Isotopic and geochemical study of geothermal fluids in Mongolia for geothermal exploration

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THESIS APPROVAL SHEET

This thesis entitled "*Isotopic and geochemical study of geothermal fluids in Mongolia for geothermal exploration*" is an original work of **Dolgorjav OYUNTSETSEG** submitted to the Department of Earth, Life and Environmental Science, Graduate School of Science and Engineering for Education, University of Toyama, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy (PhD). The thesis has been read, examined and approved by an examination comities composed of:

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DEDICATION

To my teachers Dr B.Ariyadagva and Dr D.Ganchimeg

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PREFACE

The work presented in this PhD research (Isotopes and geochemical study of geothermal fluids in Mongolia for geothermal exploration) was carried out at University of Toyama, Japan under the Society for the Promotion of Science (JSPS, RONPAKU; Dissertation PhD) Program from April 2012 to April 2015. The thesis was supervised by Prof. Akira Ueda.

The thesis is organized into four chapters.

Chapter 1 is a general introduction to the study and presents a summary of the study background, relevant literature and objectives of the study.

Chapter 2 is "Isotopic and chemical studies of hot and cold springs in western part of Khangai Mountain region, Mongolia, for geothermal exploration" which published in *Geothermics* journal.

Chapter 3 is "Chemical and isotopic characterization of hot and cold spring waters in northeastern part of Khangai area".

Chapter 4 is "Summarizes of the main conclusions and recommendations from this study."

ABSTRACT

There are 42 hot springs in Mongolia and from them 32 hot springs are located in the Khangai area. In the Khangai mountain region, geothermal fields occur in five provinces (Zavkhan, Bayankhongor, Uvurkhangai, Arkhangai and Bulgan). In this study were determined chemical and isotopic compositions in 46 hot and cold spring waters (24 hot springs, 5 cold springs and 17 river waters) of Khangai area. To identify changes of main chemical composition of hot spring waters within different times we were compared present studies results with the previous studies 25 hot spring waters results. The hot waters were of Na^+-HCO_3^- and Na^+-SO_4^{2-} type whereas cold springs and river waters were characterized as a Ca^{2+}-HCO_3^- type water. The Ca^{2+}+Mg^{2+} concentrations in the cold spring and river waters are greatest in waters with elevated HCO_3^-. This shows that cold spring and river waters are enriched in Ca^{2+}, Mg^{2+} and HCO_3^- due to dissolution of carbonate rocks such as dolomite commonly observed in the study area. In contrast, the hot waters are enriched in Na^+ and K^+ and depleted in Ca^{2+} by ion exchange with underlying clay minerals. The δD and $\delta^{18}O$ values of hot water samples in the Khangai Mountain region vary from -87 to -126‰ and -12 to -17‰, respectively and are in good agreement with those of cold springs and river water in the regions studied. The hot and cold spring waters in the Zavkhan region and at high altitude have more negative δD and $\delta^{18}O$ values than those of other regions. There is no evidence of $\delta^{18}O$ shift. This means that all water samples come from meteoric water minimal isotope exchange by interaction with surrounding rocks. The ^{13}C isotopic ratios in the study area thermal and cold waters range from -13 to -17‰. This means the carbon species (HCO_3) in hot springs is derived from organic sources. The $\delta^{34}S$ values vary from +4 to +19‰. The $\delta^{34}S$ values vary within a wide range independent of their sulfate contents. Based on the He/Ne and ^{13}C ratios, sulfur in hot springs may be of sedimentary origin. We have calculated of underground temperature were obtained using 3 different methods suggested by geothermometers, mineral saturation state and mixing model. The underground temperature in each reservoir are estimated to be 120±40℃ and indicating a low temperature geothermal resource in the study area. These resources can be used for room heating and production of electricity by a binary system.

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Chapter 1

Introduction

1.1. Main objective

The main objectives of this study are to analyze all geochemical and isotopic of thermal waters in the Khangai mountain region, Mongolia and to interpret the geochemical characteristics to apply them for future geothermal exploration and heat resources in Mongolia.

1.1.1. Specific objectives

➢ Determination of chemical composition in the hot and cold waters of the Khangai region in Mongolia and based on the comparative study with the previous research to evaluate their property and type.

➢ Determination of source in the hot springs by using stable isotopes (^{18}O, D, ^{13}C, ^{34}S and He/Ne).

➢ Calculation of underground temperature by using three different methods; chemical geothermomters, water-rock equilibrium and mixing model of deep and surface waters.

➢ Heat usage in the Khangai area.

1.1.2. Novelty of the present research

◆ By studying of He/Ne isotopes content of the Khangai region's hot waters have determined and the hot waters have radiogenic origin which means these He and Ne gas come from the decay of U-Th.

◆ The first time have determined ^{13}C and ^{34}S isotopes of the hot waters in the Khangai area. The carbon species (HCO_3) in hot springs is derived from organic sources and sulfur in hot springs may be of sedimentary origin.

◆ In the present research by using several geotheromometer methods have calculated of the subsurface temperature of the hot waters in the Khangai area and it ranges from 75 to 158^{0}C. Results indicated that the geothermal fields in the study area are classified into low temperature resources.

◆ We concluded that the hot waters in the Khangai area belong to low temperature resources. These resources can be used for room heating and production of electricity by a binary system.

1.2. Background of the study

Mongolia is situated in the northern part of Central Asia, far from oceans, on high plateau surrounded by mountain ranges. The north-west and central parts of Mongolia are high mountainous regions. Whereas the eastern part is a vast plain steppe and the southern part is a semi-desert. Mongolia has a centuries-long tradition of using geothermal water from natural springs for medical purposes. Obviously, the contribution of those facilities to the overall geothermal energy utilization is small. There are also public recreational centers where geothermal water is used for sanitary with open-air swimming pools and to heat small greenhouse using of storage hot water during the summer season. Mongolia has 42 hot springs (Pisarskii et al., 2003) but geothermal utilization is not widely developed in Mongolia. Geothermal energy, with its proven technology and abundant resources, can make a very significant contribution towards reducing the emission of greenhouse worldwide (Fridleifsson, 1998). New technology opens possibilities for more extensive use geothermal energy in Mongolia. The Khangai range is an area of extinct volcanism (repeated eruptions but not recent), earthquakes and an extensive distribution of hot springs. The 32 hot springs are located in the Khangai area. In the Khangai mountain area, geothermal field occur in five provinces (Zavkhan, Bayankhongor, Uvurkhangai, Arkhangai and Bulgan).

Knowledge of the origin of geothermal waters is important in geothermal studies because it helps to discriminate the chemical properties of the thermal waters and the source of their charge. Studies of stable isotopes play an important role in hydrogeological investigations of both thermal and non-thermal waters because the isotopes carry of fluid origin and processes.

Detailed investigation on the thermal waters in Khangai area has not been carried out earlier to establish the reservoir temperatures. This is important to plan deep exploratory program to assess the power generating capacity of the Khangai geothermal area. Towards this aim, detailed geochemical and isotopic investigations of these springs

have been carried out in order to understand their geochemical evolution and also estimate the reservoir temperatures through chemical geothermometry to apply them for future geothermal exploration and heat resources in Mongolia.

1.3. Isotopic geochemistry of geothermal water

Chemical and isotopic geochemistry plays an important role in researching origins of hot-spring fluids and temperature of geothermal reservoir (Bergfeld et al., 2001). Isotope techniques are indispensable tools in geothermal investigations. Because isotope ratios are sensitive to temperature and natural physicochemical processes, such as water-rock interaction, mixing, and steam separation, they can be efficiently used in tracing the origin of geothermal fluids and the processes that the fluids have undergone at subsurface. They are also useful in an estimation of reservoir temperature of geothermal systems, as well as the subsurface residence time of waters.

Isotopes are the atoms of an element which have the *same atomic number* but *different atomic mass*. Atoms consist of a nucleus, containing protons with positive charge and neutrons with no charge, and the electron shells surrounding the nucleus and containing negatively charged electrons. The number of protons in the nucleus is known as *Atomic Number (Z)*, and is equal to the number of electrons in a neutral atom. The sum of number of protons (Z) and number of neutrons (N) gives the *Atomic Mass (A) (A=Z+N)*. In a chart of nuclides (atoms), the notation is such that the atomic number is shown as subscript at the lower left, and the atomic mass is shown as superscript at the upper left of the symbol representing the concerned element. For example, Helium (He) isotopes with mass 3 and 4 are represented by $^{3}_{2}He$ and $^{4}_{2}He$ where the subscript 2 is the atomic number of the element Helium (Nilgun Güleç, 2013).

Isotopes are broadly classified into two groups as Radioactive Isotopes and Stable Isotopes.

1.3.1. Radioactive isotopes

Radioactive isotopes are those atoms which are transformed, in time, into other atoms through radioactive decay. The products of radioactive decay are called *Radiogenic Isotopes* which can be radioactive or stable. In isotope literature, radioactive isotope is also termed as *Parent Isotope*, and radiogenic isotope as *Daughter Isotope*. Variations in natural abundances of radioactive isotopes are governed by radioactive decay which is defined by

the equation:

$N = N_0 \, e^{-\lambda t}$ where;

N = amount of radioactive (parent) isotope at any time t,

N_0 = initial amount of radioactive (parent) isotope before the start of decay,

λ = decay constant,   t = time elapsed since the start of radioactive decay.

There are a number of decay mechanisms including α- decay, β-decay, electron catchment, positron decay and nuclear fission. For example, uranium (U) constitutes one of the major radioactive elements of the Earth and ^{238}U and ^{235}U isotopes turn into lead (Pb) isotopes by α decay:

$^{238}U \rightarrow \, ^{206}Pb + 8\alpha$

$^{235}U \rightarrow \, ^{207}Pb + 7\alpha$
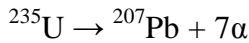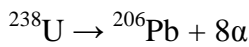
Where α particle has 2 protons and 2 neutrons, identical to $^{4}_{2}He$ isotope. Likewise, tritium (^{3}H) which is the radioactive isotope of the element hydrogen (H) is transformed into stable helium isotope $^{3}_{2}He$ by β^{-}-decay (electron emission): $^{3}H \rightarrow \, ^{3}He + \beta^{-}$

1.3.2. Stable isotopes

Stable isotopes do not undergo radioactive decay. Variations in natural abundances of stable isotopes are governed by *isotope fractionation* which is the partitioning of isotopes between two different phases during physicochemical process. Most common physicochemical processes in geothermal systems include evaporation, condensation, degassing (differentiation of a fluid into gas and residual liquid phases) and water-rock interaction. Extent of isotope fractionation is proportional to the mass difference between the isotopes ($\Delta m/m$) and is more prominent for isotopes with mass less than 40.

Isotope Fractionation is defined by the equation:

$\alpha = R_A/R_B$

Where; α = fractionation factor

R_A = heavy/light isotope ratio in substance A

R_B = heavy/light isotope ratio in substance B

For instance, for the isotope exchange reaction between two gaseous substances, carbon dioxide (CO_2) and methane (CH_4),

$^{12}CO_2 + \, ^{13}CH_4 = \, ^{13}CO_2 + \, ^{12}CH_4$
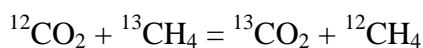
Fractionation factor is defined as: $\alpha = (^{13}C/^{12}C)_{CO2} / (^{13}C/^{12}C)_{CH4}$

Isotopic compositions of geologic materials are expressed by $\boldsymbol{\delta}$ notation as deviation of their heavy/light isotope ratio from that of a reference standard. For instance, isotopic composition of carbon in CO_2 is denoted by:

$\boldsymbol{\delta}^{13}C$ (‰) ={ [$(^{13}C/^{12}C)_{CO2} / (^{13}C/^{12}C)_{std}$] -1 } x 10^3

Positive and negative $\boldsymbol{\delta}$ (delta) values point to the enrichment and depletion, respectively, of the heavy isotope in geologic material relative to the standard.

1.3.3. Isotope studies in geothermal systems

The most commonly used isotopes in geothermal system studies are those of oxygen (O), hydrogen (H), Carbon (C) and Helium (He). Naturally occurring stable isotopes of hydrogen are ^1H (hydrogen) and ^2H = D (deuterium), those of oxygen is ^{16}O, ^{17}O and ^{18}O. Carbon and Helium each has two stable isotopes (^{12}C and ^{13}C, and ^3He and ^4He, respectively). The relative abundances of these isotopes in nature are given in Table 1.1. Hydrogen and carbon each has one radioactive isotope ^3H (tritium) and ^{14}C, respectively, which are not very common and are found in only trace amounts (Nilgun Güleç, 2013).

Table 1.1: Commonly used stable isotopes in studies of geothermal systems (Faure, 1986; Rosman and Taylor, 1998; Gerardo-Abaya et al., 2000)

Element	Stable isotopes	Natural abundance (% atom)
Hydrogen	^1H	99.985
	D	0.015
Oxygen	^{16}O	99.76
	^{17}O	0.04
	^{18}O	0.20
Carbon	^{12}C	98.89
	^{13}C	1.11
Helium	^3He	0.000137
	^4He	99.999863

Stable isotope studies performed on geothermal fluids (as well as those on the other geologic materials like groundwater, rocks and minerals) are based on the use of isotope ratios of the most abundant isotopes, namely, D/H, $^{18}O/^{16}O$, $^{12}C/^{13}C$ and $^3He/^4He$.

In geochemical applications, stable isotope compositions of H, O and C are expressed in terms of deviations of their heavy/light isotope ratios from the ratio(s) of reference standard(s) (i.e. δ notations). The reference standard is the **S**tandard **M**ean **O**cean **W**ater (SMOW) for H-and O-isotopes. For the C-isotope, the composition of the fossil *Belemnite*

from the Pee Dee Formation in South Carolina is used as reference standard (PDB: **P**ee **D**ee **B**elemnites) (Table.1.2).

Table 1.2. Parameters and standards relevant to the stable isotopes of H, O and C.

Element	Parameter	Radio	Reference standart
Hydrogen	δD	D/H	SMOW
Oxygen	$\delta^{18}O$	$^{18}O/^{16}O$	SMOW
Carbon	$\delta^{13}C$	$^{13}C/^{12}C$	PDB

SMOW: Standart Mean Ocean Water;   PDB: Pee Dee Belemnites

Isotope geology is a discipline providing significant contribution to the studies related to exploration, development and exploitation of geothermal systems. This stands from the fact that isotope fractionation is very sensitive to temperature and natural physicochemical processes (such as water-rock interaction, hot and cold water mixing, and degassing) that they can be used as potential tracers of sources of geothermal fluids and the subsurface processes to which the fluids are subjected on their circulation paths. In this respect, isotopes are used in the following studies:

I. determination of the origin of geothermal fluids,

a) sources of fluids (meteoric, magmatic, metamorphic, etc.)

b) investigation of the factors and physicochemical processes affecting the fluid composition (altitude, latitude, evaporation-condensation, water-rock interaction, mixing)

c) sources of dissolved components in geothermal fluids (dissolved solids, dissolved gases)

II. estimation of the age (subsurface residence time) of geothermal fluid,

III. geothermometry applications (estimation of the reservoir temperature).

This course is mainly focused on the use of isotopes in the determination of the origin of geothermal fluids. Estimation of age and reservoir temperature of geothermal systems is also briefly mentioned (Nilgun Güleç, 2013).

1.3.4. Origin of Geothermal Fluids

The origin of geothermal fluids refers to both the sources of fluid and its dissolved components, and the processes to which the fluids are subjected.

1.3.5. Hydrogen and oxygen isotopes

In geothermal studies, source of geothermal fluids implicitly involves the source of the (geothermal) water, as well as the source of dissolved components (dissolved solids, dissolved gases) in the fluid. Hydrogen and oxygen isotopes are the isotopes pertinent to the water molecule, and hence are used in an understanding of the source of geothermal water.

Geothermal waters have five possible sources: (1) surface water, including groundwater, commonly referred to as *meteoric water* (i.e. water forming under atmospheric conditions), (2) *seawater*, (3) *formation waters* (also called as connate or fossil waters) which are kept in deep sediments at the time of their formation, (4) *metamorphic water*, liberated during processes of metamorphism, and (5) *magmatic water*, forming at great depths.

Each of the above mentioned water sources has unique isotopic compositions, and define distinct fields on a a diagram of δD vs. $\delta^{18}O$ (Figure 1.1). The $\delta^{18}O$ and δD compositions of precipitation throughout the world are linearly correlated and distributed along a line known as the *Global Meteoric Water Line (GMWL)*, defined by the equation:

$\delta D = 8 \delta^{18}O + 10$ …… (Craig, 1961)
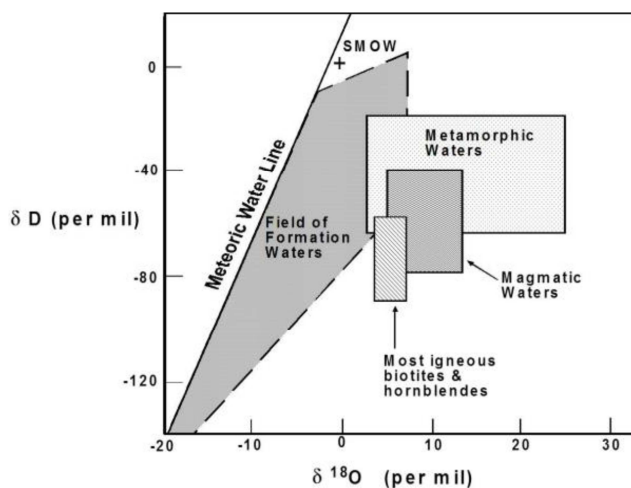
Fig.1.1. δD vs $\delta^{18}O$ diagram showing isotopic compositions of different water types (meteoric water line is rom Craig, 1961; fields are from Taylor, 1974and Sheppard, 1981).
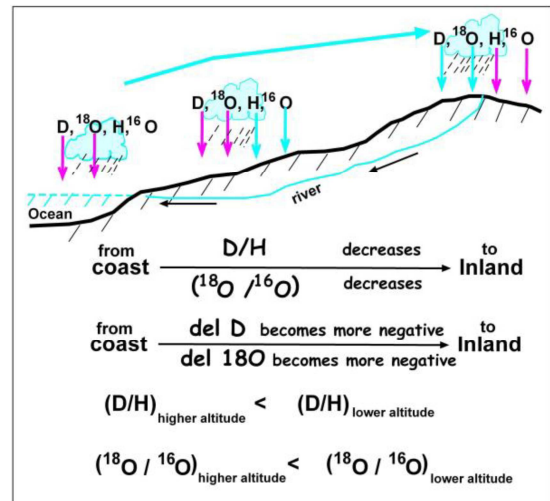
Fig.1.2. Continental and altitude effect on water composition.

Any "Local Meteoric Water Line" (LMWL), defined by precipitation collected from a specific site or region usually has similar slope as the GMWL but may have a different intercept. Seawater is enriched in heavy isotopes compared to meteoric water. The isotopic composition of magmatic water is estimated from the isotopic composition of igneous rocks

which generally falls in the range of **δD** and **δ^{18}O** values of -50 to -85‰ and +5.5 to +10‰ respectively (Taylor, 1974). Metamorphic waters have isotopic compositions controlled by equilibration with oxygen and hydrogen bearing minerals during metamorphism at temperatures from 300°C to 600°C. According to Taylor (1974) such waters are characterized by **δD** and **δ^{18}O** values of -20 to -65‰ and +5 to +25‰., respectively. Formation waters may have been originally meteoric waters, but the reactions that they have undergone give them different characters.

The position of local precipitations along meteoric water line depends on several factors such as temperature, amount of precipitation, distance from the coast (continental effect), altitude and latitude. Most water vapor in the atmosphere is derived from evaporation of low-latitude oceans. Precipitation derived from the vapor is always enriched in δD and δ^{18}O. Progressive raining (i.e. increasing amount of precipitation) results in more negative δD and δ^{18}O values. As clouds move from the coast towards inland, being associated with increasing altitude and decreasing temperature, the isotopic composition of precipitation tends to have more negative δ D and δ^{18}O (continental effect) (Figure 1.2). The latitude effect works in a similar way and increasing latitude, being associated with progressive rain-out and decreasing temperature, derives water composition towards lower (more negative) δD-δ^{18}O values (Figure.1.3).
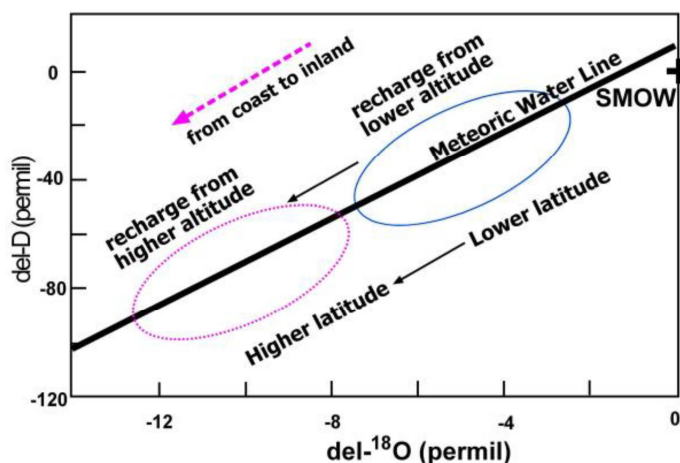
Fig.1.3. δD vs δ^{18}O diagram showing the altitude, latitude and continental effects on water composition.

Deviation from the meteoric water line can be due to several processes such as i) evaporation and condensation, ii) water-rock interaction, and iii) mixing with non-meteoric waters such

as formation (fossil) waters, metamorphic waters, magmatic waters (Albu et al., 1997).

During evaporation lighter isotopes (H, ^{16}O) preferentially partition into the vapour phase, while the residual water phase is enriched in heavy isotopes (D, ^{18}O); during condensation the first rain drops are enriched in light isotopes (H, ^{16}O) (Figure 1.4). In other words, the water's δD-δ^{18}O composition evolves towards more positive values during evaporation, while condensation shifts the composition towards more negative values (Figure 1.5).

The water-rock interaction is particularly realized at high temperatures and hence may commonly occur in geothermal systems. Given that rocks are enriched in heavy oxygen isotope, the water-rock interaction shifts the water's composition towards more positive δ^{18}O values, while δD values do not change as hydrogen is not one of the major constituents of rocks (Figure 1.5).

Regarding the mixing process, the geothermal waters of mixed origin are supposed to plot on the δD vs. δ^{18}O diagram along lines converging from meteoric water line towards the areas representing isotopic compositions of magmatic, metamorphic and fossil waters.
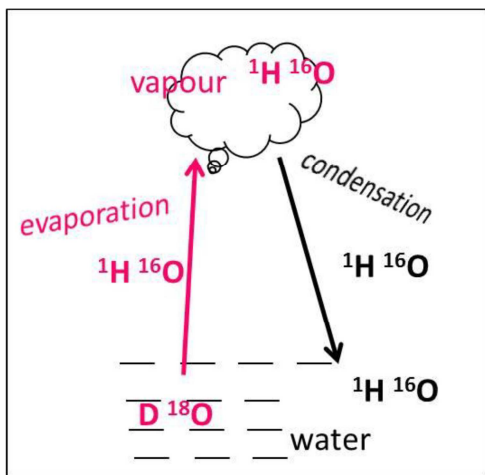
Fig.1.4. Partitioning of hydrogen and oxygen isotopes during evaporation and condensation.
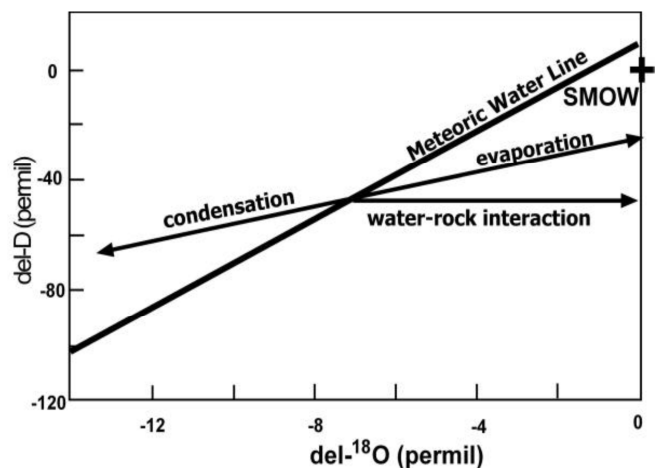
Fig.1.5. δD vs δ^{18}O diagram showing the effects of natural processes on water composition.

Given the effects of several factors and processes on water composition, hydrogen and oxygen isotope compositions can be used in geothermal exploration not only to determine the source of geothermal water but also to identify the possible recharge areas and trace the flow directions. These isotopes can also be used in monitoring studies during geothermal

exploitation (Arnorrson ve D'Amore, 2000; Gerardo-Abaya et al., 2000). For instance, because drilling and withdrawal will cause a pressure decline in the fluid pressure of geothermal reservoir, changes in deuterium and ^{18}O of fluid may reflect recharge from different aquifers into producing aquifers (at zones of depressurization). This may lead to deterioration in geothermal reservoir characteristics, particularly in case of recharge from cold aquifers which will decrease the enthalpy of system. Pressure drop may also enhance boiling in geothermal system which, in turn, will enhance scaling. Scaling is the precipitation of dissolved components (calcite, silica, etc.) in the wellbore due to oversaturation of water with respect to these components following steam separation during boiling. Because evaporation will induce an increase in δD and $\delta^{18}O$ values of residual liquid, any increase in these values during monitoring may point to a possible boiling and hence scaling. Therefore, monitoring of isotope composition of geothermal fluids during exploitation can lead to determination of, and the development of necessary precautions against decrease in enthalpy due to start of recharge from cold, shallow aquifers, or scaling problems developed as a result of subsurface boiling (Nilgun Güleç, 2013).

1.3.6. Carbon and helium isotopes

Carbon and helium isotopes are used for the investigation of the origin of dissolved components in geothermal fluids. These isotopes, particularly their combined use, are of significant importance in the investigation of not only the provenance of dissolved components, but also in assessment of natural processes to which the fluids and deep hydrothermal system might have been subjected.

There are two stable C-isotopes in nature, ^{12}C and ^{13}C (Table 1.1). C-isotopic composition is expressed as $\boldsymbol{\delta}^{13}C$ (Table 1.2). Regarding the compounds relevant to hydrological cycle, the major sources establishing the dissolved carbon content in natural waters are : i) sedimentary organic carbon ($\boldsymbol{\delta}^{13}C \approx$ -10 to -40‰) reflecting the biogenic source, ii) marine carbonates ($\boldsymbol{\delta}^{13}C \approx$ 0‰), iii) mantle CO_2 ($\boldsymbol{\delta}^{13}C \approx$ -6.5‰), and iv) atmospheric CO_2 ($\boldsymbol{\delta}^{13}C \approx$ 7-8‰) related to the global carbon cycle (Sharp, 2007; Mook, 2000) (Figure 1.6). He has two stable isotopes, ^{3}He and ^{4}He (Table 1.1); the variations in their ratio are greater than 10^3 in geologic reservoirs leading to the identification of three

major components, namely, radiogenic-He, tritiugenic-He and Primordial-He.
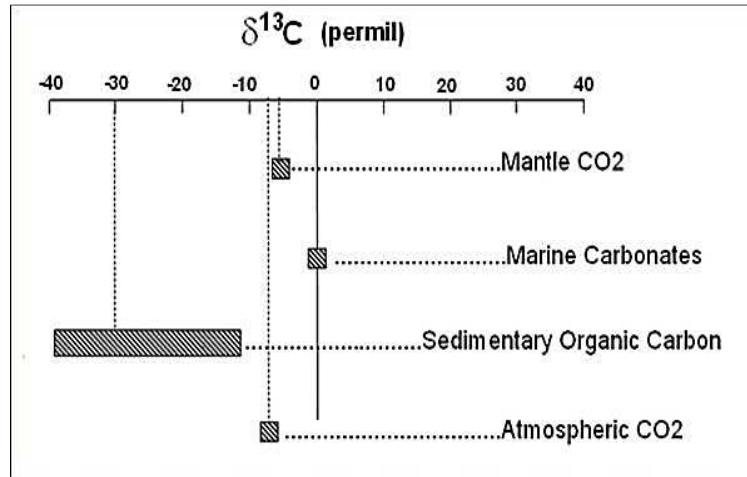
Fig.1.6. Major sources of carbon in natural waters (simplified from Sharp, 2007; Mook, 2000)

Two types of reactions are responsible for the formation of radiogenic-He: i) α-decay of uranium (U) and Thorium (Th) which produces ^{4}He, and ii) the nuclear reaction ^{6}Li (n,α) ^{3}H (β^-) ^{3}He, which produces ^{3}He. Production rate of radiogenic ^{3}He is very low compared to ^{4}He, and radiogenic-He is characterized by a ^{3}He/^{4}He ratio of about 10^{-7}-10^{-8} (Ozima and Podosek, 1983; Andrews, 1985). Because U, Th and Li are all concentrated in crust, relative to mantle, the term "radiogenic-He" is often taken to imply "crustal-H" or vice versa. Tritiugenic-He is the ^{3}He produced by the decay of tritium (^{3}H) (Craig and Lupton, 1981). Primordial-He is that component which was trapped in the interior of the Earth at the time of its accretion from solar nebula (Ozima and Podosek, 1981), and is characterized by ^{3}He/^{4}He ratio around 10^{-4}. This primordial-He is released from the mantle reservoir of the Earth essentially via magmatism. Mantle degassing occurs largely at ocean basins and - to a lesser extend - in continental areas.

Atmosphere, crust and mantle are the three major reservoirs from which He observed in terrestrial materials is derived (Figure 1.7). Atmospheric-He is characterized by a ^{3}He/^{4}He ratio of $1.39*10^{-6}$ (Ozima and Podosek, 1983). Because this ratio is rather constant over the globe, ^{3}He/^{4}He ratios measured on geologic materials are usually expressed relative to the ratio in the atmosphere (R/R_A = (^{3}He/^{4}He)$_{sample}$ / (^{3}He/^{4}He)$_{atm.}$). Crustal-He has an R/R_A range of 0.01-0.1 (Andrews, 1985). Mantle-He has ^{3}He/^{4}He ratio around 10^{-5} ($R/R_A \approx$ 8-30)

(Mamyrin and Tolstikhin, 1984; Farley and Neroda, 1998), reflecting the dilution of Primordial-He with that produced by radiogenic processes in the mantle.

Fig.1.7. Major He-components and He-reservoirs (R=(^{3}He/^{4}He)$_{sample}$, R$_A$=(^{3}He/^{4}He)$_{atmosphere}$) (Sources: Ozima and Podosek, 1983; Andrews, 1985; Mamyrin and Tolstikhin, 1984; Farley and Neroda, 1988).

Given the fact that carbon and helium have wide isotopic and relative abundance contrast between mantle and crustal reservoirs of the Earth (Table 1.3), C- and He-isotopes can be potential tracers of gas provenance. The presence of high ^{3}He/^{4}He ratios in volcanic regions, for example, may be indicative of a young volcanic heat source. C-isotope compositions can give an idea about the possible reservoir lithologies and/or the lithologies on the circulation paths of fluids. Combined He-CO$_2$ systematics can also be used to determine the possible subsurface processes in deep hydrothermal system (e.g. degassing, mineral dissolution/precipitation). Determination of such processes makes use of solubility of gases in water. Because solubility of He in water is lower than that of CO$_2$, He partitions preferentially into the gas phase during degassing leading to an increase in the CO$_2$/He ratio in the residual liquid phase. Likewise, because light isotopes more preferentially partitions into steam phase during evaporation, degassing causes the residual liquid composition to evolve towards higher ^{13}C/^{14}C and lower ^{3}He/^{4}He ratios. Mineral precipitation/dissolution processes affect the water composition in a similar way: mineral (e.g. calcite) dissolution increases, while precipitation decreases the δ^{13}C value of the water as the heavy isotopes

preferentially enters the solid phase.

Table 1.3. C- and He-isotope systematics pertinent to different reservoirs

Reservoir	R/R$_A$	δ^{13}C‰	CO$_2$/^{3}He
Crust	0.01-0.1	0 to -40	10^{11}-10^{13}
Mantle	8-10	-6.5	$2*10^9$

Crust: Andrews, 1985 (R/R$_A$); O'Nions and Oxburgh, 1988 (CO$_2$/^{3}He); Sano and Marty, 1995 (δ^{13}C).

Mantle: Farley and Neroda, 1998 (R/R$_A$); Marty and Jambon, 1987 (CO$_2$/^{3}He and δ^{13}C).

1.4. Geology of Mongolia

The Mongolian territory is located on the Central Asian folding belt, bordering with the Siberian platform to the north, and the Northern Chinese and Tarim platforms to the South. Geological setting is complex, with many lithological and structural styles, relating to plate collisions of Proterozoic to Permian age. Fold systems are formed at different times, mostly in the Paleozoic period. Also older Pre-Cambrian and younger Mesozoic movements formed fold zones, but these do not play such an important role in the geological setting (Marinov, et al., 1970). The latest active tectonic period started in Mongolia at the end of Mesozoic and the beginning of Oligocene, due to simultaneous development of the south Siberian plate form (mountain part) and the Baikal Lake region. At the time, intense tectonic development gave the Mongolian mountains their present appearance. A geophysical survey on the crystal established (affirmed) that accumulative thermal sources (magma lumps) are located near the surface under the Khangai Mountain region (Batbayar, 2001). The tectonic development periods of Mongolian land belong to the periods of Lake Baikal Rift establishments of the Eurasian Plate (PREGA, Mongolia, 2005).

The data obtained during the last few years indicate that climate changes in the Late Cenozoic were determined to a significant extent by orogenic processes in Central and South Asia, which produced the vast Inner Asian mountain belt (Zonenshain, 1990) that includes the Himalayan, Altai, Sayany, Baikal, Khangai, and Khentii mountain systems.

The total area occupied by this belt is estimated at ~9 x 10^6 km^2. Its formation likely distributed atmospheric circulation in the Northern Hemisphere and caused global climatic changes. The climatic record derived from Lake Baikal sediments shows that these changes with a cooling trend commenced approximately 3 Ma ago (Kuz'min, 2006).

In central Asia intraplate magmatism was most conspicuous in the Cenozoic. Numerous fields of volcanic rocks are found in Mongolia, Transbaikala and the Maritime territory, northwestern China. Zoneshain and Kuzmin (1983) proposed that this magmatism was related to a mantle hot spot. These volcanic rocks are widely distributed and usually grouped within enclosed areas spatially separated from other areas of the same age. The nature of these areas is not yet resolved. We consider this problem this problem using the example of a province of intraplate magmatic rocks in western Mongolia. It includes the Khangai upland and its eastern boundaries, and regions to the south to the southern frontier of Mongolian (Yarmolyuk, 1991).

1.5. Heat flow of Mongolia

Geothermal studies in Mongolia started over 35 years ago with investigation into temperatures and thicknesses of permafrost by the Institute of Permafrost (Zabolotnik, 1969). The heat flow of the region varying between 34 and 84 mW/m^2 (a mean of 62±10 mW/m^2) was first estimated in five 150-170 m deep boreholes in northern (Ardag, Erdenet), central (Harchuluun, Ihhayrhan), and southern (Tsagaan-Saburga) Mongolia (Shastkevich, 1971) (Fig.1). In 1980-1983, the Soviet-Mongolian Research Expedition run jointly by the Science Academies of the two countries the studies continued in Lake Khuvsgul (9 heat flow stations) and in its surroundings (5 boreholes in two fields), in central (26 boreholes in 11 fields), and in southern Mongolia (15 boreholes in 5 fields), and at 10 hot springs, which added 28 heat flow determinations (Lysak, 2003).

The available collection of local and regional data reported in many papers (Khutorskoi, 1986 and 1988; Dorofeeva, 1990; Golubev, 1992) and books (Khutorskoi,

1991; Golubev, 1995; Dorofeeva, 1995; Khutorskoi, 1996) is however, incomplete, as the geothermal coverage is uneven, especially in the West Country (Lysak, 2003).

The thermal state of the lithosphere in Mongolia, as elsewhere, is represented by its conductive component together with convective heat transported by ground waters that discharge in numerous hot spring along active faults in the Hangayan (Khangai), Hentiyn, and Khuvsgul uplifts (Pissarsky, 1983). Abundant data on the groundwater chemistry (Pissarsky, 1982) allowed us to use SiO_2, Na, K, and Ca chemical geothermometers for deep temperature modeling and estimation of convective and conductive heat components in 16 field. High helium enrichment of thermal waters (Pinneker, 1995) made it possible to estimate heat flows from $^3He/^4He$ ratios through special formulas (Parasolov, 1984; Polyak, 1994 and 2000), and these estimates were obtained for 22 hot springs (Lysak, 1999). Lysak (1999) investigated the geothermal field in Mongolia on the basis of data from 141 heat flow station, including 55 drilling sites, and 26 hot springs.

The heat flow distribution in Mongolia is controlled by tectonomagmatic activity associated with Mesozoic and Cenozoic rifting and active thermal faulting of the old continental crust. $^3He/^4He$ ratios show that the greatest portion of heat flow is of crustal radiogenic origin on uplifts, especially in Eastern and Central Mongolia, and the mantle component is high in rift basins, large active faults, and in provinces of Cenozoic volcanism (Lysak, 2003). The territory of Mongolia comprises different thermal activity regions. Regions of high thermal activity ($q > 60$ mW/m^2) involve narrow linear heat flow anomalies in rifts (Lake Hovsgol and Onon graben) and zones of hypothetical subsurface magmatism (Kerulen uplift and Choibalsan basin), possibly associated with mantle diapirism (Khutorskoi, 1996; Zorin, 1982; Khutorskoi, 1989). In regions of moderate thermal activity (q from 50 to 60 mW/m^2), heat flows regularly decrease with ages of rocks and crustal cooling (Khutorskoi, 1996). Regions of low thermal activity ($q < 50$-40 mW/m^2) in oceanic crust subducted beneath Northern Eurasia (Molnar, 1975).
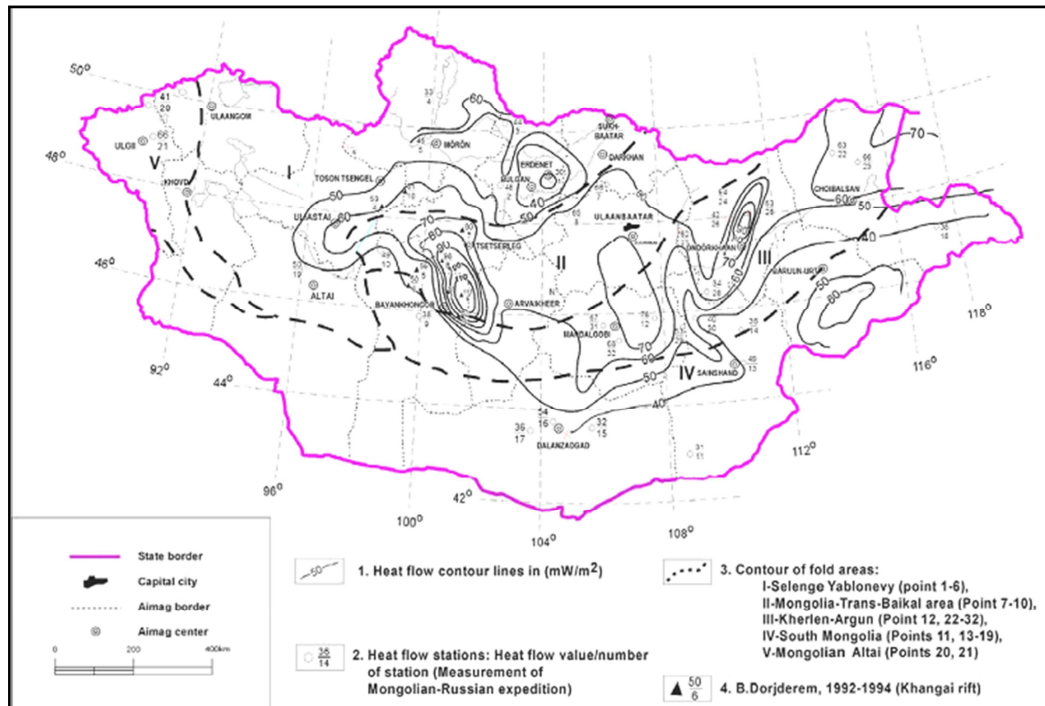
Fig.1.8. Heat flow map of Mongolia (based on information from Ministry of Agriculture and Industry of Mongolia (1999) and Dorofeeva (1992) and maps published by the Geodesy and Cartographical Institute, Mongolia (1980; 2000)

Western and Southern Mongolia was in the middle Carboniferous a zone of subduction where regions are confirmed by anomalously low heat flows. The predicted deep temperatures indicate that the lithosphere in Northern and Northeastern Mongolia is in quasi-steady thermal state and is much hotter4 than in the Western and Southern regions. Heat flow is higher in depressions within high-activity thermal regions and in uplifts within regions of moderate and low thermal activity where higher temperatures beneath uplifted areas are associated with ongoing crustal uplift. The thermal evolution of the lithosphere in Mongolia controlled its structural and compositional changes, especially at shallow depths (Lysak, 2003).

1.6. Geothermal study in Mongolia

Mongolia is rich in mineral waters and geothermal resources with a various properties including their applicability for health and energy source purposes (Figure 1.9). The first systematical study of mineral waters of Mongolia were performed by Smirnov et al. during 1926-1927. Further more detailed investigation on the formation mineral water,

their distribution and chemical composition were studied by Marinov, Namnandorj etc. In 1963 and 1966 were published monographs on mineral water resources of Mongolia. Mongolia and Soviet Union's joint hydrochemical "Khubsgul" research group was performed research on complex study of hydromineral resources of Mongolia during 1971-1974. The aim of the research was to determine physic-chemical and micrbiological properties of the mineral resources (Pinnecer, 1980). Based on all previous research were created "The map of Mineral springs of Mongolia" in 1983.

New edition of "The map of Mineral springs of Mongolia" were performed in 2004 (Pisarsky, 2004). This map is result of many years of study on "Reserves of mineral springs of Mongolia" carried out in collaboration between the international teams consisting of scientists of the Earth Crust Institute, Siberian branch of Academy of Science, Russia and Institute of Chemistry and Chemical Technology of Mongolian Academy Science, the National Balneology Center of the Ministry of Health, Mongolia. This map is rather different from the schematic map developed previously by scientists N.A. Marinov, Popv, V.N and Sh. Tseren and the variant created on scientific basis by Pisarsky, Lkhanaasuren, Ariya-Dagva, Speiser and Dorjsuren. New edited map contains newly discovered and described mineral springs objects and were used modern analytical methods for compiling borders of hydrogeologic provinces, districts and boundaries of various mineral spring areas were corrected and clarified on the scientific basis (Pisarsky, 2006).

In the results of many years of studies were established that Mongolia has about 250 mineral waters. Also Pisarsky and Ganchimeg have done gas analysis for identify gas composition of the Mongolian mineral springs and determined such as He, Ar, O_2, N_2, CH_4, H_2S, CO_2 during 1983-2000. Mongolian mineral waters by their distribution, temperature, gas composition and geochemical characterization were divide into four groups such as a hot waters with nitrogen type and cold mineral waters with carbon dioxides (CO_2), cold salty waters with methane and submineral waters with different composition (B.I.Pisarsky, B.Nambar, 2004). The gas analytical data revealed that Mongolian all hot springs are

belong into nitrogen type by their gas composition (Pissarsky and Ganchimeg, 2007).

The hot waters mainly distributed in Khangay, Khentey, around the Khuvsgul Lake and the Mongol Altay plate forms in Mongolia due to their developments during the second geodynamic Cenozoic age. Mongolia has 42 hot waters. The hot springs are divided into four areas based on their distribution and hydrogeological characteristics.
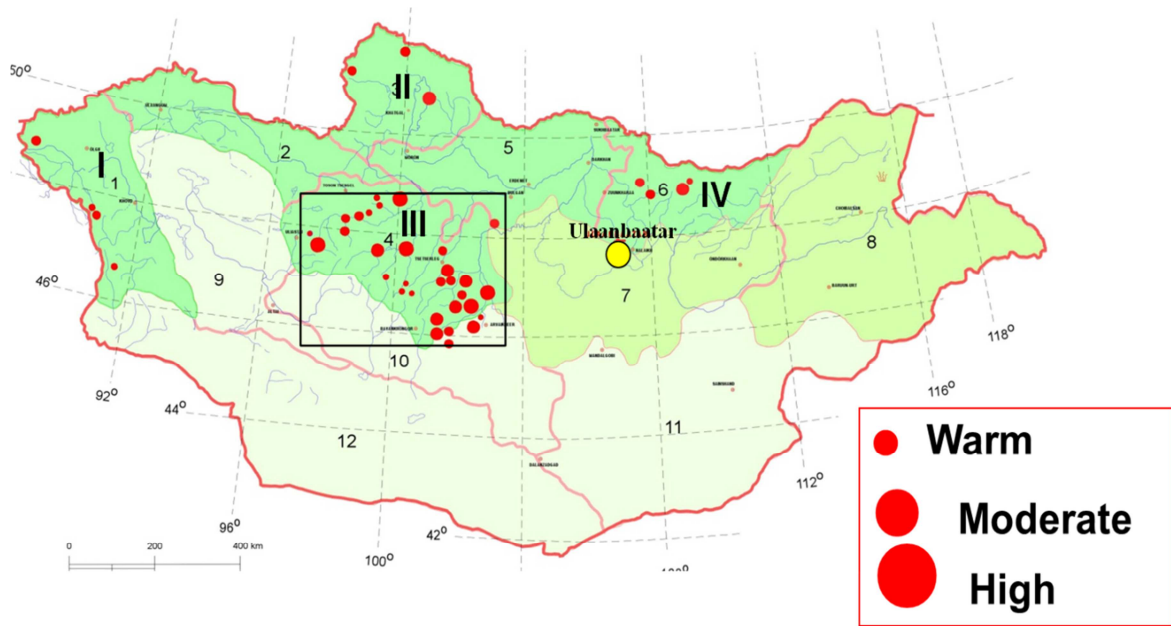
Fig.1.9. Distribution of hot springs in Mongolia (Batbayar, 2001)

I. The Mongol Altay area. It is located in the western part of the Mongolia and there are 5 hot springs which belong to sodium-bicarbonate type. The hot springs surface temperatures are varied from 29°C to 33°C.

II. The Khuvsgul lake area. It is located in the northern part of the Mongolia and there are 3 hot springs. Those hot springs are belong to sodium - sulphate, bicarbonate and sodium –bicarbonate and sulphate types according to their chemical composition. The surface temperature of these hot springs ranges from 21°C to 59°C.

III. The Khangay area. It is located in the central part of Mongolia and there are 32 hot which belong to sodium-bicarbonate and sulphate type. The most of hot springs are located in the central region of Mongolia (Khangay area). The surface temperature ranged from 30°C and 92°C.

IV. The Khentey area. It is located in the north-east part of the county and there are 4 hot springs which belong to sodium – bicarbonate type. The surface temperatures are varied from 34°C to 88°C.

1.7. Geology of the Khangai area, Mongolia

Tectonically Mongolia occupies a key position in the Central Asian Orogenic Supercollage or Altaids, and is located between the Siberian craton on the north and Katasia (Tarim and sino-Koreon cratons) to the south. The Khangai dome in west-central Mongolia is the western end of Khangai Daurian terrane of the Mongol-Okhotsk orogenic belt. The Khangai region consists of intensely deformed Carboniferous and Devonian sedimentary rocks (including carbonate rocks such as dolomite) intruded by huge bodies of late Paleozoic and early Mesozoic granites and gronadiorites. Numerous late Cenozoic, high potassium alkaline basaltic provinces are distributed throughout the Khangai area (Figure 1.10). The mantle plume beneath the region resulted in 4-5 stages of magmatic events from late Paleozoic to late Cenozoic (Holocene epoch) (Igmr-transaction, 2008).

The Khangai region has been described as "domed" (Windy & Allen, 1993; Gunningham, 2001). It is a mountainous region covering >200 000 km^2 with numerous flat-topped peaks over 3000 m (Gunningham, 2001). On the basis of the presence of titled sediments, uplift and doming began in the middle Oligocene (Devyatkin, 1975; Barsbold & Dorjnamjaa, 1993), reaching a maximum uplift of 2 km (Devyatkin, 1975). The Hangai region represents an important kinetic link between the Baikal rift province to the north and the Altai transpressional ranges to the south and west (Gunningham, 2001). Late Cenozoic uplift of the southern part of Hangai appears to be confined to an area underlain by cratonic basement, whereas the Altai region to the south and west, including the Gobi Altai, is underlain by mechanically weaker Palaeozoic arc and accretionary belts (Gunningham, 2001).

There is a number of normal NE and NW trending faults within the Khangai Mountain region (Igmr-transaction, 2008). Most of hot springs are controlled by

intersections of these types of fractures, faults and contact breccias zones between Carboniferous or Devonian sedimentary rocks and Permian-Triassic granitic rocks. The regional heat flow in the Khangai dome reaches 50-60 mW/m^2 (Khutorskoi and Yarmoluk, 1989). Of 42 hot springs with temperatures of 21-95°C in Mongolia, 32 hot springs are located in the Khangai region. The geothermal manifestations, a consequence of uplift, alkaline magmatism, high heat flow, lithospheric thinning, and neotectonic faulting are characteristic signatures of the thermal areas in the Khangai region. The Khangai region has been described as 'domed' (Windley and Allen, 1993; Cunningham, 2001). The basement of the dome consists of a Pre- cambrain block that contains tonalitic and trondhjemitic gneisses, potassic granitoids and various high grade schists and gneisses (Kepezhinskas, 1986). The geological interpretation of the isotopic data Kovalenko (1996) implies that blocks of the consolidated pre- Riphean crust were overthrust, during the accretionary-collision formation of the foldbelts, onto younger crustal complexes of sea basins between these blocks (Igmr-transaction, 2008).

In the central and southern Khangai region, batholitic bodies are widely exposed (Figure 1.10). Late Paleozoic granitoids are Carboniferous to Permian periods and early Mesozoic granitoids are Triassic to Jurassic batholites. The granitoids batholitic bodies are named the Khangai complex, the Sharus river complex and the Egiin Davaa complex in normal geological map sheets (Barsbold and Dorjnamjaa, 1993). The two main units in the study area have been ascribed to the Permian Khangai complex and the Triassic-Jurassic Egiin Davaa complex. These units are predominantly granite and granodiorites associations. The granitoids are medium enriched in aluminum, K-subalkaline and calc-alkaline series (Igmr-transaction, 2008).

Five stages of high potassium alkaline basaltic provinces are distributed throughout the Khangai region of the late Cenozoic age. Tertiary lavas occur in sequences exceeding 200 m in thickness that constitute plateaus and make up much of the high mountainous region, southeast of Chuluut Gol. Quaternary lavas are found as isolated lava fields in

topographic lows, confined by valleys carved into the pre-tertiary bedrock. Several processes have been proposed for the tectonic origin of Cenozoic volcanism in central Mongolia (also Central Asia).
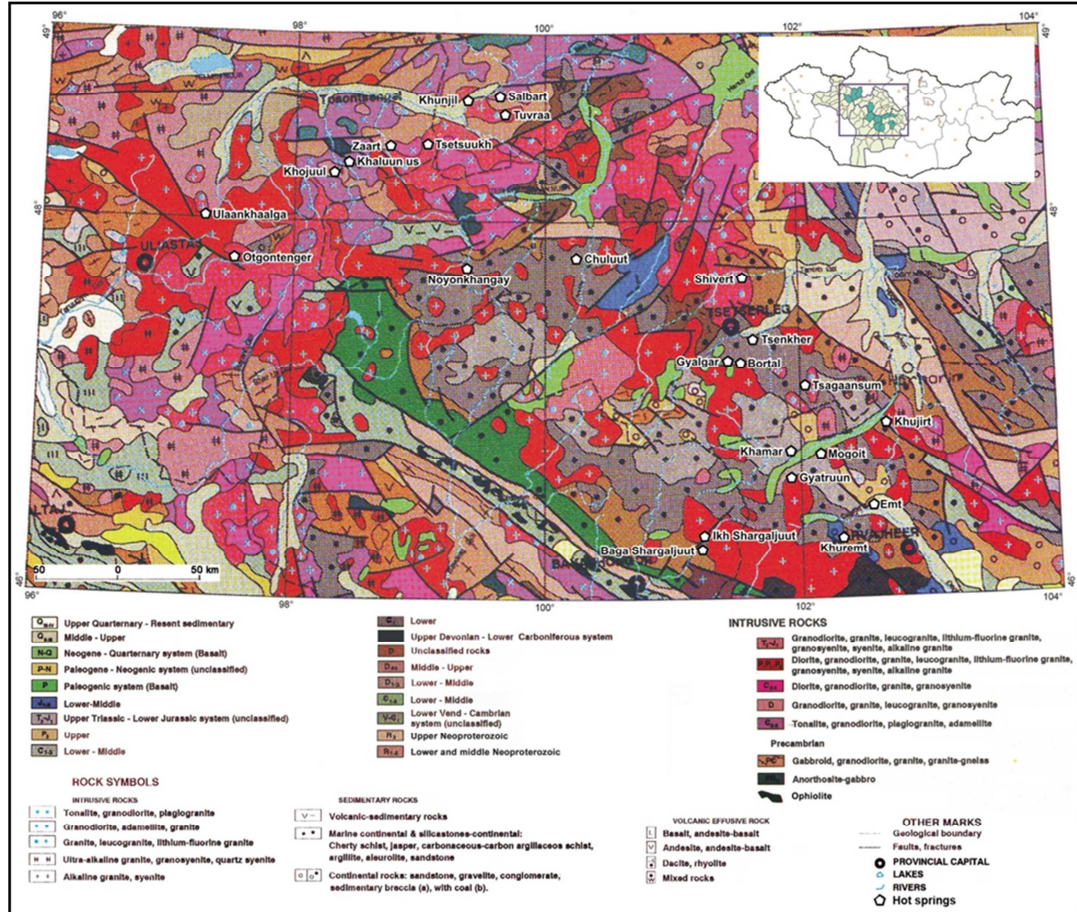
Fig.1.10. Geological map of the study area (after Barsbold and Dorjnamjaa, 1933)

The geochemical evidence such as trace elements and Sr-Nd-Pb-Hf isotope data indicates that the Mongolian basalts were generated by small degree partial melting with the garnet stability (Bary et al., 2003).

Khangai doming began in the mid Oligocene, and was contemporary with alkaline volcanism throughout the Khangai Mountains (Igmr-transaction, 2008). The young normal fault systems in the Khangai are perhaps a response to crustal uplift and doming in the range (Cunningham, 2001). In addition, the faults with the clearest evidence for Holocene activity within the Khangai region occur at relatively high elevations suggesting that these areas are extending. In contrast, the southern Khangai dome region is dominated

by Late Cenozoic normal faults that bound small half grabens (Cunningham, 2001).

Numerous small volcanic provinces are distributed throughout the Hangai area, of which the four most northerly ones are studied here: Tariat, Hanui, Togo and Orhon. The Tariat volcanic province has been the subject of several detailed studies of mantle (PreB et al, 1986; Stosch, 1986; Ionov, 1998) and crustal (Kopylova, 1995; Stosch, 1995) xenoliths. Within Mongolia, the Tariat province is exceptional for its xenolith abundance. At this locality, steeply incised river canyons cut through sequences of flat-lying lavas (up to 20 m thick); individual lavas within these sequences are commonly ~8-12 m thick. Basement rocks are exposed in the valley walls, and although their age is unknown they are inferred to be Precambrian to Carboniferous in age (Kempton, 1987).

The Khangai area in the central Mongolian part of the Central Asian orogeny stands out in the scale of Late Paleozoic graitoud magmatism, with numerous plutonic complexes in the southwestern end of Central Asia's largest Mongolia-transbaikalia igneous province of alkaline granitoids. The knowledge on the rocks is uneven and insufficient. Many intrusions lack isotope, major- and trace-element characteristics which are indispensable for correlation of the Khangai magmatism with that in the surrounding areas and for understanding its tectonic setting and related metallogeny. The Khangai Upland occupying a key geographic position in terms of geology and national economy is one such underexplored area. It is located in the hangayn Late Paleozoic basin filled with thick sequences of Devonian and Carboniferous terrigenous sediments (Orolmaa, 2008).

Diverse granotoids are key elements of the Khangai geological framework. According to their geological position and petrography, they were divided into the Late Paleozoic Tarbagatai (C_3), Shar Us Gol (P_1), Hangayn (P_2), and early Mesozoic Egiyn Davfaa (T_3-J_1) complexes. The tectonic sitting of their formation has been a point of controversy being attributed either to the Late Paleozoic orogeny (Federova, 1977; Marinov, 1973; Pavlenko, 1974) or to accretion of continental crust during closure of the Paleotethys (Kovalenko and Yarmolyuk, 1990; Kovalenko, 1996; Yarmolyuk, 2002). A later idea is that

Late Paleozoic magmatism in Central Asia, including Central Mongolia, may have been driven by a mantle hotspot (Yarmolyuk and Kovalenko, 2003).

1.8. Current geothermal usage and possibilities of using geothermal energy in Mongolia

1.8.1 Direct use of geothermal energy around the world

Geothermal utilization is commonly divided into two categories (i.e., electric production and direct application). The minimum production temperatures in a geothermal field generally required for the different types of use are shown in Figure 1.11 (Lindal, 1973). The boundaries, however, serve only as guidelines. Conventional electric power production is limited to fluid temperatures about 150°C, but considerably lower temperatures can be used with the application of binary fluids (outlet temperatures commonly at 100°C). The idial inlet temperatures into house for space heating using radiators is about 80°C; but, by using radiators of floor heating, or by applying heat pumps or auxiliary boilers, thermal waters with temperatures only a few degrees above the ambient can be used beneficially.

Geothermal energy has been produced commercially for nearly a century, and on scale of hundreds of MW for over four decades both for electricity generation and direct use. At present, there are records of geothermal utilization in 46 countries in the world (Stefansson, 1998). The electricity generated in these countries is about 44 TWh/a, and the direct use to about 37 TWh/a. Geothermal electricity generation is equally common in industrialized and developing countries, but plays more important role in the latter. The world distribution of direct utilization is different. With the exception of China, the direct utilization is serious business mainly in the industrialized, and central and eastern Europian countries. This is to some extent understandable, as most of these countries have cold winters where a significant share of the overall energy budget is related to space heating. Direct use of geothermal is very limited in Africa, Central and South America, as well as the Asian countries apart from China and Japan (Ingvar, 1998).

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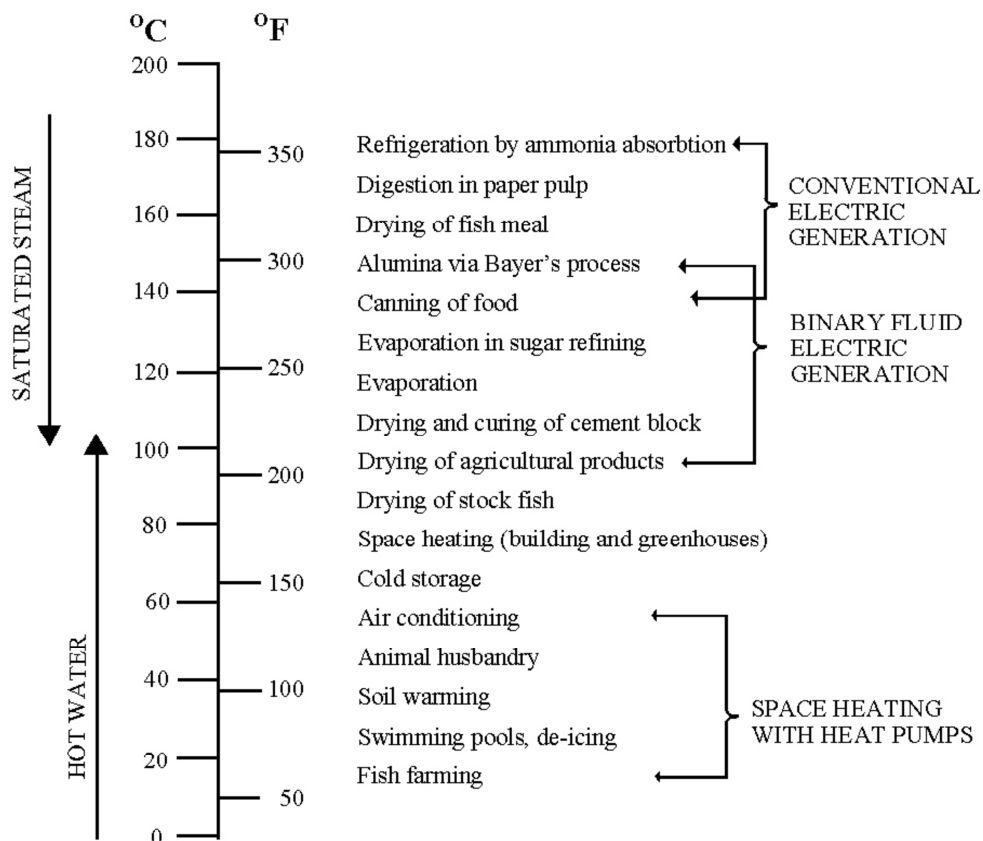
Fig.1.11. The Lindal diagram

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Lund (1996) has recently written a comprehensive summary on the various types of direct use of geothermal energy. Space heating is the dominant type (33%) of direct use in the world; but, other common types are bathing /swimming/ balneology (19%), greenhouse (14%), heat pumps for air cooling and heating (12%), fish farming (11%), and industry (10%). Table 1.4 shows the types of direct use of geothermal in the top four countries in direct utilization in the world-all of which have a well-developed tradition for direct use. Iceland is the leader in space heating. In fact, about 85% of all house in the country are heated with geothermal (Ragnarsson, 1995).

The growth rate of geothermal development has in the past been significantly affected by the prices of the competing fuels, especially oil and natural gas, on the world market (Fridleifsson, 1994). As long as the oil and gas prices stay at the present low levels, it is rather unlikely that we will see again the very high annual growth rates for geothermal electricity of 17% as was the case during oil crises of 1978-1985. The growth rate is, however, quite high due to the fact that geothermal energy is one of the cleanest energy sources available on the market. The type of conversion used depends on the state of the fluid (whether steam or water) and its temperature. There are three geothermal power plant technologies being used to convert hydrothermal fluids to electricity. The conversion technologies are dry steam, flash, and binary cycle (Fridleifsson, 1998). Björnsson, et al. (1998) maintains that if the development of hydro and geothermal energy is vigorously

pursued, these resources could fulfill a very important bridging function during the next few decades until clean fuels technology and that of other renewables have matured enough to provide a meaningful share of the world energy supply.

Table 1.4. Types of direct use in the World and the top four countries

	World	Japan	Iceland	China	USA
Space heating	33	21	77	17	10
Heat pumps (heating/cooling)	12	0	0	0	59
Bathing /Swimming/ balneology	19	73	4	21	11
Greenhouse	14	2	4	7	5
Fish farming	11	2	3	46	10
Industry	10	0	10	9	4
Snow melting	1	2	2	0	1
	100	100	100	100	100

In most countries, a significant percentage of the energy usage is at temperatures of 50-100°C, which are common in low-enthalpy geothermal areas. Most of this energy is supplied by the burning of oil, coal or gas at much higher temperatures with the associated release of sulphur, carbon dioxide and other greenhouse gases. The scope for using geothermal resources alone as well as in combination with other local sources of energy is, therefore, very large. The application of the ground-source heat pump opens a new dimension in the scope for using the earth's heat, as heat pumps can be used basically everywhere and are not as site-specific as conventional geothermal resources. Geothermal energy, with its proven technology and abundant resources, can make a very significant contribution towards reducing the emission of greenhouse worldwide (Fridleifsson, 1998).

1.8.2 Current geothermal usage in Mongolia

Mongolia has a centuries-long tradition of using geothermal water from natural springs for medical purposes. Obviously, the contribution of those facilities to the overall geothermal energy utilization is small (PREGA, Mongolia, 2005). There are also public recreational centers where geothermal water is used for sanitary with open-air swimming pools and to heat small greenhouse using of storage hot water during the summer season

(Figure 1.12). Only Khujirt and Shivert spa resorts are working during 4 seasons for bathing. In the Jargaljuut village of Bayankhongor aimag house heating is by using geothermal hot spring (T=95°C, Q=251/s) since 1960. It is one of the best examples of geothermal energy use for heating in Mongolia (Batbayar, 2001). Ample and comprehensive studies on geothermal resources and their potential uses have not been carried out in Mongolia. Some general and studies on regional geology, tectonics, geophysics, geology, hydro-geology, study of hot springs and chemical analysis carried out.
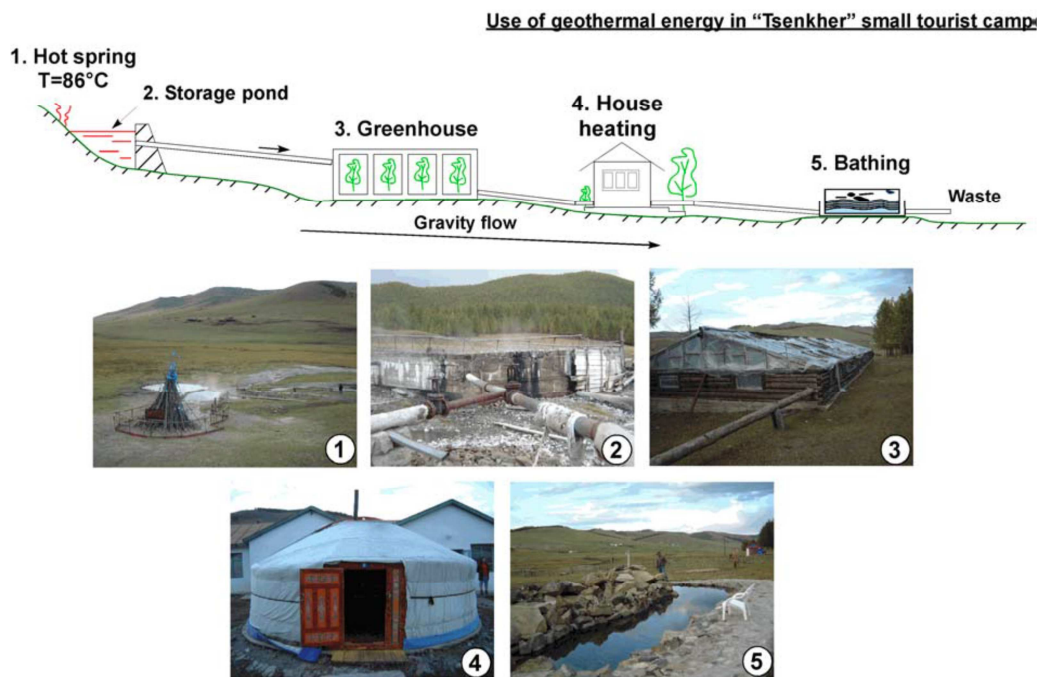
Fig.1.12. Examples of geothermal hot spring use in Mongolia from the Tsenkher geothermal field (Batbayar, 2001)

1.8.3 Possibility of using geothermal energy in Mongolia and requirements

The Mongolian Khangai area is rich in geothermal resources. New technology opens possibilities for more extensive use geothermal energy in Mongolia. Total hydrothermal resources and the utilization reserves of the springs in the Orkhon-taats take 62% of the Khangai Range Resources. Based on the reports of the geological, geophysical and geochemical surveys and exploration, contacted in the Khangai Range, it is estimated the geothermal resources in the depth of 500-5000 m on each hot spring area. The geothermal energy (depth) resources of the systems Ider-Tarvagatai, Central Khangai and

Orkhon-Taats are 817 Gcal/h, 1729 Gcal/h, respectively. Total resources of the Khangai Range is 2746 Gcal/h can be used in the economy.

In Mongolian rural areas, small users such as a Soum center (small town), "Bag" center (smallest town), rest houses, and tourist camps are located far from each other. All of them are did not connected with general electric grid lines and heating connection (Batbayar, 2001). Summarizing the results of the geological studies in Mongolia, we have considered that the Khangai Range is a promising area for geothermal direct energy utilization. From the above, we are concentrating on the Orkhon-Taats systems, which is located three province centers (Tsetserleg of Arkhangai province, Arvaikheer of Uvurkhangai province, Bayankhongor of Bayankhongor province). The Tsenkher field is near to the Tsetserleg town, the Taragt field – to the Arvaikheer of Uvurkhangai province, the Taragt field – to the Arvaikheer and the Shargalzuut area – to the Bayankhongor town. The numbers of population and families, living in the province centers, are comparatively higher than other relevant nearest settlements and there are therefore reasonable heat demands in these centers.

The heating systems are currently operating in the province centers around the Khangai area are very inefficient and not sustainably and reliably supply present and future demands. They are using coal that has to be transported long distances by truck, and their combustion are not controlled. The government of Mongolia introduced to the public drafts of Renewable Energy and Energy Conservation Law. These laws will create an environmental to develop the energy efficient and renewable technology in the wide scale in Mongolia. The National Action Plan for Renewable Energy (June 2005), adopted by the IKH KHURAL (the parliament), has the objective to build favorable investment and financial environment for renewable energy development. In 1999, The Ministry of Food and Agriculture of Mongolia has planned to develop "Geotherm" sub-program within the "Mineral Resource" Program. The investigating and research works are started in the Institute of Geology. Recently a "Sanatorium Development National Program 2003-2010"

was asserted by the 251st resolution of Mongolian government on 13 December 2002. The future developments of geothermal use will based on the total exploitation of the existing geothermal wells in the first phase, and complete geothermal field development by means of newly drilled wells as the next step (PREGA, Mongolia, 2005).

1.8.4 Future possibility of geothermal development in Mongolia

The Promotion of renewable Energy, Energy Efficiently and Greenhouse Gas Abatement (PREGA, Mongolia, 2005) had done "Hydrothermal heat supply of province center" project in Mongolia (Figure 1.13). By this project they were done pre-feasibility study on the geothermal district heating system in province center around the Khangai Range of Mongolia. In the level of the province center in the Mongolia, the geothermal district heating is more applicable compare to the individual geothermal heat pumps. It is advisable in all geothermal direct use systems to isolate the geothermal fluid from the building heating system it serves. Though the Ca and Mg contents in the fluid in the hot springs of the Khagai Range are comparatively small, this strategy greatly reduces the extent of geothermal fluid chemistry induced corrosion and scaling in the user's system. It is considered that the district heating indirect systems, which are economically reasonable against direct heating system, are more suitable in the Mongolian rural towns. By this report (PREGA, Mongolia, 2005) they consider the providing the space heating and domestic hot water to the customers and asumed that the domestic hot water will be isolated from the district water with a heat exchanger.

The units of a geothermal district heating system are geothermal water production, re-injection, heat exchanger, plant, transmission and distribution piping systems and pumps (Figure 1.13). The optional equipment is peaking capacity, which can be used the coal fired heat only boilers. The temperature of the heat exchanger plant will be used 85-90°C and in turn, the temperatures in two ends of the customers loop will be 80-85°C and 35-40°C. The result showed that the future developments of geothermal use will be based on the total exploitation of the existing geothermal wells in the first phase, and complete geothermal

field development by means of newly drilled wells as the next step. The development of geothermal applications in the economy of Mongolia greatly depends on the economic interest to be shown by private entities and government supports. Because the initial investments in geothermal heating are higher than for conventional heating systems, simulative measures by the Government would be welcome. Nearly all (99%) of commercial electricity and heat is produced in Mongolia from coal. By decreasing or offsetting the amount of energy have proven needed for space and water heating, the province economies will save the coal resources. GTESs are safe and clean because there are no combustion flames, no flues, and no odors; just safe, reliable operation year after year (PREGA, Mongolia, 2005).
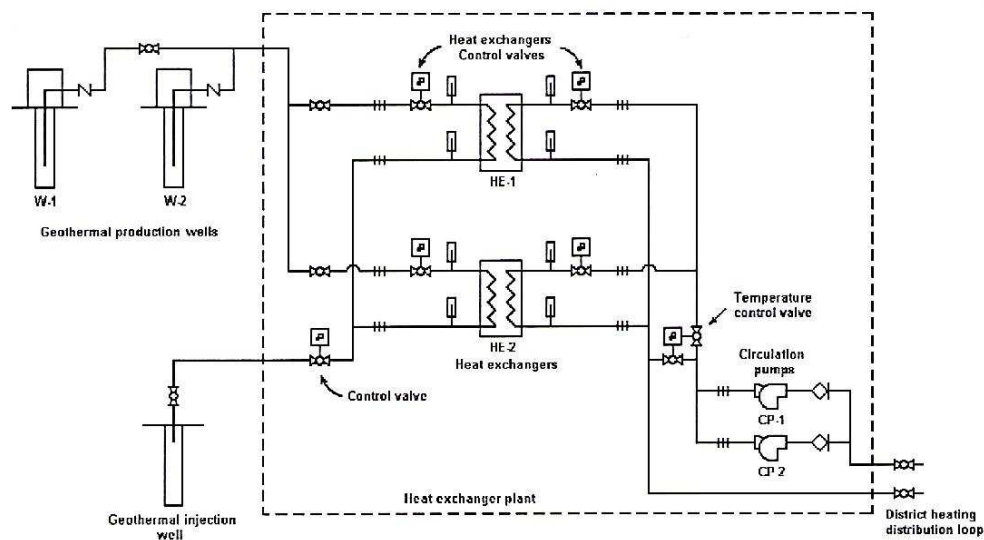
Fig.1.13. Indirect geothermal district heating system in the province center

In this report they were conclude that the direct use of geothermal energy is more acceptable in the first cases toward the successful mastering on the geothermal utilization in the areas with low temperature hydrothermal resources in Mongolia. The Khangai Range is more benefit promissing area on the geothermal energy utilization. The indirect district heating system with a central heat exchanger plant is more attractive on the heat supply of the rural towns in Mongolia. It is more efficient against to the schemes with distributed customer heat exchanger system.

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Chapter 2

Isotopic and chemical studies of hot and cold springs in western part of Khangai mountain region, Mongolia, for geothermal exploration

2.1. Introduction

Knowledge of the origin of geothermal waters is important in geothermal studies it helps to discriminate the chemical properties of the thermal waters and the source of their recharge. Studies of stable isotopes play an important role in hydrogeological investigations of both thermal and non-thermal waters because the isotopes carry a record of fluid origin and processes. There are 42 hot springs in Mongolia (Pisarskii et al., 2003) but geothermal utilization is not widely developed. Today, the hot springs are used for bathing, health resorts (balneology) and a small amount of greenhouses and building heating. Currently Mongolia has no geothermal power generation and there are few rivers suitable for hydroelectric power generation. In the western part of Khangai mountain region, hydro-geothermal resources is one of the most promising energy prospects (surface temperature of the hot spring is up to 95°C) (Badminov et al., 2011).

The aim of this study is to geochemically examine the quality and fluid sources of hot springs in the western part of the Khangai mountain region and their potential use for space heating and greenhouse cultivation. In the western part of Khangai mountain region, geothermal fields occur in three provinces (Zavkhan, Bayankhongor and Uvurkhangai). In 1977, 1978 and 2005 fifteen hot water samples were collected and analyzed at the Institute of Chemistry and Chemical Technology (Oyuntsetseg, 2009) and 29 hot and cold water samples were collected in July and August 2012 (Fig.2). The elevation of the hot and cold water sources in the study area ranges from 1643 to 2472 m above sea level. The hot springs are characterized by the high pH, low total dissolved solids, very low magnesium concentration and sodium as the dominant cation. With respect to the high pH of these

waters, bicarbonate and sulfate are the dominant anion.

2.2. Sample collection and analytical procedures

Twenty-nine water samples (15 hot spring waters, 4 cold spring waters and 10 river waters) were collected in July-August, 2012 from the Khangai area in Mongolia (Figure 2.1 and Table 2.1). At the sampling site, water temperature, pH and EC were measured by a digital thermometer, a pH meter (Shindengen, KS-701) and an EC meter (Horiba, B-173), respectively.
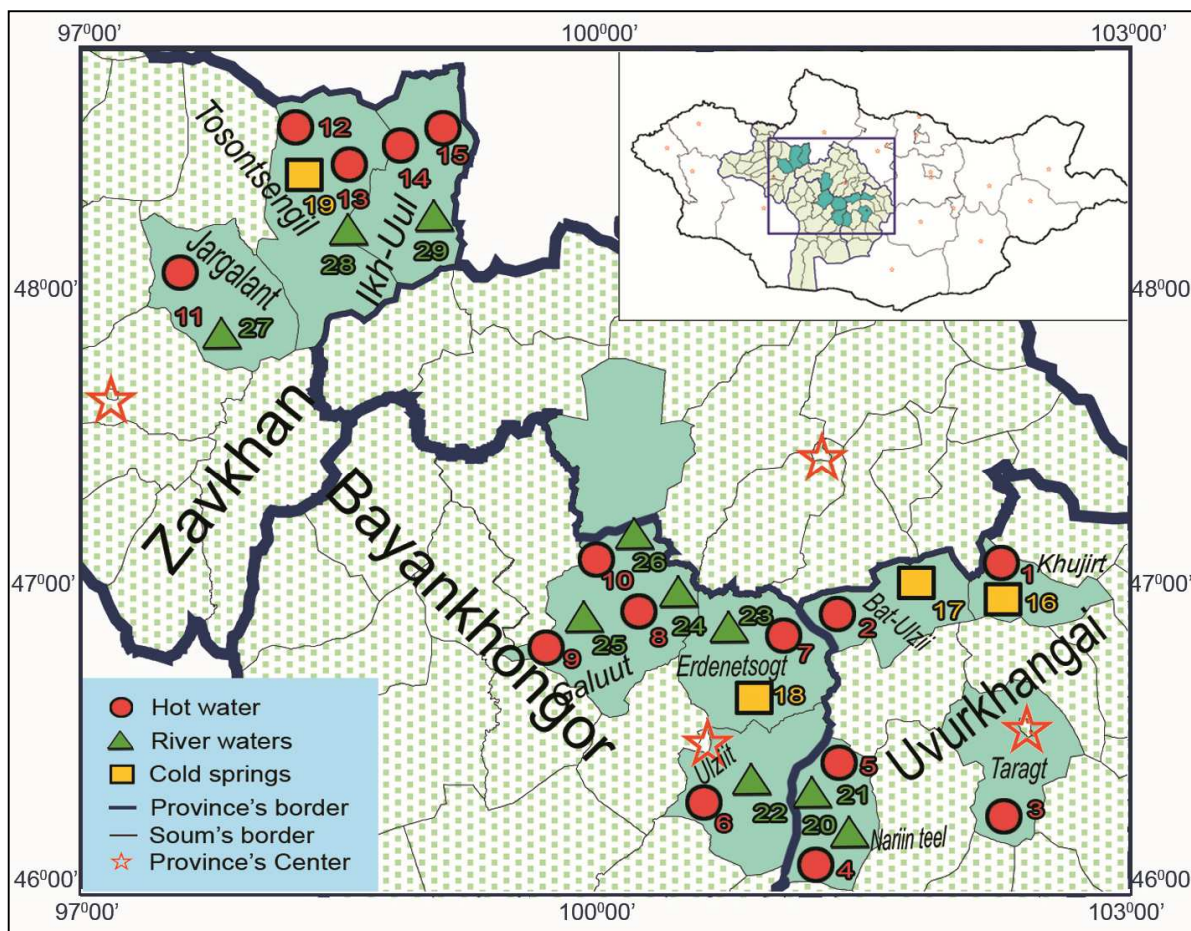
Fig.2.1. Location of sampling points in the western part of Khangai area. Numbers in the sample locality correspont to those in tables 1-4.

Water samples were collected into two plastic bottles (100 ml and 250 ml volume for isotope and chemical analysis, respectively). Water samples were filtered through a 0.45 μm filter and collected into polyethylene bottles for subsequent chemical analyses in the laboratory.

Dissolved ion concentrations were determined at the Geochemical Laboratory,

University of Toyama. The major anions Cl and SO_4 in filtered water samples were analyzed for with anion chromatograph (761 Compact IC, Metrohm) using an IonPac As22 column.

Table 2.1. Sample locality in the western part of Khangai area.

№	Sample type	Locality	Sampling date	Latitude	Longitude	Altitude (m)	Temperature (^{0}C)	pH	EC (mS/m)
1	Hot springs	Khujirt	7/22/2012	$46^0$54'02	$102^0$46'02	1643	41	9.2	39
		Khujirt	2005	$46^0$54'02	$102^0$46'02	1643	55	8.7	
2		Mogoit	7/22/2012	$46^0$44'46	$102^0$13'56	1862	74	8.9	37
		Mogoit	1977	$46^0$44'46	$102^0$13'56	1862	72	8.6	
3		Khuremt	7/24/2012	$46^0$16'19	$102^0$28'19	1945	54	9.1	40
		Khuremt	2005	$46^0$16'19	$102^0$28'19	1945	56	8.7	
4		Khaluun turuu	7/24/2012	$45^0$53'30	$101^0$40'24	1970	23	8.7	43
		Khaluun turuu	1979				30	8.5	
5		Taats	7/25/2012	$46^0$07'38	$101^0$36'18	1959	55	9	45
		Taats	1977				55	8.8	
6		Baga shargaljuut	7/25/2012	$46^0$13'57	$101^0$09'10	2049	57	8.8	39
		Baga shargaljuut	2005	$46^0$13'57	$101^0$09'10	2049	59	8.7	
7		Ikh shargaljuut	7/25/2012	$46^0$19'55	$101^0$13'32	2132	95	8.7	38
		Ikh shargaljuut	2007	$46^0$19'55	$101^0$13'32	2132	92	8.8	
8		Ukheg	7/26/2012	$46^0$47'55	$100^0$25'51	2374	58	9	51
		Ukheg	1977				57	8.9	
9		Teel	7/27/2012	$46^0$51'38	$100^0$06'57	2094	32	9.2	29
		Teel	1977				32	9.7	
10		Urguut	7/27/2012	$47^0$01'54	$100^0$06'13	2472	42	8.4	44
		Urguut	1977				42	8.6	
11		Ulaanhaalga	7/30/2012	$47^0$56'09	$097^0$16'26	2265	46	8.7	78
		Ulaanhaalga	1977				37	8.5	
12		Khojuul	7/31/2012	$48^0$19'49	$98^0$18'20	2263	44	9.8	29
		Khojuul	1978				45	9.5	
13		Khaluun us	7/31/2012	$48^0$14'51	$98^0$22'42	2200	34	8.7	51
		Khaluun us	1978				35	9.1	
14		Zart	7/31/2012	$48^0$20'02	$98^0$47'08	2059	45	8.8	40
		Zart	2005	$48^0$20'02	$98^0$47'08	2059	44	8.9	
15		Tsetsuukh	8/1/2012	$48^0$23'51	$99^0$02'36	2024	34	9.2	48
		Tsetsuukh	2005	$48^0$23'51"	$99^0$02'36"	2024	36	9.2	
16	Cold springs	Khujirt	7/22/2012	$46^0$52'48	$102^0$47'08	1662	4	6.7	31
17		Mogoit	7/23/2012	$46^0$44'56	$102^0$13'42	1838	6	6.4	11
18		Ikham	7/25/2012	$46^0$19'58	$101^0$13'37	2136	14	7.5	41
19		Khojuuliin ehnii bulag	7/30/2012	$48^0$11'58"	$98^0$18'20"	2258	8	8	41
20	River waters	Khuren tolgoi	7/24/2012	$45^0$53'45	$101^0$40'31	1968	13	7.9	31
21		Taats	7/25/2012	$46^0$07'16	$101^0$36'09	1957	12	7.9	31
22		Nariin gol	7/25/2012	$46^0$13'47	$101^0$09'16	2045	15	7.3	17
23		Shargaljuut gol	7/25/2012	$46^0$20'01	$101^0$13'33	2133	19	7.3	12
24		Ukheg	7/26/2012	$46^0$48'03	$100^0$25'48	2373	16	7.5	10
25		Tsagaan turuu	7/27/2012	$46^0$51'40	$100^0$07'00	2092	12	7.2	5.4
26		Urguut	7/27/2012	$47^0$02'12	$100^0$06'08	2471	10	7.3	11
27		Ulaanhaalga	7/30/2012	$47^0$49'04	$097^0$16'35	2263	14	7.3	7.6
28		Baruun hojuul	7/31/2012	$48^0$15'01	$98^0$22'16	2198	12	7.1	12
29		Khaluun us	8/1/2012	$48^0$19'55"	$98^0$47'17"	2049	17	7.1	7

Alkalinity was determined using a standard titration with HCl. Cations were analyzed

with the ion chromatograph (761 Compact IC, Metrohm) using a Dionex DX-320J. Dissolved silica was determined by a molybdenum yellow method using a spectrophotometer (UV-VIS Recording Spectrophotometer, Shimadzu). The charge balances of the results obtained were within ±5% and the analytical uncertainties for dissolved ion concentrations were also within 5%.

Samples were prepared for the mass spectrometry determination of $\delta^{18}O$ by the CO_2 equilibration method (Epstein and Mayeda, 1953) and that of δD by using the Zn reduction method (Coleman et al., 1982), and the determinations carried out in a mass spectrometer (VG Micromass Ltd., Optima) at the Analytical Center, Mitsubishi Materials Techno Corporation in Japan and reported relative to V-SMOW with an analytical precision of 0.1‰ and 1‰, respectively.

2.3. Results and discussion

2.3.1. Isotopic compositions

The results of isotope analysis of water samples are summarized in Table 2.2 and Figure 2.2. The δD and $\delta^{18}O$ values for hot spring samples vary from -87 to -126‰ and -12 to -17‰, respectively. The δD and $\delta^{18}O$ values of cold springs and river water samples vary from -78 to -127‰ and -11 to -17‰ respectively and are similar to those for hot spring water samples. Almost all hot and cold waters are plotted along the global meteoric water line (solid line in Fig. 3a; $\delta D = 8\delta^{18}O + 10$; Craig, 1961). Two river waters (sample numbers 22, Taats and 27, Urguut) plot far from this line. This may be due to evaporation because the water flow rates are lower than other rivers. There is no evidence of isotope shift in $\delta^{18}O$ values of hot springs from the meteoric water line (Figure 2.2a). This means that all water samples derived from meteoric water with minimal isotope exchange with reservoir rock.
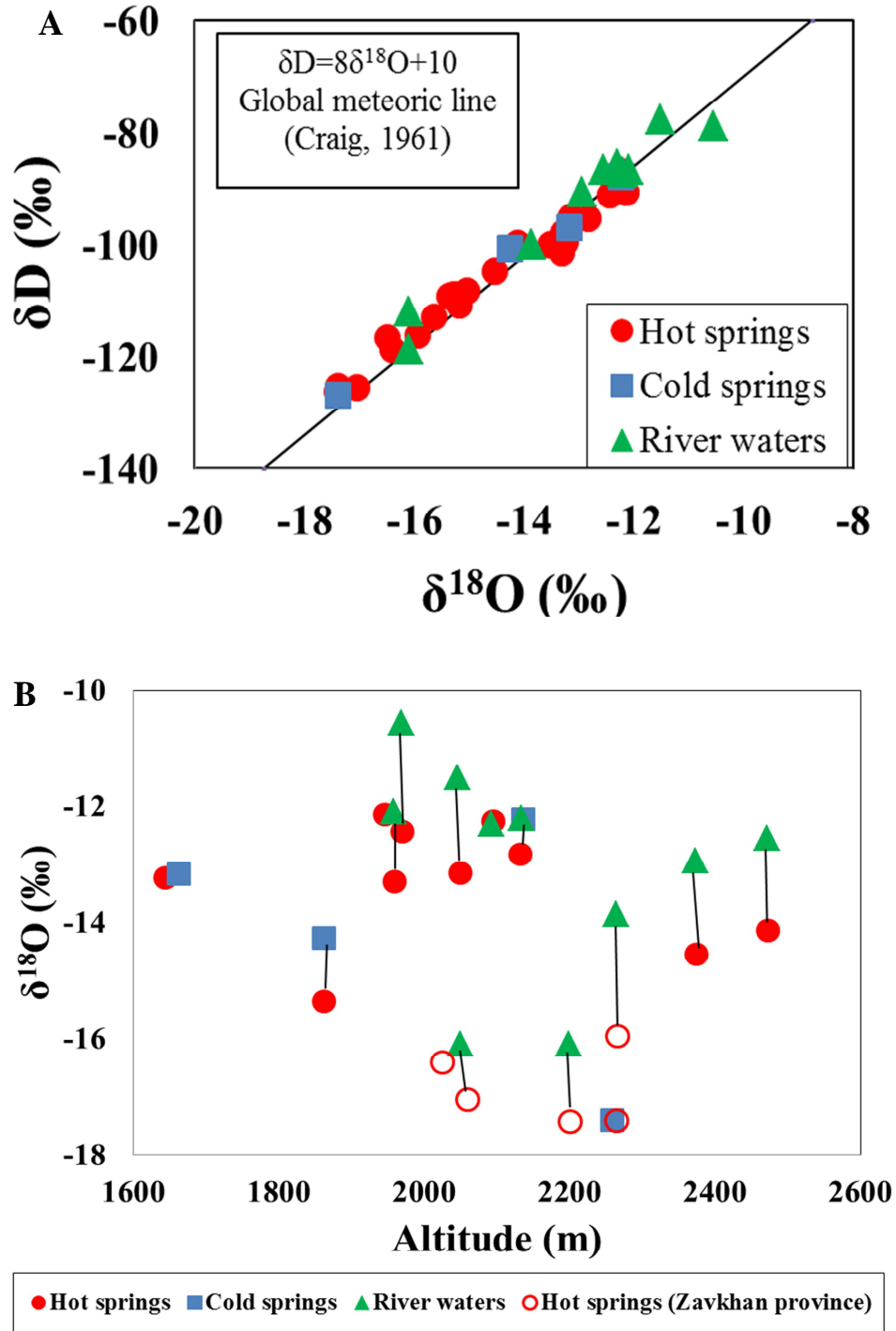
Fig. 2.2. δD vs δ^{18}O of water samples in the western part of Khangai area. (a) δD vs δ^{18}O and (b) Altitude vs δ^{18}O. The solid line in this figure shows the local meteoric water line (δD=8 δ^{18}O+10). Tie lines in (b) shows water samples from the same areas

Fig. 2.2b shows the δ^{18}O values for water samples plotted against the altitude of the sampling points. Lawrence and White (1991) reported the effects of altitude on isotope ratios between 500 and 2000 m in δD and δ^{18}O to be -1.5 ~ -5.0‰/100 m and -0.2 ~

-0.6 ‰/100 m, respectively. In the study area, there is no strong correlation among the δD and δ^{18}O values and altitude. It is noted that the hot springs located in the Zavkhan region in the study area (northern part of Mongolia) have more negative δD and δ^{18}O values than those of the other area. In contrast, cold springs and river waters in the northern part have almost the same δD and δ^{18}O values for water samples in the southern part and are independent of the altitude of the sample locality. Figure 2.2b also shows the relationship of the δ^{18}O values of water samples in the same sample locality. It is noted that the δ^{18}O values for hot spring waters are 1-4‰ lower than those for river waters. This is also shown in 8 hot and cold water samples collected in December 2008 in the Arkhangay province in the Khangay area (Dolgorjav, 2009), where the δD and δ^{18}O values are -108 to -102‰ and -14.3 to -13.5‰ for hot springs and -102 to -95‰ and -13.5 to -12.6‰ for cold water and river waters, respectively. In the Xining basin and the surrounding area, northeastern Tibetan Plateau, China (ca. 1000 km south of the present study area and 1622 to 4300 m in altitude), Tan et al. (2012) reported the δD and δ^{18}O values of geothermal waters (up to 92 °C) to be -87 to -55‰ and -12.1 to -7.7‰ which are almost the same to those of river water in the Xining basin. They concluded that the geothermal waters originate in the local meteoric waters. In general, river waters are a mixture of meteoric waters originating from different elevation and groundwater. Therefore, the δD and δ^{18}O values can be taken as those for the average composition of precipitation in the study area. In the present study, there is a large variability in the δD and δ^{18}O values between hot springs and river waters (Figure 2.2b). The depletion in D and ^{18}O in the hot spring waters may be due to a different source associated with precipitation falling at higher altitude than in the study area.

2.3.2. Chemical compositions

The chemical composition of 29 water samples is shown in Table 2.2 and Figures. 2.3-2.5. In the study area, the water temperature of hot spring water ranges from 23 to 95°C and the pH values range from 8.4 to 9.8, indicating alkaline characteristics. The total

dissolved solids (TDS) are between 228 and 529 mg/L. In contrast, the water temperatures

of cold spring and river waters are ranging from 4 to 19°C and the pH values range from

6.4 to 7.5. Their total dissolved solids (TDS) concentration is between 50 and 375 mg/L

higher than that of the hot springs.

Table 2.2. Chemical composition of hot and cold springs and river waters in the western part of Khangai area.

№	Sample type	Locality	Sampling date	Na mg/L	K	Ca	Mg	Cl	SO_4	HCO_3	NO_3	SiO_2	$\delta^{18}O$ ‰	δD
1	Hot springs	Khujirt	7/22/2012	96	2.6	6.8	0.2	22	33	121	4.8	91	-13	-100
		Khujirt	2005	98	3.9	1.6	0.1	7.2	32	120	-	104	-	-
2		Mogoit	7/22/2012	87	1.7	6.4	0.2	2.7	29	128	0.4	84	-15	-109
		Mogoit	1977	92	2.9	1.3	0.1	1.9	28	95	-	104	-	-
3		Khuremt	7/24/2012	92	1.4	2.9	0.2	8.6	41	125	0.2	75	-12	-91
		Khuremt	2005	93	2.2	1.3	0.1	8.5	43	135	-	98	-	-
4		Khaluun turuu	7/24/2012	99	2.5	13	0.2	18	27	148	0.2	60	-12	-91
		Khaluun turuu	1979	117	3.6	4.6	0.6	20	27	206	-	77	-	-
5		Taats	7/25/2012	97	1.4	4.6	0.1	24	54	97	0.2	68	-13	-98
		Taats	1977	103	2.8	2.6	0.07	21	60	92	-	91	-	-
6		Baga shargaljuut	7/25/2012	103	2.1	5.4	0.2	13	56	97	0.2	62	-13	-95
		Baga shargaljuut	2005	91	2.8	2.8	0.03	6.2	59	66	-	83	-	-
7		Ikh shargaljuut	7/25/2012	85	1.9	8.4	0.2	5.6	55	98	0.2	83	-13	-95
		Ikh shargaljuut	2007	86	3.5	2.2	0.1	3.1	59	97	-	109	-	-
8		Ukheg	7/26/2012	112	2.9	8	0.1	5.9	124	85	0.2	71	-15	-105
		Ukheg	1977	112	5.4	3.6	0.3	2.2	124	78	-	78		
9		Teel	7/27/2012	61	0.8	11	0.3	4.8	20	87	0.2	36	-12	-87
		Teel	1977	65	0.6	3.6	0.3	4.4	23	67	-	46	-	-
10		Urguut	7/27/2012	105	1.5	7.1	0.2	13	39	164	1.0	61	-14	-100
		Urguut	1977	112	2.7	2.9	0.1	9	42	167	-	78	-	-
11		Ulaanhaalga	7/30/2012	150	3.7	17	0.5	15	214	97	0.2	73	-16	-116
		Ulaanhaalga	1977	148	5.5	8.2	0.8	16	205	70	-	75	-	-
12		Khojuul	7/31/2012	65	2.2	5.8	0.2	3.3	34	110	1.2	90	-17	-125
		Khojuul	1978	60	3.1	1.4	0.06	8.7	33	115	-	102	-	-
13		Khaluun us	7/31/2012	107	2	12	0.2	11	158	137	1.2	57	-17	-126
		Khaluun us	1978	91	3	7.4	0.6	4.7	31	174	-	72	-	-
14		Zart	7/31/2012	78	1.2	13	0.3	3.1	103	71	0.2	52	-17	-125
		Zart	2005	81	1.9	6.2	0.2	4.2	103	80	-	60	-	-
15		Tsetsuukh	8/1/2012	107	2.5	5.2	0.2	9.3	115	95	0.2	75	-16	-119
		Tsetsuukh	2005	98	3.2	3.4	0.4	6.2	112	80	-	108	-	-
16	Cold spring	Khujirt	7/22/2012	12	0.7	56	8.4	13	13	181	4.3	15	-13	-97
17		Mogoit	7/22/2012	8.6	1.1	10	1.6	0.9	5.4	50	2.2	16	-14	-101
18		lkham	7/25/2012	51	1.2	47	5.4	9.2	38	171	8.7	44	-12	-88
19		Khojuuliin ehnii bulag	7/31/2012	3.7	1	20	5.5	0.6	6.2	74	2.9	16	-17	-127
20	River water	Khuren tolgoi	7/24/2012	26	2	46	8.3	19	22	142	1.4	3.3	-11	-79
21		Taats	7/25/2012	10	2	62	8.1	6.3	23	155	3.2	13	-12	-87
22		Nariingol	7/25/2012	5.4	1.3	25	5	2.5	7	85	1.9	9.3	-12	-78
23		Shargaljuut gol	7/25/2012	3.6	1.3	18	3.4	1.7	5.9	57	1.7	8.9	-12	-87
24		Ukheg	7/26/2012	2.7	0.5	18	1.9	1.1	4.1	85	0.7	8.3	-13	-91
25		Tsagaan turuu	7/27/2012	3.6	0.9	16	2.4	1.1	4.3	49	2	6.9	-12	-86
26		Urguut	7/27/2012	2.1	0.5	8.2	1.8	0.6	2.6	24	1.7	8.1	-13	-87
27		Ulaanhaalga	7/30/2012	2.6	0.9	12	1.9	0.6	4.2	33	0.9	9.9	-14	-100
28		Baruun hojuul	7/28/2012	2.4	0.5	19	3.2	0.7	11	48	2.1	12	-16	-119
29		Khaluun us	8/1/2012	2.6	0.5	9.7	1.3	0.5	7.2	27	1.5	9.8	-16	-112

The sodium concentration is up to 108 mg/L and other cation concentrations such as those

of K^+, Ca^{2+} and Mg^{2+} are very low (below the detection limit of ICP in the case of Mg^{2+}).

The highest silica concentrations are found in the hot springs, reaching values as high as 91

mg/L. Total alkalinity values (HCO_3^-) is the dominant anion (up to 164 mg/L) and chloride concentrations are always below 33 mg/L (Table 2.2).

In comparison with the previously obtained chemical composition of water samples collected in 1977, 1978 (Ariyadagva et al., 1980) and 2005 (Ganchimeg et al., 2007) at the same localities, the Na^+, K^+ and SiO_2 concentrations of hot springs in this study were slightly lower and Ca^{2+} concentrations are higher than the previous ones (Figure 2.4). Although there are several possibilities to explain the observed differences in previous and present data due to the change of chemical compositions in the hot springs, the analytical uncertainty and so on, we could not conclude the reason, so far.
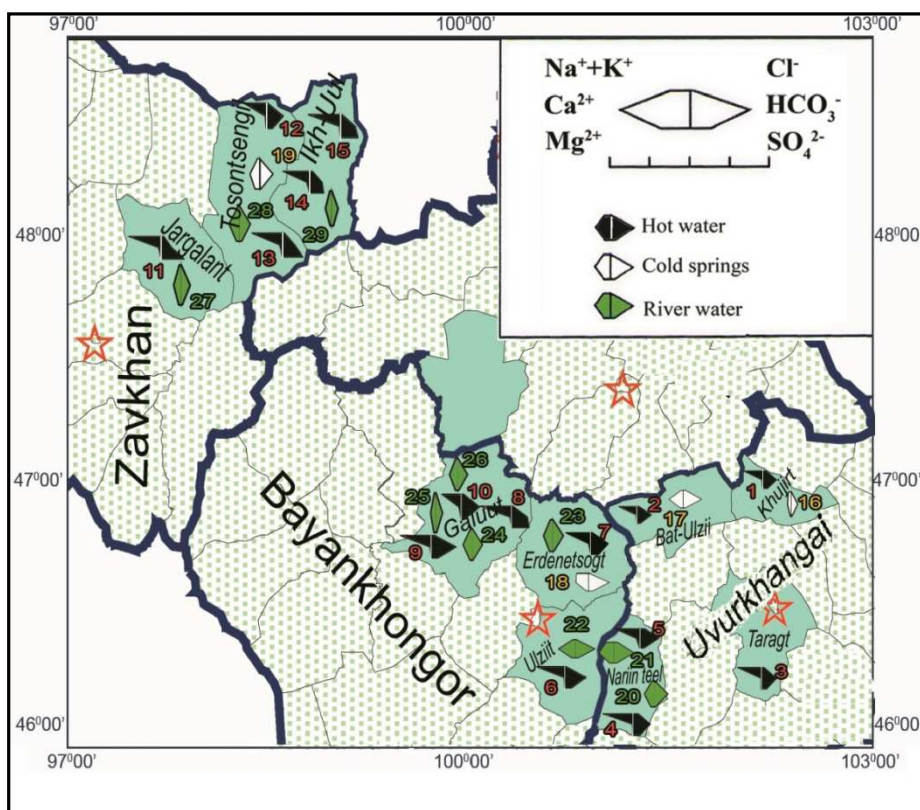
Fig.2.3. Spatial distribution of the geochemical characteristics of water samples in the western part of Khangai area. Numbers in the sample locality correspond to those in Tables 2.1-2.4.

The spatial distribution of the geochemical characteristics and a Piper diagram for the water samples in the study area are shown in Figs. 2.3 and 2.4, respectively. The chemical composition of the hot springs in the study area is characterized by two types. Most of the hot springs located in the southern part in the study area (sample Nos. 1-10;

Bayankhongor and Uvurkhangay provinces) are of the Na^+-HCO_3^- type except for one hot

spring (Na^+-SO_4^{2-} type; sample No. 8) (Fig. 2.3). The hot springs in the northern part

(Zavkhan province) are of the Na^+-SO_4^{2-} type. In this province, one hot spring water

(sample No. 12) is of the Na^+-HCO_3^- type (Figure 2.4). All river waters are of the

Ca^{2+}-HCO_3^- type. The cold spring and river waters are of the Ca^{2+}-HCO_3^- type except for

sample No. 19 ($Na+$-HCO_3^- type).
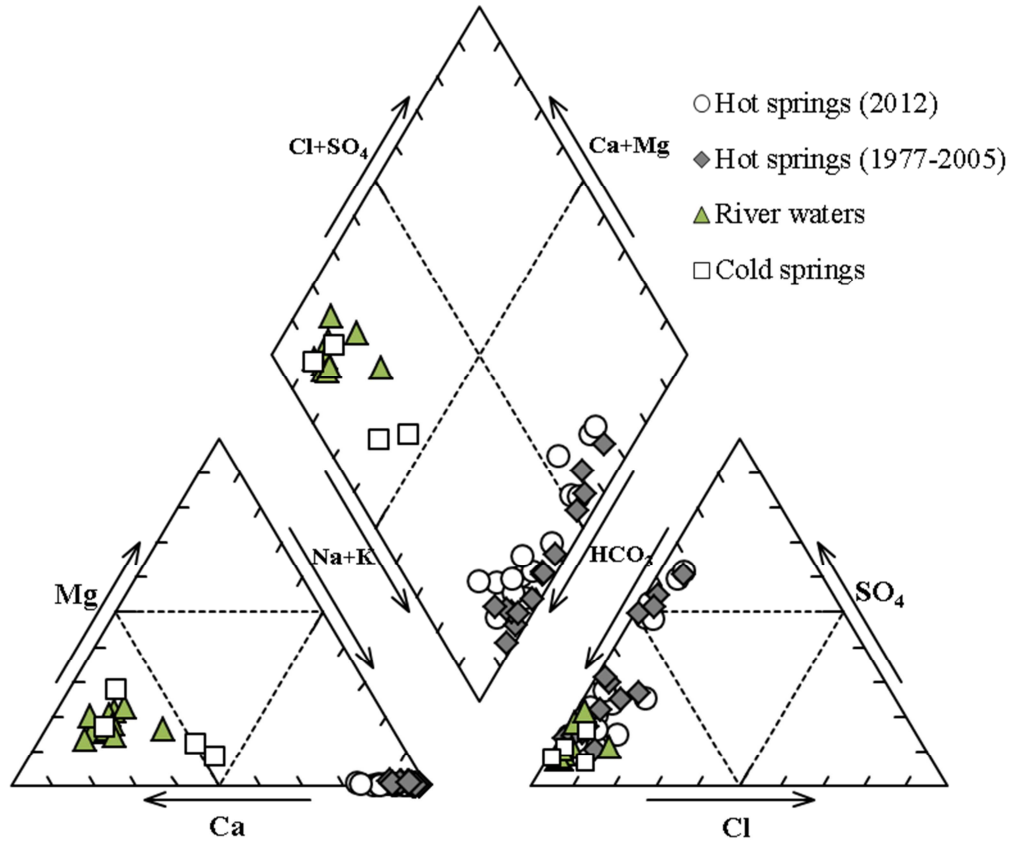
Fig.2.4. Piper diagram for water samples in the western part of Khangai area.

The HCO_3^-, Ca^{2+} and Mg^{2+} are likely to originate in the weathering of dolomite and

their constituent Ca^{2+}-Mg^{2+} silicates (chiefly calcite, plagioclase, gypsum and feldspar).

The relationship between $Ca^{2+} + Mg^{2+}$ and $HCO3^-$ concentrations is shown in Figure 2.5b,

where the broken line corresponds to the ion exchange of $Ca^{2+} + Mg^{2+}$ with $Na^+ + K^+$

following the reaction with clay minerals after dolomite dissolution. This result implies

that the cold springs are enriched in Ca^{2+}, Mg^{2+} and HCO_3^- due to dissolution of carbonate

rocks (such as dolomite), whereas all hot springs plot below the broken line in Figure 2.5a.

Sodium and potassium concentrations in hot spring waters in the study area are greater than

those in cold springs (Figure 2.5b). Figure 2.5c shows the relation between $Na^+ + K^+$ and $Ca^{2+} + Mg^{2+}$-HCO_3^-. A possible explanation for the observed result is that the hot springs are enriched in Na^+ and K^+ and depleted in Ca^{2+} and Mg^{2+} because of ion exchange with clay minerals in the soil resulting a higher pH than that of the cold spring.
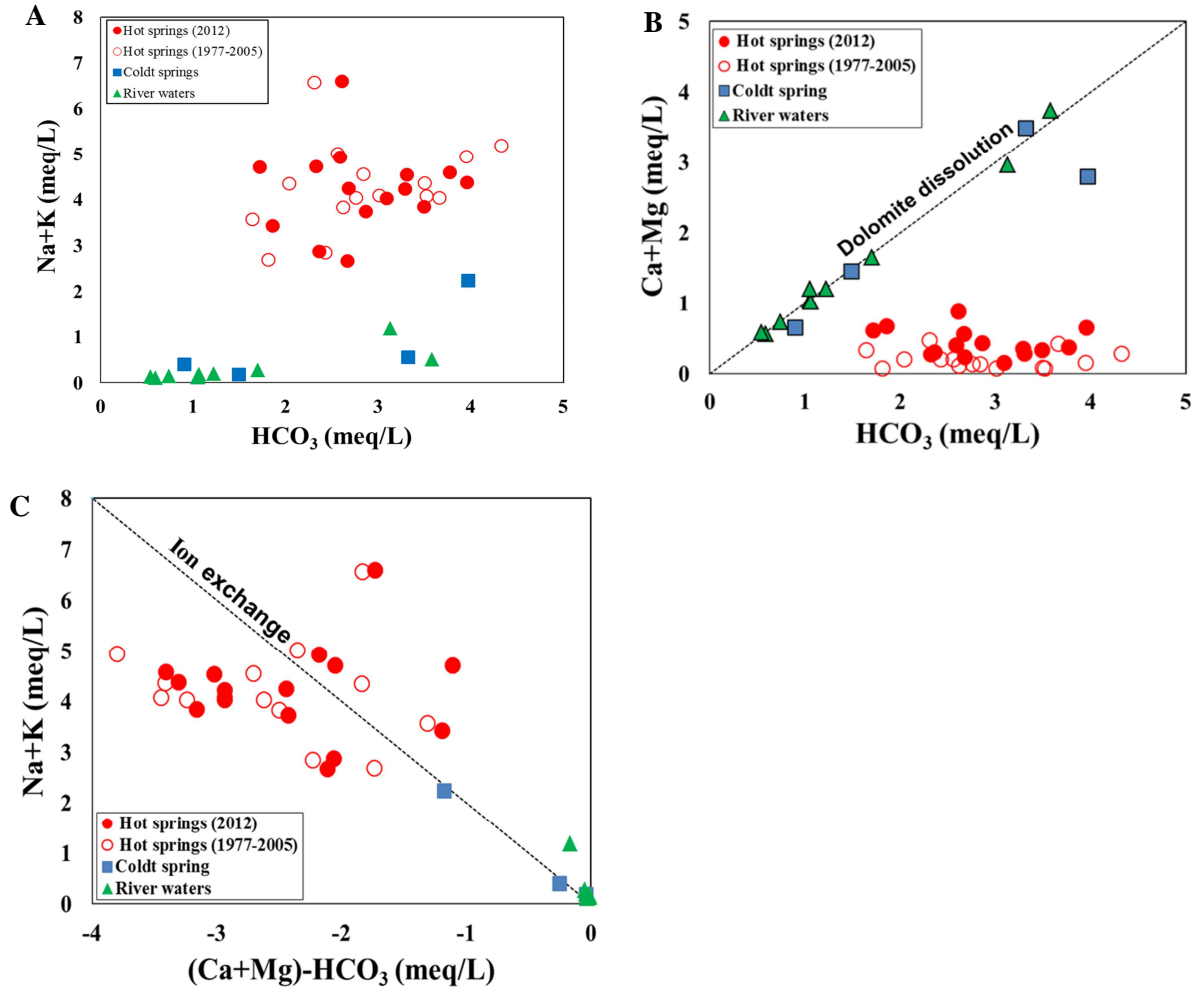
Fig.2.5. Relationships between Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO3⁻. (a) Na^++ K^+ and HCO_3 concentration, (b) Ca^{2+}+ Mg^{2+} vs HCO_3, and (c) Na^++ K^+ vs (Ca^{2+}, Mg^{2+}) - HCO_3^- for water samples in study area. The broken line (b) means dolomite dissolution. The broken line in (c) shows the ion exchange of Ca^{2+}+ Mg^{2+} with Na^++ K^+ by the reaction with clay minerals after dolomite dissolution.

2.3.3. Geothermometry

Several different chemical geothermometers were applied to chemical analyses of hot waters collected in this study, with results summarized in Table 2.3. As stated above, the temperatures obtained by applying the geothermometers based on silica concentrations may be reliable and appropriate in these geothermal systems considering the variations in silica speciation with pH and temperature. However, since their use relies completely on

the concentrations of just one element, the existence of any processes that could have modified its reservoir water concentrations must first be ruled out.

Table 2.3 Underground temperature estimated from application of solute geothermometry

№	Locality	Sampling date	T_{means} (oC)	$T_{chal\,(1)}$ (oC)	$T_{chal\,(2)}$ (oC)	$T_{Qtz\,(3)}$ (oC)	$T_{Na-K\,(4)}$ (oC)	$T_{Na-K\,(5)}$ (oC)	$T_{Na-K-Ca\,(6)}$ (oC)
1	Khujirt	7/22/2012	116	104	103	132	91	146	119
		2005	132	113	111	139	117	168	146
2	Mogoit	7/22/2012	105	100	99	127	71	128	104
		1977	126	113	111	139	102	156	137
3	Khuremt	7/24/2012	97	94	94	122	57	115	100
		2005	117	109	108	136	84	140	125
4	Khaluun turuu	7/24/2012	102	81	82	110	87	142	112
		1979	116	95	95	123	99	153	130
5	Taats	7/25/2012	93	88	88	116	56	114	97
		1977	117	105	104	132	91	146	126
6	Baga shargaljuut	7/25/2012	99	83	84	112	74	130	109
		2005	118	99	99	127	99	153	129
7	Ikh shargaljuut	7/25/2012	108	99	99	127	80	135	108
		2007	134	116	114	142	119	170	143
8	Ukheg	7/26/2012	109	90	90	119	90	144	119
		1977	130	96	95	124	131	181	151
9	Teel	7/27/2012	73	56	59	87	49	107	82
		1977	72	68	69	98	32	91	77
10	Urguut	7/27/2012	90	82	82	111	55	113	94
		1977	110	96	95	124	84	140	122
11	Ulaanhaalga	7/30/2012	108	92	92	121	86	141	115
		1977	120	93	93	122	112	164	137
12	Khojuul	7/31/2012	121	104	103	132	106	159	124
		1978	110	52	54	83	136	185	152
13	Khaluun us	7/31/2012	94	78	79	108	70	126	102
		1978	115	91	91	120	104	157	126
14	Zart	7/31/2012	86	74	75	104	57	115	89
		2005	101	81	82	111	83	138	111
15	Tsetsuukh	8/1/2012	108	94	93	122	83	138	116
		2005	127	115	113	142	104	157	132

T_{means}: Averaged values of calculated temperatures

(1),(3): Fournier (1977), (2),(4):Arnórsson et al. (1983), (5): Giggenbach (1988), (6): Fournier and Truesdell (1973)

Re-equilibrium processes affecting quartz or chalcedony do not easily occur in this type of low-temperature geothermal systems mainly due to kinetic reasons (Rimstidt and Barnes, 1980; Michard et al., 1986; Michard, 1990). However, as seen above, some of the waters studied are mixtures of thermal and cold waters, which cause considerable dilution to their silica concentrations (Table 2.2). Therefore, in the case of the geothermometers based on the SiO_2^- quartz and SiO_2-chalcedony equilibria, results obtained for the thermal waters (Table 2.3) will be considered to determine the minimum reservoir temperature.

Two chalcedony geothermometers according to those of Fournier (1977) and Arnorsson et al. (1983) give the reservoir temperature in the range 56-104°C and 59-103°C, respectively, for all hot springs in the study area. The calculated temperatures using the previous data are in the range 52-116°C (Fournier, 1977) and 54-114°C (Arnorsson et al., 1983). This difference is within the uncertainty of the geothermometer (±20°C) (e.g. Fournier, 1991). These results show that the temperature of the reservoir for each hot spring varies from 50°C to a maximum of ca. 110°C in the study area.

The quartz geothermometer (Fournier, 1977) gives the reservoir temperature in the range 87-132°C and the calculated temperatures for the previous data are in the range 83-142°C. The temperatures obtained by the SiO_2-quartz geothermometers are 26-31°C higher than those calculated for equilibrium with chalcedony for the hot springs in the study area. The chalcedony temperatures are the lowest. These differences gradually become smaller as the silica content in the water increases.

Temperatures are calculated for the hot springs based on the Na-K data and using two different calibrates (Table 2.3). The Na-K geothermometers of Arnorsson et al. (1983) and Giggenbach (1988) give the reservoir temperature in the range 49-106°C and 107-159°C, respectively. The previous database shows a range of 32-136°C (Arnorsson et al., 1983) and 91-185°C (Giggenbach, 1988). It is obvious that the Na-K geothermometer by Giggenbach (1988) yields relatively high values for all samples compared to the calibration of Arnorsson et al. (1983). The temperatures calculated (Table 2.3) using the Na-K-Ca geothermometer (β= 4/3) are similar, in the range 89-119°C (Fournier and Truesdell, 1973). The temperatures calculated for the previous data are in the range 77-152°C. These the case of all hot springs, with an anomalous Na/K ratio and a higher calculated temperature, could be the result of additional chemical reactions after mixing, including possible cation exchange reactions (e.g. Fournier, 1977; D'Amore et al., 1987; Druschel and Rosenberg, 2001). These inconsistent results with the geothermometers may be related to secondary processes (e.g.

temperature-dependent clay or aluminosilicate re-equilibration reactions) affecting dissolved calcium during the rising of the thermal waters (Giggenbach, 1988; Druschel and Rosenberg, 2001).

The average temperatures calculated from chemical geothermometers are in the range 73-134°C, indicating low temperature geothermal resources in the study area, suggesting that these resources can be used for room heating and production of electricity by a binary system.

2.3.4. *Saturation index for scale components*

It is crucial to know and take measures against probable problems such as corrosion and scaling in the pipes and pumps used in the production of water from hot springs. To find out whether to expect the precipitation of scaling materials such as calcite and silica, the saturation states of chemical components in the hot springs were examined in this study. The saturation index (SI) of a given mineral is defined in Eq. (1) as:

S.I . (Saturation Index) = Log (Q/K)   (1)

where Q and K are activity and solubility products of minerals such as calcite, $(Ca^{2+})(CO_3^{2-})$, respectively. The chemical code used for the calculation in this study is PHREEQC (Parkhurst and Appelo, 1999). An index (SI) smaller than zero indicates that the water is undersaturated with respect to a particular mineral. Such a value could reflect the character of water from a formation with insufficient amount of the mineral or solution or short residence time. An index (SI), greater than zero, specifies that the water is oversaturated with respect to the particular mineral phase and therefore incapable of dissolving more of the mineral. Nonetheless, oversaturation can also be produced by other factors that include incongruent dissolution, common ion effect and evaporation, rapid increase in temperature and CO_2 exsolution (Langmuir, 1997).

The saturation indices of anhydrite, aragonite, calcite, chalcedony, dolomite and quartz were calculated for the water samples in the study area and the results are shown in Table 2.4. All the samples of hot and cold water evaluated are undersaturated with respect

to anhydrite. The hot waters sampled in this study are oversaturated with respect to aragonite, calcite, chalcedony, dolomite and quartz, whereas the saturation index for water samples analyzed previously are calculated in this study and are found to be saturated or oversaturated with respect to calcite (Table 2.4 and Figure 2.6).

The saturation indices for water samples are plotted against pH as shown in Figure 2.6. The saturation indices for calcite and dolomite increase with increasing pH and above pH 7.9 the hot springs are saturated with respect to these minerals.

Table 2.4 Saturation indices for minerals in water samples.

№	Locality	Sampling date	pH	T_{means} (oC)	Anhydride	Argonite	Calcite	Calcedony	Dolomite	Quartz
1	Khujirt	7/22/2012	9.2	116	-2.09	0.94	1.09	-0.56	2.24	-0.35
	Khujirt	2005	8.7	132	-2.7	0.48	0.62	-0.38	1.79	-0.18
2	Mogoit	7/22/2012	8.9	105	-2.44	1.07	1.22	-0.31	2.62	-0.1
	Mogoit	1977	8.6	126	-2.81	0.24	0.39	-0.29	1.36	-0.09
3	Khuremt	7/24/2012	9.1	96	-2.58	0.88	1.03	-0.35	2.36	-0.14
	Khuremt	2005	8.7	117	-2.87	0.29	0.44	-0.28	1.47	-0.07
4	Khaluun turuu	7/24/2012	8.7	102	-2.27	1.27	1.41	-0.35	2.75	-0.13
	Khaluun turuu	1979	8.5	116	-2.56	0.82	0.97	-0.31	2.83	-0.1
5	Taats	7/25/2012	9.0	93	-2.4	0.84	0.99	-0.31	1.86	-0.09
	Taats	1977	8.8	117	-2.4	0.54	0.69	-0.35	1.44	-0.14
6	Baga shargaljuut	7/25/2012	8.8	98	-2.13	0.9	1.05	-0.32	2.11	-0.11
	Baga shargaljuut	2005	8.7	118	-2.26	0.44	0.59	-0.36	0.76	-0.15
7	Ikh shargaljuut	7/25/2012	8.7	108	-1.92	1.01	1.15	-0.26	2.23	-0.05
	Ikh shargaljuut	2007	8.8	134	-2.29	0.62	0.76	-0.42	1.81	-0.22
8	Ukheg	7/26/2012	9.0	108	-1.67	1.13	1.28	-0.76	2.07	-0.55
	Ukheg	1977	8.9	130	-1.85	0.76	0.91	-0.59	2.2	-0.39
9	Teel	7/27/2012	9.2	73	-2.73	1.19	1.33	-0.4	2.72	-0.17
	Teel	1977	9.7	72	-3.35	0.68	0.83	-0.58	2.33	-0.34
10	Urguut	7/27/2012	8.4	89	-2.35	0.84	0.98	-0.14	1.95	-0.08
	Urguut	1977	8.6	110	-2.65	0.6	2.74	-0.28	1.75	-0.07
11	Ulaanhaalga	7/30/2012	8.7	108	-1.09	1.25	1.4	-0.33	2.52	-0.12
	Ulaanhaalga	1977	8.5	120	-1.36	0.78	0.92	-0.36	2.14	-0.15
12	Khojuul	7/31/2012	9.8	121	-2.7	1.34	1.49	-1.1	3.45	-0.89
	Khojuul	1978	9.5	110	-3.42	0.5	0.65	-0.65	1.91	-0.44
13	Khaluun us	7/31/2012	8.7	94	-1.73	1.12	1.26	-0.29	2.22	-0.07
	Khaluun us	1978	9.1	115	-2.34	1.1	1.25	-0.59	3.21	-0.38
14	Zart	7/31/2012	8.8	86	-1.65	0.96	1.1	-0.27	1.96	-0.04
	Zart	2005	8.9	101	-1.9	0.54	0.69	-0.41	1.36	-0.2
15	Tsetsuukh	8/1/2012	9.2	107	-2.41	1.08	1.22	-0.55	2.71	-0.33
	Tsetsuukh	2005	9.2	127	-2.1	0.84	0.99	-0.6	2.68	-0.4

T_{means}: **Averaged values of calculated temperatures**

Hot springs in the present study are particularly oversaturated with respires to calcite due to their high Ca^{2+} and HCO_3^- concentrations. The cold waters and low pH values (<7.9) are clearly undersaturated with respect to these minerals. These results

imply that groundwater essentially derived from river waters infiltrating into underground and enriched in Ca^{2+} and HCO_3^- due to dissolution of carbonate minerals such as calcite and dolomite which are commonly observed in the study area. The hydrolysis and dissolution reactions of limestone and dolomite to form dissolved bicarbonate, calcium and magnesium ions can be described as follows; (e.g., Appelo and Postma, 2005):

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^- \qquad (2)$$

$$CaMg(CO_3)_2 + 2H_2O = Ca^{2+} + Mg^{2+} + 2HCO_3^- + 2OH^- \qquad (3)$$

$$CO_2 + H_2O = HCO_3^- + H^+ \qquad (4)$$
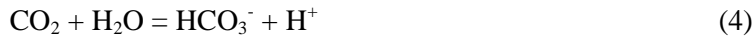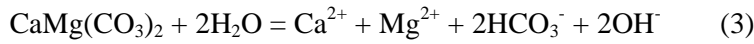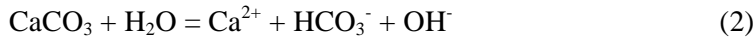
Under the system of CO_2 addition from air and/or decomposition of organic matter, the equations are;

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^- \qquad (5)$$

$$CaMg(CO_3)_2 + H_2O + CO_2 = Ca^{2+} + Mg^{2+} + 2HCO_3^- \qquad (6)$$
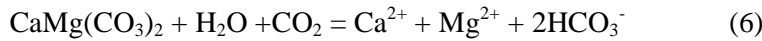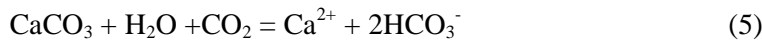
The hot spring waters are characterized by a high pH and HCO_3^- concentration compared to those of the cold spring waters as demonstrated by field measurements.
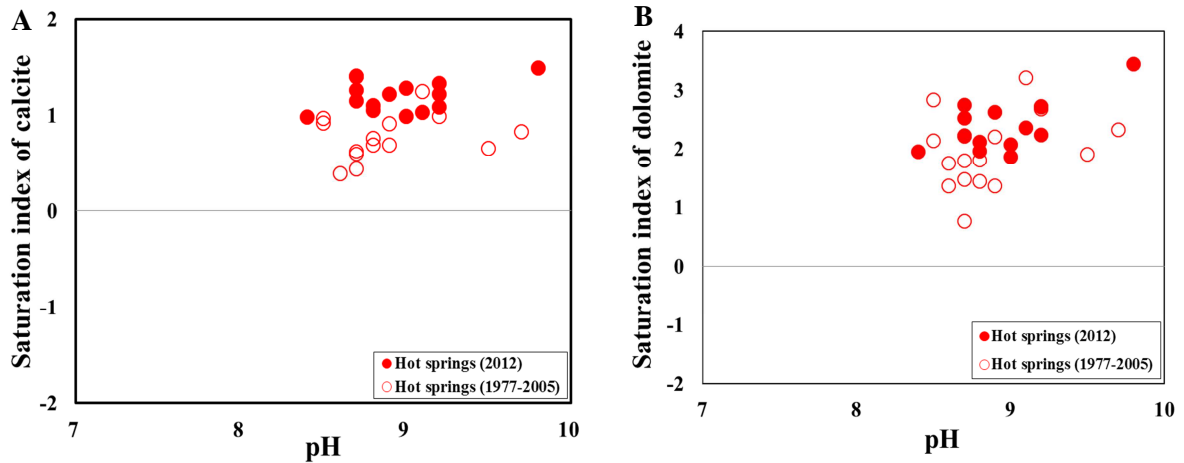
Fig.2.6. Saturation indexes of calcite (a) and dolomite (b) of water samples in the study area.

2.3.5. Characteristics of hot springs and the geothermal resources in the study area

The characteristics of hot springs in the study area are summarized; (1) the δD and δ^{18}O values for water samples indicate that the hot and cold springs are of meteoric origin without isotope exchange with rock, (2) the hot springs were of the

Na^+-HCO_3^- and Na^+-SO_4^{2-} type whereas all river waters were characterized as the Ca^{2+}-HCO_3^- type, (3) the ion concentrations of hot springs were higher than those in the cold springs and river waters, and (4) the underground temperatures in each reservoir for hot springs vary from 75 to 140°C, indicating a low temperature resource.

The average temperatures calculated from several geothermometers are in the range 75-140°C confirming that the geothermal resources in the study area are low temperature. Thus these resources can produce electricity by a binary system and the spent hot water can be applied to space heating and other uses.

2.4. Conclusions

Hot springs, cold springs and river waters in the western part of the Khangai Mountain region of Central Mongolia were examined for their stable isotope composition and chemical characteristics. The hot and cold spring waters in the Zavkhan province and at high altitude have more negative δD and $δ^{18}O$ values than those of other provinces. There is no evident $δ^{18}O$ shift which means that the geothermal water is meteoric water in which little water-rock isotope exchange has taken place. The hot spring waters are of the Na^+-HCO_3^- and Na^+-SO_4^{2-} types, although all ion concentrations in the hot spring waters were higher than those in the cold spring and river waters. River waters are characterized as of the Ca^{2+}- HCO_3^- water type. The cold springs are enriched in Ca^{2+}, Mg^{2+} and HCO_3^- due to dissolution of carbonate rocks such as dolomite. The hot springs are enriched in Na^+ and K^+ and depleted in Ca^{2+} by ion exchange with underlying clay minerals and become more alkaline (higher pH) than the cold springs. The calculated equilibrium temperature is in the range 75-140°C, indicating that the geothermal springs should be classified as low temperature springs.

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Chapter 3

Chemical and isotopic characterization of hot and cold spring waters in northeastern part of Khangai area

3.1. Introduction

Chemical and isotopic geochemistry plays an important role in researching origins of hot spring fluids and temperature of geothermal reservoir. Studies of stable isotopes play an important role in hydrogeological investigations of both thermal and non-thermal waters because the isotopes carry of fluid origin and processes (Bergfeld et al., 2001). Mongolia is rich in mineral waters and geothermal resources with a various properties including their applicability for health and energy source purposes. The first systematical study of mineral waters of Mongolia was performed by Smirnov et al. during 1926-1927. Further more detailed investigation on the formation mineral water, their distribution and chemical composition were studied by Marinov, Namnandorj etc. In 1973 and 1966 were published monographs on mineral water resources of Mongolia. Mongolia and Soviet Union's joint hydrochemical "Khubsgul" research group was performed research on complex study of hydromineral resources of Mongolia during 1976-1980. The aim of the research was to determine physic-chemical, gas and microbiological properties of the mineral resources (Pinnecer, 1980). In the results of many years of studies were established that Mongolia has about 250 hot and cold mineral waters. Based on all previous researches were created "The map of Mineral springs of Mongolia" in 2003 (Pisarskii., 2003). At present, the thermal wasters are being used for balneological and space heating purposes in Mongolia.

Mongolia has 42 hot springs and mainly distributed in Khangai, Khentii, around the Khuvsgul Lake and the Mongol Altai plate forms and temperature ranges from 21-to 95°C. The 32 hot springs are located in the Khangai area. In the Khangai mountain area, geothermal field occur in five provinces (Zavkhan, Bayankhongor, Uvurkhangai, Arkhangai and Bulgan).

The north-eastern part of Khangai area, geothermal fields occur in two provinces (Arkhangai and Bulgan). The elevation of the hot and cold waters sources in the study area ranges from 1424 to 2285 m above sea level. Detailed investigation on the thermal waters in the north-eastern part of Khangai area has not been carried out earlier to establish the reservoir temperatures. This is important to plan deep exploratory program to assess the power generating capacity of the Khangai geothermal area. Towards this aim, detailed geochemical and isotopic investigations of these springs have been carried out in order to understand their geochemical evolution and also estimate the reservoir temperatures through chemical geothermometry to apply them for future geothermal exploration and heat resources in Mongolia.

Previous studies have determined only chemical composition in hot springs of north-eastern part of Khangai area (Ariyadagva, 1980; Ganchimeg, 2007) and did not carry isotopic study. At the present study first time we have determined isotopic characterization such as a He, Ne, ^{13}C, ^{34}S, ^{18}O and D. To identify changes of main chemical composition of hot spring waters within different times we were compared present studies results with the previous studies 9 hot spring waters results.

3.2. Geology of study area

The Mongolian territory is located on the Central Asian folding belt, bordering with the Siberian platform to the north, and the Northern Chinese and Tarim platforms to the South. Geological setting is complex, with many lithological and structural styles, relating to plate collisions of Proterozoic to Permian age. Fold systems are formed at different times, mostly in the Paleozoic period. Also older Pre-Cambrian and younger Mesozoic movements formed fold zones, but these do not play such an important role in the geological setting (Marinov, et al., 1970).

The Khangai region has been described as "domed" (Windy & Allen, 1993; Gunningham, 2001). It is a mountainous region covering >200 000 km2 with numerous flat-topped peaks over 3000 m (Gunningham, 2001). On the basis of the presence of titled

sediments, uplift and doming began in the middle Oligocene (Devyatkin, 1975; Barsbold&Dorjnamjaa, 1993), reaching a maximum uplift of 2 km (Devyatkin, 1975). The Khangai region represents an important kinetic link between the Baikal rift zone to the north and the Altai transpressional ranges to the south and west (Gunningham, 2001).
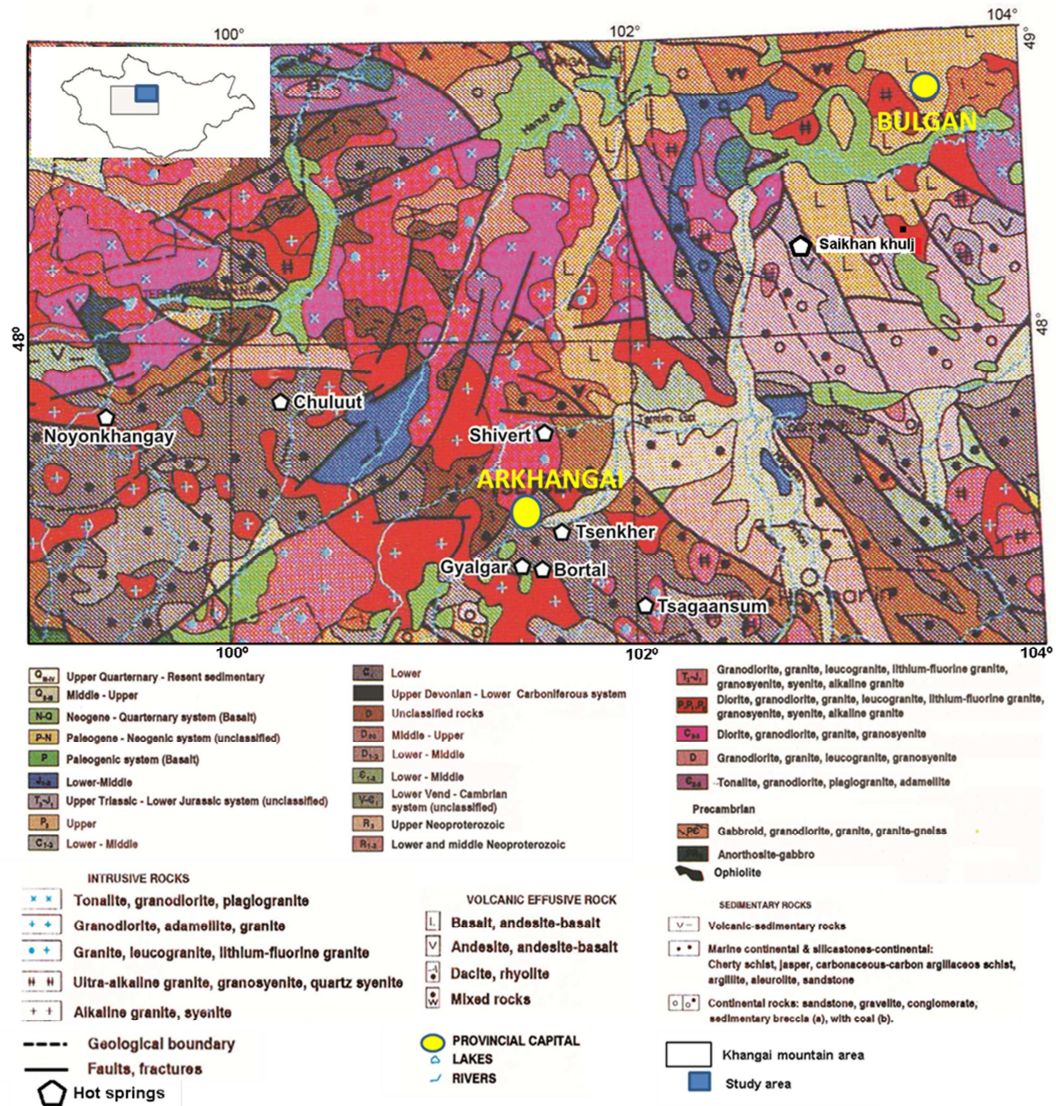
Fig.3.1. Geological map of the northeastern part of Khangai area (after Barsbold and Dorjnamjaa, 1933)

Numerous small volcanic provinces are distributed throughout the Khangai area, of which the four most northerly ones are studied here: Tariat, Hanui, Togo and Orhon. The Tariat volcanic province has been the subject of several detailed studies of mantle (PreB et al, 1986; Stosch, 1986; Ionov, 1998) and crustal (Kopylova, 1995; Stosch, 1995) xenoliths. Within Mongolia, the Tariat zone is exceptional for its xenolith abundance. At this locality,

steeply incised river canyons cut through sequences of flat-lying lavas (up to 20 m thick); individual lavas within these sequences are commonly ~8-12 m thick. Basement rocks are exposed in the valley walls, and although their age is unknown they are inferred to be Precambrian to Carboniferous in age (Kempton, 1987).

The Khangai region consists of intensely deformed Devonian-Carboniferous and not wide distributed Permian-Triassic sedimentary rocks intruded by late Paleozoic and early Mesozoic granites and granodiorites huge bodies. Late Cenozoic numerous high potassium alkaline basaltic provinces are distributed throughout the Khangai area (Figure 3.1). They are covered by unconsolidated Quaternary sediments. According to existing data, mantle plume beneath the region resulted in developing of 4-5 stages of magmatic processes from late Paleozoic to Late Cenozoic (Holocene epoch) in this region. It shows still active longliving mantle plume manipulating geothermal gradient in the crust. Therefore, India-Asian collision stress from the southwest (Algay transpressional belt) and Baikal extensional structures from the north are playing an important role for neotectonic faulting and perhaps Tertiary magmatic activation in the Khangai dome. There are number of NE and NW-trending normal faults within the Khangai mountain region. Most of hot springs controlled by intersections of such kind of fractures, faults and contact brecciated zones between Permian, Carboniferous and Devonian sedimentary rocks and Permian-Triassic granitic rocks. The regional heat flow in the Khangai dome reaches 60-70 mW/m^2 (Khutorskoi and Yarmoluk, 1989). The high heat flow in the north-eastern part of Khangay dome is reflected in localization of 9 hot and warm springs from 32 known in whole Khangai mountain area territory with temperatures of 34-88°C. Uplift, alkaline magmatism, high heat flow, asthenosphere upwelling and neotectonic faulting are showing that characteristic signatures of geothermal ability in Khangai region (Ganbat, 2010).

Five stages of high potassium alkaline basaltic provinces are distributed throughout the Khangai region of the late Cenozoic age. Tertiary lavas occur in sequences exceeding

200 m in thickness that constitute plateaus and make up much of the high mountainous region, southeast of Chuluut Gol. Quaternary lavas are found as isolated lava fields in topographic lows, confined by valleys carved into the pre-tertiary bedrock. Several processes have been proposed for the tectonic origin of Cenozoic volcanism in central Mongolia (also Central Asia). The geochemical evidence such as trace elements and Sr-Nd-Pb-Hf isotope data indicates that the Mongolian basalts were generated by small degree partial melting with the garnet stability (Bary et al., 2003).

3.3. Sample collection and analytical procedures

For this study, seventeen water samples (9 hot spring waters, 1 cold spring waters and 7 river waters) were collected in June-July, 2013 from the northeastern part in the Khangai area (Figure 3.2 and Table 3.1).
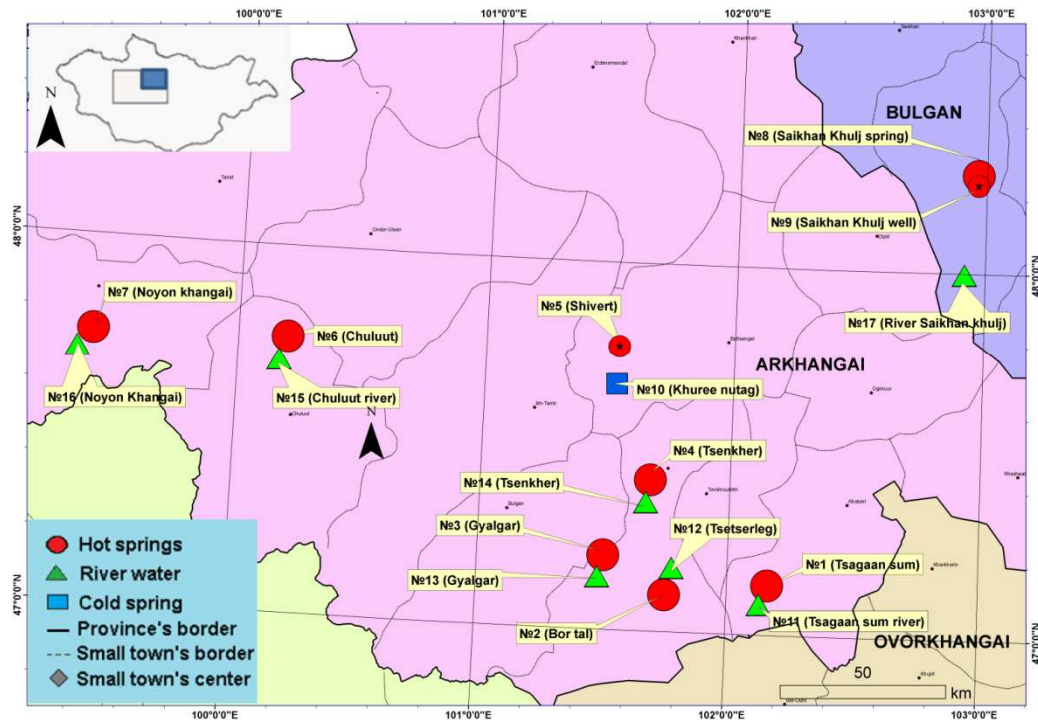
Fig.3.2. Location of sampling points in the northeastern part of Khangai area. Number and names in the sample locality correspond to those in Tables 1-3.

At the sampling site, water temperature, pH, EC and ORP were measured by a digital thermometer, a pH meter (TOA, HM-30P), an EC meter (TOA, CM-31P) and an ORP meter (TOA, RM-30P), respectively. All the samples were collected in high density polyethylene bottles for subsequent chemical analyses in the laboratory. 100ml samples

were collected for oxygen, hydrogen and carbon isotope analyses. 250 ml samples were collected for cation and anion analyses. Also 500ml samples were collected for sulfur isotope analyses. Gas samples were collected by a displacement method in water using a 50 ml lead glass container with vacuum valves at both ends. Spring waters were sampled in copper tubes (about 20 cm^3) when care was taken to avoid air contamination by air bubbles attaching themselves to the inner wall of the tubes. The tube was sealed at both ends using stainless-steel pinch clamps.

Table 3.1. Sample locality in the northeastern part of Khangai area.

№	Sample type	Locality	Sampling date	Latitude	Longitude	Altitude (m)	Temperature (^{0}C)	pH	EC (mS/m)	ORP (mV)
1	Hot springs	Tsagaan sum	7/7/2013	$47^004'02$	$102^005'56$	1700	67	9.2	45	-311
			2000				69	9.3		-18
			1977				69	8.8		10
2		Bor tal	7/7/2013	$47^011'19$	$101^035'25$	1773	45	9.5	43	-156
			7/22/2005				52	9.6		
			1977				46	9.0		65
3		Gyalgar	7/7/2013	$47^012'06$	$101^030'15$	1796	39	9.4	37	-172
			7/26/2005				52	9.4		
			1977				52	9.0		80
4		Tsenkher	7/7/2013	$47^019'01$	$101^039'07$	1797	88	9.0	54	-136
			Dec-08				84	9.4		-112
			7/25/2005				84	8.9		-275
			1977				86	8.8		70
5		Shivert	7/8/2013	$47^038'42$	$101^031'33$	1644	56	9.3	60	6
			Dec-08				62	9.0		-270
			2000				57	9.5		-12
			1977				48	8.8		160
6		Chuluut	7/8/2013	$47^045'22$	$100^014'37$	1971	48	9.3	46	-35
			8/8/2002				44	9.3		-243
			1977				45	8.8		-45
7		Noyon khangai	6/18/2013	$47^044'32$	$99^024'52$	2285	36	9.0	31	
			8/17/2002				37	9.3		-145
			1978				38	9.5		310
8		Saikhan khulj (spring)	7/9/2013	$48^015'48$	$102^058'18$	1421	34	8.1	34	144
9		Saikhan khulj (well)	7/9/2013	$48^015'54$	$102^058'17$	1413	52	8.8	116	105
			7/22/2002				57	8.8		-350
			1977				53	8.8		140
10	Cold spring	Khuree nutag	7/9/2013	$47^036'32$	$101^030'40$	1761	3.0	7.0	12	2.9
11	River waters	Tsagaan sum	7/7/2013	$47^003'59$	$102^006'01$	1707	8.3	7.9	36	72
12		Tsetserleg	7/7/2013	$47^012'21$	$101^035'22$	1766	14	7.3	13	131
13		Gyalgar	7/7/2013	$47^012'15''$	$101^030'17$	1785	12	7.6	7.1	234
14		Tsenkher	7/8/2013	$47^019'02$	$101^038'58$	1735	8.6	7.9	26	231
15		Chuluut	7/8/2013	$47^044'43$	$100^013'13$	1995	16	7.8	11	186
16		Noyon khangai	6/18/2013	$47^044'32$	$99^024'44$	2274	14	7.2	4.5	
17		40 km east from Saikhan khulj	7/10/2013	$47^059'30$	$102^051'43$	1572	15	8.6	55	225

Out of these, one river water (sample No17) is located far (about 40 km) from the hot spring (sample No8) and the cold spring (sample No10) is located far (about 1 km) from hot spring (sample No5). All other cold groundwater sampling sites were selected from the

nearest possible location (<100 m) to the sampled hot springs (Figure 3.2).

The $^3He/^4He$ and $^4He/^{20}Ne$ ratios of the samples were measured by a noble gas mass spectrometer at the University of Tokyo. The ^{13}C and ^{34}S isotopes of the samples were measured by mass spectrometry at the Kyuden Cooperative limited. The samples were prepared for the mass spectrometry determination of $\delta^{18}O$ by the CO_2 equilibration method (Epstein and Mayeda, 1953) and that of δD by using the Zn reduction method (Coleman et al., 1982), and the determinations carried out in a mass spectrometer (VG Micromass Ltd., Optima) at the Analytical Center, Mitsubishi Materials Techno Corporation in Japan and reported relative to V-SMOW with an analytical precision of 0.1‰ and 1‰, respectively.

Dissolved ion concentrations were determined at the Geochemical Laboratory, University of Toyama. The major anions Cl and SO_4 in filtered water samples were analyzed with ion chromatograph (761 Compact IC, Metrohm) using an IonPac As22 column. Cations (Na, K, Ca, Mg) were analyzed with the ion chromatograph (761 Compact IC, Metrohm) using a Dionex DX-320J. Alkalinity was determined using standard titration with HCl. Dissolved silica was determined by a molybdenum yellow method using a spectrophotometer (UV-VIS Recording Spectrophotometer, Shimadzu). The charge balances of the results obtained were within ±5% and the analytical uncertainties for dissolved ion concentrations were also within 5%.

3.4. Results and discussion

3.4.1. Chemical compositions

Descriptions of sampling locations and geochemical results of hot and cold waters are listed in Tables 3.1 and 3.2. The discharge temperature of hot springs varied from 34°C to 88°C while their pH varied from 8.4 to 9.6, indicating alkaline characteristics. The electric conductivity (EC) of hot springs varied from 31 mS/cm to 116 mS/cm. In contrast, the water temperatures of cold spring and river waters are ranging from 3 to 16°C and the pH values range from 7 to 8.6. The electric conductivity (EC) of cold spring and river waters varied from 4.5 mS/cm to 55 mS/cm (Table 3.1). This indicates a low mineralization of hot, cold springs and river waters.

Table 3.2. Chemical and isotope composition of the hot and cold springs and river waters in the northeastern part of Khangai area

№	Sample type	Locality	Sampling date	Na mg/L	K	Ca	Mg	Cl	SO$_4$	HCO$_3$	SiO$_2$	δD ‰	δ^{18}O	δ^{13}C	δ^{34}S
1	Hot springs	Tsagaan Sum	2013/7/7	80	2.3	0.1	0.1	6.8	47	105	80	-109	-15	-14	19
			2000	72	1.9	3.2	0.2	2.5	29	80	83				
			1977	97	3.2	2	0	7.5	48	97	106				
2		Bortol	2013/7/7	83	1.2	0.1	0.1	1.9	42	109	72	-113	-16	-14	8.8
			2005/7/22	76	1.4	2.4	0.1	27	37	60	61				
			1977	97	1.6	2.5	0.1	19	39	84	94				
3		Gyalgar	2013/7/7	75	2.1	0.1	0.1	15	37	114	85	-117	-16	-14	6.0
			2005/7/26	71	2.1	3.6	0.2	18	30	78	76				
			1977	87	2.8	1.9	0.1	15	4.6	94	112				
4		Tsenkher	2013/7/7	94	3.1	0.1	0.1	18	48	108	114	-108	-15	-14	9.1
			2008	84	2.9	2.2	0.5	18	45	76	114	-108	-14		
			2005/7/25	86	3.0	2.4	0.1	20	40	73	112				
			1977	107	4.2	2.1	0	18	49	105	133				
5		Shivert (well)	2013/7/8	100	4.4	0.4	0.1	16	89	98	96	-109	-15	-13	9.3
			2008	96	3.8	2.4	0.1	18	84	88	93	-106	-14		
			2000	96	4.1	3.2	1.2	20	77	71	87				
			1977	123	6.0	2.4	0.1	16	73	86	106				
6		Chuluut	2013/7/8	92	2.9	0.5	0.1	12	50	116	88	-109	-15	-13	18
			2002/8/8	93	2.6	2.4	0.1	15	14	124	63				
			1977	105	3.9	1.9	0.1	12	51	112	92				
7		Noyon khangai	2013/6/18	65	1.3	0.3	0.1	5.9	42	99	66	-111	-15	-16	7.6
			2002/8/17	61	0.9	1.6	0.4	6.7	19	94	81				
			1978	63	1.3	2	0.5	5.9	40	107	94				
8		Saihan Khulj (spring)	2013/7/9	190	6.5	45	0.4	43	440	53	63	-100	-14		4.4
9		Saihan Khulj (well)	2013/7/9	190	4.9	40	0.1	41	420	27	63	-101	-13	—	5.5
			2002/7/22	198	4.3	44	0.2	45	415	29	65				
			1977	215	5.9	42	2.2	43	431	22	64				
10	Cold spring	Khuree Nutag	2013/7/9	4.3	0.9	15	2.9	0.8	4.6	61	14	-105	-15	-16.5	—
11	River waters	Tsagaan Sum	2013/7/7	14	1.2	44	10	1.6	6.7	228	9.9	-92	-12	-13.4	—
12		Tsetserleg	2013/7/7	3.6	1.1	13	5.2	0.8	6.5	72	10	-101	-14	-13.1	—
13		Gyalgar	2013/7/7	3.9	0.9	6.8	1.9	0.8	3.7	37	9.2	-102	-15	—	—
14		Tsenkher	2013/7/8	7.1	1.0	32	7.5	0.6	5.8	159	11	-99	-13	-13.7	
15		Chuluut	2013/7/8	4.4	1.5	12	2.7	1.2	4.6	52	4.1	-97	-14	—	—
16		Noyon khangai	2013/6/18	1.5	0.6	9.3	1.1	0.7	4	32	9.4	-86	-12		
17		40km east of Saihan khulj	2013/7/10	44	6.0	39	32	6.4	13	369	4.8	-113	-12		—

We compared the results of the present study on hot springs with the previous results (hot spring samples collected in 1977, 1978 (Ariyadagva et al., 1980) and 2000, 2002, 2005 (Ganchimeg et al., 2007) and cold water data which located at the same area and showed by the Figure 3.3 and Table 3.2. These results are no significant difference in the chemical compositions of water samples collected in 1977 and 2005 and the present study at the same localities. The sodium concentration of hot springs (№1,2,3,4,6,7) in Arkhangai province are dominant cation range from 61 mg/L to 107 mg/L and other cation concentrations such as those of K^+, Ca^{2+} and Mg^{2+} are very low (below the detection limit of ICP in the case of Mg^{2+}). Total alkalinity values (HCO_3^-) is the dominant anion (up to 124 mg/L), chloride concentrations are always below 27 mg/L and sulfate concentrations are range from 19 mg/L to 50 mg/L except for one hot well in the Arkhangai province

(sample №5: dominant cation Na up to 123 mg/L and dominant anion HCO_3 up to 98 mg/L and SO_4 up to 89 mg/L). The total dissolved silica content of hot springs ranged from 63 mg/L to 114 mg/L and from 4.1 mg/L to 14 mg/L for cold waters. The bicarbonate (HCO_3) concentration of cold waters at the same localities area dominant cation range from 32 mg/L to 228 mg/L and dominant anion Ca^{2+} is range from 9.3 mg/L to 44 mg/L.

The sodium (Na) concentration of hot spring and well (№8,9) in Bulgan province are dominant cation range from 190 mg/L to 215 mg/L and Ca^{2+} concentration are up to 45 mg/L than higher that other hot springs (Arkhangai province). Sulfate concentration (SO_4) is the dominant anion (up to 440 mg/L), bicarbonate (HCO_3) concentrations are range from 27 mg/L to 53 mg/L and chloride concentration up to 43 mg/L. The total dissolved silica content of hot spring and well is ranged from 63 mg/L to 65 mg/L and up to 4.8 mg/L for river waters. The bicarbonate (HCO_3) concentration of cold waters at the same localities area dominant cation up to 369 mg/L and dominant anion Na is 44 mg/L, Ca^{2+} 39 mg/L and Mg 32 mg/L, receptivity.
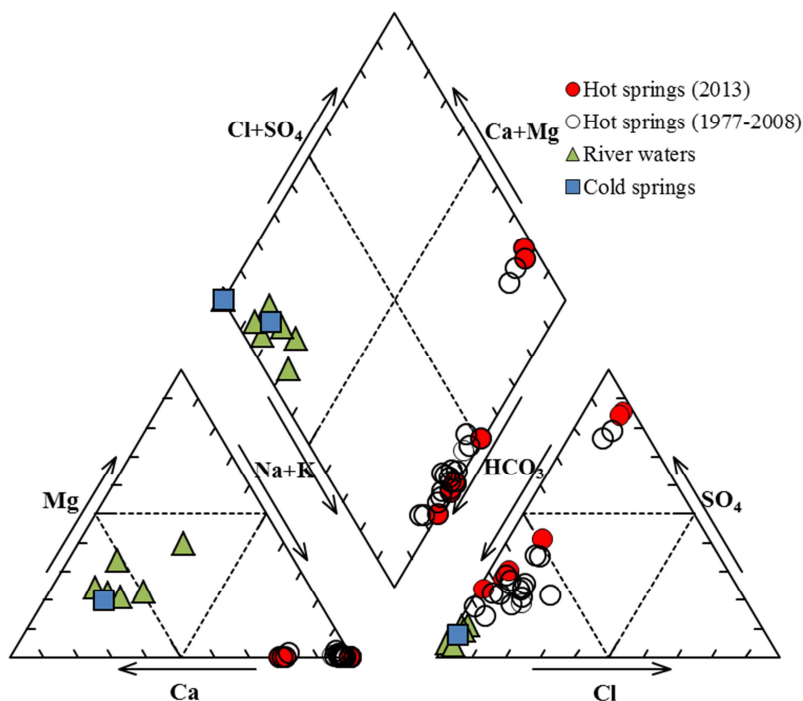

Fig.3.3. Piper diagram for water samples in the northeastern part of Khangai area.

In comparison with the previously obtained chemical composition of water samples collected in 1977, 1978 (Ariyadagva et al., 1980) and 2000, 2002, 2005 (Ganchimeg et

al., 2007) at the same localities, the Ca and SiO_2 concentrations of hot springs in this study were slightly lower (Table 3.2). Although there are several possibilities to explain the observed differences in previous and present data due to the change of chemical compositions in the hot springs. The main ions of the hot springs were HCO_3, Na and silica and concentrations of Ca and Mg were negligible in the hot springs. The reason for this behavior is related with high content of sodium and siliceous compounds in the granite massive which contains the hot springs were under the weak tectonically region and high temperature. Those factors were influenced to dissolve granite massive into hot water and it increased content of sodium and silica in the hot water. (Lkhagva, 1975).

Piper diagram for the water samples in the study area are shown in Figure 3.3. The chemical composition of the hot springs in the study area is characterized by two types. Most of the hot springs located in the southern part in the study area (sample Nos. 1-7; Arkhangai province) belongs to Na^+-HCO_3^- type except for one hot spring (Na^+-HCO_3, SO_4^{2-} type; sample №.5). The hot springs in the north-eastern part (Bulgan province) in the study area belong to Na^+-SO_4^{2-} type. All cold waters are of the Ca^{2+}-HCO_3^- type.
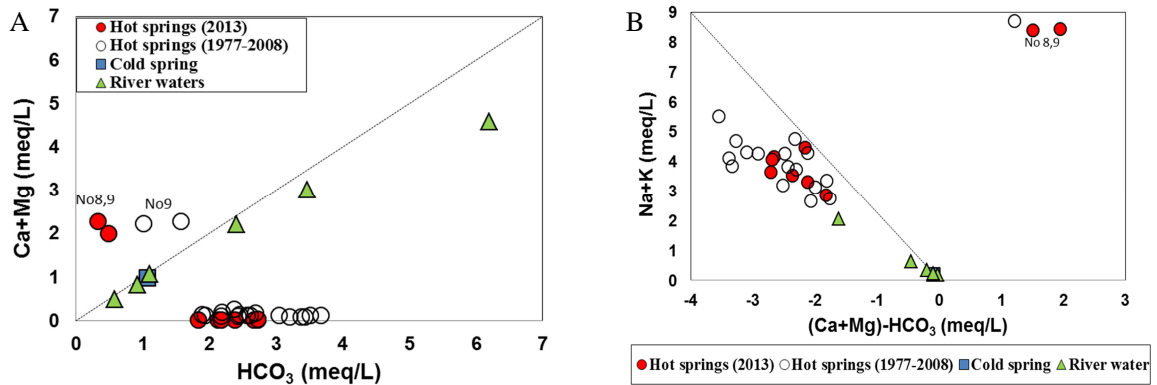

Fig.3.4. Relationship between Na^+, K^+, Ca^{2+}, Mg^{2+}, and HCO_3. (a) Ca^{2+}, Mg^{2+} vs HCO_3^- concentration, (b) Na^+, K^+ vs (Ca^{2+}, Mg^{2+}) - HCO_3 for water samples in the study area. The broken line in the (a) means dolomite dissolution. The broken line in the (b) shows the ion exchange of Ca^{2+}, Mg^{2+} with Na^+, K^+ by the reaction with clay minerals after dolomite dissolution.

The relationship between Ca^{2+} + Mg^{2+} and HCO_3^- concentrations is shown in Figure 3.4(a), where the broken line is dolomite dissolution. This result implies that the cold springs are enriched in Ca^{2+}, Mg^{2+} and HCO_3^- due to dissolution of carbonate rocks (such as dolomite), whereas all hot springs plot below the broken line except for sample No8 and

9 in Figure 3.4a. Fig. 3.4b shows the relation between $Na^+ + K^+$ and $(Ca^{2+} + Mg^{2+})$-HCO_3^- and the broken line corresponds to the ion exchange of $Ca^{2+} + Mg^{2+}$ with $Na^+ + K^+$ by the reaction with clay minerals after dolomite dissolution. The water chemical types evolve to Na–SO_4 for long residence time and long period of evolution and also water–rock interactions and the TDS content increases, the content of Na^+, Ca^{2+} and SO_4^{2-} increases correspondingly. These types of waters are including samples from Saikhan hulj (sample No8 and 9) in Bulgan province. Due to strong water–rock interactions to increase the cation exchange under high temperature, the sample plots of all other hot springs locate in Arkhangai province. A possible explanation for the observed result is that the hot springs are enriched in Na^+ and K^+ and depleted in Ca^{2+} and Mg^{2+} because of ion exchange with clay minerals in the soil resulting a higher pH than that of the cold spring.

3.4.2. Isotopic compositions

Isotope techniques are indispensable tools in geothermal investigations. Because isotope ratios are sensitive to temperature and natural physicochemical processes, such as water-rock interaction, mixing, and steam separation, they can be efficiently used in tracing the origin of geothermal fluids and the processes that the fluids have undergone at subsurface. The most commonly used isotopes in geothermal system studies are those of oxygen (O), hydrogen (H), Carbon (C) and Helium (He). During exploration, O and H isotope studies are utilized in determining the source of geothermal water, identifying possible recharge areas and flow directions, and estimating age and reservoir temperature of the system, while C- and He-isotopes are potential tracers of volatile provenance which in turn can be used in assessing the possible heat source and reservoir lithology (Nilgun Güleç, 2013).

3.4.2.1. Oxygen and hydrogen isotope ratios

Results of the $\delta^{18}O$ and δD ratios of water samples are presented in Table 3.2 and Figure 3.5 (a, b). The $\delta^{18}O$ ratio of hot springs ranges from -13 to -16‰ and that of cold

waters is between -12 and -15‰. Deuterium values for hot and cold waters are -100 to -117‰ and -86 to -113‰ respectively. Most of the hot and cold waters (located in the Arkhangai province) are plotted on the Global Meteoric Water Line (Figure 3.5a; $\delta D = 8\delta^{18}O + 10$; Craig, 1961) and some the hot (sample No8 and 9) and river waters close to the Local Meteoric Water Line (LMWL) which has a regression equation $\delta D = 7.98\delta^{18}O + 4.19$. A local meteoric water line has been proposed for Central Mongolian basin (Dubinina et al, 2007). These hot and cold waters are indicate a common meteoric origin and out of these, one river water (Saikhan hulj river, sample No17) plot far from these lines. The unusual position of the Saikhan hulj river water with an ^{18}O shift about 2‰ units from the hot springs (sample No8 and 9, located in the Bulgan province) at the same localities is explained by water-rock interaction which has resulted in an increase of $\delta^{18}O$ content of this water (Figure 3.5 (a.b)). In comparison with the 4 hot spring samples collected in August 1987 at the same localities (Pinneker. E.I, 1995), where the **δD** and **δ^{18}O** values are -75 to -107‰ and -12 to -15‰ for hot spring and these **δD** and **δ^{18}O** and ratios of hot springs are slightly higher than those for the present study. This is also shown in 29 hot and cold water samples collected in July 2012 of the western part in the Khangai mountain area, Mongolia (D.Oyuntsetseg et al, 2015), where the δD and $\delta^{18}O$ values are -87 to -126‰ and -12 to -17 % for hot springs and -78 to -127‰ and -11 to -17‰ for cold and river waters, respectively. These are almost the same to those of hot and cold waters in the western part of Khangai area. They concluded that the all water samples derived from meteoric water with minimal isotope exchange with reservoir rock. Figure 3.5b shows the $\delta^{18}O$ values for water samples plotted against the altitude of the sampling points. In the study area, **δD** and **δ^{18}O** ratios of cold waters are slightly higher than those of hot springs. Enrichments for D and ^{18}O are about 4 to 25‰ and 1 to 4‰ respectively. This may indicate that thermal waters are recharged from a different source probably from a higher elevation.
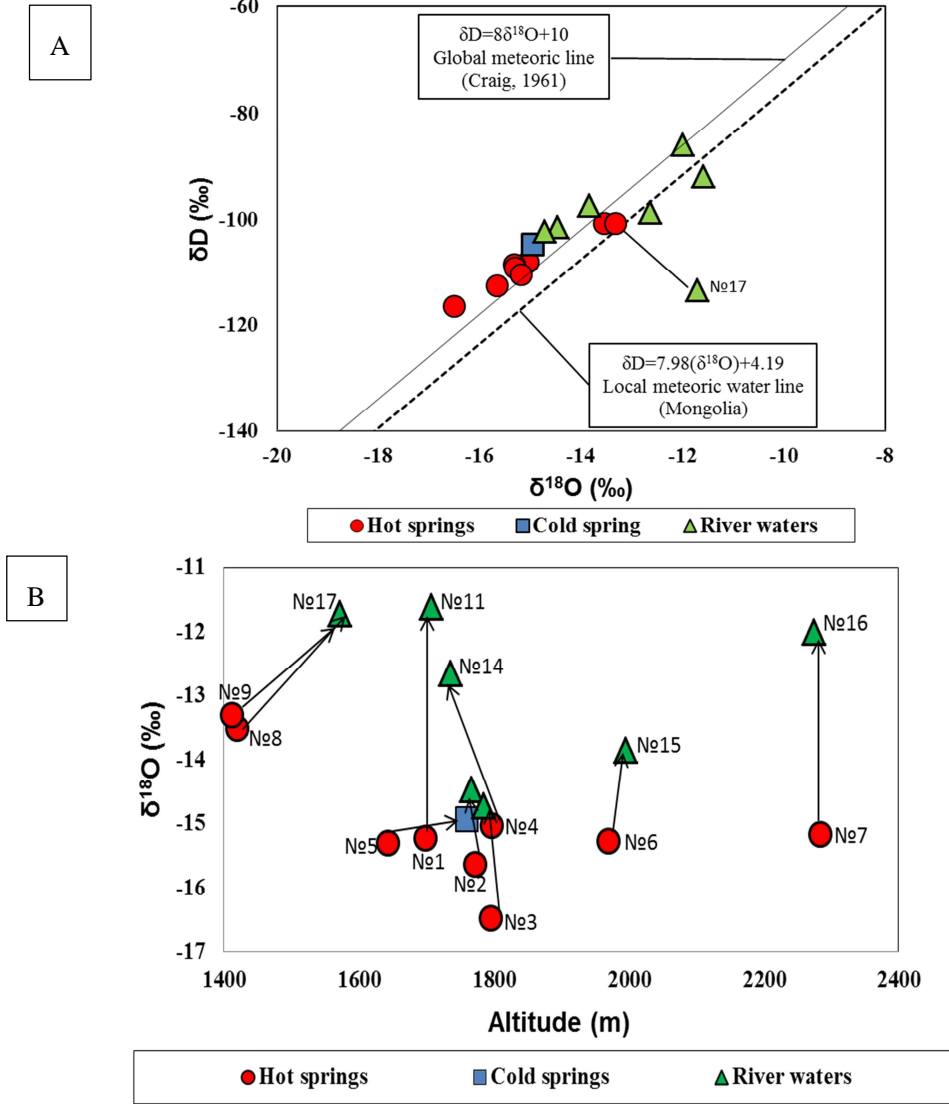
Fig.3.5. δD vs δ^{18}O of water samples in the northeastern part of Khangai area. (a) δD vs δ^{18}O and (b) Altitude vs δ^{18}O. The solid line in this figure shows the local meteoric water line (δD=8 δ^{18}O+10). Tie lines in (b) shows water samples from the same areas

3.4.2.2. Helium and neon isotope ratios

He has two stable isotopes, ^{3}He and ^{4}He the variations in their ratio are greater than 10^3 in geologic reservoirs leading to the identification of three major components, namely, radiogenic-He, tritiugenic-He and Primordial-He (Nilgun Güleç, 2013). Atmosphere, crust and mantle are the three major reservoirs from which He observed in terrestrial materials is derived (Figure 3.6). Atmospheric-He is characterized by a ^{3}He/^{4}He ratio of 1.39*10^{-6} (Ozima and Podosek, 1983). Because this ratio is rather constant over the globe, ^{3}He/^{4}He ratios measured on geologic materials are usually expressed relative to the ratio in the atmosphere (R/R$_A$ = (^{3}He/^{4}He)$_{sample}$/(^{3}He/^{4}He)$_{atm.}$). Crustal-He has an R/R$_A$ range of

0.01-0.1 (Andrews, 1985). Mantle-He has $^3He/^4He$ ratio around 10^{-5} (R/R_A ⫼ 8-30) (Mamyrin and Tolstikhin, 1984; Farley and Neroda, 1998), reflecting the dilution of Primordial-He with that produced by radiogenic processes in the mantle.

In 1980–83, the Soviet-Mongolian Research Expedition run jointly by the Science Academies of the two countries the studies continued in Lake Khovsgol (9 heat flow stations) and in its surroundings (5 boreholes in two fields), in central (26 boreholes in 11 fields), and in southern Mongolia (15 boreholes in 5 fields), and at 10 hot springs, which added 28 heat flow determinations. The high helium enrichment of thermal waters made it possible to estimate heat flows from $^3He/^4He$ ratios, and these estimates were obtained for 22 hot springs (Pinneker et al. 1995, Lysak and Pissarsky 1999). Thus, they investigated the geothermal field in Mongolia on the basis of data from 141 heat flow station, including 55 drilling sites, and 26 hot springs. The 12 hot springs are located in the Khangai area, where $^3He/^4He$ radios range from $4.9*10^{-8}$ to $36*10^{-8}$ respectively. They concluded that $^3He/^4He$ ratios show that the greatest portion of heat flow is of crustal radiogenic origin on uplifts, especially in Eastern and Central Mongolia, and large active faults, and in provinces of Cenozoic volcanism (Lysak, 2003).
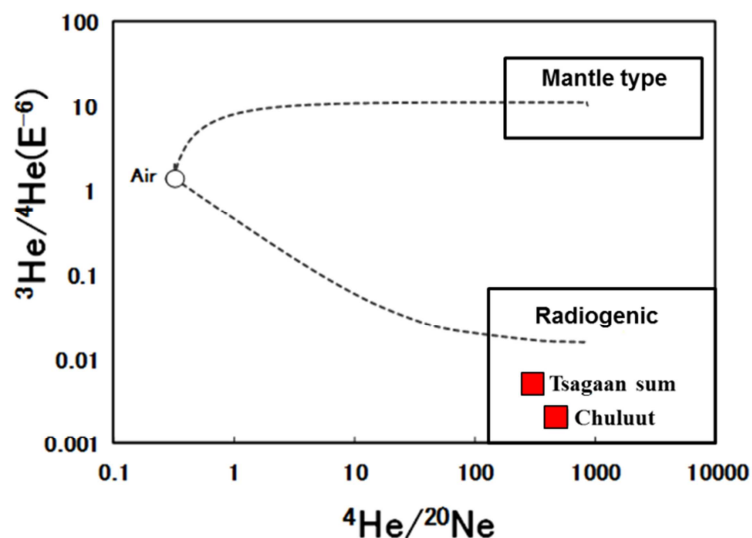

Fig.3.6. Relationship between $^3He/^4He$ and $^4He/^{20}Ne$ ratios in the northeastern part of Khangai area.

The relationship between $^3He/^4He$ and $^4He/^{20}Ne$ ratios is given in Figure 3.6. In the study area, $^3He/^4He$ ratios are range R/R_A from 0.007 to 0.009 ($0.069*10^{-6}$ to $0.15*10^{-6}$)

and $^4He/^{20}Ne$ ratios are range from 450 to 672 respectively. In comparison with the 2 hot spring samples collected in July 1989 and July 1990 at the same localities (Pinneker. E.I, 1995), where the $^3He/^4He$ ratios are $0.12*10^{-6}$ to $0.14*10^{-6}$ which are almost the same to those for the present study. In summary, two samples have been analyzed so far and plotted below radiogenic origin (Figure 3.6) which means these He and Ne gas come from the decay of U-Th. This means no volcanic contribution to the Mongolian geothermal waters and the heat source is derived from the radiogenic one.

3.4.2.3. Carbon isotope ratios

Carbon isotope is used for the investigation of the origin of dissolved component in geothermal fluids. Regarding the compounds relevant to hydrological cycle, the major sources establishing the dissolved carbon content in natural waters are : I) sedimentary organic carbon ($δ^{13}C ≈ -10$ to $-40‰$) reflecting the biogenic source, II) marine carbonates ($δ^{13}C ≈ 0‰$), III) mantle CO_2 ($δ^{13}C ≈ -6.5‰$), and IV) atmospheric CO_2 ($δ^{13}C ≈ 7-8‰$) related to the global carbon cycle (Sharp, 2007; Mook, 2000).

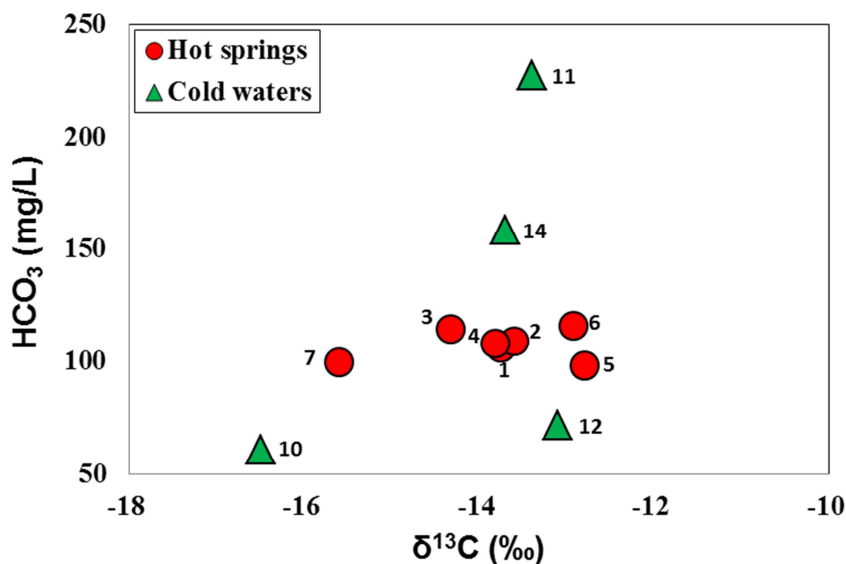**Fig.3.7.** Relationship between HCO_3 and $δ^{13}C$ ratios in the northeastern part of Khangai area. Numbers in the sample point correspond to those in Tables 1-4.

The major sources of carbon contributing to DIC in the waters are CO_2 derived from the decay of organic matter in soils and from the dissolution of carbonate, while in general the contribution of atmospheric CO_2 is negligibly small.

The $\delta^{13}C$ values of total dissolved inorganic carbon are plotted versus alkalinity (expressed as HCO_3) in Figure 3.7. The isotopic ratios in dissolved inorganic carbon (DIC) in the study area thermal waters range from -13 to -16‰. The $\delta^{13}C$ values of cold springs and river water samples vary from -13 to -17‰ (Table 3.2). These values are corresponding to sedimentary organic carbon ($\delta^{13}C \approx$ -10 to -40‰) (Sharp, 2007; Mook, 2000). This means the carbon species (HCO_3) of the hot springs in the study area is derived from organic sources.

4.2.3. Sulfur isotope ratios

Sulfur is present in nearly all nature environments: as a minor component in ingneous and metamorphic rocks, mostly as sulfides; in the biosphere and related organic substances, like crude oil and coal; in ocean water as sulfate and in marine sediments as both sulfide and sulfate. It may be a major component: in ore deposits, where it is the dominant nonmetal, and as sulfates in evaporates. These occurrences cover the whole temperature range of geologic interest. Sulfur is bound in various oxidation states, from sulfides to elemental sulfur, to sulfates. From these facts it is quite clear that sulfur is of special interest in stable isotope geochemistry (Hoefs, 1987). The distribution of sulphur isotopes in a number of natural materials is shown by Thode et al. (1949) and Trofimov (1949). For a schematic diagram, see Figure 3.8.
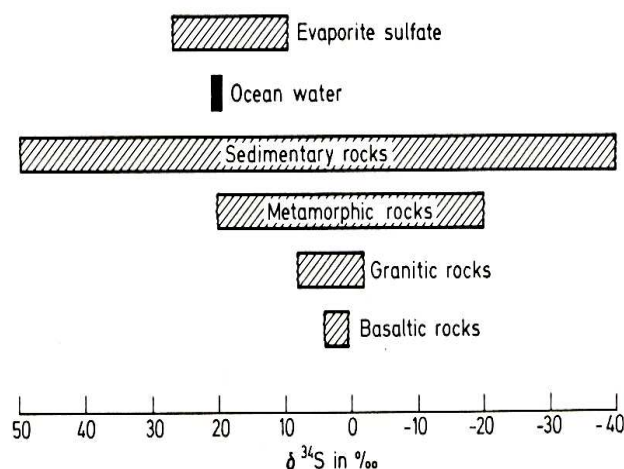

Figure 3.8. $^{34}S/^{32}S$ ratios in some geologically important materials ($\delta^{34}S$ relative CD troilite)

The source of sulfate in thermal waters is highly variable. It could be derived from dissolution of sulfate minerals (e.g., gypsum and anhydrate), oxidation of sulfides (e.g., pyrite) and biological activity.
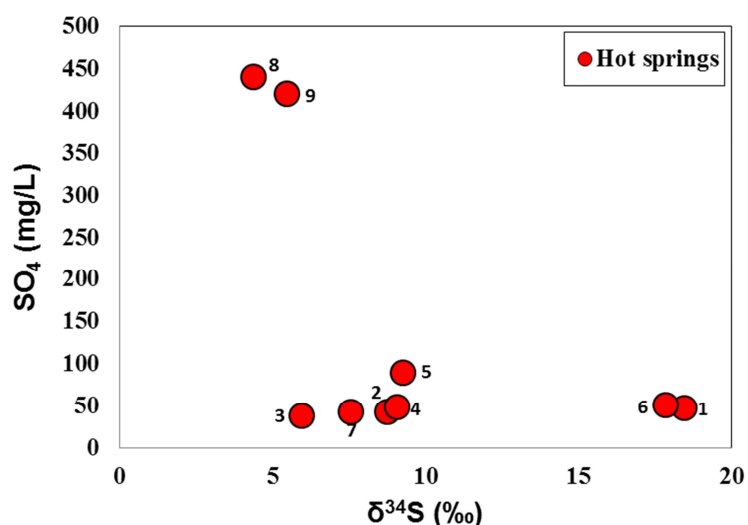

Fig.3.9. Relationship between SO_4 and $\delta^{34}S$ ratios in the northeastern part of Khangai area

In Figure 3.9, $\delta^{34}S$ values of waters are plotted versus SO_4 contents in the study area. The $\delta^{34}S$ values of thermal waters range from +4.4 to +19‰ in the study area (Table 3.2). Compared with the figure.10, the $\delta^{34}S$ values vary within a wide range independent of their sulfate contents. Therefore, based on the He/Ne and ^{13}C ratios, sulfur in hot springs may be of sedimentary origin.

3.4.3. Geothermometers

In the last few decades, various geothermometers were introduced to calculate reservoir temperatures of geothermal waters based on the chemical constituents (Arnorsson, 1983; Fournier, 1977; Giggenbach, 1988; Fournier and Truesdell, 1973). Among these, the silica (quartz, chalcedony, amorphous silica etc.) and alkali geothermometers (Na–K, Na–K–Ca etc.) are the most commonly applied. These temperature equations, based on empirical or semi-empirical laws, rely on specific equilibrium constants that refer to specific mineral-solution reactions in geothermal reservoirs. Silica-quartz/chalcedony-based geothermometers are widely applied to calculate the temperature of low enthalpy reservoirs (Fournier, 1977, 1979; Giggenbach, 1988; Truesdell and Fournier, 1973). Most

of these geothermometers were based on water–rock equilibrium in geothermal reservoirs in volcanic geothermal terrains. The Na/K ratio and Na–K–Ca geothermometers proposed by Giggenbach (1988) can also be used to calculate the possible equilibrium temperatures.

The results of chemical geothermometers applied to the thermal waters in the northeastern part of Khangai area are given in Table 3.3. These estimates were obtained using methods suggested by Fournier (1977), Arnorsson (1983), Fournier and Truesdell (1973) and Giggenbach (1988).

The silica quartz geothermometer of Fournier, (1977) yielded the highest reservoir temperatures that range from 111^OC (Bortal) to 154^OC (Tsenkher) for all geothermal springs in the study area and higher than those calculated for equilibrium with chalcedony. For comparison, the silica–chalcedony temperature two equation proposed by Fournier (1977) and Arnorsson, (1983) gave reservoir temperature ranges from 84^OC (Saikhanhulj) to 129^OC (Tsenkher). It is obvious that the chalcedony geothermometer by Fournier (1977) yields relatively almost similar values for all samples compared to the calibration of Arnorsson et al. (1983). The calculated temperatures using the previous data (1977, 1978) are higher than other previous and present data of each hot spring in the study area. The solubility of silica in thermal waters increases with an increase in temperature (Fournier, 1977 and Arnorsson, 1983).

Temperatures are calculated for the hot springs based on the Na-K data and using two different calibrates (Table 3.3). The Na-K geothermometers of Arnorsson et al. (1983) and Giggenbach (1988) give the reservoir temperature in the range 62-308°C and 120-315°C, respectively. It is obvious that the Na-K geothermometer by Giggenbach(1988) yields relatively high values for all samples compared to the calibration of Arnorsson et al. (1983) except for sample No8 (Saikhanhulj hot spring (2013) 368^OC by Arnorsson et al. (1983) and 355^OC by Giggenbach (1988)).

Table 3.3. Underground temperature estimated from application of solute geothermometry.

№	Locality	Sampling date	T_{means} (^{o}C)	$T_{chal\,(1)}$ (^{o}C)	$T_{chal\,(2)}$ (^{o}C)	$T_{Qtz\,(3)}$ (^{o}C)	$T_{Na-K\,(4)}$ (^{o}C)	$T_{Na-K\,(5)}$ (^{o}C)	$T_{Na-K-Ca\,(6)}$ (^{o}C)
1	Tsagaan Sum	7/7/2013	120	97	97	125	99	152	149
		2000	109	99	99	127	76	133	118
		1977	115	114	112	140	65	123	135
2	Bortol	7/7/2013	101	91	91	120	62	120	120
		7/22/2005	97	82	83	111	71	128	106
		1977	108	107	105	134	71	128	106
3	Gyalgar	7/7/2013	121	101	100	128	98	152	147
		7/26/2005	115	94	94	122	102	156	122
		1977	118	118	116	144	71	127	134
4	Tsenkher	7/7/2013	122	119	116	144	70	127	159
		2008	124	119	117	145	86	142	135
		7/25/2005	134	118	116	144	121	172	135
		1977	130	129	126	154	84	140	145
5	Shivert (well)	7/8/2013	120	108	106	135	77	133	163
		2008	116	106	105	133	78	134	143
		2000	115	102	101	130	78	134	144
		1977	143	114	112	140	144	191	156
6	Chuluut	7/8/2013	158	102	102	130	220	252	143
		8/8/2002	106	84	84	113	86	141	126
		1977	188	105	104	133	321	324	143
7	Noyon khangai	6/18/2013	132	86	86	115	168	211	122
		8/17/2002	164	98	97	126	274	291	98
		1978	180	107	105	134	307	314	111
8	Saihan Khulj	7/9/2013	189	84	85	113	368	355	125
9	Saihan Khulj (well)	7/9/2013	156	84	84	113	259	280	114
		7/22/2002	169	86	86	114	306	314	108
		1977	171	85	85	114	308	315	118

T_{means}: averaged values of calculated temperatures.

(1),(3): Fournier (1977), (2), (4): Arnórsson et al. (1983), (5): Giggenbach (1988), (6): Fournier and Truesdell (1973)

The temperatures calculated (Table 3) using the Na-K-Ca geothermometer (β= 4/3) are similar, in the range 98-163°C (Fournier and Truesdell, 1973). These the case of all hot springs, with an anomalous Na/K ratio and a higher calculated temperature, could be the result of additional chemical reactions after mixing, including possible cation exchange reactions (e.g., Fournier, 1977; D'Amore et al., 1987;Druschel and Rosenberg, 2001).

The result shows that averaged values of calculated temperature ranges from 101°C (Bortal) 156°C (Saikhan hulj) among the studied hot springs.

3.4.4. Mineral saturation states

Mineral saturation indices for the hot spring waters in the eastern part of Khangai area were calculated using the computer program "PHREEQC" (Parkhurst and Appelo, 1999). In this study the "PHREEQC" (Parkhurst and Appelo, 1999) program was used to calculate the log (Q/K) for the temperature range 20-180°C. The speciation technique was only applied of water samples on 2013. The calculated saturation index (SI=logQ/logK) vs. temperature for hot water from springs are shown in Figure 3.10.

Based on a subset of selected chemical analyses, multicomponent geothermometry coupled with numerical optimization has been applied at hot springs to estimate the extent of dilution and degassing processes, to evaluate potential mineralogical assemblage controlling the fluid chemistry at depth, and possibly define the equilibrium temperature of the reservoir. The results of this approach are sensitive to the minerals considered in the calculations. The minerals albite low, aragonite, anhydrite, calcite, K-feldspar, laumontite, montmorillonite-Na, muscovite, chalcedony and quartz were selected to calculate the equilibrium state.

Best results were obtained by selecting a mineral assemblage consisting of K-feldspar, montmorillonite-Na and quartz. Also some cases were obtained by selecting a mineral assemblage consisting of albite low, muscovite and chalcedony at the low temperature. The minerals calcite and aragonite are within the undersaturation zone and other minerals were cuttings equilibrium line.
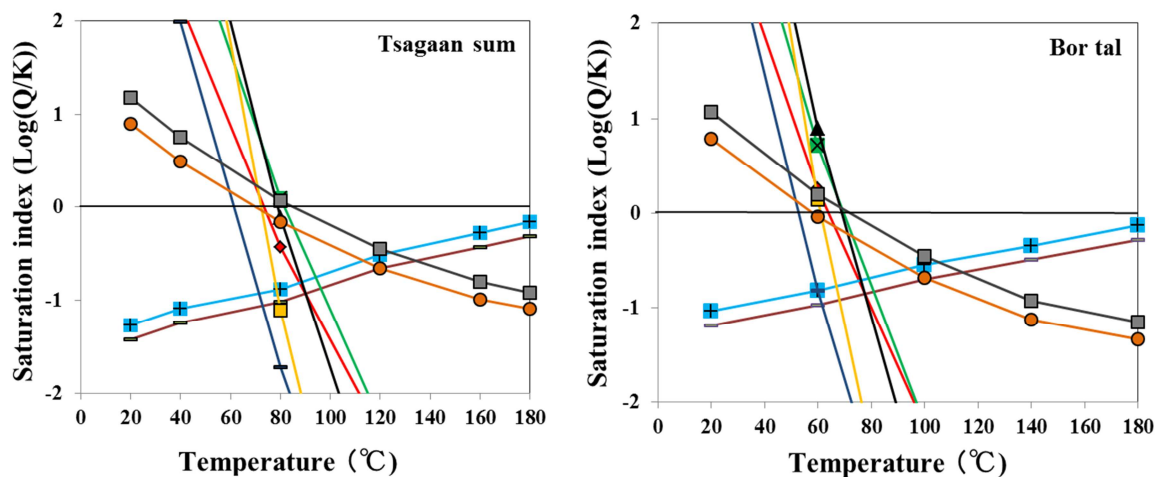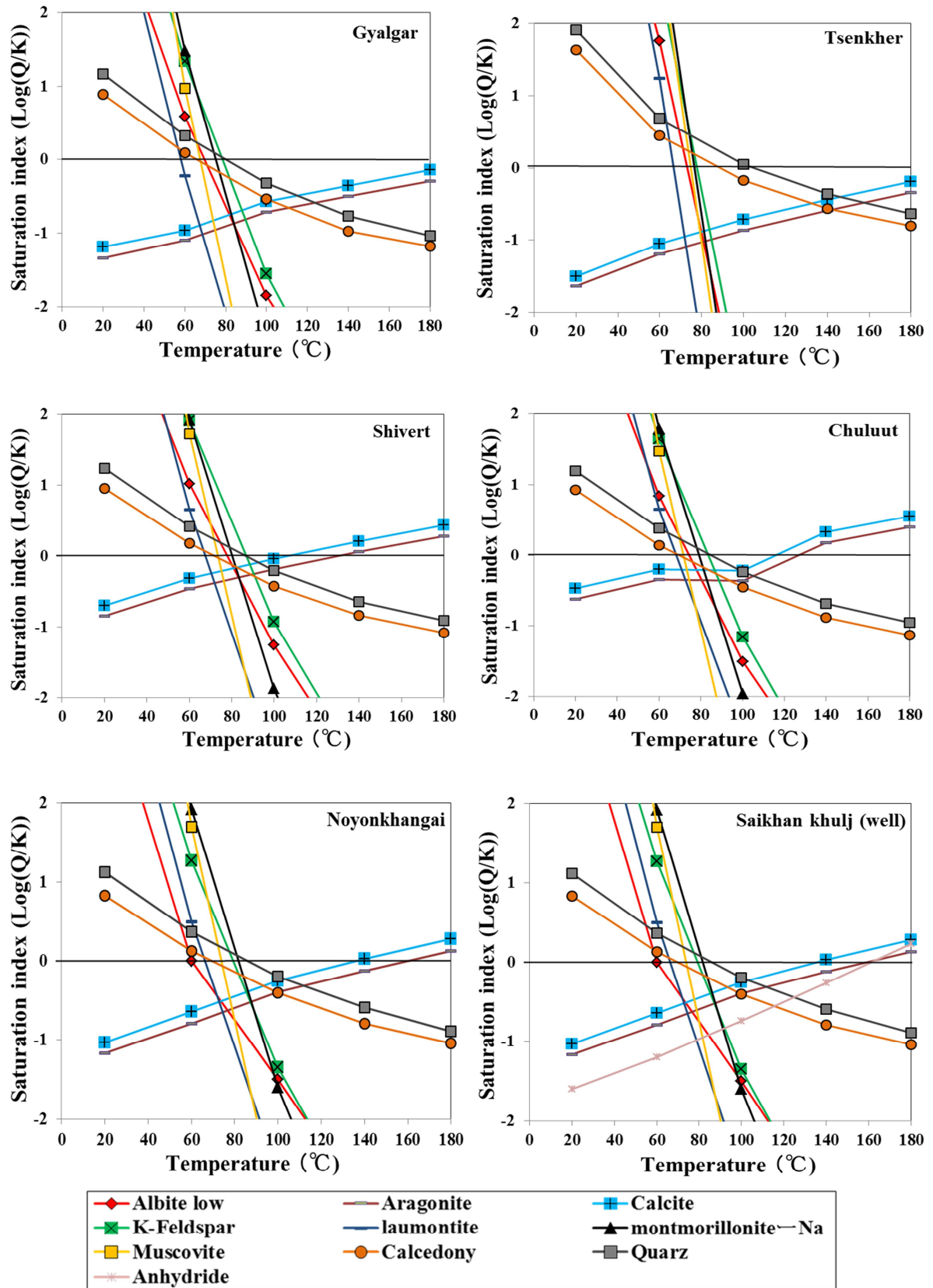
Fig.3.10. Saturation index (log Q/K) vs temperature calculated with the PHREEQC (Parkhurst and Appelo, 1999) program for hot springs in the northeastern part of Khangai area.

Anhydrite was also considered but not found to cluster, except for Saikhan hulj and

as well as the other minerals. The minerals anhydrite and aragonite are in equilibrium (SI=0) at 160°C of the Saikhan hulj. The calculated equilibrium temperatures range from 70 to 90°C of the hot springs in the study area. The chalcedony temperature estimates (Table 3.3) lie within (or close to) the subsurface temperature range estimates from the SI.

3.4.5. The silica-enthalpy mixing model

The silica-enthalpy mixing model proposed by Fournier (1977) may be used as an aid to evaluate subsurface temperatures. The silica-enthalpy mixing model may be used to determine the temperature of the hot water component, provided the silica has not precipitated before or after mixing, and there has been no conductive cooling of the water (Truesdell and Fournier, 1977).
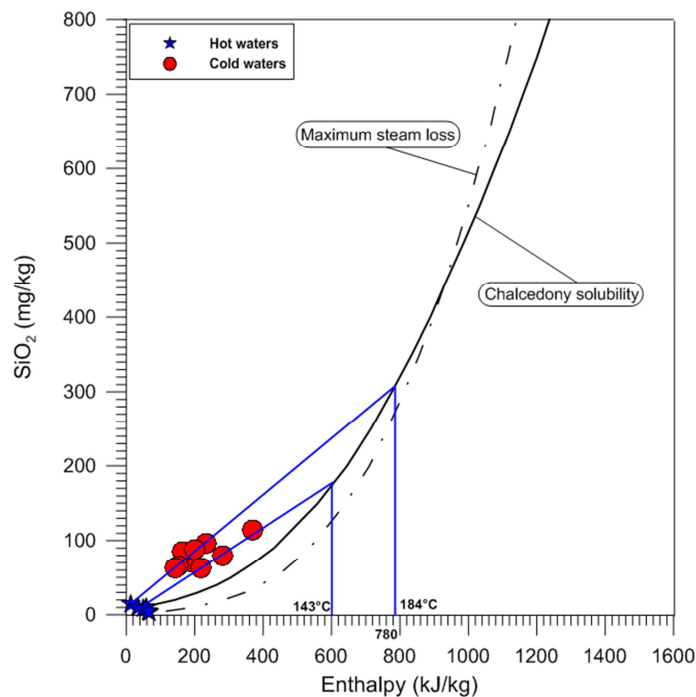

Fig.3.11. The silica-enthalpy mixing model for samples from the northeastern part of Khangai area

Figure 3.11 depicts the silica-enthalpy mixing model based on chalcedony solubility. The cold groundwater sample was assumed to be represented by the available data for the chemical composition of cold springs in the area. The blue line between the cold water and the mixed thermal water intersects the chalcedony solubility curve where enthalpy is equal, from 600 to 780kJ/kg, and corresponds to the estimated reservoir temperature from 143 to 184°C. Subsurface temperature estimates using this method are higher than those obtained using the chalcedony geothermometer, indicating that most of the hot waters have probably mixed with cooler water in the reservoir or that conductive cooling probably took place

during the up flow of the hot water.

In summary, these estimates of underground temperature were obtained using 3 different methods suggested by geothermometers, mineral saturation state and mixing model. The result shows that calculated geothermometers temperature ranges from 101^OC - 156^OC, calculated equilibrium temperatures range from 70 to 90^oC and mixing model temperature between 143 and 184°C respectively. The large range of convergence temperature is probably mixed with shallow cold and deep thermal groundwater. The underground temperature in each reservoir is estimated to be $120 \pm 40℃$ and indicating a low temperature geothermal resource in the study area.

3.5.   Summary and conclusions

Characteristics of hot springs and the geothermal resources of the north eastern part in the Khangai area, Mongolia

➢ The hot springs belong to the Na^+-HCO_3^- and Na^+-SO_4^{2-} type whereas all river waters were characterized as the Ca^{2+}-HCO_3^- type.

➢ The hot springs are enriched in Na^+ and K^+ and depleted in Ca^{2+} by ion exchange with underlying clay minerals and become more alkaline (higher pH) than the cold springs.

➢ The ion concentrations of hot springs were higher than those in the cold springs and river waters

➢ The δD and $δ^{18}$O values for water samples indicate that the hot and cold springs are of meteoric origin without isotope exchange with rock

➢ The heat source is derived from the radiogenic and He and Ne gas come from the decay of U-Th.

➢ The carbon species is derived from organic sources.

➢ The underground temperatures in each reservoir are estimated to be $120 \pm 40℃$, indicating a low temperature resource.

➢ The hot waters in the Khangai area belong to low temperature resources. These resources can be used for room heating and production of electricity by a binary system.

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Chapter 4

Summarizes of the main conclusions and recommendations

from this study

The geology of hot springs in the Khangai area comprises Devonian sedimentary units, Upper Carboniferous granite and quartz-diorite, which are covered by unconsolidated Quaternary sediments. Upper Carboniferous granitic rocks are common, and intrude the older sedimentary unit. Intrusive rocks include leucocratic biotite-hornblende granite, quartz-diorite and granodiorite (Lhagva, 1975).

There are 42 hot springs in Mongolia and from them 32 hot springs are located in the Khangai area. In the Khangai mountain region, geothermal fields occur in five provinces (Zavkhan, Bayankhongor, Uvurkhangai, Arkhangai and Bulgan).
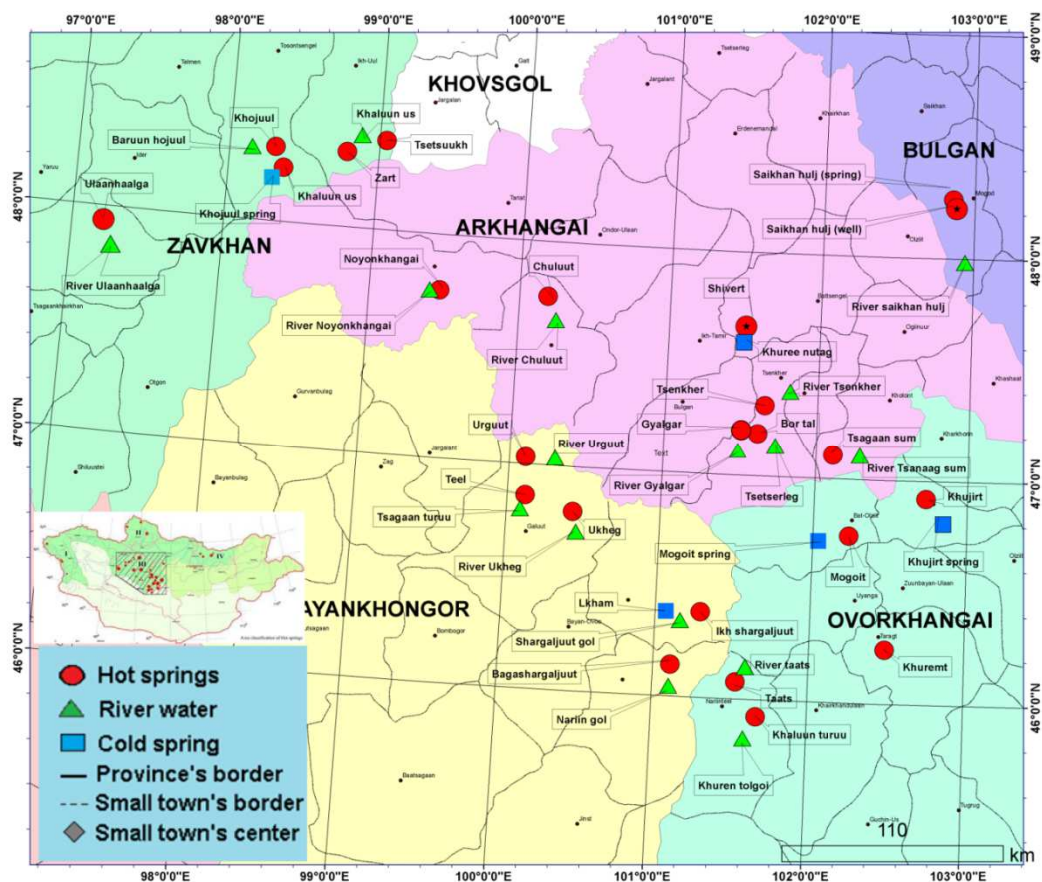

Fig.4.1. Location of sampling points in the Khangai area.

In this study were determined chemical and isotopic compositions in 46 hot and cold spring waters (24 hot springs, 5 cold springs and 17 river waters) of Khangai area (Figure 4.1). To identify changes of main chemical composition of hot spring waters within different times we were compared present studies results with the previous studies 25 hot spring waters results.

The δD and $\delta^{18}O$ values of hot water samples in the Khangai Mountain region vary from -87 to -126‰ and -12 to -17‰, respectively. The δD and $\delta^{18}O$ values of cold springs and river waters vary from -78 to 127‰ and -11 to -17‰, respectively and are similar to those for hot spring water samples. The hot and cold spring waters in the Zavkhan province and at high altitude have more negative δD and $\delta^{18}O$ values than those of other provinces. There is no evidence of $\delta^{18}O$ shift which means that geothermal water is meteoric water in which little water-rock isotope exchange has taken place. In the study area, $\boldsymbol{\delta}D$ and $\boldsymbol{\delta^{18}O}$ ratios of cold waters are slightly higher than those of hot springs. Enrichments for D and ^{18}O are about 4 to 25‰ and 1 to 4‰, respectively. The depletion in D and ^{18}O in the hot spring waters may be due to a different source associated with precipitation falling at higher altitude than in the study area.

$^3He/^4He$ ratios are range R/RA from 0.007 to 0.009 ($0.069*10^{-6}$ to $0.15*10^{-6}$) and $^4He/^{20}Ne$ ratios are range from 450 to 672 respectively. The He and Ne gas come from the decay of U-Th. The heat source is derived from the radiogenic of hot waters in the study area. The ^{13}C isotopic ratios in the study area thermal and cold waters range from -13 to -17‰. This means the carbon species (HCO_3) in hot springs is derived from organic sources. The $\delta^{34}S$ values vary from +4 to +19 ‰. The $\delta^{34}S$ values vary within a wide range independent of their sulfate contents. Based on the He/Ne and ^{13}C ratios, sulfur in hot springs may be of sedimentary origin.

The water temperature of hot spring water ranges from 23 to 95 °C and the pH values range from 8.1 to 9.8, indicating alkaline characteristics. The total dissolved solids

(TDS) are between 214 and 778 mg/L. In contrast, the water temperatures of cold spring and river waters are ranging from 3 to 19°C and the pH values range from 6.4 to 8.6. Their total dissolved solids (TDS) concentration is between 40 and 509 mg/L lower than that of the hot springs.
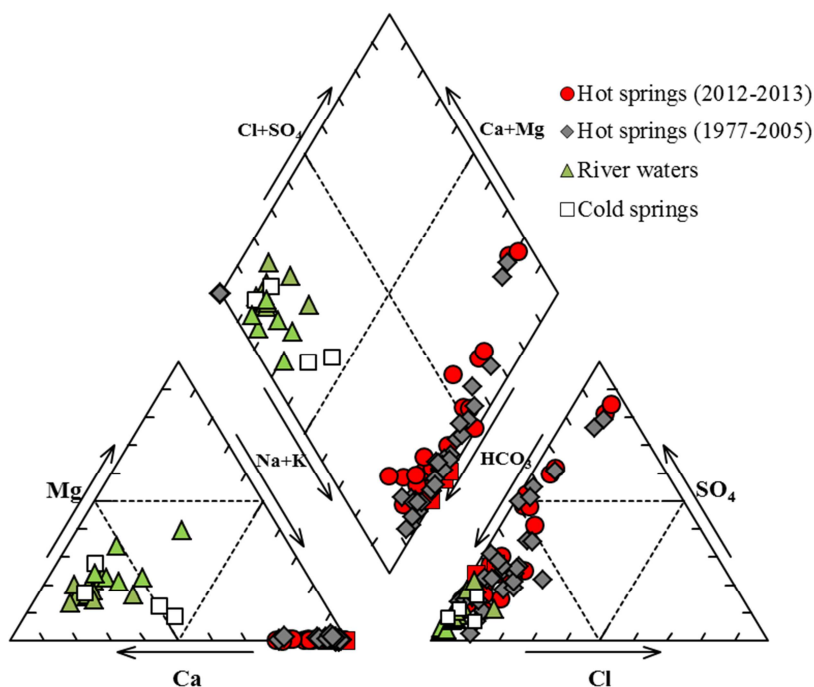

Fig.4.2. Piper diagram for water samples in the Khangai area

The chemical composition of the hot springs in the Khangai area is characterized by two types (Figure 4.2.). Most of the hot springs located in the southern and central part in the study area (Chapter II; sample Nos. 1-10 or located in the Bayankhongor and Uvurkhangai provinces and Chapter III; sample Nos. 1-7 or located in the Arkhangai province) are of the Na^+-HCO_3^- type except for one hot spring (Na^+-SO_4^{2-} type; sample No. 8 of Chapter II). The hot springs in the west northern and east northern part (Chapter II; sample Nos 11-15 or located in the Zavkhan province and Chapter III; sample No 8 and 9 or located in the Bulgan province) are of the Na^+-SO_4^{2-} type except for one hot spring water (Chapter II; sample No. 12 or located in the Zavkhan province) is of the Na^+-HCO_3^- type. The cold springs and river waters are of the Ca^{2+}-HCO_3^- type except for sample No. 19 of Chapter II ($Na+$-HCO_3^- type). The Ca^{2+} concentration of hot springs and well (Chapter II; sample No 11-15 and Chapter III; sample No 8 and 9) in Zavkhan and Bulgan provinces

are up to 45 mg/L than higher that hot springs in the other provinces (Chapter II; sample No 1-10, Bayankhongor, Uvurkhangai and Chapter III; sample No 1-7, Arkhangay province). The cold spring and river waters are enriched in Ca^{2+}, Mg^{2+} and HCO_3^- due to dissolution of carbonate rocks such as dolomite commonly observed in the study area. In contrast, the hot waters are enriched in Na^+ and K^+ and depleted in Ca^{2+} by ion exchange with underlying clay minerals.

We have calculated of underground temperature were obtained using 3 different methods suggested by geothermometers, mineral saturation state and mixing model. The result shows that calculated geothermometers temperature ranges from 73^oC – 156^oC, calculated equilibrium temperatures range from 70 to 90^oC and mixing model temperature between 117 and 184°C respectively (Figure 4.3). The large range of convergence temperature is probably mixed with shallow cold and deep thermal groundwater. The underground temperature in each reservoir are estimated to be $120\pm40^{\circ}\mathrm{C}$ and indicating a low temperature geothermal resource in the study area.
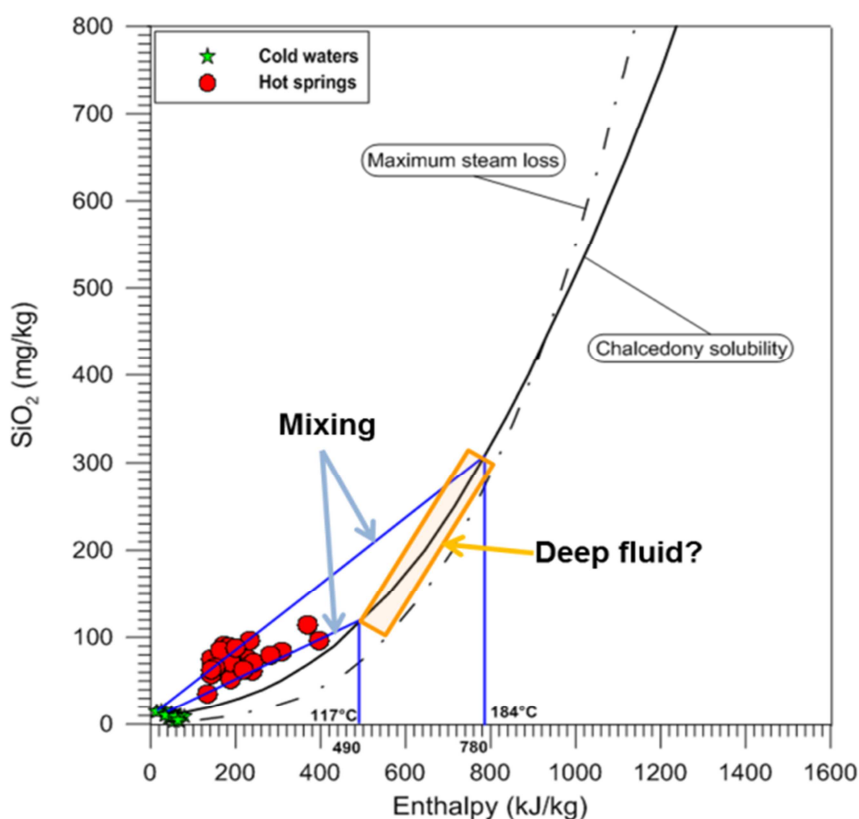

Fig.4.3. Silica-enthalpy mixing model for hot spring in the Khangai area, Mongolia

We concluded that the hot waters in the Khangai area belong to low temperature resources. These resources can be used for room heating and production of electricity by a binary system. It is advisable in all geothermal direct use systems to isolate the geothermal fluid from the building heating system it serves. Though the Ca and Mg contents in the hot springs of the Khagai area are comparatively small, this strategy greatly reduces the extent of geothermal fluid chemistry induced corrosion and scaling in the user's system. It is considered that the district heating indirect systems, which are economically reasonable against direct heating system, are more suitable in the Mongolian rural towns.

List of published articles

1. Dolgorjav Oyuntsetseg, Darmaa Ganchimeg, Amgalan Minjigmaa, Akira Ueda and Minoru Kusakabe (2015) Isotopic and chemical studies of hot and cold springs in western part of Khangai Mountain region, Mongolia, for geothermal exploration. *Geothermics*, 53, 488–497. http://doi.dx.org/10.1016/j.geothermics.2014.08.010

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