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Comparison Characterization and Interpretation of Geothermal Fluid Geochemistry in Sedimentary Environments of Kibiro, Panyimur and Öxarfjördur

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ABSTRACT

Geochemical data interpretation of representative chemical analytical and isotopic results for geothermal waters and gas in sedimentary environments obtained by standard analytical methods were studied in this research work. Techniques like: - Chemical geothermometers (silica and cation geothermometers) and gas geothermometers were used in the prediction of variation of temperatures in these geothermal systems. The speciation programme WATCH was used to calculate the different species of anions and cations, Na/K, Quartz and Chalcedony temperatures, Ternary diagram for Na/1000-K/100-$\sqrt{Mg}$ based on the equilibration conditions for these cations in these waters at particular temperatures, and a Cl-SO_4-HCO_3 ternary plot constructed. Different mixing models and plots of different constituent relationships were used in the comparison characterization and interpretations of the geochemistry of these different geothermal areas. The geochemistry of magmatically driven geothermal systems may be used to develop effective exploration techniques for the geothermal systems that are driven by temperature gradients like the East African Rift System (EARS) the western branch of which Kibiro and Panyimur are part.

The chemical and isotopic composition of the water samples from Kibiro, Panyimur and Öxarfjördur, suggest mixing of cold ground water with geothermal waters. Major ions and isotope parameters were used to characterize the waters from Kibiro and Panyimur as Na-Cl-HCO_3 waters and waters from Öxarfjördur as Na-Cl waters. The main processes affecting the geothermal system in the sedimentary geological environment are:-dilution and conductive cooling

1. INTRODUCTION

The term geothermal basically refers to any system that transfers heat which is within the earth to the surface , and . Where the heat transfer may involve water, hydrothermal features indicating geothermal system may be formed at the surface. Some examples of hydrothermal features which may include the followings: - hot springs, geysers, mud pools, fumaroles, and hot and warm ground. The DSIR Report 38D catalogued New Zealand geothermal systems and later Mongillo and Clelland describe the geothermal system.

For future exploration, building up of a conceptual model and utilization of geothermal resources in the area were they exist , a sound understanding of the chemistry of that geothermal fluids need to be established in the beginning of the exploration phase for better facilitation and approaches . Water and gas chemistry has been used for the last decades to verify the following : - origin of the geothermal fluids, the mixing effects in the geothermal system, to evaluate the subsurface temperature and to predict corrosion and scaling problem during the use of these fluids . and .

Chemical composition of geothermal steam and water from natural manifestations provides initial constraints on reservoir temperature, production properties and potential environmental concerns related to utilization of the geothermal fluid . And this can only be attained by carrying out geochemical exploration which is one of the exploration techniques applied in search for any geothermal resource for any utilization

This project aimed at investigating the geochemical relationship of the geothermal waters of Kibiro and Panyimur geothermal areas and compared it with the low temperature geothermal system of the Öxarfjördur located in North Iceland. The formation conditions of the geothermal fluids differ from one area to another and this can only be proven by analysing the chemical characteristics and comparing the findings with the different formation conditions. Geology of these geothermal areas where briefly described, together with classification of the geothermal waters. The speciation program WATCH , , , and geothermometers were mainly used for the determination of the reservoir temperatures and equilibrium conditions, .

Geothermal systems all over the world is mostly associated with the rift system where there is very high heat source closed to the surface of the earth,, and . The geothermal activities in Panyimur and Kibiro are more restricted largely to the rift system of the western branch of the EARS, with geothermal manifestations like: hot springs and altered ground , occurring along some of the border faults of the rift valley and within the volcanic fields . The geothermal system of Öxarfjördur area in north Iceland too is within a major graben which is associated with the current volcanic activity

Geochemical principles can also be applied to interpretation of chemical data from producing wells and may yield information on scaling in pipes or a gradual chemical change in the geothermal fluids that could indicate an impending change in production temperature. The use of geochemistry in the exploration as many geochemical processes affect the concentrations and ratios of reactive and un reactive gases in fluids of volcanic geothermal systems. They include supply of gases from the magma heat source , from the atmosphere and from the rock with which the geothermal fluid interacts.

According to the main tasks of water chemistry in geothermal exploration, drilling and utilization may be grouped as. a) Surface exploration, which may include the followings: - Evaluate origin of water, Estimate underground temperature, Cold water composition, Map the extent of the geothermal system, . Characterize the reservoir chemistry with respect to utilization and Define environmental impact with respect to utilization. b) Drilling, under which we have we have the followings:-

Assess water composition with reference to utilization, Establish changes in total well discharge composition during long term testing, Provide chemical data for construction design , , define scaling and corrosion problems, methods for disposal of geothermal water and c) Utilization, which involves:- Monitoring chemical changes, Monitoring chemical parameters of the fluid in the distribution system and Participating in solving problems arising from utilization.

1.1 Geothermal fluids

In geothermal system, for the heat to be transported to the subsurface of the earth, there is need for transport media which in most cases is the geothermal fluids, and , hence it is a very essential substance of geothermal energy production. These geothermal fluids consist of a mixture of gas and condensed phases having complex chemical compositions, and The clear understanding of the chemical tendencies and physical properties of the geothermal fluids which are necessary in the modelling of many processes that occur during the fluid movement to the subsurface. Those models are developed in order to reduce on the risks during different operations and improve on the plant sustainability.

When carrying out research on the physical properties and chemical behaviour of geothermal fluids , the competency cluster “Fluids” system may be used . The cluster fluid system is also responsible for the online fluid and gas monitoring at the research platform Groß Schönebeck . This group have analytical- experimental orientation with several laboratories, where measurements and experiments may be carried out at in-situ reservoir conditions.

2.0 GEOLOGY OF THE WESTERN BRANCH OF THE EASTERN AFRICAN RIFT SYSTEM

The western arm of the EARS where Kibiro and Panyimur area under this study are located, has Cenozoic rift faults , , starts from the north along the Sudan border , and then curves to the west and southwest along the border with the Democratic Republic of Congo , and south to Rwanda and Burundi for about 100 km. The western branch of EARS is considered to be at an early stage in development , and is younger, that is Late Miocene to Recent than the more mature eastern branch . The rifting region has a higher heat flow than the surrounding Pre-Cambrian terrain . Two different enechelon strands are found in the Western Rift, separated by the Rwenzori Mountains , which rise from base of less than 1000 m in the Rift to over 5000 m elevation and . Within the rift valley there are thick layers of late Tertiary and Quaternary sediments fresh water and saline crater lakes, volcanics, and plutonic bodies have been identified beneath L. Albert and L. Edward. The majority of geothermal areas in Uganda are found in the Western Rift Valley.

2.1 Geology of Kibiro

The area has some volcanic rocks injected through Pleistocene lacustrine rocks in the rift valley and granitic gneisses on and above the escarpment at , big dykes of basic intrusive rocks can be traced in some cases for mile in the argillites and gneisses trending NNE to SSW. The mineralogical compositions of the rocks in Kibiro area are mostly: - porphyritic augites, pyroxexes, ilmenite, and titaniferous minerals. In addition to the more basic intrusive, there is also other granitic type like charnockites, 4.8 km South East of Kibiro with very large intrusion running east and west, and are presumed late date intrusions related of faults. The geology of Kibiro geothermal area is quiet unique in its tectonic setting , this is from the geological and geophysical studies carried out in this area which revealed that the geothermal activities may be associated with the block faulted granites away from the main rift system.

2.2 Geology of Panyimur

The area is characterized by fractured crystalline basement rocks such as coarse hornblende gneisses, coarse hornblende garnet rocks, talcose rocks and pegmatitic veins in a gorge that dips into the escarpment . In the area, there is foliation/basement schistose which trends NNE-SSW. In addition, others schistose trend almost NE, parallel to the local major faults. and the major rocks in the area include crystalline basement rocks which are coarsely jointed granitic-gneiss with outcrops to the west and Pleistocene sediments to the east of the Rift fault boundary . There are some mylonite gneisses which is intruded by pegmatitic dykes, quartz veins and garntiferous amphibolite dykes on the escarpment, with the minor faults cross cutting the rift faults (upper panyimur fault and the lower panyimur fault) all striking north east

2.3 Geology of Öxarfjördur

The Öxarfjördur area is characterized by historical lavas of younger to older age, with thick sediment of about 1000 m, from glacial river and by fissure swarms from active central volcanoes further in land. It is located at the junction between the NE-SW spreading zone, which crosses Iceland, and a right – lateral transform zone, the Tjörnes Fracture Zone. Today the waters round the island are oxygen saturated. This could be due to the fact that major climate change during the Pleistocene could have changed the paths of ocean currents and may that of oxygen cycle too.

The Öxarfjördur sedimentary graben falls in the transform zone of lateral transform movement, spreading and volcanism in the zone between the North Iceland Volcanic Zone in Öxarfjördur and the spreading axis along Kolbeinsey Ridge. The geological model of Öxarfjördur sedimentary trough basing on the tectonic settings and geophysical data indicates that it is younger than 1 Ma, with probably thickness of up to 1 km at the shore inside the Krafla and Theistareykir fissure swarms, while thinning southwards where the sediments are expected to be more frequently inter bedded with lavas and hyaloclastites . The Öxarfjördur lowlands in NE-Iceland are characterized by sediments from a glacial river and by fissure swarms from active central volcanoes

2.3.1 Surface geothermal manifestations in Kibiro and Panyimur

The hot springs in the Panyimur geothermal area are located within a stretch of about of 1.5 km along the main fault and all are aligned in the north-east direction in the western escarpment of the Rift Valley, which probably means that they are controlled by the intersection of the traverse fault together with the main rift. In addition to that, deposits of travertine, sulphurous algae, smell of hydrogen sulphide and all the discharges are characterized by gas bubbling .

The geothermal manifestations in Kibiro area are mainly concentrated at Kibiro and Kachuguru, west of the escarpment, on the shores of Lake Albert, with some fumarolic activity at Kachuru and along the escarpment for approximately 1.5 km from the intersection of the Kachuguru fault and the main escarpment to the Kibiro hot springs. There are some calcite deposits observed in cracks and fissures in many locations along the escarpment, the Kachuguru fault, the Kitawe fault and in the crystalline rocks located south-southeast of Kibiro, indicating extinct thermal fluid discharges. The hot springs at Kibiro are apparently related to a secondary fault , oblique to the main Rift fault, and most likely controlled by their intersection. The total flow measured from the hot springs is approximately 7 l/s and the maximum surface temperature is 86.4˚C .

2.3.2 Surface geothermal manifestations in Öxarfjördur

The surface geothermal manifestations in the Öxarfjördur region are meagre, mainly in the form of warm springs and warm ground within the active fissure swarms . Geothermal manifestations are known at thirteen different locations, which can be divided into 3 groups. These groups are: 1) The Krafla fissure swarm which has the most important sites like Skógalón, where water at shallow level has temperatures up to 100°C covering an area of several hundred square metres and Bakkahlaup with warm ground covering a wide area with temperatures of up to 80°C in the uppermost part having been considerably lower before the Krafla fires. 2) The Theistareykir fissure swarm in the western part of the Öxarfjördur area, with the most important one at Ytra Lón close to the coast, with recently measured temperatures of 50°C, older records showing temperatures above 80°Cand 3) Geothermal sites found outside active fissure swarms.

2.4 Brief overview of geothermal fluids chemistry

The chemistry of geothermal fluids is diverse and largely reflects the geological setting of particular area, . And most of these chemical differences depend on the source of recharge waters and some contribution of gases from magmatic or metamorphic sources. Geothermal fluids contain a number of different constituents with varying concentrations, with important chemical parameters which characterize geothermal fluids such as pH which describes the acidity or alkalinity of the fluid and TDS, which gives a measure of the amount of chemical constituents dissolved in the fluids.

The constituents of the geothermal waters can be grouped into two categories with respect to their properties, that is:-

1) Reactive constituents, which are also used as geo-indicators, due to the fact that they tend to equilibrate with some of the minerals in the geothermal system, and . Information on the temperature and steam fraction, which constitute the physical state of the geothermal system , may be provided by these constituents .
2) Conservative constituents such as Br, Cl, B, N_2, ^2H, ^{13}C, ^{40}Ar, and ^{18}O, , and may be used to trace the origin and flow of the geothermal fluids as they do not take part in water-rock interaction , ,

The geothermal fluids or natural waters may be classified using the $CI-SO_4-HCO_3$ ternary plot diagram . This diagram is used to distinguish a number of different types of thermal waters , like: - immature unstable waters giving it an indication of mixing relationships or the geological groupings, steam heated waters, volcanic waters and the peripheral (Stober 2013) waters . And this leads to the provision of a trend and preliminary statistical evaluation of the grouping of geothermal waters , , . Water circulating in high enthalpy geothermal reservoirs is mostly of meteoric origin and in some geothermal system, it may be oceanic or evolved connate waters which is present, . For geothermal system which are located along the convergent plate boundaries and are closed to the volcanic-magmatic association , the deep magmatic heat source tend to add some acidic gases like CO_2, SO_2, HF, H_2S and HCl, with some andesitic waters in the system.

In high enthalpy geothermal systems, four different types of geothermal waters have been classified (Truesdell, 1991., Henley et al., 1984; Ellis and Mahon, 1977):-

1) Acid sulphate waters, this is the type of the thermal waters which are mainly found in the upflow part of the geothermal system, . These types of geothermal waters are characterized by a low pH of 0 to 3 and a low concentration of chloride . They react very fast with the host rocks giving advanced argillic alteration paragenesis mainly composed of alunite and kaolinite. CO_2 and H_2S are the two main types of gases in this geothermal environment , . The H_2S may undergo oxidization in the up flow zone to form SO_4 , and near the surface and it contain constituents mostly dissolved from the surrounding rock with which it is in contact
2) Sodium – Chloride waters, waters with chloride concentration of up to 10,000 mg/kg, and pH of approximately ±1 or ±2 units to a neutral pH at depth for example 5.5-5.6 at temperature of 200°C to 300°C, . These types of waters contain the following constituents in high concentration than in cold waters: - Na, B, F, Li, Si, K, Ca , but with low Mg and with CO_2 and H_2S as the main dissolved gases .
3) Acid Chloride – Sulphate waters are those types of waters in the deepest part connected with the neutral pH that is NaCl system, there and in inflow of magmatic gases rich in sulphur and hydrochloride species, namely H_2S and SO_2, . The acid Chloride – Sulphate waters are mainly found in crater lakes. The formation of neutral NaCl waters , , and is due to more neutralization in the system .
4) Sodium Bicarbonate waters , the condensation of geothermal steam in a free oxygen ground water at a relatively deep zone may be due the dissolution of CO_2 , present in some of the gases in the system, leading to origin of bicarbonate rich

waters. Lack of oxygen in this system prevents the oxidation of H_2S, meaning that, the acidity in the aqueous solution is from the dissociation of the H_2CO_3 , as shown in equation 1.

$$H_2CO_{3(aq)} \rightleftharpoons CO_{2(g)} + H_2O_{(l)} \qquad (1)$$

The conversion of feldspars to clay is aided by this weak acid especially in medium to high temperature geothermal reservoir , and giving rise to neutral aqueous solutions.

2.4.2 Water rock interaction

When geothermal fluids move through the rock , they may chemically react with the rock with which they come into contact and some of the rock themselves are chemically complex . This may lead to the following: - 1) dissolution of some selective minerals from the rock. 2) precipitation of some minerals from the solution and 3) substitution of certain chemical elements, in the fluids by other elements in the minerals. All these three processes , may lead to secondary mineral formation that is by depletion of some of the chemical composition from the fluids or enrichment of the chemical composition in the rock due to the dissolution of the primary minerals . Series of chemical reactions associated with the interactions between water and rocks of the chambers in which it is

located and the path to reach the earth surface may occur , for example reaction which typically involves sulphur and /or metal cations. Water - rock interactions occur generally slowly, that is primary rock dissolves very slowly in water, but like most reactions it´s dissolution occurs more readily at higher temperatures. The changes in the chemical and/or mineralogical may or may not lead to volume change of the rock. If the volume of the rock is changed then, the porosity and permeability may too be affected. When the reaction between water and rock is prolonged, some of the ionic species and saturated silica are liberated into solution an example of reaction equation 2 below. And the same reactions like the above provide $Na^+_{(aq)}$ and $Ca^{2+}_{(aq)}$ to the geothermal water.

Most geothermal system need heat, permeability, and water for the heat extraction from the Earth's core to continuously flows outward of the earth´s surface , but the molten magma sometimes reaches the surface as lava, but it usually remains below the Earth's crust, heating nearby rock and water to levels as hot as 700°F sometimes.

Physic-chemical conditions like temperature once changed in this case if it´s decreased, may lead to precipitation of some mineral due to low solubility in the solution like in reaction equation 4. When boiling upon pressure decreases, then re-partitioning of the ligands between the vapour and liquid phase may occur leading to solubility decrease of some metals for example gold.

$$\underset{\text{Feldspar rock}}{2H^+_{aq} + 2KAlSi_3O_8} + 9H_2O \rightarrow 2K^+_{aq} + \underset{\text{kaolinite clay}}{Al_2Si_2O_5(OH)_4} + \underset{\text{dissolved silica}}{4H_4SiO_{4\,(aq)}} \qquad (2)$$

Water may be in equilibrium with the rock for sufficiently long period of time that is hundreds to thousands of years and the reactions are sufficiently slow for them to be used to calculate the temperature of the water. In effect, the ratios of the concentrations of the liberated cations like: - Ca^{2+}, Na^+, $Mg^{2+}$and K^+ which are temperature dependent. The most important process governing their relative contents is rock dissolution and equilibration.

The solubility of silica is also temperature dependent, but this equilibrium is attained rather more rapidly than the dissolution of most other silicate minerals.

$$\underset{\text{dissolved silica}}{H_4SiO_{4(aq)}} + 2H_2O \rightarrow \underset{\text{siliceous sinter}}{SiO_2} \qquad (3)$$

This reaction (equation 3) may be used as a geothermometer. Any difference in temperatures obtained from the two geothermometers is related to the sampling of the water relative to the deep aquifer: waters that have moved away from the aquifer are likely to have lower temperatures derived from silica concentrations than temperatures derived from concentrations of Na, K and Ca. And this is simply because of the fact that, the solubility of silica in solution is dependent on temperature.

Iron and manganese ions may be liberated from silicate minerals and ultimately precipitate as their highly coloured oxides. The example below shows the oxidative liberation of iron from a silicate mineral under acid conditions. Iron (II) is oxidized to iron (III).

$$O_{2(aq)} + 7H_2O + 2H^+ \rightarrow 2KFe_2AlSi_3O_{10}(OH)_2 + Al_2Si_2O_5(OH)_4 + 3Fe_2O_3 + 2K^+ + H_4SiO_4 \qquad (4)$$

geothermal water Fe-bearing silicate clay (kaolinite) hematite geothermal water
(ferric oxide)

When water in a geothermal system has attain a high temperature that is above 100°C, it will react with the rock to a greater extent, leading to production of significant oxygen shift, which can be prove by the equation (4), (Stefán Arnórsson. 2000) and this may tell us if the geothermal water shows precipitation which has fallen from the present day climate or under different conditions of the climate.

$$\delta = \delta^2H - 8\,\delta^{18}O \qquad (5)$$

2.4.3 Mixing models

Geothermal waters may be mixed with cold water after a certain period of conductive cooling of the hot water, before, after or during boiling . Depending on pressure and temperature conditions, the main component of geothermal fluids, H_2O, can be present in different physical states . The presence of a single liquid phase in the geothermal reservoir is the most frequent situation, but it is not the only one, since either a two-phase liquid vapour mixture or a single vapour phase can be present in the reservoir. These possibilities can be ascertained by accurate enthalpy data or by gas geochemistry (Giggenbach, 1980; Bertrami et al., 1985).

Large variations in the temperature and flow rates of thermal springs in a particular field that can be linked with the parallel variations in the concentration of the non-reactive components in the water , like Cl, usually constitute the best evidence that mixing has occurred . Mixing models have been developed to allow estimation of the hot water component in mixed waters emerging in springs or discharged from the shallow drill holes, . And there are basically three types of the mixing model and these are: - 1) chloride-enthalpy model, 2) silica-enthalpy warm springs mixing model, and 3) silica – carbonate mixing model.

The enthalpy versus chloride plot is a suitable tool to distinguish the effects of boiling (steam loss) and mixing , since both steam and cold waters, which generally have low chloride contents, are characterized by very different enthalpy values. The enthalpy-chloride shows that boiling moves the liquid from the point representative of the 265°C geothermal liquid toward higher chloride contents and lower enthalpies, whereas addition of cold, dilute waters determine a decrease in both enthalpy and chloride. If discharged water is cooled, mainly through conductive heat loss, chloride concentration of the deep hot water remains unchanged.

In many geothermal hot springs, mixing of the hot and cold water leads to dilution and cooling , for this to be proved by using the different mixing model techniques, the chemical composition of each component in the geothermal water need to be to be carried out thoroughly . And for better use of mixing models, to establish whether there is mixing in the up flow zone of any geothermal systems , large number of samples from one geothermal area is required . The chloride enthalpy plot is used in mixing prediction due to the fact that, chloride concentration increases gradually with continuous rock dissolution with increase in temperature.

3.0 FIELD SAMPLING METHODOLOGY

In all these areas of research work, geochemical sampling of the hot springs, and the wells was carried out by GSMD geochemistry team together with Halldór Ármannsson from the Iceland Geo-Survey in Uganda while the sampling from the Öxarfjördur area North of Iceland were carried out by the Iceland Geo-Survey geochemistry team. Measurement of the physical parameters and analysis of the volatile components were carried out in the field laboratory of the water samples collected, and rock samples were collected for mineralogy analysis to determine the source of salinity in these geothermal waters from Kibiro and Öxarfjördur, though it was not used in this research work

Untreated samples were collected for pH, carbonate, H_2S and conductivity measurements and also for the analysis of Mg and SiO_2. During the sampling process, were the concentration, of SiO_2 were expected to be more than 100 ppm, the samples were then, and diluted with distilled or deionized water to bring concentration in the range of 30 to 100 ppm in triplicate and the dilution factor recorded. Samples were also collected and filtered anions, for the cations, the filtered samples were acidified with nitric acid. All the samples used in the determination of sulphate were precipitated with Zn $(CH3COO)_2$ and then sulphate analysed for from after filtration of the samples. For the analyses of stable isotopes (δ^2H, $\delta^{18}O$) the isotope laboratory needed 60 ml of filtered sample. Summary of sample treatment and preservation method in the geothermal sampling of hot spring and hot water wells.

3.1 Analytical methods

The department of Geological Survey and Mines carried out the determination of the TDS and conductivity of the geothermal waters in their laboratory at Entebbe. The samples were, and then divided into different portions for analysis. The samples were then sent for complete chemical analysis at the Institute of Geological and Nuclear Science, New Zealand, but the samples collected from Öxarfjördur area were analysed in the Orkustofnun Laboratory. The methods and instruments summarized in (Table 2, appendix 3) were used in the analysis of these samples.

4.0 RESULTS AND DISCUSSION

4.1 The aqueous chemistry of the geothermal fluids in these areas

The results for selected hot springs and hot water wells presented in (Table 1, appendix 2) from Kibiro, Panyimur and Öxarfjördur are generally in the range of neutral – alkaline with pH of 6.7- 9.5. General summary of the different chemical component ranges in the samples from Kibiro, Panyimur and Öxarfjördur are presented in (Table 5). Samples from Öxarfjördur contain very low H_2S (<0.03 – 0.07) mg/kg, CO_2 (5.1 – 30.8) mg/kg, the $\delta^{18}O$ is -12 - -9.3 ‰, and δ^2H -114.1 - -87.8 ‰, and very high TDS (1283 – 6401) mg/kg and samples from Kibiro contain very high CO_2 (115 – 367) mg/kg and H_2S (0.0 – 17.3) mg/kg. Panyimur samples in general contain very low concentration of all the chemical components. And in general, the samples from Panyimur and Öxarfjördur contain lower concentrations of Mg than the samples from Kibiro. There is a relatively higher concentration of fluoride in some of the samples from Panyimur compared to the samples from Kibiro and Öxarfjördur. The chemistry of these water samples differ mainly in the samples from Öxarfjördur in general contain almost not or very little H_2S in all of them, but contain the highest amount of Na, K, TDS, concentrations of SiO_2, Na, Cl, CO_2, Mg and TDS.

4.2 Use of Ternary diagram in classifying geothermal waters of Kibiro, Panyimur and Öxarfjördur

4.2.1 Cl-SO_4-HCO_3 ternary diagram.

The Cl-SO_4-HCO_3 ternary plot diagram has been used in the classification of geothermal and natural waters (Giggenbach, 1991). Compositions of many water types are shown as one of the following in the triangular plot (Figure 1, in appendix 1): mature waters, steam-heated waters, volcanic waters and peripheral waters. From the Cl-SO_4-HCO_3 ternary plot, the degree of separation of the plotted points for high-chloride and bicarbonate waters shows some indication of relative degree of interaction of the fluids at lower temperature with CO_2 charged, of the HCO_3 contents increasing with time and the distance travelled by the waters underground.

In waters from Kibiro, Panyimur and Öxarfjördur, there is a great degree of variation among the HCO_3 and CI waters. With the waters from the Öxarfjördur areas, plot in the volcanic region of the diagram, with two samples in the CI portions, one in the SO_4 and another one in the HCO_3 part. Four of the Kibiro samples, which are plot in the chloride portion of the diagram, bur three in the HCO_3 region, but more towards the SO_4 and the HCO_3 section. Two of the Panyimur samples, plot in the Cl area, two in the peripheral water zone.

4.2.2 The Na-K-Mg triangular diagram

This technique for the derivation of Na-K-Mg-Ca geoindicators was initiated by, as one of the classification techniques for different kinds of waters depending on whether they are: - 1) immature waters, 2) partially equilibrated and 3) fully equilibrated waters. Using the plots, one may apply geothermometers to the equilibrated and partially equilibrated waters only.

In the triangular plot, the area of partial equilibrium indicates that there could be some mineral that has dissolved, though it has not yet attained equilibrium or it may be that it is geothermal water, but has been diluted with waters that has not yet reached equilibrium for example it may be cold ground water. For those points which plots close to the √Mg corner indicates that there is very high proportion of relatively cold groundwater mixed in the water system.

In (Figure 2, found in appendix1), samples from Panyimur and Öxarfjördur all plot in the partially equilibrated region of the diagram, probably meaning that there is some recharge from cold ground waters into the geothermal systems in those areas. In Kibiro, some of the samples plotted in the immature region, hence contain cold ground water while six of the samples plotted in the partially equilibrated portion. The t_{km} temperature for samples from Kibiro varies in many range 160°C to 140°C, and then 100°C to <100°C, the tkn is from 100°C to 240°C, for Panyimur, the t_{km} is 120°C to 70°C and the t_{kn} is from 100°C to 160 °C and for Öxarfjördur t_{km} varies in the range of <100°C to 200°C and the t_{kn} is from 100°C to 200°C. The t_{km} temperature for all these samples varies considerably. This could be due to the fact that the K-Mg geothermometer tends to react faster to change than the K-Na geothermometer in the same system.

4.3 Calculated geothermometers temperatures

Fifteen different geothermometer equations (eight for quartz geothermometers, two chalcedony, three Na/K, K-Mg and Na-K-Mg) were applied in the prediction of the subsurface temperatures of the geothermal water from Kibiro, Panyimur and Öxarfjördur. The average calculated quartz geothermometer temperatures for hot springs and wells in Öxarfjördur are 150°C, in or Kibiro samples is 123and in Panyimur 129°C. The Na-K geothermometer temperatures, for Kibiro and Panyimur are high while the Na-K-Ca, geothermometer gives very high temperatures for Öxarfjördur. This may due to loss of CO_2 leading to calcite precipitating out of the solution. This affects the concentration of calcium in the solution leading to abnormally high geothermometer temperatures. The calculated chalcedony geothermometer the remperatures for these samples are: - for Öxarfjördur 116°C, for Kibiro 114°C, and Panyimur 101°C. The calculated Na-K geothermometertemperatures are: - for Öxarfjördur 148°C, for Kibiro 197°C and Panyimur 116°C.

In many instances there is no good agreement between the Na-K temperatures and the silica temperatures for samples from Öxarfjördur, but the cation geothermometers seem to agree quite closely. The quartz geothermometer temperatures for Kibiro seem to agree quite well, and for Panyimur samples there are great variations in all the calculated geothermometer temperatures. The magnesium concentration is high in these samples suggesting a substantial influence of cold groundwater rendering the Na/K geothermometer unreliable, and for low temperatures the silica geothermometers are not dependable either. The anomalously high estimates from the Na-K-Ca geothermometer for all the samples could be due to calcium carbonate deposited during the ascent which prevents the aqueous K and Na from interacting with the country rock.

4.4 Mixing model interpretations

Assuming that, the silica has not precipitated before or after mixing and there has been no conductive cooling of the water, then the dissolved silica concentration of mixed water and silica – enthalpy diagram may be used to determine the temperature of the hot water component. However, it is not easy to determine whether a given spring is a mixture of hot and cold spring water and also to prove that silica has not precipitated or conductive cooling has not occurred.

From the enthalpy – silica mixing model (Figure 3, found in appendix 1), the samples from Kibiro indicate a geothermal system with temperature of about 191-220°C, samples from Panyimur, indicate temperatures of about 150-160°C and samples from Öxarfjördur show temperatures of 190-220°C.

The silica – carbonate plot for all the samples from Panyimur indicates that boiling has not occurred, for Kibiro, two of the samples show boiling in the hot spring while some show equilibration and the others suggest no boiling and mixing. Samples from Öxarfjördur suggest that boiling has occurred meaning that some of the CO_2 has been lost in the steam phase, hence lowering the CO_2, concentration in some of those samples.

4.5 Gas geothermometer tempearture results based on this analysis.

One sample from Kibiro gas geothermometer was calculated and the results were: $T_{CO2} =$199°C, $T_{CH4/C2H6}$ = 208°C and $T_{H2/Ar} =$ 221°C. And for the samples from Öxarfjörfjördur, the following estimates of $T_{CH4/C2H6}$ have been made on three samples from the wells, and these are were in the following temperature ranges: Well ÆR-01 = 150°C -170°C, Well ÆR-03: = 175°C -180°C and Well ÆR-04: = 200°C -220°C. This was done basically to confirm the variations of gas geothermometers and the chemical or solute geothermometers.

4.6 Binary plots

A mixing trend could clearly be seen in all the areas under study with, K^+ vs. Cl^- and Na^+ vs. Cl^-, giving a positive correlations for Öxarfjördur and Kibiro, which may mean that there is a high Cl^- concentration being either added into these system like in the case of Öxarfjördur, it could be that seawater is mixing with the geothermal waters and for Kibiro it may be from the salt mining in that area and/or sodium chloride geothermal waters. For Panyimur, it may be from sodium chloride geothermal waters mixing at depth.

The concentration of HCO_3 in four samples from Kibiro and two samples from Panyimur is relatively higher than of other samples, suggesting that there could be CO_2 absorption from the gases that the fluid carries or from the condensation of geothermal steam containing the CO_2, geothermal waters samples containing high concentrations of HCO_3, due to the condensation of the geothermal steam in that area. There is an increase in the concentration of chloride in the samples from Öxarfjördur which may mean that there is either mixing of the geothermal waters with sea water or with deep geothermal fluids. The relationship of Ca – Na for Öxarfjördur samples showed a high ratio which may be due to limited albitization, a process in which alkali feldspar or plagioclase feldspar are completely or partially replaced with albite. This seems to be the case too for Kibiro, but not for Panyimur.

Looking at the relationships of different elements in the geothermal waters from Kibiro, Panyimur and Öxarfjördur, the following conclusion may be drawn from these results. There are some linear relationships between B and Cl which may mean that there is mixing of cold water with hot geothermal fluid in the up flow zones in these systems. While for Kibiro samples, there is linear relation between Li and B that may be due to the uptake of lithium from the waters by the surrounding rocks in the area suggesting that there could be some water rock interaction in the system.

The relationships between Na – B and Ca – B in which B is a conservative element and a linear relationship in these plots of these samples may mean that Ca and Na are present in the environment in which these waters occur too, the increase in B concentration suggests that there is water-rock interaction since Ca and Na are less mobile compared to B, and may be removed from the water during secondary mineral precipitation out of the solution.

4.7 Mineral saturation

In the log (Q/K) plots showing the equilibrium state of some of the minerals r calculated by the WATCH programme for Kibiro samples (Figure 4, found in appendix 1), most of the curves intersect the line of log (Q/K) equal to zero for Kibiro area in rhe temperature range 140°C – 160°C, and some the minerals converge below the log (Q/K) equal to zero line at 180°C – >200°C.

For Panyimur, most of the curves cross the log (Q/K) equal to zero line at 120°C - 160°C and converge below it at 180°C - > 200°C. For Kibiro and Panyimur it may be inferred that there is some mixing of cold water with a geothermal component. The anhydrite in the samples from Kibiro and Panyimur are undersaturated. Samples from Öxarfjördur (Figure 5, appendix 1) show that most of the minerals have not yet reached equilibrium. The curves for the different minerals intersect the log (Q/K) line equal to zero at temperatures of about 120°C - 150°C. And some of the curves converge below the log (Q/K) line equal to zero at temperatures of about 90°C - 180°C, with some curves converging above 200°C. There is some mixing of cold water with geothermal component in the Öxarfjördur area. And most of the minerals are under saturated, that is their solubility for example of hydrate, talc, and calcite decreases with increasing temperature leading to them being precipitated out of the solution. And this may be due to mixing of hot water with cold water in the area.

4.8 Isotope data interpretations.

I the Öxarfjördur area, the $\delta^{18}O$ ranges from -12.0 to -0.8 ‰ and δ^2H from -100.4 to -7.1 ‰, Kibiro $\delta^{18}O$ (5.5 to -1.0) ‰ and δ^2H (+39.8 to - -3.9) ‰ and that for Panyimur, $\delta^{18}O$ values range from -18.8 to -2.0 ‰ then, δ^2H from 2.5 to -16.6 ‰. There is a significant variation in the $\delta^{18}O$ values of these areas, i.e. Öxarfjördur with those from Kibiro and Panyimur both located in the western arm of the EARS**.**

All Kibiro samples plot close to all the lines that is: - the WML, KRL and CARL, with some slight shift from the WML (Figure 6, in appendix 1) which may mean that there is some oxygen shift due to water rock interaction within the system as a result of a low water rock ratio or a high temperature. All amples from Panyimur plot above the lines suggesting that there could be some good permeability in the area this could mean that there is excess deuterium.

The samples from Öxarfjördur all plot below the KRL and CARL, but close to the WML. This could mean that the water samples from Öxarfjördur has undergone water rock interaction for a relatively longe time and there may be a high temperature at depth, hence leading to oxygen shift due to exchange of oxygen between water and the rock.

5.0 CONCLUSION

The geothermal waters of Kibiro, Panyimur and Öxarfjördur are classified as sodium-chloride-bicarbonate waters. The geothermal samples from Öxarfjördur are more mature than the water samples from Kibiro and Panyimur.

From geothermometer temperature prediction, and interpretation, quartz and Na/K geothermometers are applicable in a very wide range of geological environment for example from rhyolitic, classic sediments to a basaltic geological setting.

The mineral saturation plots for Kibiro and Panyimur show that all waters have almost reached equilibration with most minerals but in Öxarfjördur they have not yet attained equilibrium.

The chemical composition of the water samples from Kibiro, Panyimur and Öxarfjördur from the different sedimentary geological settings are much affected by the strata through which these fluids flow.

Despite the fact that the Öxarfjördur geothermal system is located in a sedimentary graben, there is considerable water- rock interaction at depth beneath the sedimentary system compared to the situation at Kibiro and Panyimur.

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APPENDIX 1: FIGURES USED IN THIS RESEARCH WORK

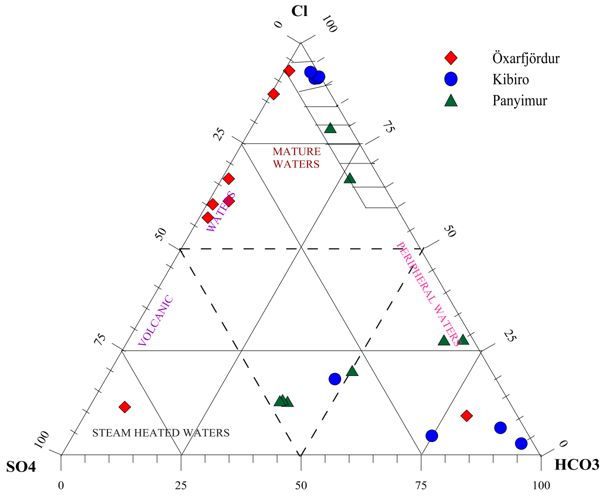

Figure 1: Cl-SO$_4$-HCO$_3$ ternary plot (Giggenbach, 1991) for water samples from Öxarfjördur.Kibiro and Panyimur

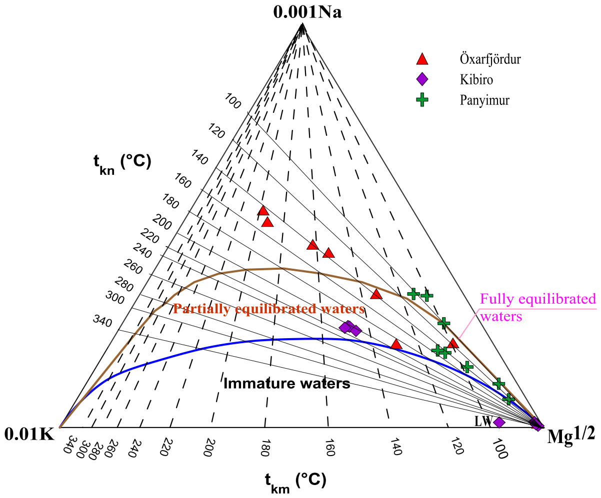

Figure 2: Na-K-Mg triangular diagram for water samples from Öxarfjördur.Kibiro and Panyimur

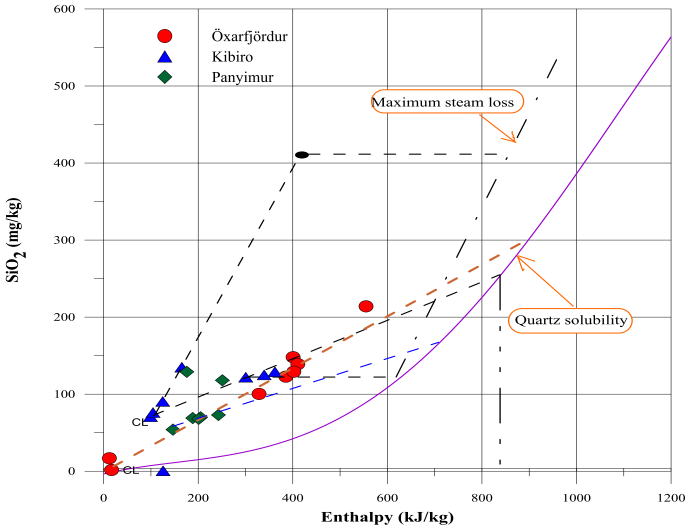

Figure 6: Silica-Enthalpy mixing model applied to water samples from Öxarfjördur.Kibiro and Panyimur

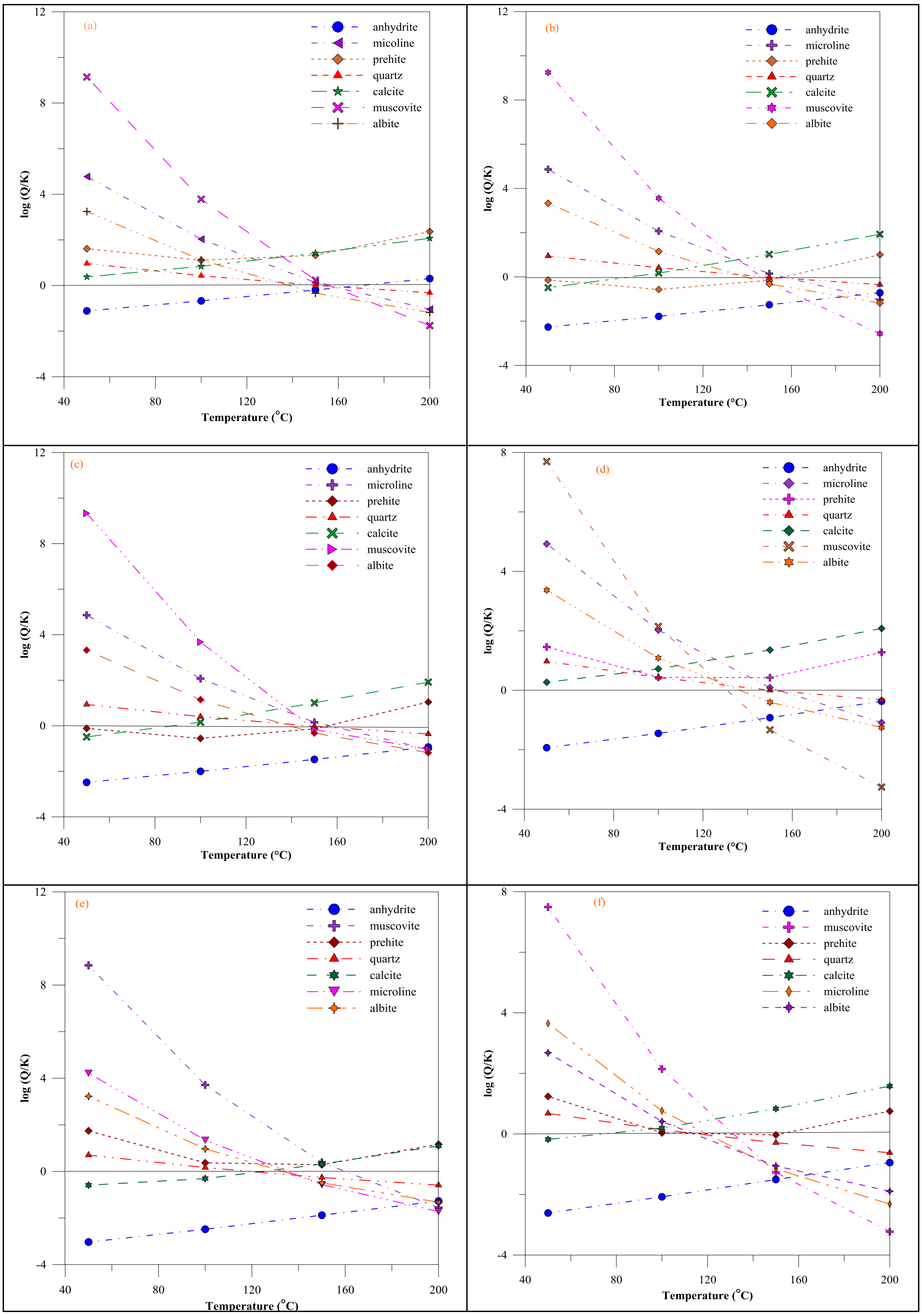

Figure 4: Mineral equilibrium plots for Kibiro samples (a-d) and Panyimur samples (e and f)

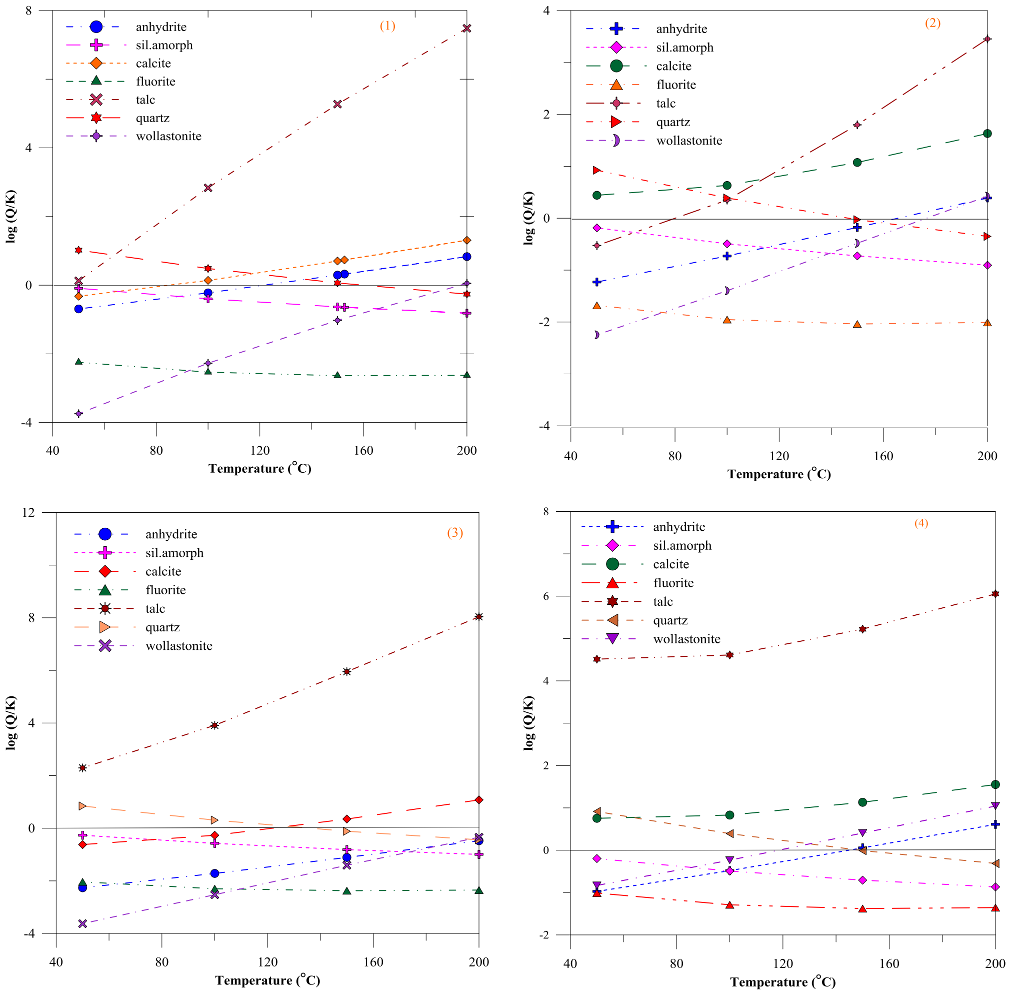

Figure 5: Mineral equilibrium plots for Öxarfjördur

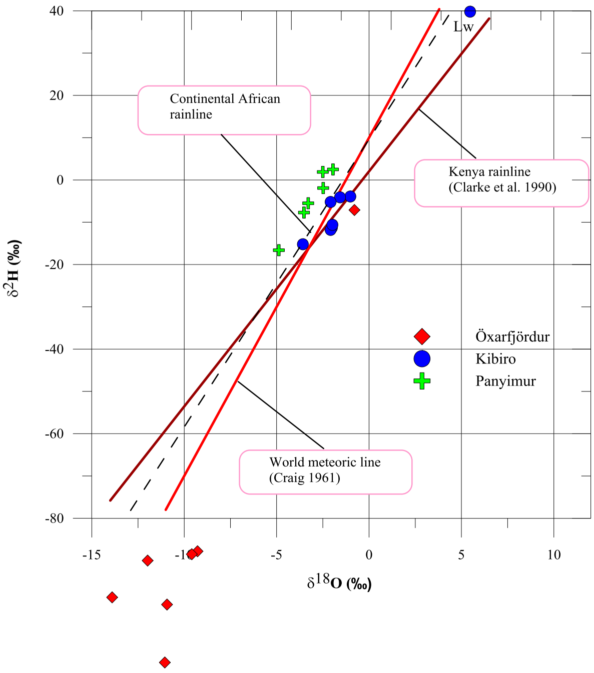

Figure 6: Plot of δ2H vs δ18O for samples from Kibiro, Panyimur and Öxarfjördur

APPENDIX 2, TABLE 1: CHEMICAL COMPOSITION (MG/KG) OF SELECTED SAMPLES FROM ÖXARFJÖRDUR KIBIRO AND PANYIMUR AND ISOTOPE VALVES IN ‰ SMOW)

LOC	T(°C)	PH	CO_2	H_2S	NH_3	Cl	SO_4	F	Br	Na	K	Ca	Mg	Al	Fe	SiO_2	B	Li	TDS	δ^2H	$\delta^{18}O$
ÖXA																					
ISK	95.7	7.3	30.3	0.05	0.00	3539	232	0.41	12.1	1818	98	400	7.14	0.00	0.00	148	1.77	0.00	6401	-87.8	-9.3
ISG	92.0	8.7	30.6	0.05	0.00	1807	85.9	0.33	6.2	950	55	186	0.07	0.00	0.00	123	1.40	0.00	3326	-88.5	-9.6
IBK	78.5	8.4	30.8	<0.05	0.00	658	46.1	0.59	2.2	427	41	17	1.47	0.00	0.00	100	0.53	0.00	1283	-90.0	-12.0
IA1	98.0	9.5	12.4	<0.05	0.00	2460	138	0.65	<0.0	1250	77	259	0.18	0.00	0.00	139	<0.0	0.00	4630	0.0	-10.0
IA3	96.0	7.9	24.3	0.07	0.00	1534	96.6	0.27	5.3	833	44	154	0.42	0.00	0.00	129	1.00	0.00	2709	-100.4	-10.9
IA4	132.0	8.6	5.1	<0.03	0.00	2110	150	0.12	8.23	1222	67	185	0.63	0.00	0.00	214	1.36	0.00	4085	-114.1	-11.1
IJÖ	2.9	7.8	42.1	<0.03	0.00	6.9	7.9	0.16	<0.0	19.8	1.4	6.1	3.62	0.00	0.00	16.8	<0.0	0.00	104	-98.7	-13.9
ISW	4.0	8.1	105	<0.03	0.00	18288	2545	0.70	<0.0	10113	396	378	1162	0.00	0.00	1.6	<0.0	0.00	36110	-7.1	-0.8
KIB																					
KM1	86.5	7.06	146	10.4	0.00	2500	46.6	5.12	16.7	1530	169	62.0	8.1	0.037	0.00	129	2.26	1.500	4576	-11.3	-2.01
KM2	81.1	7.14	155	13.0	0.00	2450	26.4	5.02	16.4	1490	164	62.9	7.96	0.041	0.02	125	2.23	1.480	4436	-11.8	-2.08
KM3	71.8	7.14	155	17.3	0.00	2440	15.4	4.74	16.2	1480	165	66	9.21	0.044	0.00	122	2.21	1.460	4384	-10.6	-1.98
KM4	39.5	8.05	115	<0.0	0.00	2580	49.9	5.37	17.3	1570	182	76	8.71	0.029	0.03	135	2.47	1.530	4548	-3.9	-1.01
KM4	29.8	6.89	367	<0.0	0.00	31.2	139	0.37	0.26	87.5	7.7	76	39.5	0.010	1.50	90.5	<0.0	0.02	662	-15.2	-3.58
KM6	23.6	6.26	130	<0.0	0.00	5.2	5.3	0.12	0.04	12.4	2.6	15	8.03	0.007	0.74	70.8	<0.0	0	124	-4.1	-1.57
KM7	24.9	6.72	232	<0.0	0.00	123	227	0.12	0.64	50.6	7.5	138	39.5	0.014	0.72	76.1	<0.0	0.02	680	-5.2	-2.08
KM8	30	8.93	236	<0.0	0.00	24.2	19.3	0.83	0.13	72.3	49	9.8	27.3	0.015	0.07	0.5	<0.0	0.01	338	39.8	5.47
PAN																					
PA1	58	8.66	71	5.61	2.1	470	26	5.2	1.5	352	11	4.5	0.36	0.47	0.1	73	0.65	0.12	890	-7.7	-3.5
PA2	45	8.45	109	2.48	1.6	379	36	4.7	0.93	321	9.5	8.5	0.68	0.17	0	69	0.58	0.00	794	-5.5	-3.3
PA3	35	7.56	142	<0.0	0.25	83	19	2.4	0.17	138	7.3	8.4	3.1	0.21	0.2	54	0.22	0.00	337	1.9	-2.5
PA4	49	9.06	95.5	<0.0	0.12	53	4.4	6.6	0.29	110	2.6	1.4	0.04	0.17	0	70	<0.1	0.00	nd	-1.9	-2.5
PA5	48	8.23	91.1	<0.0	<0.1	51	73	8.0	0.45	111	3.9	6.6	0.76	0.21	0.2	68	0.2	0.00	nd	2.5	-2.0
PA6	60	8.35	216	<0.0	<0.1	95	341	13.0	<0.2	322	18	24	2.7	<0.1	0.1	118	0.18	0.19	815	-4.9	-18.8
PA7	42	8.39	207	<0.0	<0.1	97	343	13.8	<0.2	323	19	21	1.5	<0.1	0.2	129	<0.1	0.2	812	-4.8	-17.2
PA8	38	8.44	207	<0.1	<0.1	96	352	13.0	<0.02	342	22	21	1.5	<0.1	0.3	129	0.76	0.22	825	-16.6	-4.9

APPENDIX 3: TABLE 2, METHODS AND INSTRUMENTS WERE USED IN THE ANALYSIS OF THESE SAMPLES.

Constituents	Laboratory	Method	LOD	PR RSD%
Conductivity	GSMD	4 electrode		
pH	GSMD	GE		
CO_2 and H_2S	GSMD	Titration	0.02 – 1.0	3.8 – 13.7
SiO_2, B and NH_3	OS and GSMD	SP	0.01- 0.5	0.7 – 8.3
Na, K, Ca, Mg, Sr, Li	OS	AAS	0.0005-0.1	1.5 – 2.7
SO_4, Cl and Br	OS	IC	0.02 – 0.025	0.8 – 5.4
TDS	OS	GR	2.5	3.4
F	OS	ISE	0.05	0.9
Fe, Al and Mn	OS	FAAS	0.001	
$\delta^{18}O$ and δ^2H	USI	MS		
$CO_{2,\ n.c.,}$ H_2S, n.c., CH_4, H_2, N_2, Ar, and C_2H_6	OS	GC	0.01 – 0.02	