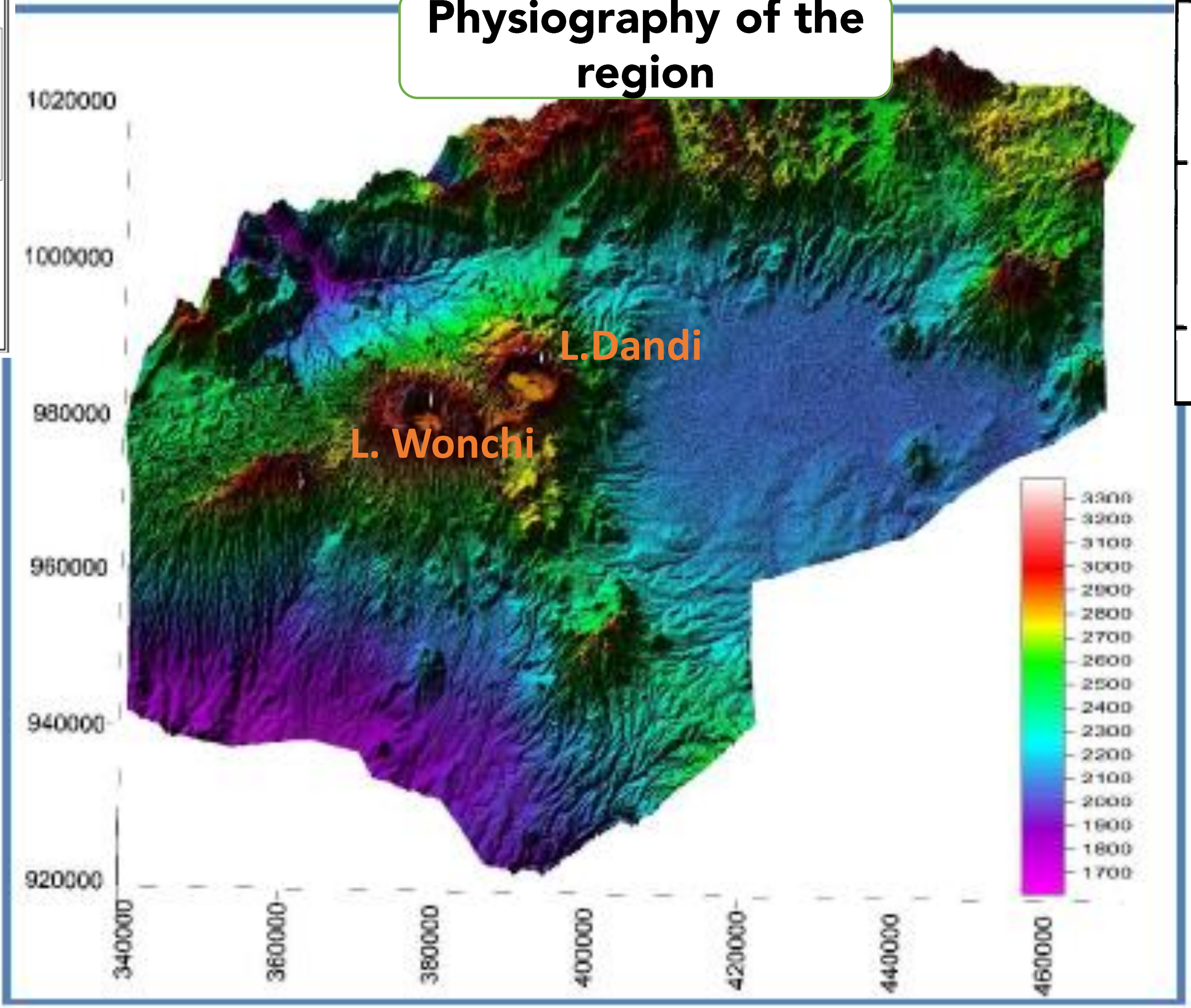
- CO_2 can be emitted to the atmosphere by degassing of magma and metamorphic decarbonation.
- Through volcanoes, associated fissures and hydrothermal sites, geothermal systems.
- CO_2 - Water form by mixing of mantle-derived, magmatic or metamorphic CO_2 and high T geothermal fluids with ground or surface waters.

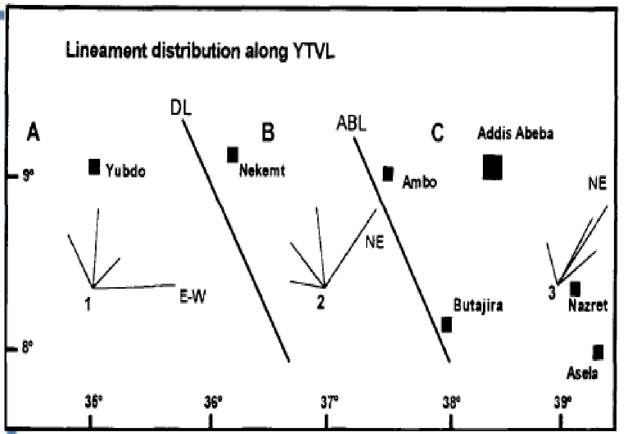
- Wonchi system is one of the natural analogues with Natural sparkling waters which diffuses CO2 to the atmosphere
- Thermal-gaseous springs are associated to this structures.
- CO2-Water-rock interaction is investigated in the Wonchi System of mineralized thermal and gaseous groundwater.

Introduction



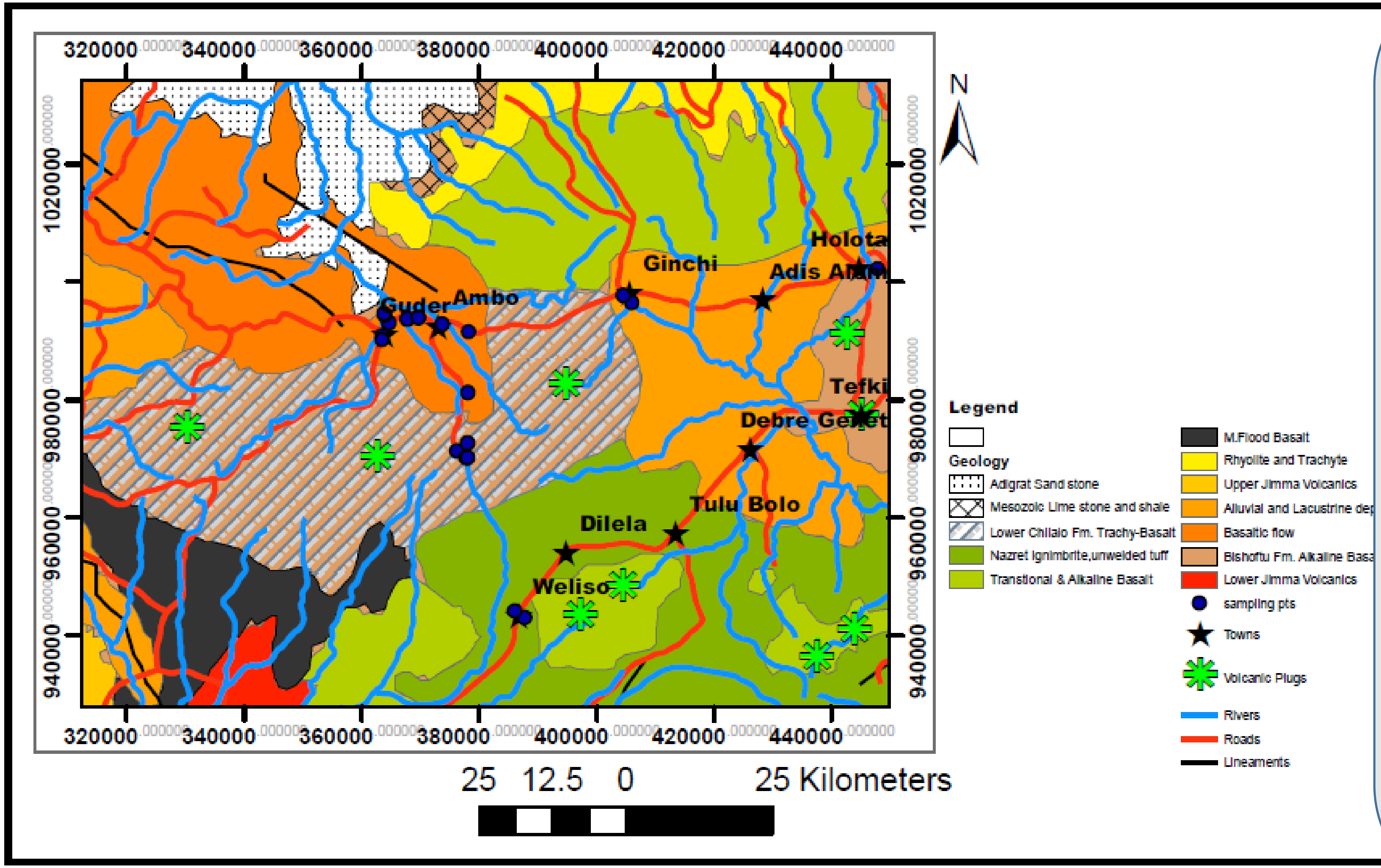
Physiography of the region





Lineament distribution along the YTVL. Bars represent the azimuthal peaks. (modified after Tsegaye Abebe et al., 1998)

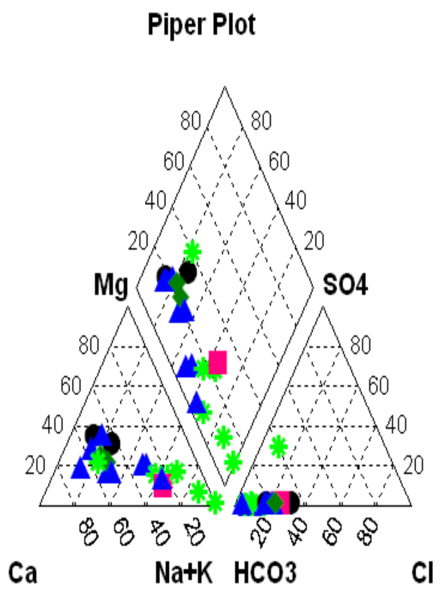
Geology and Hydrogeology

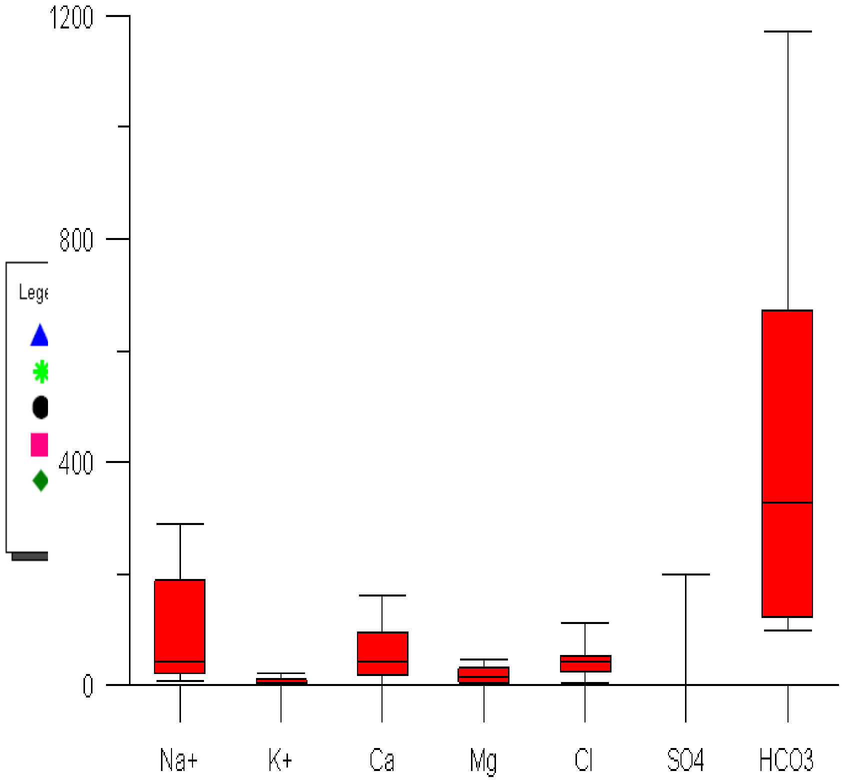


- Adigrat Sandstone in Ambo and Senkele area with medium productivity.
- Rhyolite and trachyte between Ambo, Wonchi and Dandi volcanic centers and Wolisso with low productivity.
- Tarmaber scoraceous Basalt exposed across Ambo fault and Wolisso area.
- Tertiary ignimbrite(low productivity) overlien by Becho plain quaternary basalt and alluvial deposits with moderate to high productivity.
- Geological structures along the Ambo-Wonchi-Wolisso and AA-Ambo fault syatems.

Methods and Results

- **Water samples were collected and analyzed for δ^2H and $\delta^{18}O$, geochemical data, $\delta^{13}C$ isotope and trace element.**
- **HCA analysis**
- **Inverse geochemical modeling (Phreeqc)**
- **^{13}C analysis to identify the CO_2 Source.**





- Deep groundwaters: thermal and gaseous: low pH (CO2), high alkalinity, TDS, EC and DO.
- Shallow groundwaters: cold, fresh: high pH, low alkalinity, TDS, DO

- Deep ground waters: NaHCO3 and NaCaHCO3 water types.
- Shallow ground waters: NaCaHCO3Cl, Ca-Mg-Na-HCO3-Cl and Ca-Na-Mg-HCO3-SO4 water types.

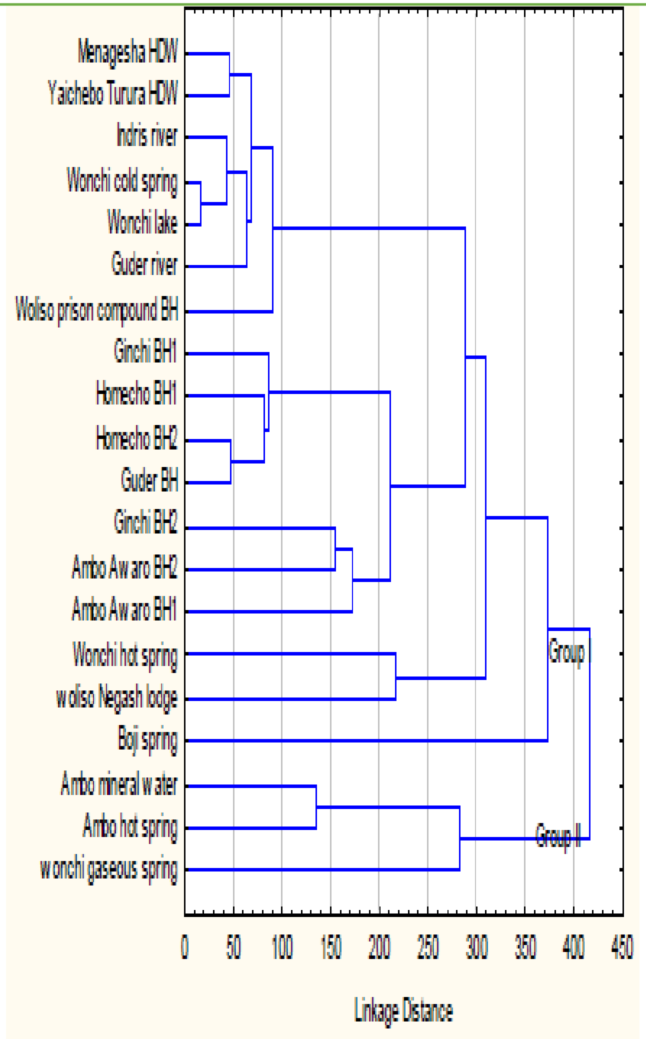
Results and Discussion

HCA classified the waters in to **two major groups and six sub groups**

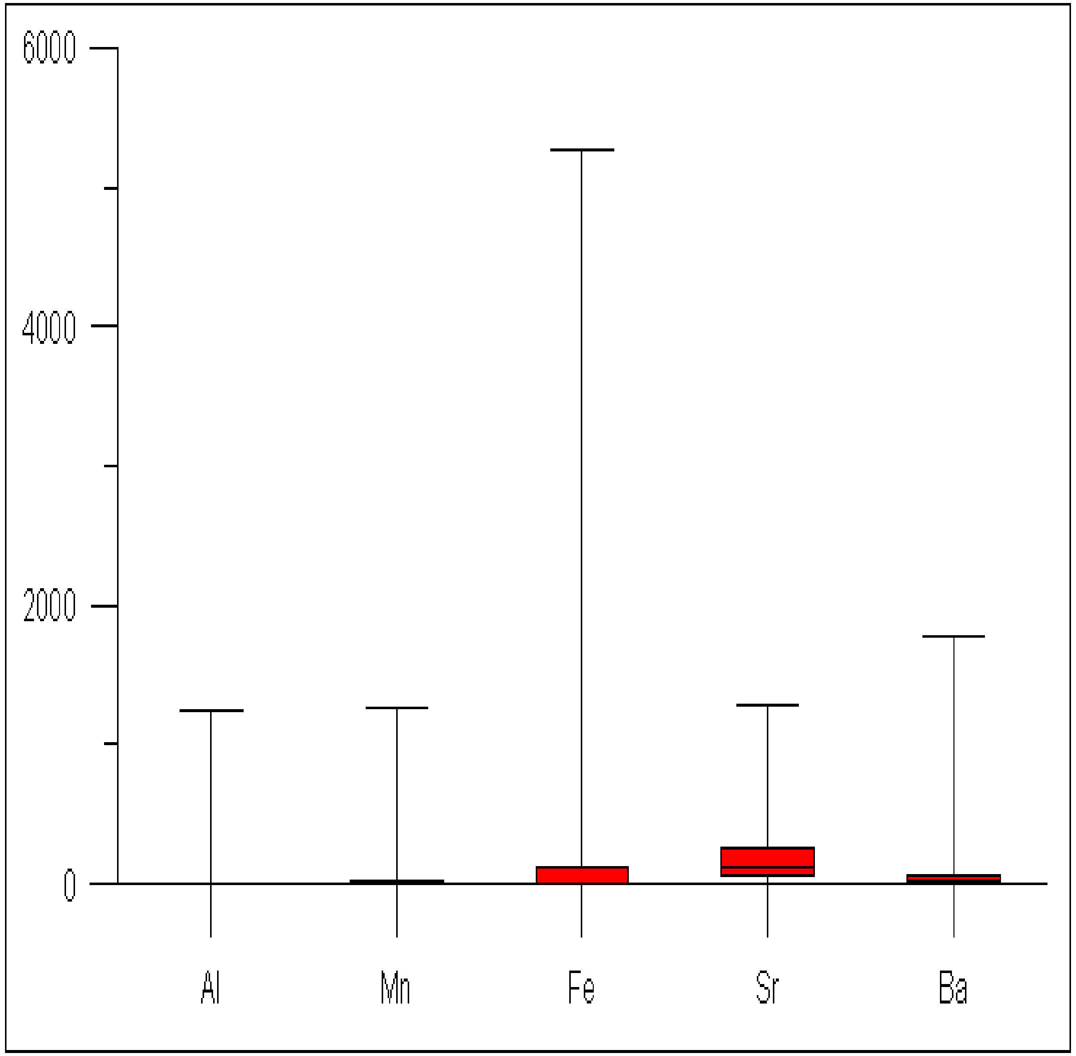
- **Group 1: low TDS<850mg/l**: shallow ground waters, rivers hand dug wells and lakes situated around Wonchi, Guder, Ambo and Woliso area.
  - **Cold, shallow and fresh ground waters**: **$CaHCO_3$, $CaMgHCO_3$** water types except in **some mixed ground waters.** They undergo short residence time and shallow subsurface circulation.

- **Group II: high TDS >850mg/l**: **thermal and gaseous springs** which represent the deep ground water circulation.
  - **Ground waters around Ambo area**: **$NaCaHCO_3$ type;** high TDS, alkalinity and low pH; representing the highly evolved, deep ground waters.
  - **Ground waters around Wonchi and Woliso**: **$NaHCO_3$** water type, **high TDS** and long subsurface circulation.

Hierarchical cluster analysis



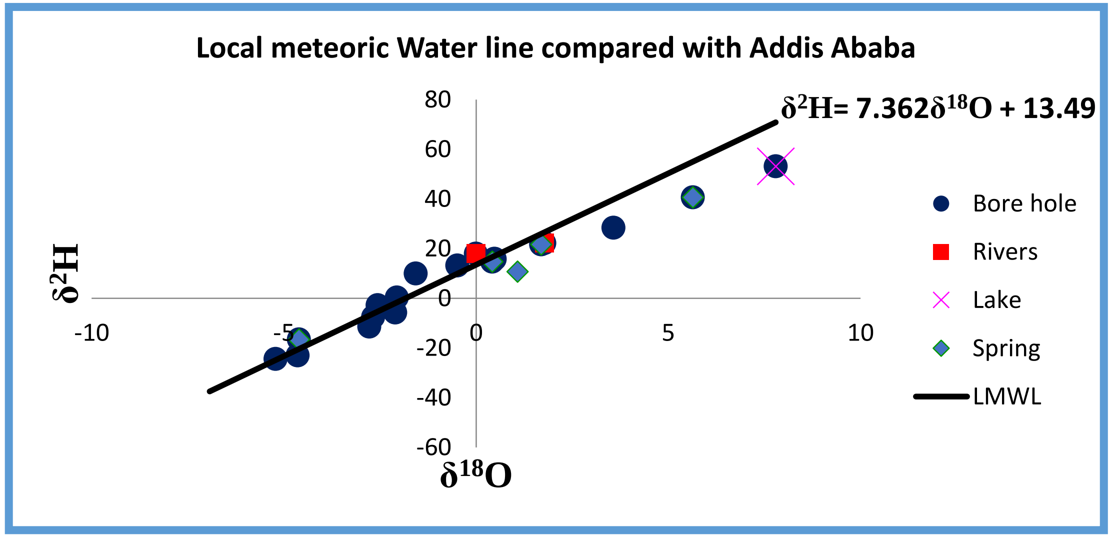
Trace element mobility



- **Low pH thermal and gaseous ground waters: higher trace element mobility**
- **Origin of heavy metals: geogenic source** like the weathering of silicate rocks, ferromagnesian minerals and weathering of calcite.
- **Sr, Ba, Fe, Mn and Al:** sometimes above WHO standard due to oxidation of sulphides
- **Li, Cu, Ni and B**: relatively higher but less than WHO standard.

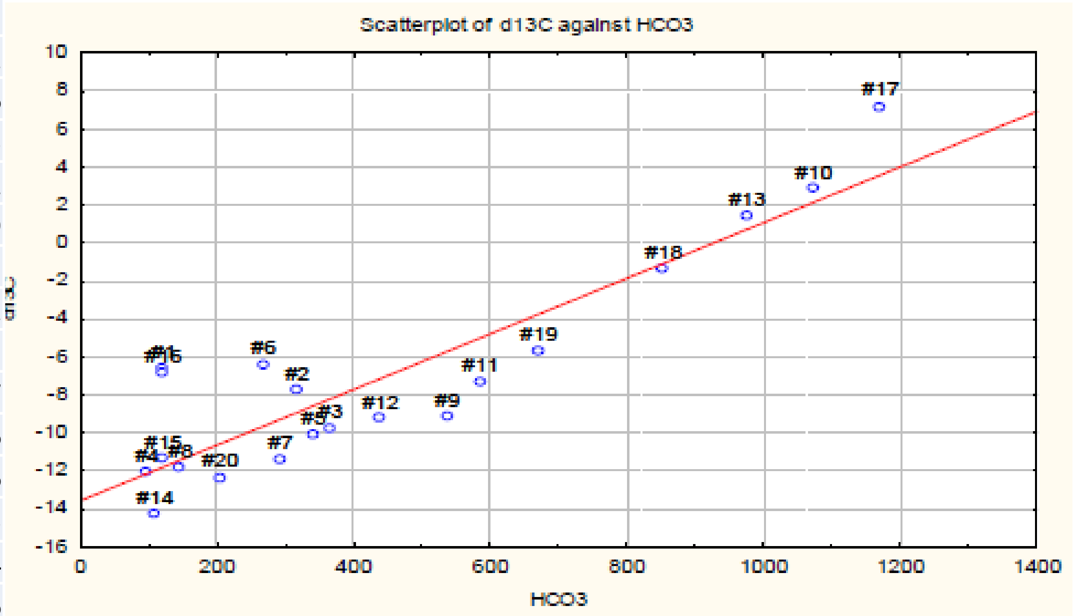
Results and Discussion

- **The $\delta^{18}O$ and δ^2H: thermal and gaseous ground waters** show **depletion:** recharge at higher altitude
- Thermal and gaseous ground waters **around Wonchi crater lake** show **enrichment in $\delta^{18}O$ due to** hydraulic connection of the lake water to ground waters.
- **cold and shallow ground waters and surface waters: enrichment in $\delta^{18}O$ and δ2H isotopes due to local evaporation effect.**
- Thermal and gaseous ground waters around Ambo: **negative oxygen shift** due to the effect of CO2 gas



Results and Discussion

ID	^{13}C
W1-HDW1	-6.62
W2-BH1	-7.76
W3-BH2	-9.75
W4-R1	-12.11
W5-BH3	-10.09
W6-BH4	-6.43
W7-BH5	-11.41
W8-R2	-11.83
W9-S1	-9.17
W10-BH6	2.86
W11-BH7	-7.36
W12-BH8	-9.25
W13-S2	1.44
W14-HDW2	-14.26
W15-S2	-11.36
W16-L1	-6.81
W17-S3	7.18
W18-S4	-1.36
W19-S5	-5.71
W20-BH9	-12.37



- The **δ^{13}C isotope:** high TDS gaseous ground waters **Ambo mineral water, Ambo hot spring and Wonchi gaseous spring**: CO2 from **metamorphic decarbonation source**.

- **Woliso Negash lodge and Wonchi thermal spring:** CO2 is from **magmatic source i.e. mantle origin**.

- **shallow ground water bore holes, hand dug wells, lake water and river waters:** CO2 to this ground water is from **soil and C3 plants.**

- The δ^{13}C of the ground waters
  - **Shallow aquifers: depleted = -14.26 to -6.43‰ and**
  - **Deep thermal and gaseous : enriched =-5.71 to 7.18‰.**

Inverse geochemical modeling

- **The initial and final waters** of the aquifer system
- **PHREEQC computer code**: simulate the geochemical evolution among HCA identified waters.
- **Four models** are conducted on selected ground water flow path
- The major phases of **dissolution** in most of the model results are **CO2(g), halite, K-mica, pyroxene, K-feldspars, plagioclase, albite, fluorite and dolomite.**
- **Calcite and clay minerals like illite** are among the major phases of **precipitation.**

Models	Water types
Model A	NaCaHCO3
	NaCaHCO3
Model B	CaMgHCO3Cl
	NaCaHCO3
Model C	NaCaHCO3Cl
	NaHCO3
Model D	NaCaHCO3Cl
	NaHCO3

Model A

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

Model B

Phase	mole transfers:	
alcite	-1.116e-002	CaCO3
02(g)	3.523e-002	CO2
alite	2.161e-003	NaCl
llite	-2.925e-002	K0.6Mg0.25Al2.3Si3.5O10(OH)2
-feldspar	1.479e-003	KAlSi3O8
lagioclase	1.274e-002	Na0.62Ca0.38Al1.38Si2.62O8
yroxene	1.634e-002	Mg0.5Ca0.5SiO3
-mica	1.607e-002	KAl3Si3O10(OH)2

Model C

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

Model D

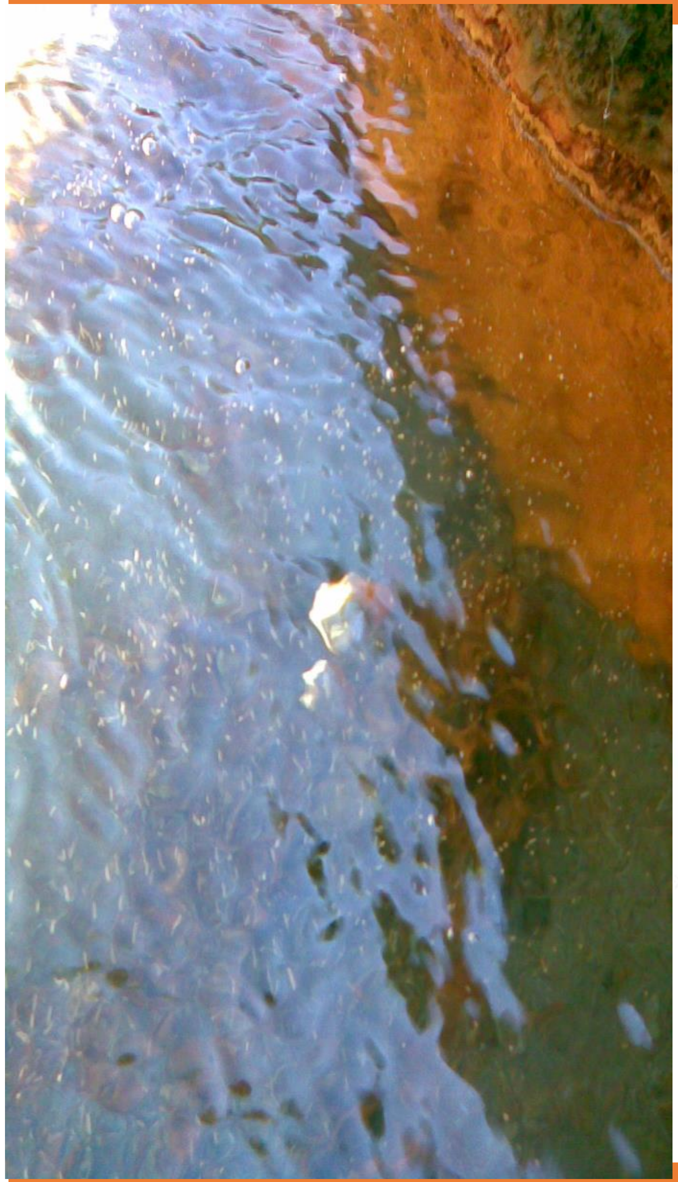
Phase		
Calcite	-1.317e-002	CaCO3
CO2(g)	1.215e-002	CO2
Dolomite	6.897e-003	CaMg(CO3)2
Halite	7.576e-004	NaCl
Illite	-2.624e-002	K0.6Mg0.25Al2.3Si3.5O10(OH)2
K-mica	1.065e-002	KAl3Si3O10(OH)2
Fluorite	1.196e-004	CaF2
K-feldspar	5.412e-003	KAlSi3O8
Plagioclase	1.667e-002	Na0.62Ca0.38Al1.38Si2.62O8

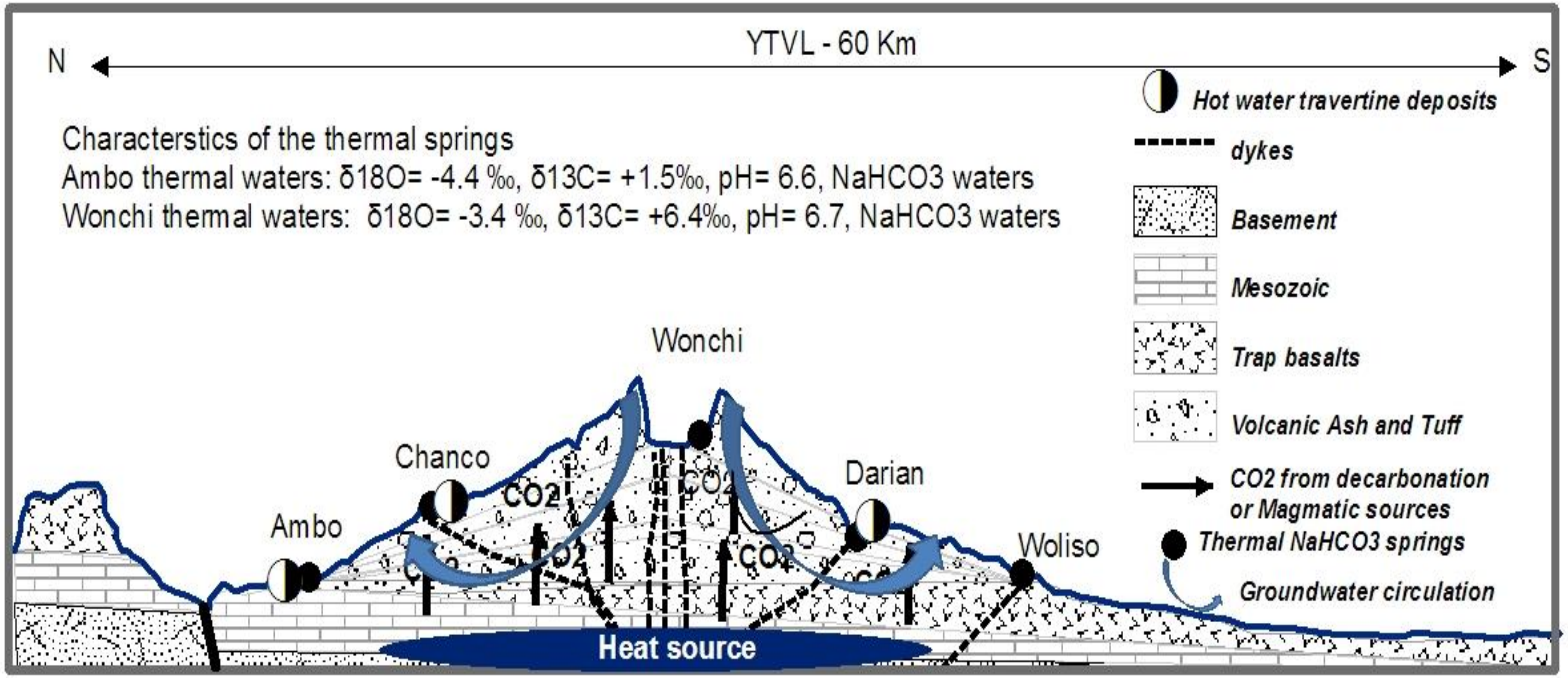
CO2-water-rock interaction

- **Deep groundwaters**
  - Thermal and gaseous groundwaters: **open to the influx of CO2 gas from external source:** from Mantle source and Metamorphic decarbonation
  - **Hydration of CO2 gas to form H_2CO3 and then dissociated to HCO3** and silicate hydrolysis reaction is activated.
  - Gaseous and thermal ground waters are **depleted in $\delta^{18}O$ and enriched in $\delta^{13}C$ isotopes,** except in Wonchi gaseous and thermal springs.
  - **CO2 is the major phase of dissolution** and 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.

- **Shallow and cold ground waters are closed to CO2 influx from external source** and undergo slight CO2-water-rock interaction and short sub-surface circulation.

CO_2 -water-rock Interaction





Conclusion

- **Thermal and gaseous ground waters along the Ambo-Woliso-Butajira fault: Highly evolved with significant CO_2-water-rock interaction; source of CO_2 is from metamorphic decarbonation and magmatic source**

- **shallow and cold ground waters: slight CO_2-water-rock interaction and short subsurface circulation;** the **CO_2 source in shallow** ground waters is from **soil and C3** plants.

- **Trace element mobility** is higher in low pH thermal and gaseous ground waters and origin of these trace metals is geogenic

- **Geochemical reactions like strong silicate hydrolysis by $CO_2(g)$** .
  - **The major phases of dissolution**: $CO_2(g)$, pyroxene, K-mica, K-feldspars, albite and dolomite.
  - **The major phases of precipitation**: calcite and clay mineral like illite.

Thank You