



GEOCHEMICAL CHARACTERIZATION OF THERMAL FLUIDS FROM THE KHANGAY AREA, CENTRAL MONGOLIA

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ABSTRACT

In the current study, chemical analyses of water samples from 32 hot springs located in the Khangay area in Central Mongolia were used for interpretation. The Cl-SO₄-HCO₃ and Na-K-Mg ternary diagrams, silica and cation geothermometers, mixing models, saturation index plots, and the relationship between Cl and B and stable isotopes were used to characterize the waters and estimate the subsurface temperature. The results show that most of the waters are in partial equilibrium with the rock. The hot waters in the study area can be classified as bicarbonate-sodium type and sulphate-sodium type waters. Values for the chalcedony geothermometer and the Na/K geothermometer values are quite different. According to the relationship between Cl and B, all the waters indicated have low B/Cl ratios, suggesting that they originate from old hydrothermal systems. The $\delta^{18}\text{O}$ and δD ($\delta^2\text{H}$) are used to trace and determine the origin and movement of groundwater. Thermal waters have more negative $\delta^2\text{H}$ values than cold waters. All the waters are close to the local meteoric line, parallel to the world meteoric line, indicating that the hot and cold waters are of local meteoric origin, with no apparent $\delta^{18}\text{O}$ shift. This may indicate that hydrothermal alteration reactions have long ceased occurring, that aquifer temperatures are not high, or that good permeability exists in the reservoir. The silica-enthalpy mixing model predicts a subsurface reservoir temperature between 143 and 245°C and most of the hot waters have probably mixed with cold water.

1. INTRODUCTION

Mongolia is a large (1,570,000 km²), sparsely populated central Asian country, with most of its people engaged in agriculture-related industries (accounting for 33% of GDP). Mongolia has no geothermal power generation and there are few rivers suitable for hydroelectric power generation. Mongolia has a centuries-long tradition of using geothermal water from natural springs for medical purposes. Direct use for heating and bathing is at present the only utilization of geothermal energy in Mongolia (Bignal et al., 2004).

In the current study, 32 hot springs located in the Khangay area, Central Mongolia, were selected. These are hot springs with surface temperatures ranging from 32 to 92°C, pH values between 8 and 9.6 and total dissolved solids (TDS) between 210 and 830 ppm. The sampling was carried out in 1977-2008, as a part of the scientific collaboration between the Earth Crust Institute, the Siberian

branch of the Russian Academy of Science and the Institute of Chemistry and Chemical Technology of the Mongolian Academy of Science. The sampling for isotope analysis was carried out in 2008 by the Laboratory for Stable Isotope Geochemistry of the Institute of Geology and Geophysics of the Chinese Academy of Science. The main objective of this study is the interpretation of this data. The report consists of the following main parts:

- The geology of the area;
- Geochemical and sampling methods for thermal waters;
- Evaluation of chemical classification of the thermal fluid;
- Estimation of subsurface temperatures by chemical geothermometry and equilibrium calculations;
- Relationship between Cl and B concentrations;
- Evaluation of mixing processes;
- Analysis of stable isotopes of oxygen and hydrogen.

2. BACKGROUND AND STUDY AREA

Mongolia is situated in the northern part of Central Asia, far from the oceans, on a high plateau surrounded by mountain ridges. Surrounded by Russia in the north and China in the south, the mountainous country's mean elevation is about 1,600 m above sea level and it has a population of 2.9 million. The northwest and central parts of Mongolia are high mountainous forest regions, whereas the eastern part is a vast plain steppe and the southern part is a semi-desert. The lowest point is Huhk Lake, at 560 meters above sea level, and the highest point is Huiten peak in the Mongolian Altay mountain range (4,374 m). The Mongolian lands are of plicate uplift (mountainous) zones and lakes and concave zones (Ministry of Agriculture and Industry of Mongolia, 1999). The territory of Mongolia is divided into eight zones by way of the geological, tectonic and hydro-dynamic systems, the thermal fluid zones and the physico-chemical states (Dorjderem, 2001). The Khangay and Khenty range zones have open systems of hydrothermal resources. The Khuvsgul zone is a semi-open structure, while closed geothermal systems are in the Dornod–Dariganga zones, which consist of the areas and basins of the Orkhon and Selenge rivers and the Great Lake concaves. In the areas of recent tectonic activity and extinct volcanism, namely Khangay, Khenty, Khuvsgul and Mongol Altay, in the Mongolian plicate uplifts with convective hydrological systems, there are dynamic systems where the geothermal hot water is continually being discharged to the surface, to rivers and fills. Geothermal resources in Mongolia are mainly distributed in Khangay and Khenty, around the Khuvsgul Lake and the Mongol Altay plate forms, due to tectonic developments during the second geodynamic Cenozoic age. A geophysical survey on the crustal structure has established that accumulative heat sources (magma intrusions) are located near the surface under the Khangay Khenty mountain region.

Mongolia has 44 hot springs and one steam field in these uplifts (Figure 1). The hot springs are divided into four areas based on distribution and hydrogeological characteristics:

- I. The Mongol Altay area is located in the western province of the country. This area has five sodium-bicarbonate type hot springs, with surface temperatures between 29 and 33°C.
- II. The Khuvsgul lake area is located in the northern part of the country. This area has three hot springs, with surface temperatures between 21 and 59°C. They are of sodium-sulphate, bicarbonate, and sodium–bicarbonate and sulphate type.
- III. The Khangay area is located in the central province of the country. This area has 32 sodium-bicarbonate and sulphate type hot springs. The surface temperatures range between 30 and 92°C.
- IV. The Khentey area is located in the northeast province of the county. This area has four sodium-bicarbonate type hot springs. The surface temperatures are between 34 and 88°C.

In this paper, data from 32 hot springs in the Khangay area in Central Mongolia are used (Figures 1 and 2). The Khangay geothermal field extends into six provinces (Zavkhan, Arkhangay, Bayankhongor, Uvurkhangay, Bulgan and the southern part of the Khuvsgul). The elevation of the hot springs in the Khangay area is in the range of 1,335-2,500 m above sea level (Popov, 1963).

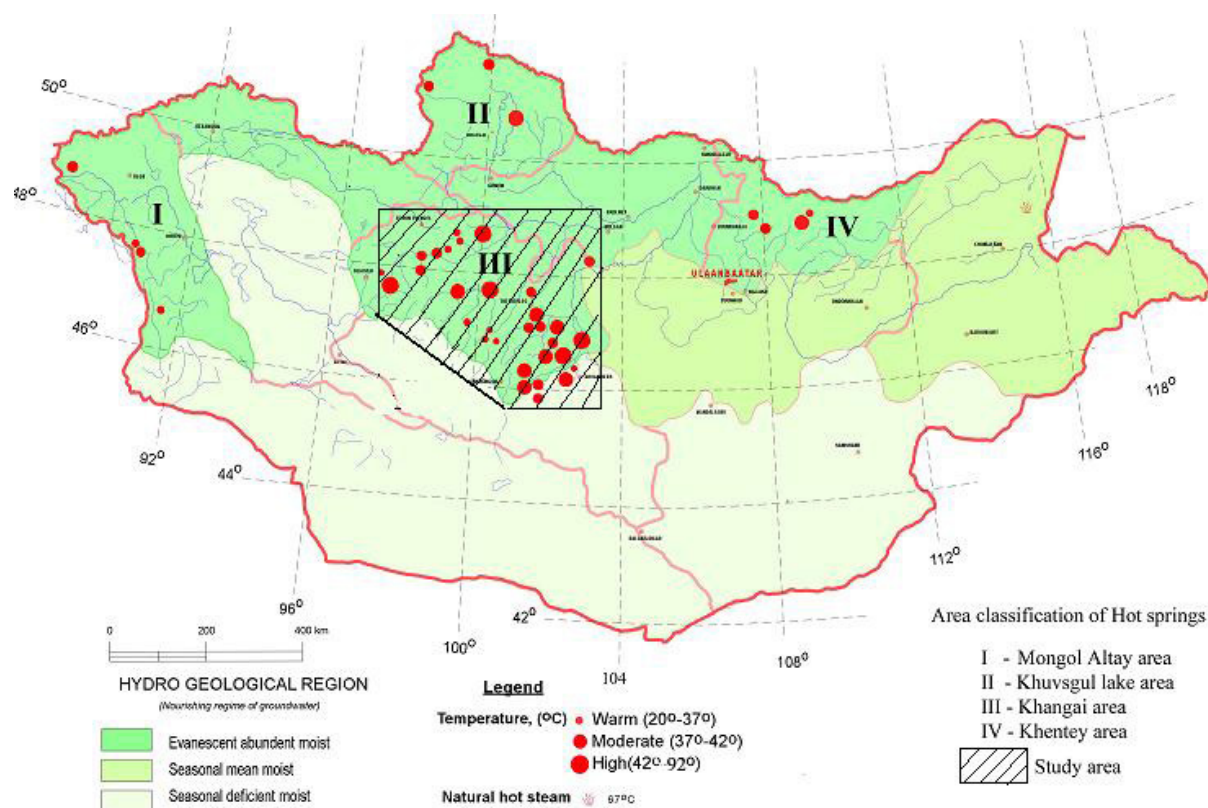


FIGURE 1: Districts of hot springs in Mongolia (Tseesuren, 2001)

The total area of the Khangay Range is 350,000 km² (Figure 2). The Khangay Range is an area of extinct volcanism (repeated eruptions), severe earthquakes and has a wide distribution of hot springs. The area has a specific zone with abundant renewable hydrothermal resources. The chemical composition of low-temperature tectonic geothermal waters from the hot springs in the Khangay Range area is influenced mainly by the chemistry of the rocks that the water has come into contact with, and the temperatures to which the water has been raised.

3. GEOLOGICAL PROPERTIES OF THE STUDY AREA

Tectonically the territory of Mongolia occupies a key position in the Central Asian Orogenic Supercollage or Altaids, located between the Siberian craton in the north and Katsasia (Tarim and sino-Korean cratons) in the south. The Khangay dome in west-central Mongolia is the western end of the Khangay Daurian terrain of the Mongol-Okhotsk orogenic belt. The Khangay region consists of intensely deformed Carboniferous and Devonian sedimentary rocks intruded by huge bodies of granites and granodiorites from late Paleozoic and early Mesozoic periods. Numerous late Cenozoic, high potassium alkaline basaltic provinces are distributed throughout the Khangay area. According to existing data, the mantle plume beneath the region resulted in developing 4-5 stages of magmatic processes from the late Paleozoic to the late Cenozoic (Holocene epoch) in this region. It still shows an active, long-living mantle plume affecting the geothermal gradient in the crust. Therefore, the India-Asian collision stress from the southwest (Algay transpressional belt) and the Baikal extensional

structures from the north are playing an important role for neo-tectonic faulting and perhaps Tertiary magmatic activation in the Khangay dome. There are a number of normal northeast and northwest trending faults within the Khangay mountain region. Most of the hot springs are controlled by intersections of those 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 Khangay dome reaches 50-60 mW/m². The high heat flow of the Khangay dome is reflected in the localization of over 32 hot and warm springs of the 44 known in the entire Mongolian territory with temperatures of 21-92°C. Uplift, alkaline magmatism, high heat flow, lithospheric thinning and neo-tectonic faulting are characteristic signatures of the geothermal resources in the Khangay region. The Khangay region has been described as 'domed'. The basement of the dome is a problematic issue for many geologists and consists of a Precambrian block that contains tonalitic and trondhjemitic gneisses, potassic granitoids and various magmatites and high grade schist and gneisses. According to Kovalenko (1996), the geological interpretation of the isotopic data 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). The Khangay region consists of intensely deformed Carboniferous and Devonian sedimentary rocks which were deposited on a basement intruded by huge bodies of granite and granodiorite from the late Paleozoic and early Mesozoic. Numerous late Cenozoic, high potassium alkaline basaltic provinces are distributed throughout the Khangay area (Figure 2). They are covered by unconsolidated Quaternary sediments.

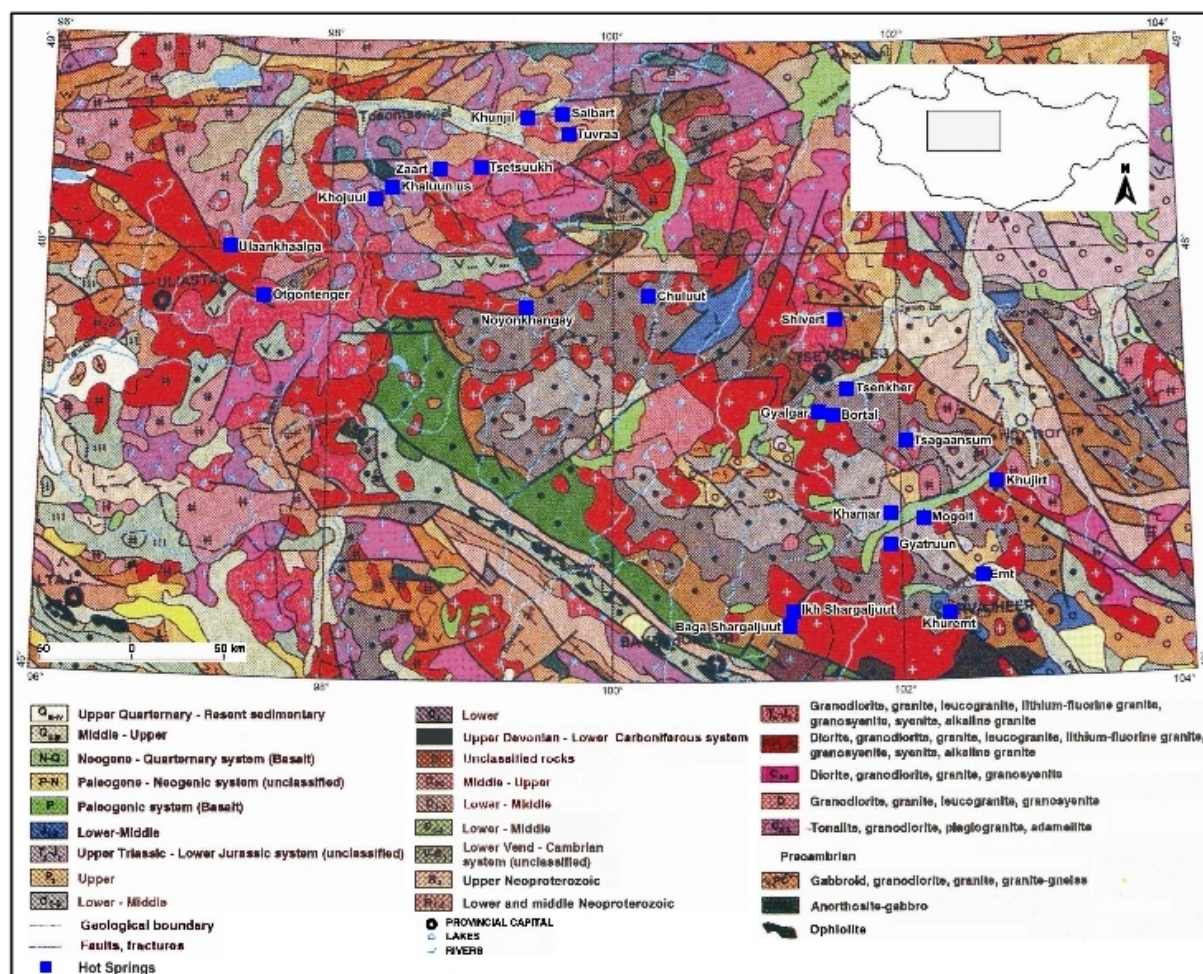


FIGURE 2: Geological map of the Khangay area in Mongolia (Barsbold and Dorjnamjaa, 1993)

3.1 Granitoid magmatism

In the central and southern Khangay region, batholithic bodies are widely exposed (Figure 2). Late Paleozoic granitoids are Carbon to Permian and early Mesozoic granitoids are Triassic to Jurassic batholithic. The batholithic bodies are named the Khangay complex, the Sharus river complex and the Egiin davaa complex in usual geological map sheets (Barsbold and Dorjnamjaa, 1993). The two main units in the study area have been ascribed to the Permian Khangay complex and the Triassic- Jurassic Egiin Davaa complex. These units are predominantly granite and granodiorite associations (Figure 2). The granitoids are medium enriched in aluminium, K-subalkaline and chalk-alkaline series. The granitoids are slightly enriched in Pb, Th, Nd, Sm, Tb, but depleted in Nb, P, Ti, Ba (especially the granites). Its REE composition is relatively higher than the HREE in the granitoids, but it also has a large, negative Eu anomaly in the granite, and slight or no Eu anomaly in the granodiorites (Igmr-transaction, 2008).

3.2 Cenozoic volcanism

Five stages of high potassium alkaline basaltic provinces are distributed throughout the Khangay region from the late Cenozoic period. Their general characteristics are tholeiite basalts of Oligocene (28.5 ± 1 Ma, Devyatkin, 1981), alkali trachybasalts, trachyandesite-basalts and trachyandesite of Miocene (15-11 Ma, Yarmolyuk et al., 1994) and Pleistocene (2.5-1.75 Ma, Devyatkin, 1981) and K-alkaline basalts of Holocene (110 ka, Enkhtuvshin, 1995). Tertiary lavas occur in sequences exceeding 200 m in thickness that constitute plateaus making up much of the high Khangay, 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). Proposals include: a mantle plume, mantle plume processes combined with effects of the India-Asia collision; a shallow thermal anomaly heating a metasomatized lithosphere; a hot spot volcanism; and a crustal weakness along cratonic boundaries resulting in a thin lithosphere as well. Generally, a geochemical analysis of the Cenozoic basalts in Khangay shows that the basalt fields were supplied from the enriched mantle (Igmr-transaction, 2008).

3.3 Neo-tectonic

The Khangay doming began in the middle Oligocene, and was contemporary with alkaline volcanism throughout the Khangay Mountains. The young, normal fault systems in the Khangay are perhaps a response to crustal uplift and doming in the range. In addition, the faults with the clearest evidence for Holocene activity within the Khangay occur at relatively high elevations suggesting that these areas are most actively extending. West-central Mongolia has been the site of four great earthquakes ($M_s > 8.0$) and many moderate sized ones (M_s 5.3-7.5) in the 20th century. This activity is related to the peculiar position of Mongolia, between the extensional structure of the Baikal rift system and the transpressional mountain belt of Central Asia (the collision zone between India and Asia). The active faulting in western to west-central Mongolia forms a pattern resembling a parallelogram of conjugate strike-slip faulting surrounding the Khangay dome. NW-SE or N-S right-lateral faulting occurs in the west (Mongolian Altay) and east (Mogod), while E-W left lateral faulting occurs to the north (Bulnay) and south (Gobi-Altay). There are a number of northeast and northwest trending normal fault scarps within the Khangay area and probably many more that have not been discovered yet. Northeast-striking Cenozoic normal faults at a high elevation are the most recently active. The southern Khangay dome region is dominated by Late Cenozoic normal faults that bound small half grabens. India-Asian collision stress from the southwest (Gobi-Altai) and Baikal extensional structures from the north as well as uplifting are playing an important role for neo-tectonic faulting and perhaps tertiary magmatic activation in the Khangay area (Igmr-transaction, 2008).

4. GEOCHEMICAL METHODS IN GEOTHERMAL EXPLORATION

Geochemical methods are relatively inexpensive and can provide valuable information on the temperature conditions in a geothermal reservoir and the source of the geothermal fluid. The use of geochemistry in geothermal exploration has a profound importance in inferring subsurface conditions by studying the chemistry of surface manifestations or discharge fluids that carry the signature of the deep geothermal system.

Chemically inert constituents that are conserved and not changed by chemical reactions provide information on the sources of the fluid. Such sources are termed tracers. On the other hand, reactive components, such as SiO_2 , CO_2 , H_2S etc., react with the minerals and other reactive constituents and can contain information about the subsurface conditions. Such components are called geointicators (Arnórsson, 2000a). Geothermometers are geointicators that can be used to estimate subsurface temperature using the chemical and isotopic compositions of discharges.

4.1 Classification of thermal waters

4.1.1 Cl-SO₄-HCO₃ ternary diagram

The Cl-SO₄-HCO₃ ternary diagram is used to classify geothermal fluids on the basis of the major anion concentrations (Giggenbach, 1988). It helps to discern immature unstable waters and gives an initial indication of mixing relationships or geographic groupings. The position of a data point in this plot is obtained by first calculating the sum, Σ , of the concentrations, C (mg/kg) of all the species involved:

$$\Sigma_{anion} = C_{Cl} + C_{SO_4} + C_{HCO_3} \quad (1)$$

The next step is to obtain the percent (%) of every constituent using the following equation:

$$\%Cl = \frac{100C_{Cl}}{\Sigma_{anion}}; \%SO_4 = \frac{100C_{SO_4}}{\Sigma_{anion}}; \%HCO_3 = \frac{100C_{HCO_3}}{\Sigma_{anion}} \quad (2)$$

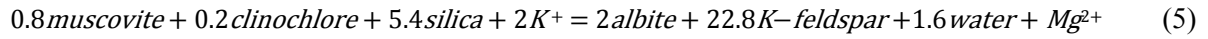
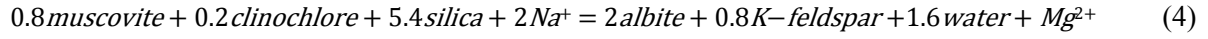
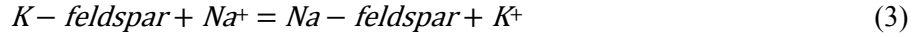
This plot indicates the compositional ranges for the different kinds of waters typically found in geothermal areas, such as:

1. Mature NaCl waters of neutral pH, which are rich in Cl and plot near the Cl vertex. This water type, also known as “alkali-chloride” or “neutral-chloride”, is typical of the deep geothermal fluid found in most high-temperature systems. Chloride is used as a tracer in geothermal investigations because it is a conservative ion in geothermal fluids, as it does not take part in reactions with rocks after it has dissolved. Chloride does not precipitate after it has dissolved; it does not return to the rock so its concentration is independent of the mineral equilibrium that controls the concentration of the rock-forming constituents.
2. Na-HCO₃ waters are indicated as peripheral waters.
3. Volcanic and steam heated waters are generated through the absorption of either high-temperature HCl-bearing volcanic gases or lower-temperature H₂S-bearing geothermal vapours into the groundwater.

4.1.2. Na-K-Mg equilibrium diagram

This triangular diagram is used to classify waters into fully equilibrated, partially equilibrated and immature waters. It can be used to predict the equilibrium temperature and also the suitability of thermal waters for the application of ionic solute geothermometers. It is based on the temperature dependence of the full equilibrium assemblage of potassium and sodium minerals that are expected to

form after the isochemical recrystallization of average crustal rock under conditions of geothermal interest (Giggenbach, 1988). The use of the triangular diagrams is based on the temperature dependence of the three reactions:



The Na-K-Mg triangular diagram shows attainment of the water-rock equilibrium if the data point plots on the full equilibrium line, or suggests a field of immature water below the “immature water curve” which indicates an initial dissolution of minerals before equilibrium reaction sets in. No geoindicators can be used in the latter case. The field of partial equilibrium lies between the curves, and suggests either a mineral that has dissolved, equilibrium reactions have set in but equilibrium has not been reached, or a mixture of a water that has reached equilibrium (e.g. a geothermal water) with a dilute unequilibrated water (e.g. cold groundwater). Geothermometer temperatures may often be deduced from such a position. Points close to the \sqrt{Mg} corner usually suggest a high proportion of relatively cold groundwater, not necessarily “immature”.

Again, it is based on the use of triangular diagrams. Because of the non-linear term C_K^2 , the square root is taken of the Mg contents and the coordinates for the ternary diagram are calculated according to (Giggenbach, 1991):

$$S = C_{Na^+}/1000 + C_{K^+}/100 + \sqrt{C_{Mg^{2+}}} \quad (6)$$

$$\begin{aligned} \% Na &= C_{Na^+}/10S \\ \% K &= C_{K^+}/S \\ \% Mg &= \sqrt{C_{Mg^{2+}}}/S \end{aligned} \quad (7)$$

where C_{Na^+} , C_{K^+} and $C_{Mg^{2+}}$ represent concentration of the cation expressed as ppm.

4.2 Geothermometers

The application of chemical geothermometers is one of the most important methods for the exploration and development of geothermal resources. It is useful for predicting subsurface or reservoir temperatures and obtaining valuable information about what is happening in the reservoir during exploitation. Cooling of the water in the upflow zones of a geothermal system may occur by conduction, boiling and/or mixing with cold water. The basic assumption is that a temperature dependent equilibrium is attained between the fluid and the minerals in the reservoir. The temperatures in geothermal reservoirs are generally not homogeneous, but variable, both horizontally and vertically, so geothermometry is useful for revealing the temperature of the aquifer feeding drillholes. Temperatures encountered in a deep drillhole may be higher than those indicated by chemical geothermometry, particularly if the waters investigated are fed by shallow aquifers (Arnórsson, 1991). The silica (quartz and chalcedony), Na/K and Na-K-Ca geothermometers are the most important. These geothermometers are all based on the assumption that specific temperature-dependent mineral-solution equilibria are attained in the geothermal reservoir.

4.2.1 Quartz geothermometers

The quartz geothermometer is based on the solubility of quartz and is used to estimate subsurface temperatures in hot spring systems. The solubility of quartz is dependent on pressure, temperature and

salinity. The quartz geothermometers work best for waters in the subsurface temperature range of 120-250°C (Arnórsson, 2000b). The basic reaction for the dissolution of silica minerals is:



For many silicate-water reactions, it is a good approximation, at least up to about 250°C, to take the enthalpy of such reactions to be constant. This expression is particularly useful when experimental or drillhole data, which are used to calibrate geothermometers, only cover a limited temperature range and need to be extrapolated, either to lower or higher temperatures.

In this study, the following equation for the quartz geothermometer was used.

Quartz – no steam loss (Fournier, 1977):

$$t^{\circ}\text{C} = \frac{1309}{5.19 - \log\text{SiO}_2} - 273.15 \quad (9)$$

4.2.2 Chalcedony geothermometers

This geothermometer is based on the solubility of chalcedony. Fournier (1991) suggested that there is ambiguity in the use of silica geothermometers at temperatures below 180°C as chalcedony appears to control dissolved silica in some places and quartz in others. Chalcedony is a very fine-grained variety of quartz, which is probably not a separate mineral but a mixture of quartz and moganite and, with time, it will probably all change to quartz (Gíslason et al., 1997). Temperature, time and fluid composition all affect different crystalline forms of silica. Thus, in old systems, where water has been in contact with rock at a given temperature for a relatively long time, quartz may control dissolved silica at temperatures down to 100°C. In younger systems, chalcedony may control dissolved silica at temperatures up to 180°C. In this study, the following equations for chalcedony geothermometers were used.

Chalcedony – no steam loss (Fournier, 1977):

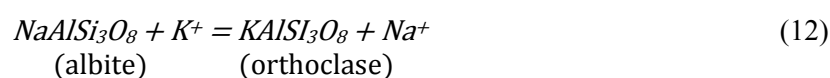
$$t^{\circ}\text{C} = \frac{1032}{4.69 - \log\text{SiO}_2} - 273.15 \quad (10)$$

Chalcedony – no steam loss (Arnórsson et al., 1983):

$$t^{\circ}\text{C} = \frac{1112}{4.91 - \log\text{SiO}_2} - 273.15 \quad (11)$$

4.2.3 Cation geothermometers

Cation geothermometers are based on ion exchange reactions with temperature-dependent equilibrium constants. A typical example is the exchange of Na^+ and K^+ between co-existing alkali feldspars:



Two assumptions are made, that the activities of the solid reactions are in unity and the activities of the dissolved species are equal to their molal concentrations in an aqueous solution. The equilibrium constant, K_{eq} for this reaction is:

$$K_{eq} = \frac{(KAlSi_3O_8)(Na^+)}{(NaAlSi_3O_8)(K^+)} \quad (13)$$

If the activities of the solid reactants are assumed to be in unity and the activity of the dissolved species is about equal to their molal concentrations, the equation will be reduced to:

$$K_{eq} = \frac{(Na^+)}{(K^+)} \quad (14)$$

Several authors have suggested empirical Na/K geothermometers based on experiments and obtained different results due to work with different minerals. Basaltic minerals usually give low values (Arnórsson et al., 1983) but andesitic ones high values (Giggenbach, 1988) at low temperatures. At high temperatures they converge and give similar values. The Na/K ratio works generally well for estimating temperatures of water above 200°C.

The following formulae, based on empirical correlations presented by Arnórsson et al. (1983) and Giggenbach (1988), are used in this report. The concentrations of Na and K are in mg/kg:

Na-K temperature (Arnórsson et al., 1983):

$$t^{\circ}C = \frac{933}{0.993 - \log\left(\frac{Na}{K}\right)} - 273.15 \quad (15)$$

Na-K temperature (Giggenbach, 1988):

$$t^{\circ}C = \frac{1390}{1.75 - \log\left(\frac{Na}{K}\right)} - 273.15 \quad (16)$$

4.2.4 Na-K-Ca geothermometer

The Na-K-Ca geothermometer was developed by Fournier and Truesdell (1973) for application to waters with elevated Ca^{2+} contents that give an anomalously high calculated temperature for the Na/K geothermometer. The relationships of Na^+ , K^+ and Ca^{2+} were explained in terms of the Ca^{2+} participating in aluminium silicate reactions. The amounts of dissolved Na and K are therefore influenced by the dissolved Ca, even though the final amount of aqueous Ca may be controlled largely by carbonate solubility and carbon dioxide (Nicholson, 1993). The geothermometer is entirely empirical and assumes one type of base exchange reaction at temperatures above about 100°C (concentrations are in mg/kg):

$$t^{\circ}C = \frac{1647}{\log\left(\frac{Na}{K}\right) + \beta \left[\log\left(\frac{\sqrt{Ca}}{Na}\right) + 2.06 \right] + 2.47} - 273.15 \quad (17)$$

where $\beta = 4/3$ for $Ca^{1/2}/Na > 1$ and $t < 100^{\circ}C$;
 $\beta = 1/3$ for $Ca^{1/2}/Na < 1$ or if $t > 100^{\circ}C$.

4.3 Mineral-solution equilibria

Geothermometers have been developed to predict reservoir temperature. However, various geothermometers can give different values for the temperature of a reservoir. This may be due to different reaction rates, or the reservoir mixing with cold water in the upflow zone. Reed and Spycher

(1984) have suggested that the best estimate of a reservoir temperature can be attained by considering simultaneously the state of equilibrium between specific water and many hydrothermal minerals as a function of temperature. Therefore, if a group of minerals converges to equilibrium at a particular temperature, this temperature corresponds to the most likely reservoir temperature. The rising fluid has reacted chemically with rock. The equilibrium state of minerals can be estimated by the ratio of the reaction quotient (Q) to the equilibrium constant (K). The equilibrium constant and the reaction quotient are related to the Gibbs energy through:

$$\Delta G_r = -RT \ln K + RT \ln Q = RT \ln \left(\frac{Q}{K} \right) \quad (18)$$

where R = Gas constant;
 T = Temperature (K).

The equilibrium state for a given reaction of a mineral and a solution in a geothermal system can be evaluated by the ratio of the equilibrium constant (K) for the given reaction to the reaction quotient (Q) (Arnórsson, 2000a). The saturation indices (SI) for minerals in aqueous solutions at different temperatures were computed as:

$$SI = \log \frac{Q}{K} = \log Q - \log K \quad (19)$$

where Q = Calculated ion activity product;
 K = Equilibrium constant.

All minerals that are in equilibrium at the same temperature converge to $SI = 0$; $SI < 0$ for an undersaturated solution, and $SI > 0$ for a supersaturated solution. If fluid mixes with dilute water, mineral curves will intersect at $SI < 0$, but if it has boiled at $SI > 0$.

4.4 Speciation and equilibrium - the WATCH program

The computer program WATCH (version 2.3) calculates the speciation of waters at a given temperature (Arnórsson and Bjarnason, 1993; Bjarnason, 1994). It is quite useful for the interpretation of the chemical composition of geothermal fluids, as well as for non-thermal waters. A chemical analysis of samples collected at the surface can be used to compute the composition of aquifer fluids. The program calculates aqueous speciation, using mass balance equations and chemical equilibrium. WATCH can also be used to calculate the composition of the sample after cooling or boiling, and is, thus, useful for modelling the behaviour of fluid for different designs of geothermal plants. The WATCH program can also be used to compute the concentrations of the resulting species, activity products and solubility products when the equilibrated fluid is allowed to cool conductively or by adiabatic boiling from the reference temperature to some lower temperature.

4.5 Relationship between Cl and B

The Cl/B ratio is a convenient tool for distinguishing between aquifer systems, as neither Cl nor B participates in any important mineral/solute equilibria. Thus, the boiling and cooling of the geothermal water should not change the relative concentrations of the elements (Kristmannsdóttir and Johnsen, 1982). Available literature agrees that Cl acts as incompatible in practically all natural water-rock environments, i.e. once in a solution, it stays there both at ambient and elevated temperatures (Ellis, 1970). It is not adsorbed to any marked degree on mineral surfaces (Hem, 1970) and usually does not enter common rock-forming minerals due to its large size. High-temperature water-rock interaction experiments have shown that B in common types of igneous rocks is highly

mobile and probably also incompatible. However, there is evidence that at temperatures below some 100-150°C, B is taken up from solution into secondary minerals, particularly illite and mica (Arnórsson and Andréðóttir, 1995 and references therein). B concentrations in surface and non-thermal groundwaters are, therefore, either equal to or higher than those found in precipitation water. The Cl/B ratios of water interacting with common types of igneous rocks are equal to or lower than that of sea water because the Cl/B ratio of such rocks is lower than that of seawater.

4.6 Mixing models

Mixing models have been developed to allow for the estimation of the hot water component in mixed waters in springs, or discharges from shallow drillholes. Two kinds of mixing models are used here:

1. The silica-enthalpy mixing model, (Fournier, 1977);
2. The silica-carbonate mixing model (Arnórsson, 1985).

When applying mixing models to estimate subsurface temperatures, several simplifying assumptions are made. Conservation of mass and heat is always assumed, both during and after mixing. Therefore, it is assumed that chemical reactions occurring after mixing are insignificant and do not modify the water composition.

4.6.1 The silica-enthalpy mixing model

Truesdell and Fournier (1977) proposed a plot of dissolved silica versus the enthalpy of water to estimate the temperature of the deep hot water component. There are some criteria for hot spring waters which may be appropriate for the application of this model:

- A measured water temperature which is at least 50°C less than the calculated silica and Na-K-Ca geothermometer temperatures;
- A silica geothermometer temperature which is lower than the Na-K-Ca temperature;
- A mass flow rate which is high enough to allow for only a little conductive cooling.

This model cannot be used for boiling springs because the heat is carried away in the steam after mixing.

4.6.2 The silica-bicarbonate model

This model is based on the relationship between silica and total carbonate concentrations (Arnórsson, 2000a). It is based on the assumption that practically all silica in geothermal water occurs as H_4SiO_4 and all carbonate as CO_2 . This model can be used to estimate the temperature of the hot water component in mixed waters and also to distinguish between boiled and non-boiled waters.

4.7 Stable isotopes of oxygen and hydrogen

Geothermal fluids originate mainly from meteoric water and sea water (Craig, 1963). The determination of the recharge to geothermal systems is an important aspect of geothermal investigations. This is done by measuring the hydrogen and oxygen isotope composition of the steam and water of a geothermal field; the isotopic ratio is the number of atoms of a given isotope divided by the number of atoms of the most abundant isotope of that element. It is not easy to measure absolute isotopic ratios accurately, but differences in isotopic ratios between a particular sample and a standard can be measured accurately. For this reason isotopic concentrations are conveniently expressed in the delta notation (δ) as part per thousand, or

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad (20)$$

where R stands for the isotopic ratio of the sample and standard, respectively (Craig, 1961a).

Thus, for example if water has a deuterium delta value, $\delta^2\text{H} = -50\text{‰}$, this means that its deuterium ratio is 50‰ lower than that of the standard. A positive delta value shows that the sample is more enriched in the respective isotope than the standard. Craig (1963) established the isotopic characteristics ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) of precipitation relating to latitude and altitude as well as to continental effects. Samples from higher latitudes and elevation or those collected further inland were progressively lighter (more negative values of δ). The values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in precipitation were approximately related by the meteoric water line (Craig, 1961b):

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10 \quad (21)$$

The expression above is recognized as the *World meteoric line* abbreviated as WML. It describes the global meteoric water line, and in spite of the complex interactions that occur during the meteoric process, there is a remarkably good correlation worldwide. The applications of water isotopes in geothermal studies do not only involve tracing the origin of water, but are also useful in characterizing the boiling process and in monitoring the flow of injected fluids.

5. SAMPLING AND METHODS

Thirty two water samples were collected from the Khangay area in Mongolia (Figures 1 and 2). Of these, 17 samples were collected in 2005, 2006 and 2007, while the other samples were collected in 1977 and 1978 and are characterized as the older dataset in this study. All samples were collected from thermal springs. The analyses were carried out in the field and in the laboratory. On-site analyses comprised temperature, pH, and unstable components such as CO_3^{2-} , HCO_3^- , NH_4^+ , CO_2 , H_2S and SiO_2 . The unstable components were determined by titration and by comparison methods. Water samples were passed through a 0.45 μm filter and collected in polyethylene bottles for subsequent laboratory analyses. Major cation concentrations (Ca^{2+} , Mg^{2+}) were determined by trilon-B titration, Na^+ and K^+ by inductively coupled plasma optical emission spectrometry, anions (Cl^- , SO_4^{2-} , Br^- , and F^-) by ion chromatography and CO_3^{2-} and HCO_3^- by titration using 0.1N HCl. The total dissolved solid content was determined by evaporating 1 litre of a filtered water sample at 100°C. The residue was dried at 180°C for 2 hours. Analyses of major compositions were carried out at the hydrological laboratory of the Institute of Chemistry and Chemical Technology of the Mongolian Academy of Science. Analyses of minor components and dissolved gas compositions were carried out by ion chromatography, atomic absorption spectrometry and mass spectrometry at the hydrological laboratory of the Earth Crust Institute, Siberian branch of the Russian Academy of Science. The results of the chemical analysis of thermal springs from the Khangay area in Mongolia are presented in Table 1.

TABLE 1: Chemical composition of geothermal waters from the Khangay area in Central Mongolia (in ppm)

No.	Province	Name of hot springs	Year	T _{meas} (°C)	pH	HN ₄	Na	K	Mg	Ca	HCO ₃	CO ₃	Cl	SO ₄	F	SiO ₂	H ₂ S	B	Li	TDS
1		Ulaan haalga	1977	37	8.45	1.1	147.7	5.5	0.8	8.2	10.5	59.5	16.3	204.8	13.0	75	11.54	0.2	0.35	600
2		Otgon tenger	1976	56	8.45	0.1	104.4	2.3	0.1	3.7	68.6	28.5	8.7	72.7	10.5	76	13.33	0.5	0.14	440
3	Zavkhan	Hojuul	1978		9.45	0.2	60	3.1	0.06	1.4	82.4	33	2.76	32.5	6.5	102	1.7	0.3	0.08	380
4		Haluun us	1978	35	9.14	0.2	91	3	0.61	7.41	156	18	7.3	30.7	0.02	72	7.55	0.5	0.09	440
5		Zart	2005	44	8.85	0.15	81	1.9	0.24	6.21	64.7	15	4.18	103	10.5	60	1.4	0.3	0.05	390
6		Tsetsuuh	2005	36	9.2		97.5	3.2	0.4	3.41	56.7	23	3.24	112	10.5	108	1.3	0.45	0.08	500
7	Khuvsugul	Hunjil	2007	59	8.9	0.1	152.8	4.58	0.36	11.02	48.21	1.5	28.4	253.5	9.05	95	0.17	0.3	0.24	658
8		Salbart	2007	44	8.4	0.1	207.3	4.42	0.36	28.06	35.39	1.2	70.2	392.3	9.4	52	0.57	0.4	0.74	832
9		Tsuuraa	1978	35	9	0.15	181	5.7	0.36	26.1	26.8	18	44.6	339	12.5	80	3.75	0.2	0.5	790
10	Arkhangai	Noyon Khangai	2002	38	9.2	0.4	64.93	1.3	0.24	1.8	84.21	8.4	8.86	18	4.5	84		0.6	0.12	326
11		Chuluut	2006	45	8.8		93.1	2.75	0.12	2.4	54.9	45	20.2	30.26	17.8	73	3.74	0.7	0.78	393
12		Shivert	2007	62	9	0.1	102.2	3.74	0.24	2	93.36	4.5	19.8	81.48	17.8	96	0.86	0.75	0.49	479
13		Tsenkher	2005	87	9.4	0.1	86.4	2.99	0.12	2.41	65.29	8.1	19.8	40.33	21	112	0.68	0.8	1.43	425
14		Bor tal	2005	52	9.6	0.1	76.2	1.35	0.12	2.41	50.04	10.2	27.3	36.62	14.7	61	0.85	0.75	0.55	318
15		Gyalgar	2005	52	9.4	0.1	70.55	2.07	0.24	3.61	69.56	8.4	17.7	30.04	10.3	76		0.65	0.6	334
16		Khuiten	2005	13	9.6	0.1	60.2	1.7	0.12	2.81	79.93	16.2	6.38	39.09	6.4	82	0.27	0.5	0.34	343
17		Tsagaan sum	2005	69	8.85	1.3	97.2	3.16	0.25	2	81.7	13.5	7.5	47.6	19	106	17.4	0.8	0.5	450
18	Bayan Khongor	Ih Shargaljuut	2007	92	8.75	0.2	85.8	3.53	0.1	2.22	79.3	18.0	3.1	59.1	10.5	109	16.71	0.82	0.2	450
19		Baga Shargaljuut	2005	59	8.65	0.1	91	2.78	0.03	2.75	65.9	12	6.2	59.1	13.5	83	7.5	0.78	0.18	400
20		Ukheg	1977	57	8.85	1	111.7	5.43	0.28	3.63	63.4	14.1	2.12	124.4	8	78	9.71	0.6	0.18	470
21		Urguut	1977	42	8.6		111.7	2.69	0.1	2.9	158	9	9	41.5	9	78	2.78	0.3	0.2	470
22		Teel	1977	32	9.7	0.2	65.1	0.56	0.27	3.55	48.8	18	4.4	23.2	11.5	46	11.9	0.2	0.1	250
24	Uvur-khnagai	Khujirt	2005	55	8.7	0.4	97.9	3.9	0.1	1.6	100	19.5	7.17	32.1	13.5	104	12.27	0.8	0.5	420
25		Huremt	2005	56	8.7	0.7	92.5	2.23	0.1	1.3	112.2	22.54	8.48	43.4	8.5	98	13.63	0.6	0.4	470
26		Sharga	1979	30	8.5		117.3	3.6	0.6	4.6	198.3	7.5	19.8	27.4	16	77	1.36			520
27		Gyatraun	1977	36	8	0.01	29.7	0.34	0.55	4.8	73.8	0.3	8.83	41.55		34	0.5	0.8	0.6	210
29		Mogoit	1977	72	8.6	0.01	92	2.97	0.1	1.33	75	19.5	1.96	27.5	15	104	15.85	0.79	0.6	420
30		Taats	1977	55	8.75		103.1	2.78	0.07	2.62	78.7	13.5	21.2	59.9	15	91	8.86	0.7	0.2	460
31		Emt	1977	39	8.8	0.7	123.2	5.29	0.17	1.86	151.3	22.5	12.6	22.9	18.5	101	14.24	0.37	0.2	530
32	Bulgan	Saikhan hulj	2005	53	8.3	0.1	169.8	4.04	0.12	44.89	29.29		44.7	425.9	2.15	54	0.49	0.62	0.09	810

6. CHEMICAL PROPERTIES OF THE GEOTHERMAL WATERS

6.1 Classification of thermal waters

6.1.1 The Cl-SO₄-HCO₃ triangular diagram

A classification of the waters was carried out on the basis of relative contents of the three major anions Cl-SO₄-HCO₃ and a diagram based on the relative Na+K, Ca and Mg concentrations, as shown in Figure 3. From Figure 3a, different types of the thermal waters can be distinguished, such as peripheral or bicarbonate (HCO₃) waters. Sodium and potassium are the dominant cations in all the thermal springs as shown in Figure 3b.

Peripheral or bicarbonate (HCO₃) waters. Most of the samples are located within the region of high bicarbonate concentration and they can be classified as peripheral waters that may have mixed with cold groundwater. Some samples are located near the sulphate or steam heated water regions (some hot springs) of the diagram but still within the bicarbonate water region. In these cases the dominant ions are bicarbonate and sulphate. These bicarbonate waters found in non-volcanogenic, high-temperature systems are more problematic in origin and may constitute the deep reservoir fluid. These thermal springs have measured temperatures ranging from 12.5 to 92°C, pH from 8.45 to 9.7 and TDS from 210 to 600 mg/l. The major cation is sodium (Figure 3b). The waters were classified as bicarbonate and sodium type waters with a relatively high sulphate content and low chloride, typical of high-temperature systems.

Steam heated or sulphate (SO₄) waters. The hot springs of the Khuvsgul and Bulgan provinces are located in the region of sulphate and steam heated waters. The dominant cation is sulphate and they

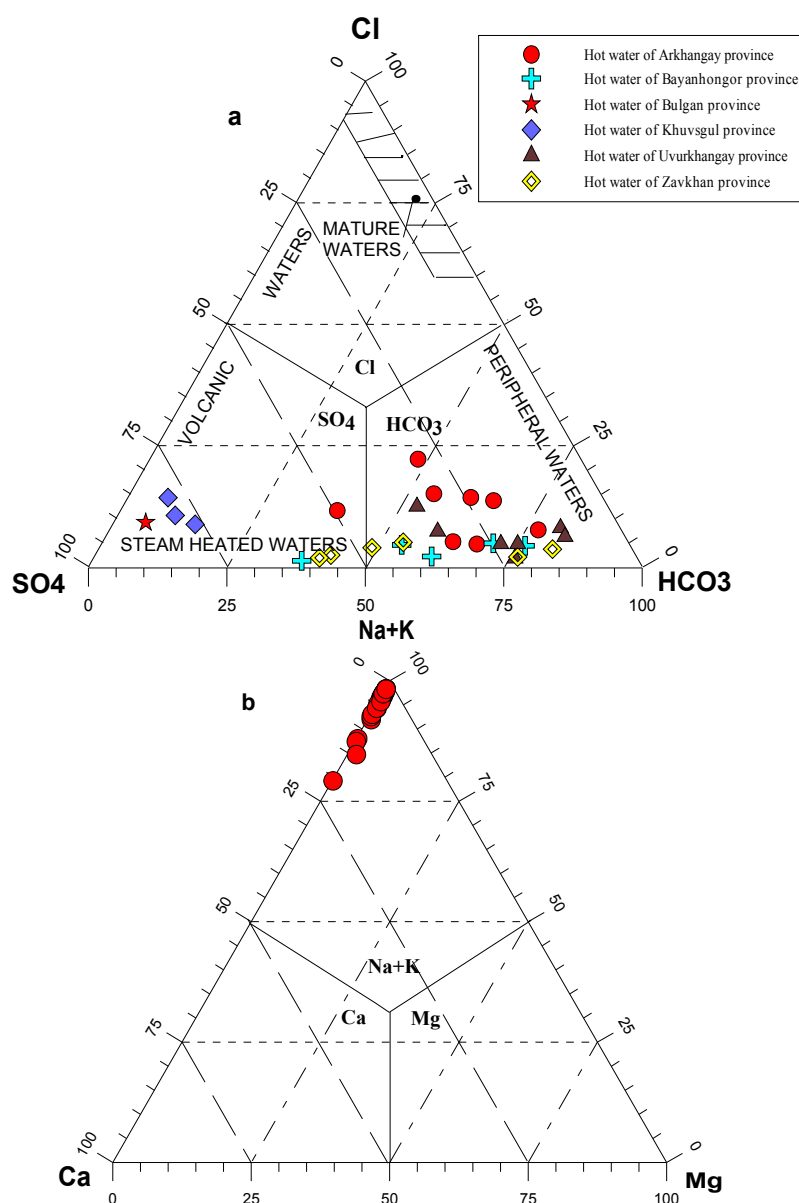


FIGURE 3: Classification of thermal springs from the Khangay area in Central Mongolia on the basis of a) Relative Cl, SO₄ and HCO₃ content (in ppm); b) Relative Ca, Mg and Na+K content (in ppm)

are of the sulphate-sodium water type. Some springs are located near to the bicarbonate water region but are still within the sulphate water region. These waters are of a sulphate-bicarbonate and sodium water type. These fluids are surface fluids often formed by the condensation of geothermal gases into the liquid near the surface, i.e. oxygenated groundwater, but sometimes their origin can be related to equilibria deep down in the geothermal systems and that may even be useful for interpretation. They are found on the margins of a field some distance from a major upflow area, at topographic levels high above the water table, in perched water tables and over boiling zones. Although usually found near the surface at < 100 m depth, sulphate waters can penetrate to depth through faults into the geothermal system. Since the concentration of silica and most cations is only the product of near-surface leaching, such steam-heated waters cannot be employed in geothermometry as the concentrations of the dissolved constituents bear no relation to mineral-fluid equilibria in the reservoir (Nicholson, 1993). The waters from the Khuvsgul and Bulgan provinces were classified as a sulphate and sodium type and the temperature was between 35 and 59°C. The pH values for these waters range from 8.3 to 9.0 and TDS from 390-832 mg/l.

6.1.2 Na-K-Mg equilibrium diagram

The Na-K-Mg triangular diagram of Arnórsson (2000a) indicates the equilibrium temperatures of minerals (feldspars, clay) containing these elements, and was used to identify the equilibrium between the geothermal fluids and rock and to determine the reservoir temperature. Most of the hot springs plot on the full equilibrium line which means that these waters have attained equilibrium between water and rock (Figure 4a). However, other hot springs plot close to the full equilibrium curve and are probably also at equilibrium. The calculated equilibrium temperature is in the range of 75-140°C, indicating that the geothermal springs are classified as a low-temperature springs. As seen from the Giggenbach (1988) diagram (Figure 4b), the data for the hot springs are located between immature waters and fully equilibrated waters, in the field of

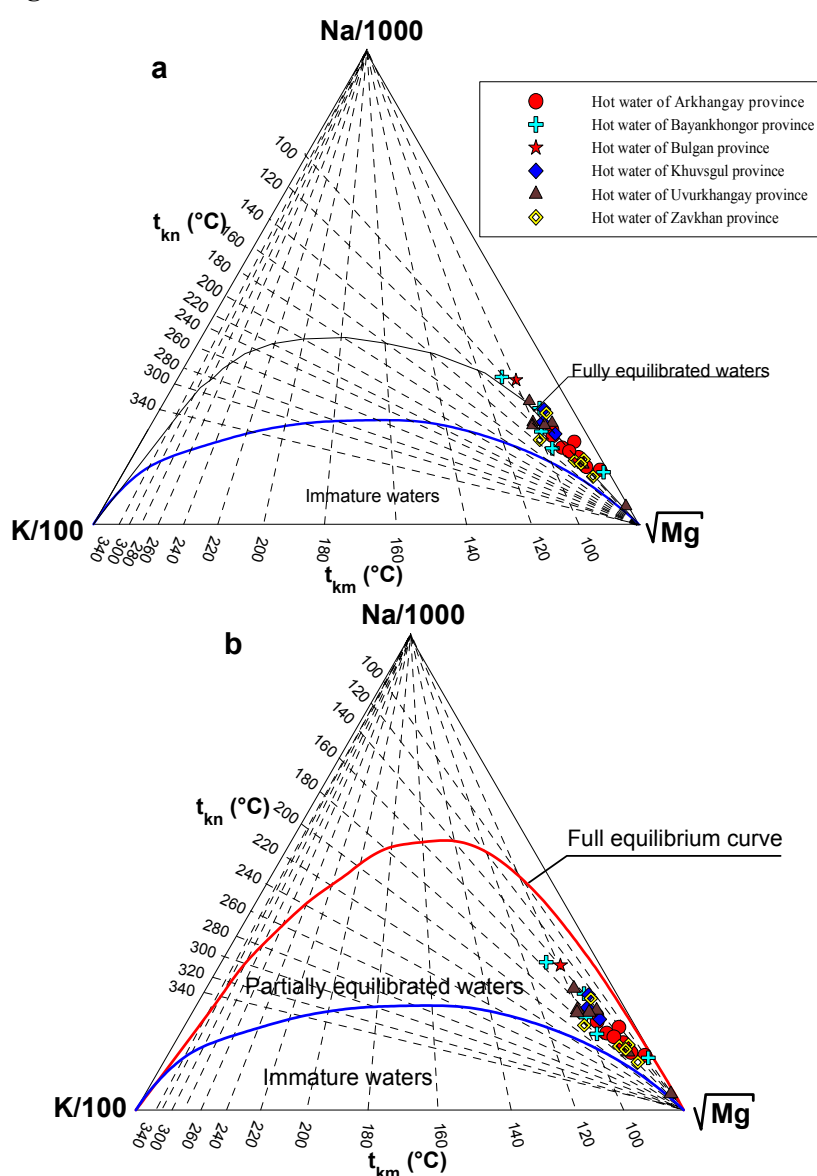


FIGURE 4: Na-K-Mg equilibrium diagram for the hot springs from the Khangay area in Central Mongolia; a) Arnórsson (2000a) diagram; b) Giggenbach (1988) diagram

partially equilibrated waters, indicating that these waters have mixed with cold water and have not reached equilibrium with the rock. The calculated equilibrium temperature is in the range of 100-180°C.

6.2 Geothermometers

Chemical geothermometry was used to estimate subsurface temperatures and predict possible cooling in the reservoir during production, as described in Section 4.2. The WATCH computer program (Arnórsson and Bjarnason, 1993) was used for calculations of silica (quartz and chalcedony) and Na-K temperatures. The Na-K-Ca temperature and different geothermometers (quartz, chalcedony and Na-K) were calculated using the equations in Section 4.2 (Equations 10, 11, 12, 15, 16 and 17).

The measured temperatures of the hot springs and results for the solute geothermometry (calculated subsurface temperatures) are summarised in Table 2.

TABLE 2: Geothermometer temperatures for thermal waters from the Khangay area in Central Mongolia

No.	Province	T _{meas} °C	T _{qtz} ¹	T _{qtz} ²	T _{chal} ¹	T _{chal} ²	T _{chal} ³	T _{Na-K} ¹	T _{Na-K} ³	T _{Na-K} ⁴	T _{Na-K-Ca} ⁵
1	Zavkhan	37	119	122	91	93	93	103	112	164	137
2		56	118	122	91	94	94	70	79	135	116
3		45	124	138	95	112	110	134	136	185	152
4		35	107	120	78	91	91	103	104	157	126
5		44	107	111	79	81	82	50	83	138	111
6		36	131	142	103	115	113	98	104	157	132
7	Khuvs-gul	59	130	134	104	107	106	87	98	152	126
8		44	101	104	72	74	75	69	77	133	110
9		35	116	125	86	97	97	89	101	154	124
10	Arkhangai	38	117	128	87	100	99	61	73	130	110
11		45	117	120	89	92	92	72	91	146	127
12		62	115	135	83	108	107	95	111	163	141
13		87	111	144	77	118	116	82	107	160	135
14		52	97	111	66	82	83	53	67	124	106
15		52	108	122	77	94	94	94	96	150	122
16		13	120	126	92	99	98	64	93	147	119
17		69	135	140	109	114	112	98	103	156	135
18	Bayan Khongor	92	136	142	109	116	114	107	119	170	143
19		59	123	127	96	99	99	77	99	153	129
20		57	120	124	93	96	95	125	131	181	151
21		42	119	124	92	96	95	67	84	140	122
24	Uvur-khnagai	55	134	139	109	113	111	98	117	168	146
25		56	131	136	105	109	108	77	84	140	125
26		30	119	123	92	95	95	86	99	153	130
29		72	134	139	108	113	111	77	102	156	137
30		55	128	132	101	105	104	71	91	146	126
31		39	133	138	107	111	110	118	122	173	152
32	Bulgan	53	103	105	73	76	77	81	83	139	109

¹WATCH program; ²Fournier (1977); ³Arnórsson et al (1983);

⁴Giggenbach (1988); ⁵Fournier and Truesdell (1973)

- The quartz geothermometer gives reservoir temperatures of hot springs in the study area in the range of 97-136°C (WATCH program) and 104-144°C (Fournier, 1977).
- The chalcedony geothermometer gives reservoir temperatures in the range of 66-109°C (WATCH program), 74-116°C (Fournier, 1977) and 75-116°C (Arnórsson et al., 1983).

- The Na-K geothermometer temperatures are in the range of 50-135°C (WATCH program), 67-136°C (Arnórsson et al., 1983) and 124-185°C (Giggenbach, 1988).
- The Na-K-Ca geothermometer gives reservoir temperatures between 106 and 152°C (Fournier and Truesdell, 1973).

Calculated temperatures for the hot springs are quite variable. The temperatures predicted by the chalcedony geothermometer are the lowest. These differences gradually become smaller as the silica content in the water increases. The results from the three Na-K geothermometers are quite variable. It is obvious that the Na-K geothermometer by Giggenbach (1988) yields relatively high values for all samples compared to the other two. The reason is that they are based on different mineral assemblages, and the results depend on which minerals control the mineral-fluid equilibration.

6.3 Mineral-solution equilibrium

The log (Q/K) diagram can be calculated by computer programs like WATCH and SOLVEQ. In this study the WATCH program was used to calculate the log (Q/K) for the temperature range 20-120°C. The speciation technique was only applied to 12 water samples with a high measured temperature. The minerals calcite, fluorite, silica amorphous, chalcedony and quartz were selected to calculate the equilibrium state. The calculated saturation index ($SI = \log Q/\log K$) vs. temperature for hot water from springs are shown in Figure 5. Results based on this method should be interpreted with caution as follows:

- *Otgon tenger (2)*: The minerals calcite and fluorite intersect each other at 67°C within the undersaturation zone and most minerals plot within this zone, which may indicate mixing with cold groundwater.
- *Hojuul (3)*: Calcite and chalcedony are almost in equilibrium at 82°C.
- *Hunjil (7)*: Calcite and fluoride intersect at 85°C and calcite and chalcedony at 98°C. These intersections are very near the equilibrium line of $SI=0$.
- *Shivert (12)*: The minerals calcite and quartz intersect at 72°C within the saturation zone.
- *Tsenkher (13)*: The water sample of this spring shows a very scattered pattern, suggesting that it has not attained equilibrium. This can be deduced because the SI lines for the minerals do not intersect the equilibrium line ($SI=0$) at the same temperature.
- *Gyalgar (15)*: The minerals calcite and quartz intersect at 64°C within the saturation zone.
- *Ih Shargaljuut (18)*: The minerals calcite and chalcedony intersect at 105°C on the equilibrium line.
- *Baga Shargaljuut (19)*: Calcite and silica amorphous intersect at 73°C and calcite and fluoride at 96°C within the undersaturation zone.
- *Ukheg (20)*: The minerals calcite, fluoride and silica amorphous intersect at 62°C within the undersaturation zone.
- *Mogoit (29)*: The minerals calcite, fluoride and silica amorphous intersect at 89°C within the undersaturation zone.
- *Taats (30)*: Calcite and silica amorphous intersect at 74°C and calcite and fluoride at 96°C within the undersaturation zone.
- *Saikhan hulji(32)*: The minerals calcite and chalcedony intersect at 62°C within the saturation zone.

The diagrams (Figure 5) appear to have a similar pattern for most samples and do not show a clear conversion to the zero saturation index by any group of minerals. In other words, the fluid is not in equilibrium with the assumed subsurface mineral assemblage at a certain temperature. The limitation of mineral choices, due to the absence of aluminium analysis data, impacts the results.

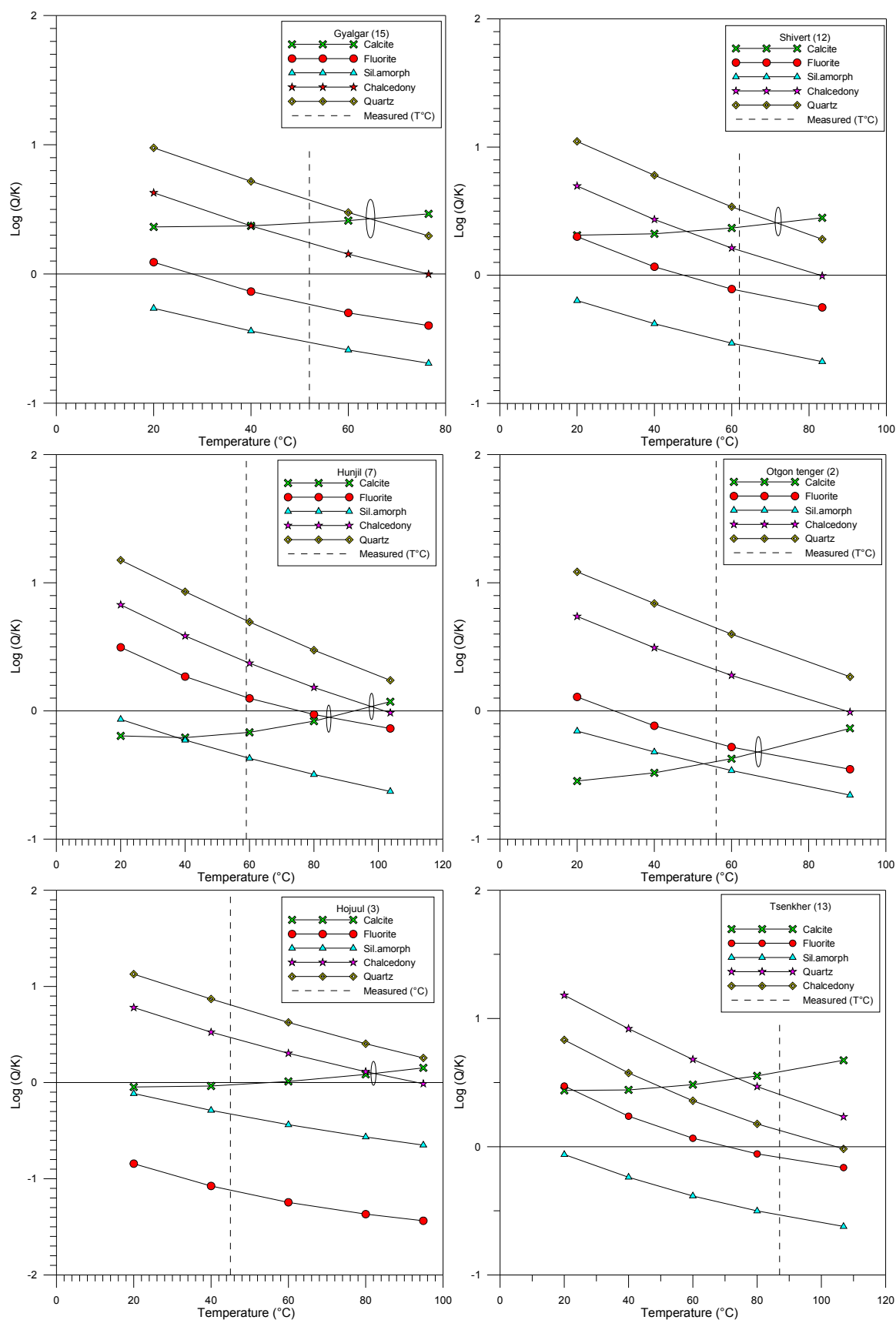


FIGURE 5: Saturation index ($\log Q/K$) vs. temperature calculated with the WATCH program for hot springs in the Khangay area, Central Mongolia

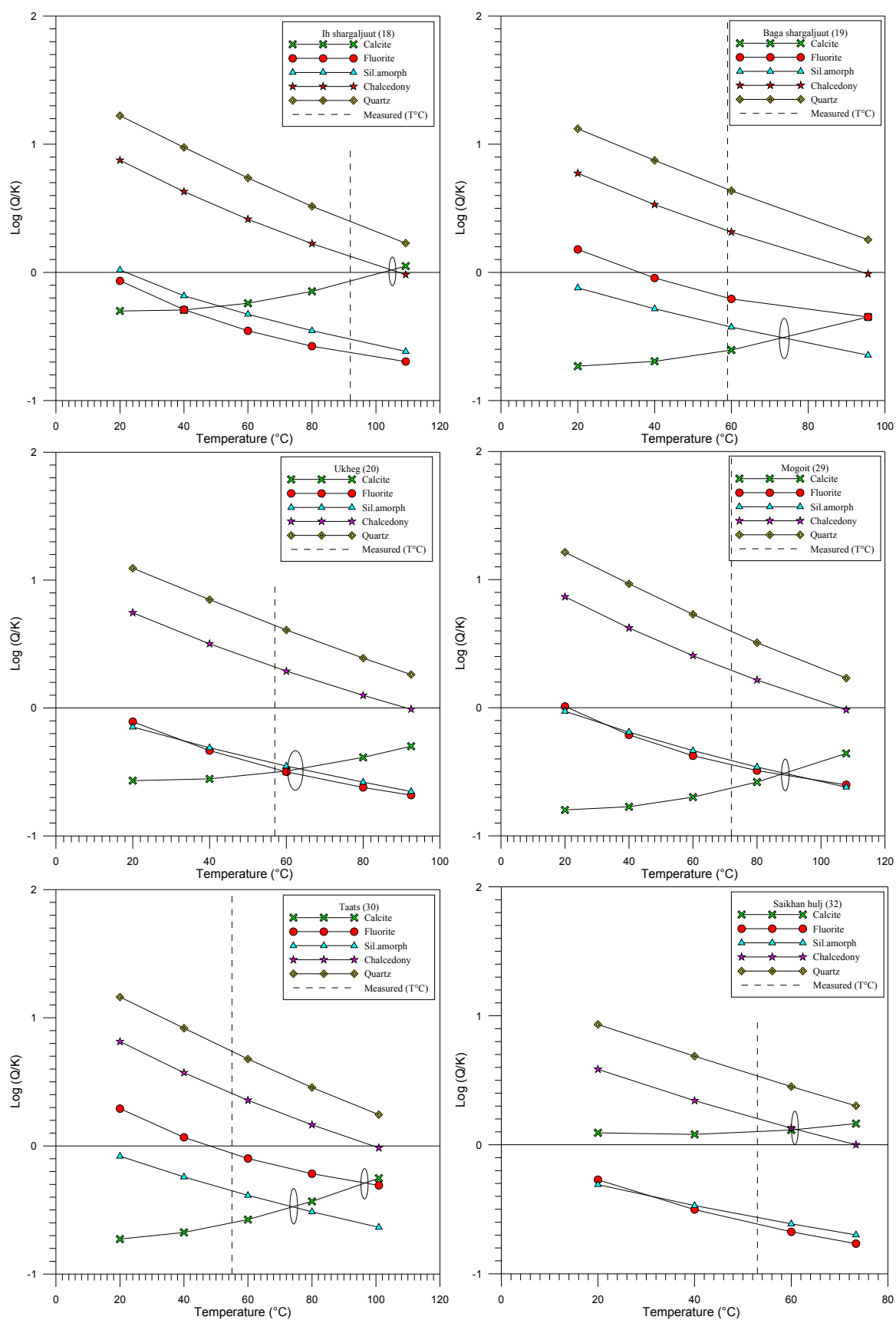


FIGURE 5: Continued; saturation index (log Q/K) vs. temperature calculated with the WATCH program for hot springs in the Khangay area, Central Mongolia

In almost all cases, lines for the minerals quartz and chalcedony are within the saturation zone whereas most other minerals plot and intersect within the undersaturation zone, which may indicate mixing with cold groundwater. In fact, the calculated temperatures are only a little bit higher than measured temperatures for the selected hot springs in the study area. The calculated equilibrium temperatures range from 62 to 105°C.

6.4 Mixing models

Two mixing models were tested for comparison and further classification of the hot springs in this study, the silica-enthalpy warm spring mixing model (Fournier, 1977) and the silica carbonate mixing model (Arnórsson, 2000a).

6.4.1 The silica-enthalpy mixing model

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). Figure 6 depicts the silica-enthalpy mixing model based on chalcedony solubility and quartz 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 long, black broken line between the cold water and the mixed thermal water intersects the chalcedony solubility curve where enthalpy is equal, from 600 to 1060 kJ/kg, and corresponds to the estimated reservoir temperature from 143 to 245°C. Subsurface temperature estimates using this method are higher than those obtained using e.g. 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 upflow of the hot water.

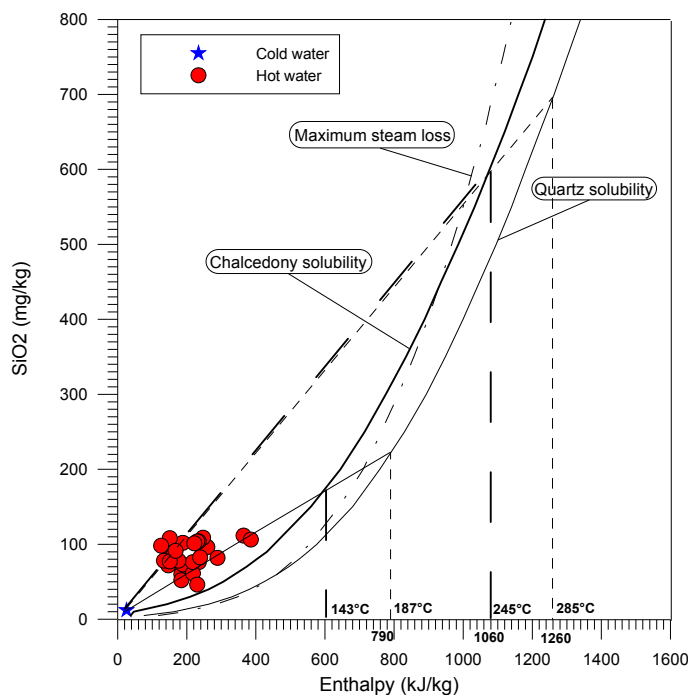


FIGURE 6: The silica-enthalpy mixing model for samples from the Khangay area Central Mongolia

The small, broken line between the cold water and the mixed thermal water intersects the quartz solubility curve where the enthalpy is equal, from 790 to 1260 kJ/kg, and corresponds to the estimated reservoir temperature from 187 to 285°C, here using the quartz geothermometer (see Equation 10 in Section 4.2.1). The hot waters of the Khangay area in Central Mongolia have a difference of less than 50°C between the measured and calculated quartz geothermometer temperatures; therefore, this model is not applicable (Fournier, 1991).

6.4.2 The silica-carbonate mixing model

The silica-carbonate mixing model is based on the relationship between the silica and the total carbonate concentrations, assuming that practically all the silica in geothermal systems occurs as H_4SiO_4 and practically all the carbonate as CO_2 , and that the concentrations are fixed by a temperature dependent solute/mineral equilibrium in the reservoir (Arnórsson, 2000a). This model not only serves

to estimate the temperature of the hot water component in mixed waters but also distinguishes between boiled and non-boiled waters. Figure 7 shows that the points plot below and far from the curve. This means that the waters in the hot springs in this study are not boiled but have mixed with cold groundwaters. An extrapolation of the line through the data points indicates that the temperature of the hot water component ranges from 227 to 241°C.

6.5 Relationship between Cl and B

Chloride and boron are considered to essentially act as mobile elements in the surface and groundwater environment. This implies that they do not enter to any extent secondary minerals forming as a result of weathering and hydrothermal alteration processes. A linear relationship in a particular geothermal field between Cl and B indicates the mixing of geothermal water with cold water. A Cl-B plot (Figure 8) of the low temperature thermal waters of the Khangay area of Central Mongolia depicts three distinct sets of data, possibly representing their geographic locations. Thermal water samples from the Arkhangay, Bayanhongor, Uvurkhangay Zavkhan provinces are similar and contain the lowest Cl concentrations and the relatively highest B concentrations, 0.25-0.82 and 2-27.3 ppm, respectively, and the Cl/B weight ratios range from 4 to 36, comparable to the average ratio of basalt and granite. It was observed that the aqueous B concentrations of springs in these provinces are generally higher and the Cl concentrations lower than in the other provinces, and the temperatures in these springs are higher. These provinces are located in the central and western parts of the study area.

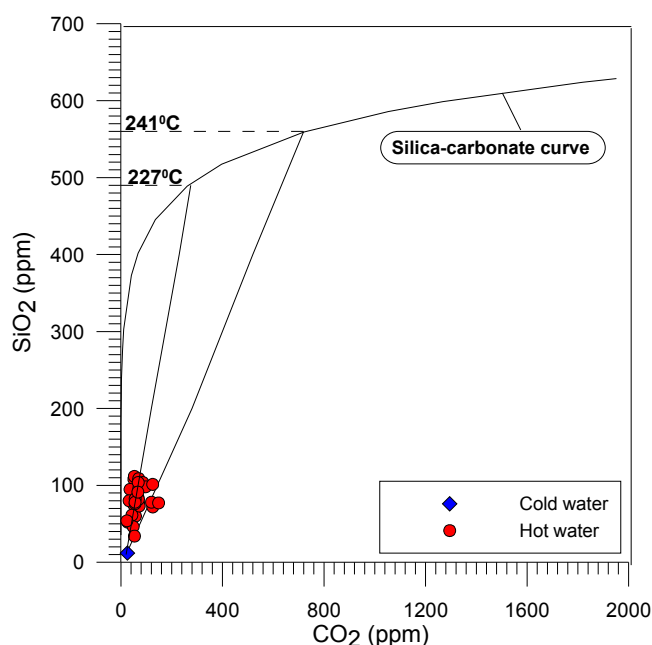


FIGURE 7: The silica-carbonate mixing model for samples from the Khangay area, Central Mongolia

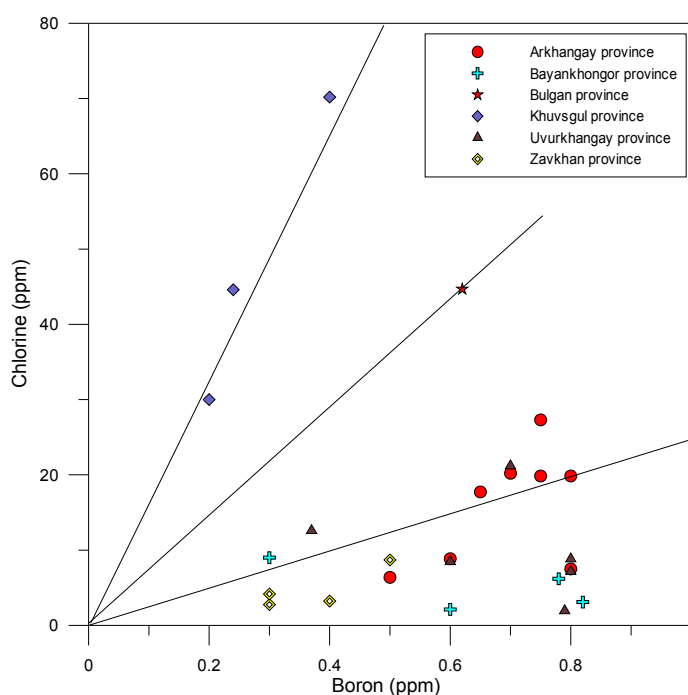


FIGURE 8: The relationship between Cl and B concentrations from the Khangay area in Central Mongolia

The B and Cl concentrations of the Bulgan province are high, Cl 45 ppm and B 0.62 ppm, and the Cl/B weight ratios of the waters in this spring is 72. This province is located in the northeastern part of the study area.

Thermal water samples from the Khuvsgul province of the study area contain the highest Cl concentrations and relatively low B concentrations, 0.24-0.4 and 30-70 ppm, respectively, and the

Cl/B weight ratios range from 95 to 186. It was observed that the aqueous Cl concentrations of these provinces are generally higher and the B concentrations lower than in the other provinces. It was also noted that within this area the B concentrations correlate with distance and elevation. This province is located in the northern part of the study area. Most of the hot springs in Mongolia discharge from granite rock, and there is always a relationship between hot water and granite rock. Therefore, the hot springs of the Khuvsgul province are rather found in older rocks than in the other provinces in the Khangay area. Possible explanations for the higher Cl/B ratios are either the removal of B from the solution or the addition of Cl from other sources. It is known that B is not significantly removed from the solution in the granitic environment of Mongolia. So, the cause is likely the addition of Cl from other sources. According to the Cl-B diagram, all waters indicated have low B/Cl ratios and suggest old hydrothermal systems.

6.6 Stable isotopes of oxygen and hydrogen

Knowledge of the origin of geothermal waters is very important in geothermal studies because it helps in discriminating the chemical properties of the thermal waters and also their sources of recharge. Studies of stable isotopes play an important role in hydrogeological investigations of both thermal and non-thermal waters because the isotopes carry imprints of the origin of the waters. The stable isotope compositions of oxygen and hydrogen for samples from the Arkhangay province in the Khangay area were represented by eight water samples collected in December, 2008. The isotope analyses were carried out in 2008 in the laboratory for Stable Isotope Geochemistry of the Institute of Geology and Geophysics of Chinese Academy of Science. Isotopic compositions of geothermal water in the study area are presented in Figure 9 and Table 3, from which the following conclusions are clear:

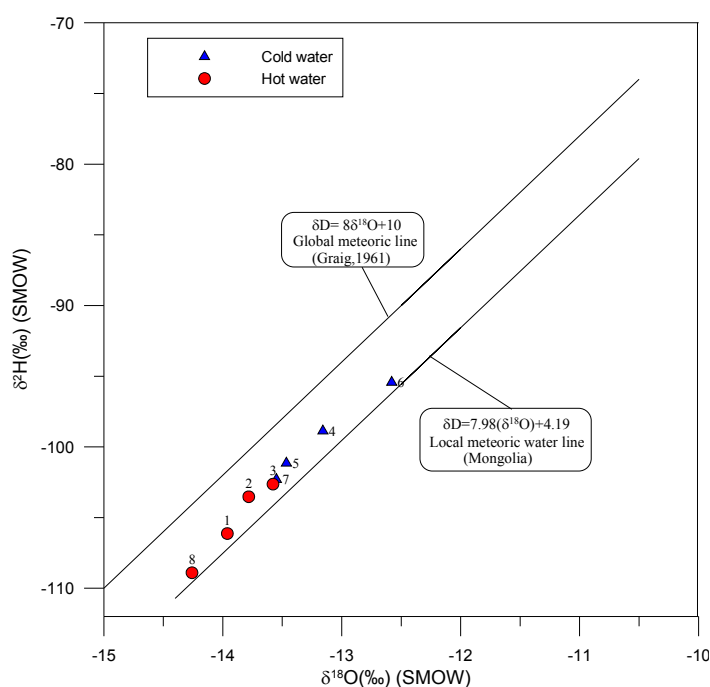


FIGURE 9: The $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ relationship for hot and cold springs of the Arkhangay province in the Khangay

- 1) Thermal waters have more negative $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values than cold waters. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ratio of hot and cold waters in the study area plot parallel below the global meteoric line as $\delta\text{D} = 8(\delta^{18}\text{O}) + 10$. A local meteoric water line has been proposed for the Central Mongolian basin (Dubinina et al., 2007). This line has the formula $\delta\text{D} = 7.98(\delta^{18}\text{O}) + 4.19$ and is below but almost parallel to the world meteoric water line, indicating that the meteoric water has already evaporated before falling onto the Earth's surface.
- 2) Stable isotope composition of samples from surface water, groundwater with a normal temperature and geothermal water in the study area, is approximately parallel to the local meteoric regression line (LMOW), indicating that different kinds of water in the district are derived from meteoric water and that the replenishment process has been generally balanced since the replenishment.

- 3) Characteristics of oxygen and hydrogen isotopes in thermal water are similar to that of the local meteoric line. The δ values in thermal water have a linear distribution characteristic along the LMOV in the $\delta^2\text{H}$, $\delta^{18}\text{O}$ relationship diagram (Figure 9), and there is no evident $\delta^{18}\text{O}$ shift phenomenon which means that the geothermal water comes from meteoric water and little water-rock isotope exchange has taken place.
- 4) The lowest δ values are from the sample with the highest temperature of the geothermal water of Tsenkher (sample 8). It means that no sea water component is in the thermal water and the salts in the thermal water mainly come from the dissolution of rocks and minerals.

TABLE 3: The stable isotope composition of the Arkhangay province in the Khangay area

Sample no.	Sample name	T _{meas} (°C)	Altitude (m)	δD (‰)	δO (‰)
ShHW-1bp	Shivert hot water	62	1749	-106	-13.9
ShHW-2a	Shivert hot water	51	1747	-103	-13.7
ShHW-3	Shivert hot water	57	1748	-102	-13.5
CWW-4	Cold water of well	4	1872	-98	-13.2
CSW-5	Har hulganat cold spring	2	1808	-101	-13.5
CSW-6	Usan turuu cold water	1	1807	-95	-12.6
CSW-7	Gants mod cold water	3	1937	-102	-13.5
TSHS-8	Tsenkher hot spring	86	1913	-108	-14.3

7. CONCLUSIONS

Chemical analyses of water samples from 32 hot springs located in the Khangay area in Central Mongolia were used for interpretation. The following are the main conclusions of this study:

- The hot waters in the study area can be classified as bicarbonate-sodium type and sulphate-sodium type waters. Most of the samples are located in the region of high bicarbonate or they can be classified as peripheral waters that may have mixed with cold groundwater. These bicarbonate waters are found in typical, non-volcanogenic, high-temperature systems. The hot springs of the Khuvsgul and Bulgan provinces are located in the region of sulphate and steam heated waters.
- In Arnórsson's (2000a) Na-K-Mg ternary diagram, most of the hot springs plot on the full equilibrium curve and other hot springs plot close to the full equilibrium curve and are probably at equilibrium. The calculated equilibrium temperature is in the range of 75-140°C. In the Giggenbach (1988) diagram, all the hot springs are located between immature waters and fully equilibrated waters, in the partially equilibrated water area. The calculated equilibrium temperature is in the range of 100-180°C.
- The most common geothermometers were applied. The quartz, chalcedony, Na-K and Na-K-Ca geothermometers showed results that were reasonably close. The chalcedony and quartz geothermometers predict maximum subsurface reservoir temperatures of 116 and 136°C and minimum subsurface temperatures of 74 and 97°C, respectively. The results from the three Na-K geothermometers are quite different. It is obvious that the Na-K geothermometer by Giggenbach (1988) yields relatively high values, or a minimum temperature of 130°C and a maximum temperature of 185°C for all samples compared to the other two which yielded a minimum temperature of 61°C and a maximum temperature of 136°C. But the chalcedony geothermometer provided the most reliable temperature for these fields, with predicted temperature average values ranging from 92 to 112°C.

- The saturation indices (Log (Q/K)) were applied to 12 of the 32 water samples with a high measured temperature. The mineral assemblage indicates that equilibrium has been attained in the temperature range of 62-105°C.
- The silica-enthalpy mixing model, predicts a subsurface reservoir temperature between 143 and 245°C. Subsurface temperature estimates using this method are higher than those obtained using the other geothermometers, 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 upflow of the hot waters.
- The Cl-B plot of the low temperature thermal waters of the study area depicts three distinct sets of data, possibly representing their geographical locations. According to the Cl-B diagram, all waters indicated have low B/Cl ratios which suggest old hydrothermal systems.
- The waters are meteoric and of a local origin, with no apparent $\delta^{18}\text{O}$ shift which may indicate that, hydrothermal alteration reactions have long ceased occurring, aquifer temperatures are not high, or good permeability exists.

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REFERENCES

- Arnórsson, S., 1985: The use of mixing models and chemical geothermometers for estimating underground temperature in geothermal systems. *J. Volc. Geotherm. Res.*, 23, 299-335.
- Arnórsson, S., 1991: Geochemistry and geothermal resources in Iceland, In: D'Amore, F. (coordinator), *Applications of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 145-196.
- Arnórsson, S. (ed.), 2000a: *Isotopic and chemical techniques in geothermal exploration, development and use. Sampling methods, data handling, interpretation*. International Atomic Energy Agency, Vienna, 351 pp.
- Arnórsson, S., 2000b: The quartz and Na/K geothermometers. I. New thermodynamic calibration. *Proceedings of the World Geothermal Congress 2000, Kyushu-Tohoku, Japan*, 929-934.

Arnórsson, S., and Andréðóttir A., 1995: Processes controlling the distribution of boron and chlorine in natural waters in Iceland. *Geochim. Cosmochim. Acta*, 59, 4125-4146.

Arnórsson, S., and Bjarnason, J.Ö., 1993: *Icelandic Water Chemistry Group presents the chemical speciation programme WATCH*. Science Institute, University of Iceland, Orkustofnun, Reykjavík, 7 pp.

Arnórsson, S., Gunnlaugsson, E., and Svavarsson, H., 1983: The chemistry of geothermal waters in Iceland III. Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta*, 47, 567-577.

Barsbold, R., and Dorjnamjaa, D., 1993: Geological map of the Khangay highland, scale 1:500000, Geodesy and Cartographical Institute, Ulaanbaatar, Mongolia.

Signal, G., Batkhishig, B., and Tsuchiya, N., 2004: Character of surface thermal manifestations and spring waters at the Shargaljuut hot springs, Mongolia. *Geothermal Resources Council, Trans.* 28, 449-453.

Bjarnason, J.Ö., 1994: *The speciation program WATCH, version 2.1*. Orkustofnun, Reykjavík, 7 pp.

Craig, H., 1961a: Standards for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science*, 133, 1833-1834.

Craig, H., 1961b: Isotopic variations in meteoric water. *Science*, 133, 1702-1703.

Craig, H., 1963: The isotopic geochemistry of water and carbon in geothermal areas. In: Tongiorgi, E. (ed.), *Nuclear geology on geothermal areas*. Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa, 17-53.

Devyatkin, E.V., 1981: The Cenozoic of Inner Asia (stratigraphy, geochronology and correlation). *Transactions of the Joint Soviet-Mongolian Scientific-Research Geological Expedition (in Russian)*, 27, 196 pp.

Dorjderem, B., 2001: *Possibility of the hydrothermal resources of new tectonic structures in the Khangai Region (in Mongolian)*. University of Science and Technology Annual Report, Ulaanbaatar, Mongolia, 113-119.

Dubinina, E.O., Petrov, V.A., and Golubev, V.N., 2007: Isotopic parameters of meteoric waters in fractured porous rocks of the Tulukuev ore deposit (in Russian). *Doklady Earth Sciences*, 421a, 914-918.

Ellis, A.J., 1970: Quantitative interpretation of chemical characteristics of hydrothermal systems. *Geothermics*, 2, 516-527.

Enkhtuvshin, Kh., 1995: *A petrological study on the late Mesozoic and Cenozoic volcanic rocks of the Mongolian plateau*. Shimane University, Japan, MSc. thesis, 92 pp.

Fournier, R.O., 1977: Chemical geothermometers and mixing model for geothermal systems. *Geothermics*, 5, 41-50.

Fournier, R.O., 1991: Water geothermometers applied to geothermal energy. In: D'Amore, F. (coordinator), *Applications of Geochemistry in Geothermal Reservoir Development*. UNITAR/UNDP publication, Rome, 37-69.

- Fournier, R.O., and Truesdell, A.H., 1973: An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta*, 37, 1255-1275.
- Giggenbach, W.F., 1988: Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim. Cosmochim. Acta*, 52, 2749-2765.
- Giggenbach, W.F., 1991: Chemical techniques in geothermal exploration. In: D'Amore, F. (coordinator), *Applications of geochemistry in geothermal reservoir development*. UNITAR/UNDP publication, Rome, 119-142.
- Gíslason, S.R., Heaney, P.J., Oelkers, E.H and Schott, I.I., 1997: Kinetic and thermodynamic properties of moganites, a novel silica polymorph. *Geochim. Cosmochim. Acta*, 61, 1193-1204.
- Hem, J.D., 1970: *Study and interpretation of the chemical characteristics of natural water*. U.S. Geol. Survey, water supply paper 1473.
- Igmr-transaction, 2008: *The magmatic evolution and geothermal conditions of Tamir river basin* (in Mongolian). Institute of Geology and Mineral Resources, Ulaanbaatar, Mongolia, 127 pp.
- Kovalenko, D.V., 1996: Paleomagnetism and kinematics of the central part of the Olytorsky Range (Koryak Highlands) (in Russian). *Geotectonics*, 3, 82-92.
- Kristmannsdóttir, H., and Johnsen, S., 1982: Chemistry and stable isotope composition of geothermal waters in the Eyjafjörður region, North Iceland. *Jökull*, 32, 83-90.
- Ministry of Agriculture and Industry of Mongolia, 1999: *Geothermal sub-programme of Mineral resource programme (in Mongolia)*. Ministry of Agriculture and Industry, Ulaanbaatar, Mongolia, report, 25 pp.
- Nicholson, K., 1993: *Geothermal fluids: chemistry and exploration techniques*. Springer-Verlag, Berlin, 268 pp.
- Popov, V.N., 1963: *Mongolian hydrogeology*. Moscow State Scientific Press of the Oil and Mining Fuel Literature, Moscow, 208 pp.
- Reed, M.H., and Spycher, N.F., 1984: Calculation of pH and mineral equilibria in hydrothermal water with applications to geothermometry and studies of boiling and dilution. *Geochim. Cosmochim. Acta*, 48, 1479-1490.
- Truesdell, A.H., and Fournier, R.O., 1977: Procedure for estimating the temperature of a hot water component in a mixed water using a plot of dissolved silica vs. enthalpy. *U.S. Geol. Survey J. Res.*, 5, 49-52.
- Tseesuren, B., 2001: Geothermal resources in Mongolia and potential uses. Report 15 in: *Geothermal Training in Iceland 2001*. UNU-GTP, Iceland, 347-374.
- Yarmolyuk, V.V., Ivanov, V.G., Kovalenko, V.I., Samoilov, V.S., 1994: Dynamics of formation and magmatism of the Late Mesozoic-Cenozoic southern Khangay mantle hot spot, Mongolia (in Russian). *Geotectonics*, 5, 28-45.