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Geochemical Analysis for Understanding Prospectivity of Low Enthalpy Geothermal Reservoirs of Dholera

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ABSTRACT

Geochemical Methods are crucial methods applied during various stages of exploration and exploitation to evaluate reservoir characteristics. It is used concurrently with geological and hydro-geological appraisals to supplement available information regarding the prospectivity of potential region of investigation at relatively low costs compared to geophysical methods or drilling. Dholera is an ancient port city which has historically been associated with natural thermal springs and wells with hot water flowing at appreciably high temperatures. Studies from pre-existing wells and surveys have suggested the presence of a sizable low enthalpy geothermal resource base. Geochemical methods are applied to waters, gases, and secondary minerals. One of the most prominent use of geochemical sampling is the determination of subsurface temperatures using Geothermometry. In this study commonly accepted concepts of Ionic and Silica Geothermometry are applied to understand conditions in the reservoir. Care has been taken to undertake tests while preserving native conditions by preserving sample using accepted standards. This paper seeks to present an interpretation on the results obtained as well as a give an outlook of the resource in place waiting to be utilized in this region. Interpretation of the data has given us some input on the Reservoir characteristics like: Reservoir Temperature, Type of reservoir rock, mixing process, multiple fluid origin and elevation of the basin.

1. INTRODUCTION

Gujarat is endowed with a huge potential of wide range of geothermal resources. Figure 1 shows the various thermal springs located in Gujarat. Out of the 17 thermal spring, Dholera was chosen as the study area and a preliminary study of the subsurface reservoir conditions was attempted on the basis of Ionic and Silica Geothermometry. The field survey of the study area involved sampling 4 thermal spring in the resource area. The samples were analyzed for color, pH, conductivity, hardness, salinity and various other physical also, detailed study in the presence of various cations and anions present in the sample were done. The variation in the chemistry of geothermal fluids provides information regarding the origins, mixing and flow regimes of the systems (Arnosson et al., 2007).In order to keep the predictions of the study precise great diligence has been taken in collection as well as testing of the samples. The present study includes the Collection of samples, their chemical analysis and the interpretation of the results.

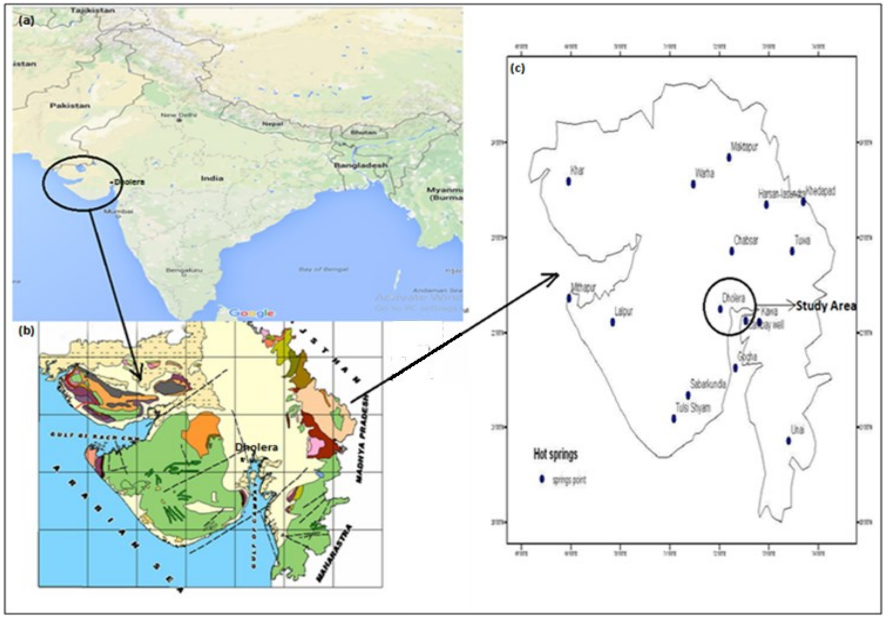


Figure 1: The Location of the Study Area in (a) within the political boundaries of India (Source- Google Maps, 2016) , (b) In the geological map of the state of Gujarat(Geological Survey of India, 2005) (c) Among the known hot springs in the state of Gujarat. (Sircar et al.,2014)

2. AREA OF STUDY

There are 22 thermal provinces in Gujarat having 17 thermal spring (Table 1) that stretch from Archean to Quaternary in provenance within the Cambay basin as its main tectonic structure(Chandrsekharam, 2005) . The Geothermal Fields at Dholera, Figure 1, lies 30 km south-west of the Dhandhuka Village in the Ahmedabad District and is around 60 km to the north of the city of Bhavnagar. Villages here show an easterly trend in elevation changes, wherein the low-lying plain falls gradually from the 8m contour on the western boundary to 4m in the east. The area is marked by the presence of old mud flats, flood plains and salt flat areas. The soil in this region mainly consists of alternate layers of gravels, fine to coarse grained sand and clay. Chemically the soil is loamy, mixed montmorillonitic, calcareous and mostly saline.

Location	LAT / LON
Chabsar	22°48’ 72°16’
Cambay Wells	22°14’ 72°41’
Gogha	21°41’ 72°16’
Harsan	23°22’ 73°05’
Kawa	22°04’ 72°47’
Khedapad	23°20’ 73°56’
Khar	23°33’ 69°00’
Maktapur	23°50’ 72°22’
Warha	23°43’ 71°43’
Mithapur	22°32’ 74°01’
Unai	20°51’ 73°24’
Tuwa	22°51’ 73°34’
Tulsishyam	21°08’ 71°05’
Savarkundla	21°20’ 71°19’
Lasundra	22°55’ 73°12’
Lalpur	22°12’ 69°48’
Dholera	22°15’ 72°12’

Table 1- List of thermal springs in Gujarat, (GSI 2001)

The Dholera Springs were first discovered more than a century ago, the first drilled well in this area flows to this day at an appreciable rate. A total of four springs have been demarcated in a radius of 4 km, viz. Dholera, Uthan, Swaminarayan temple and Bhadiyad, Figure 2. Of all identified hot springs in Gujarat, the springs in the areas around Dholera have the highest geothermal flow rate in Gujarat (Vaidya et al., 2015). The area of study falls on the western margin of the Cambay basin. Cambay basin rests on the Deccan trap, which lies at a depth of 500-600 m. Quaternary alluvial deposits of a thickness up to 100 m occur by the side of the basin (Sircar et at, 2015). The subsurface lithology of the area is mostly sand dominant consisting of alternating layers of coarse and fine sand. The alkaline magnetism causes presences of granitic basement rocks and a shallow mantle.

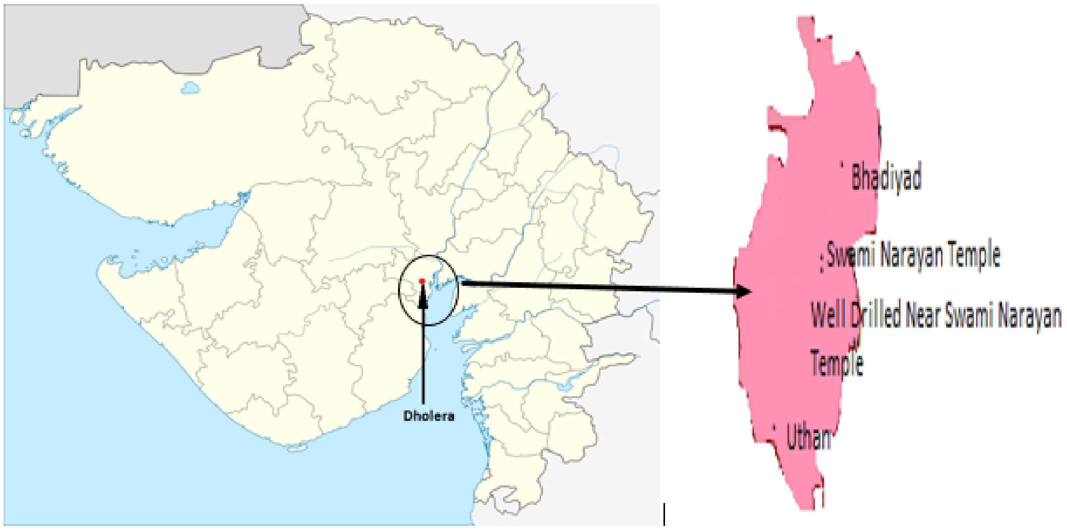


Figure 2: Area of study for geochemical analysis, Dholera and the various hot water springs that were examined in this study. (Map not to scale)

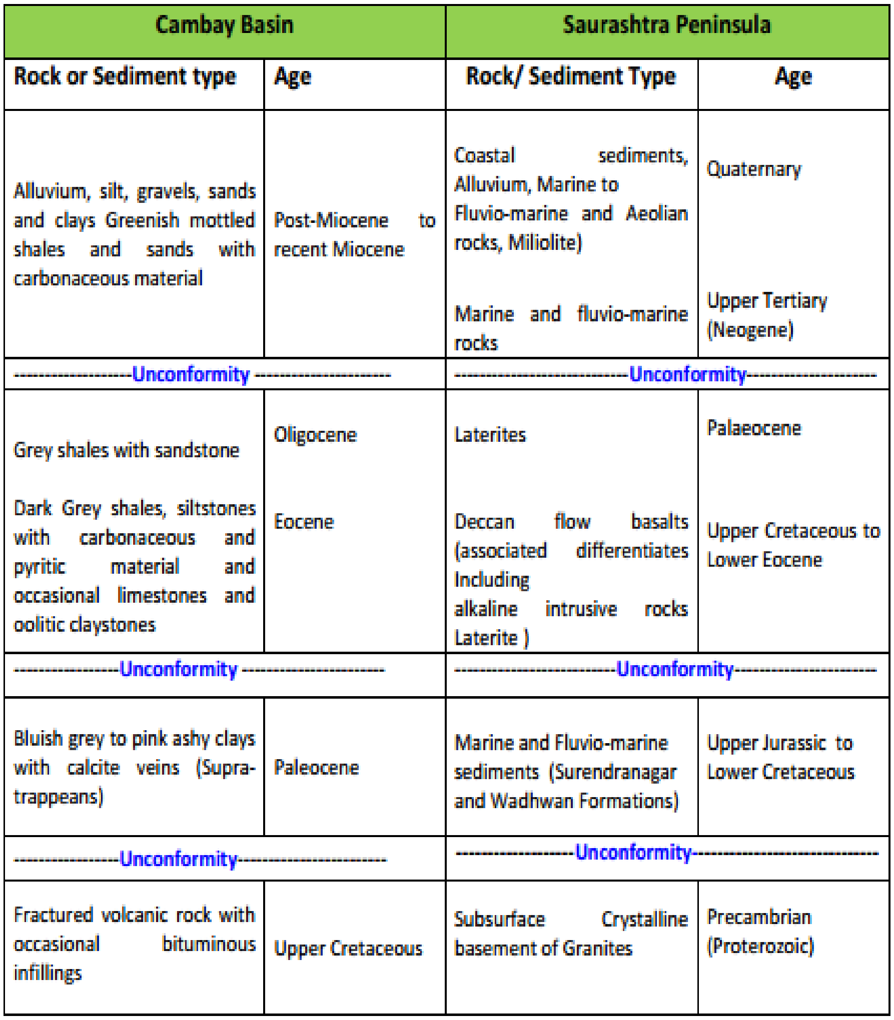
2.1 Geology and Geomorphology

In the present day the terrain in Dholera is marked by recent to sub recent alluvium and mud flats. It lies in the in the deltaic region of five rivers, namely Sukhbhadar, Lilka, Utavali, Padaliyo and Keri. The area is also marked by the presence of quaternary soils deposited in the subsiding area on the margins of the Cambay basin for over a thickness of 100 m (approx.) over the tertiary sediments which rest on Deccan Traps at a depth of about 500- 600m (Biswas, 1988). The area is located along the margin of the Saurashtra Peninsula which is in the vicinity of the West Coast lineament and to the west of the West Marginal fault of the Cambay Basin. The presence of granitic basement rocks and shallow mantle depth underlying the springs are indicated by the presence of high gravity reading over the area (400 m x 400 m) (Sharma, 2013).

Dholera is located in the Saurashtra Peninsula and adjacent to the Cambay Basin. The sediment deposition in the area took place in two cycles, namely, a Major Jurassic Transgressive cycle (deposition of carbonate and shales) followed by a Late Jurassic- Early cretaceous regressive cycle (deposition of deltaic clastics).

The geotectonic configuration of the region is largely responsible for the abundant presence of the minerals as per the historical database of the state mineralogical development on the region maintained by the Government of India. (GMDC, 2010) Also, due to tectonic upliftment, the presence of mantle at shallower depths causes the presence of high heat flow (Chandrasekharam, 2005). The high heat flow rates, presence of rift systems and deep lithosphere piercing gravity fault systems are surmised to have given rise to the various thermal springs in the our study area.

The Cambay Basin is an intra-cratonic basin. The configuration of this basin is controlled by three major tectonic trends. (Biswas et al, 2011). The basin has an age range between Paleocene to Holocene in which a Mesozoic sequence is overlain by a thick flow of basaltic lava on which a complete Tertiary sequence rests. Besides deep seated faults, which brackets the basin, older granite intrusive (~ 955 Ma; Gopalan et al., 1979), such as those at Tuwa and Miocene- Pliocene basic intrusive, contribute partly to the high thermal gradient (> 60^{o}C) and heat flow value (>80 mW/m^{2}) of this basin (Chandrasekharam, 1977).



Cambay Basin		Saurashtra Peninsula	
Rock or Sediment type	**Age**	**Rock/ Sediment Type**	**Age**
Alluvium, silt, gravels, sands and clays Greenish mottled shales and sands with carbonaceous material	Post-Miocene to recent Miocene	Coastal sediments, Alluvium, Marine to Fluvio-marine and Aeolian rocks, Miliolite) Marine and fluvio-marine rocks	Quaternary Upper Tertiary (Neogene)
-------------------Unconformity ---------------------		---------------------------Unconformity--------------------	
Grey shales with sandstone Dark Grey shales, siltstones with carbonaceous and pyritic material and occasional limestones and oolitic claystones	Oligocene Eocene	Laterites Deccan flow basalts (associated differentiates Including alkaline intrusive rocks Laterite)	Palaeocene Upper Cretaceous to Lower Eocene
----------------Unconformity ----------------------		-------------------------Unconformity---------------------	
Bluish grey to pink ashy clays with calcite veins (Supra-trappeans)	Paleocene	Marine and Fluvio-marine sediments (Surendranagar and Wadhwan Formations)	Upper Jurassic to Lower Cretaceous
----------------Unconformity-----------------------		------------------Unconformity----------------------------	
Fractured volcanic rock with occasional bituminous infillings	Upper Cretaceous	Subsurface Crystalline basement of Granites	Precambrian (Proterozoic)

Figure 3: Generalized Stratigraphy of Cambay Basin (right) and Saurashtra Peninsula (left), After Sircar et *al* (2015)

Saurashtra Basin is located in the northern part of western continental margin of India which trends NNW-SSE. The on-land part of the basin is also known as Saurashtra Peninsula. The tectonic movements during the tertiary age was milder and cyclic which is represented in the stratigraphy with large unconformities. After the early Middle Miocene, the western margin as a whole experienced a heavy influx of clastics and manifests basin-ward rapid shift of the shelf considerably long distance to its present position. (DGH, 2009). The Stratigraphic sequence of Cambay and Saurashtra (Figure 3) exhibit a case where the formation of large unconformities and basaltic base in the system cause a strong chance of presence of a geothermal system, as can be witnessed in Dholera. There are places in Dholera where the upper sequence has been completely eroded and the Deccan Traps can be realized at a shallower depths itself.

3. GEOCHEMICAL STUDY

Geochemical methods are applied during various stages of exploration, evaluation and exploitation. When they are used for geological and hydro-geological appraisals concurrently they are capable of supplying valuable information at comparative lower costs in comparison to geophysical methods or even drilling. These techniques are used to understand physicochemical parameters, the dissolved chemical species (spanning all concentrations) as well as isotope content. Geochemical interpretations provide an approach towards developing insights on fluid chemistry, which in the exploration phase facilitates developing a reservoir model and approached the future conditions during exploitation.

Geochemical tool	Selected parameter	Information on the EGS reservoir
Secondary minerals	Mineral assemblages (silica, silicates, carbonates, sulfides, zeolites, clays)	Qualitative estimation of reservoir temperatures, reservoir heterogeneity
Fluid and gas chemical composition	Major and minor species	Rock type, chemical equilibrium, fluids mixing processes
Fluid and gas isotopic composition	Hydrogen, carbon, sulfur, strontium isotopes	Elevation of the infiltration zone, underground residence time, origin of the minerals, fluids mixing processes, crustal/mantle origin
Gas composition	N_2, CO_2, H_2S, H_2, He, Ar, Rn	Fracture monitoring during drilling
Water-stable isotopes	$D/^{18}O$	Oxygen shift enrichment
Solute geothermometers	SiO_2, Li, Na, K, Ca, Mg, F, SO_4	Reservoir temperature, fluid uprising processes, mixing processes
Isotope geothermometers	$^{18}O(H_2O)$, $^{18}O(SO_4)$	-
Gas geothermometers	CO_2, H_2S, H_2, CH_4, Ar	-
Mud and fluid logging	Major specie, CO_2, He	Fracture monitoring during drilling

Table 2: Geochemical tools and interpretation. (Giggenbech, 1988)

In the past, the water and gas chemistry of geothermal fluids has proved to be extremely effective in determining water provenance, identify mixing processes and eliminating their effects, type of reservoir rock, multiple fluid origin, elevation of the infiltration basin, underground transit time, evaluating subsurface temperatures, and predicting scaling and corrosion during project conceptualization. (Fournier, 1977; Rybach, and Muffler, 1981; Arnorsson, Gunnlaugsson, and Svavarsson, 1983; Arnorsson, 2000; Giggenbach, 1988). Table-2 sums up the uses of various geochemical tools and techniques. These methods provides information that could support future EGS developments

3.1 Geothermal Fluid Chemistry

Geothermal fluids contain a number of different constituents with varying concentrations, with important chemical parameters which characterize geothermal fluids, such as (Nicholson, 1993)

- 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.
- Chemical composition of waters is expressed in terms of major anion and cation contents.

3.2 Geothermometry

One of the most prominent methods of the temperature analysis from the geochemical sampling is the determination of the temperature of the subsurface by geothermometers. Geothermometers are thermometers that are designed to measure the temperatures of the borehole by the various minerals that are present in the water sample. The geothermometer works because of the relative equilibrium concentration of the chemical species change with respect to the temperature (Powell, 2010). The temperature at which these different species react may also vary with silica reacting at lower temperature and the cations reacting at higher temperatures.

The geothermometry can be of broadly of 3 types:

1. Water or solute geothermometers
2. Steam or gas geothermometers
3. Isotope geothermometers

Water and Steam Geothermometers compose Chemical Geothermometers. Application of Chemical and Isotopic Geothermometry techniques help during exploration stages to estimate reservoir temperatures below the zone of cooling. The application of these geothermometers though need assumption that the water composition does not change during conduction cooling while being transported, the boiling is considered to be adiabatic (Cyrus, 2009).

3.4 Water Analysis

Analysis of water samples to understand the chemical composition of water is of utmost importance. This composition is majorly expressed in terms of the cation and anion concentrations – Na^+, Ca^{++}, Mg^{++}, HCO_3^-, Cl^-, SO_4^{--} etc. The ionic concentrations, in turn, helps to draw conclusions on water source – if it belongs to a surface water aquifer or is a major geothermal aquifer contributor. For example, water from surface aquifers has a higher magnitude of Mg concentration as compared to a geothermal reservoir. Also, conservative components or stable isotopes such as ^2H, ^{13}C, ^{18}O along with B, Cl, Br etc. are key to trace back the water origin as they do not take part in water-rock interaction. Furthermore, the rock forming constituents SiO_2, Na, K, Ca, Mg, etc. can be used to infer subsurface temperature and potential problems that can be encountered during production.

3.5 Methodology

The major challenge encountered while conducting laboratory analysis is collecting a water sample representative of the geothermal reservoir. The water tends to loose certain components (say, H_2S gas content) as it reaches the surface through a hot water spring.

Moreover, maintaining the sample temperature to original is also significant as temperature changes directly affect the percentage solubility of various compounds. Hence, when geothermal water or fluid move through the rock they may have chemically react with the rock with which they come into contact. This may lead to following

- Dissolution of some selective minerals from the rock.
- Precipitation of some minerals from the solution.
- Substitution of certain chemical elements in the fluid by other elements in the mineral.

Above three processes leads secondary mineral formation by depletion or enrichment of some of the chemical component from the fluids. (Arnórsson, 2000). Thus emerges a need to specify a sampling procedure while collecting water samples. Discussed further is the sampling procedure followed in Dholera, Uthan and Unai along with elaborated interpretation method. Water samples from hot springs at Dholera, Unai and Uthan were collected. These springs have been active for more than 50 years and the water collected from the surface might not mimic the subsurface aquifer conditions but collecting a preserved sample straight from the aquifer was not possible. The sampling methods used are as outlined in Giggenbach and Goguel, 1988. There were four samples collected from each water source.

- Raw untreated sample for determination of pH and conductivity
- Filtered untreated sample for determining anionic concentrations
- Filtered and diluted sample for determining silica content, and
- An acidified sample with nitric acid reduced to pH 2 for determination of cationic concentrations

Preservation of samples was critical in order to reduce the rate of any biological or chemical reactions. After collecting the samples, these were evaluated in our laboratory where all the chemical tests were carried out in order to obtain concentration values.
The general method for determining the concentration of Aluminum is by carrying out Flourometric Analysis with Lumogallion. The concentration of Ammonia (NH_3), Boron, Calcium, Magnesium, Silica, Potassium, etc. can be estimated by conducting a Spectrometric Analysis using different reagents – for example Nessler Reagent, Carmine, Curcumin, etc. Titrimetric Tests are conducted to understand the composition of Bicarbonates, Carbonates, total Carbon Dioxide, Chloride, etc. Also, Ion Chromatography is widely acceptable to estimate percent composition of Chloride, Fluoride, Calcium, Sulphate, Magnesium, etc. Silica, being very crucial in water source determination, could be determined using UV-Visible Spectroscopy. (UNUGTP, 2005 and Chatterjee *et.al.*, 2015)

3.6 Results

A Total of 8 Samples were collected from the Wells, two samples from each instance, in and around the study area to understand the ionic parameters. The two samples were taken to ensure the repeatability and accuracy of the data that was obtained during analysis. Study was done in accordance to accepted standards for sample preservation and to ensure accuracy of the results. The results of the study are shown in Table 3.

The results of the ionic compositions served as the input for the calculations for the Geochemical Cross Plots and Geothermometry based temperature predictions. The gaps in the plot represent data that were considered erroneous due to sample contamination during transport to the laboratories which caused results to be anomalous to what is seen normally.

Parameters	Uthan		Temple		Bhaliyad		Dholera	
	S1	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**
pH	7.07	7.05	7.22	7.22	7.27	7.32	7.24	7.25
TDS	~	5012		5120		4952		4844
Chlorides (mg/l)	2426	3019	2510	3158	2635	4319	2476	2926
Sulphates (mg/l)	30	31	13	12	56	48	16	16
Fluoride (mg/l)	0.21	0.11	0.17	0.01	0.22	0.24	1.16	0.19
Conductivity	12150	12100	12300	12600	12600	12900	12400	12300
Sodium (mg/l)	1139	1811	~	1901	1156	1902	1107	1792
Pottasium (mg/l)	26.5	18.4	25.7	17.9	21	16.6	23.7	17.5
Calcium (mg/l)	107	95	107	116	125	146	100	111
Magnesium (mg/l)	49	52	50	49	72	60	46	39
Carbonate (mg/l)	60	~	~	~	60	~	20	~
Bicarbonate (mg/l)	190	~	~	~	140	~	170	~
Boron (mg/l)	3.88	1	3.76	~	4.44	~	4.8	~
Strontium (mg/l)	<0.002	~	<0.002	~	<0.002	~	<0.002	~
Cesium (mg/l)	<0.002	~	<0.002	~	<0.002	~	<0.002	~
Rubidium (mg/l)	<0.002	~	<0.002	~	<0.002	~	<0.002	~
Arsenic (mg/l)	<0.01	~	<0.01	~	<0.01	~	<0.01	~
Barium (mg/l)	<0.002	~	<0.002	~	<0.002	~	<0.002	~
Iron (mg/l)	0.505	~	0.482	~	<0.01	~	0.647	~
Manganese (mg/l)	<0.02	~	<0.02	~	<0.02	~	<0.02	~
Silica (mg/l)	12.32	14	16.85	16	9.98	15	12.79	17
Lead (mg/l)	~	0.08	~	0.11	~	0.09	~	0.19
Nickel (mg/l)	~	0.06	~	0.13	~	0.07	~	0.04
Salinity	5010	5012	5300	5421	7612	7604	4887	4801
Carbonate Hardness	150	150	160	160	70	40	180	200

Table 3: Results of Analysis of water samples

3.7 Analysis and Interpretation

3.7.1 Piper Plot

The Piper Plot is extensive used to understand the composition of geothermal waters. The lower left part of the plot represent the cations while the lower right represents the anions. The Diamond plot in the middle represents the combination of the two lower parts. Different portions of the diamond diagram conveys different interpretations. The top quadrant represents calcium sulfate waters (gypsum ground water and mine drainage), the left quadrant calcium bicarbonate waters (shallow fresh ground water), the right quadrant sodium chloride waters (marine and deep ancient ground water), and the bottom quadrant sodium bicarbonate waters (deep ground water influenced by ion exchange). The results from the analysis on samples from the study area (Figure 4) show a higher concentration of Sodium and Potassium cations and Chloride anion. All the four thermal springs of Dholera in this study falls in the same block indicating that they are similar in geochemical nature and composition.

3.7.2 Tcsh

The Tcsh plot (Giggenbach, 1991a) illustrates the proportion of major anions present in the sample, Giggenbech 1991. As it can be seen from the Plot in Figure 5 that the samples from the thermal springs fall under the mature water region. It has moderate to high chloride and bicarbonate content while a very low sulfate content. Giggenbech et al (2010), has stated that these types of waters provide more reliable cation Geothermometry results than a spring that is mainly bicarbonate or sulfate.

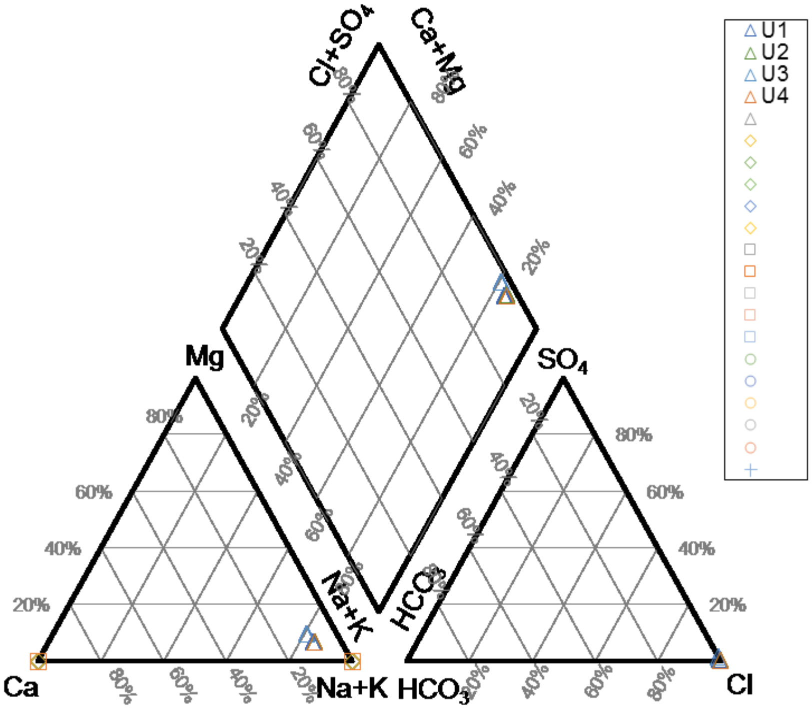


Figure 4: Piper plot

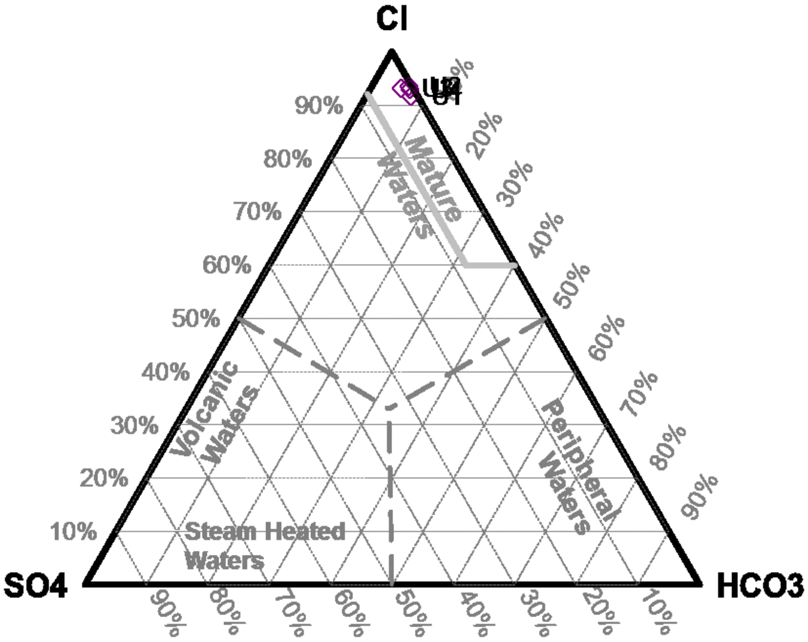


Figure 5: Tcsh Plot

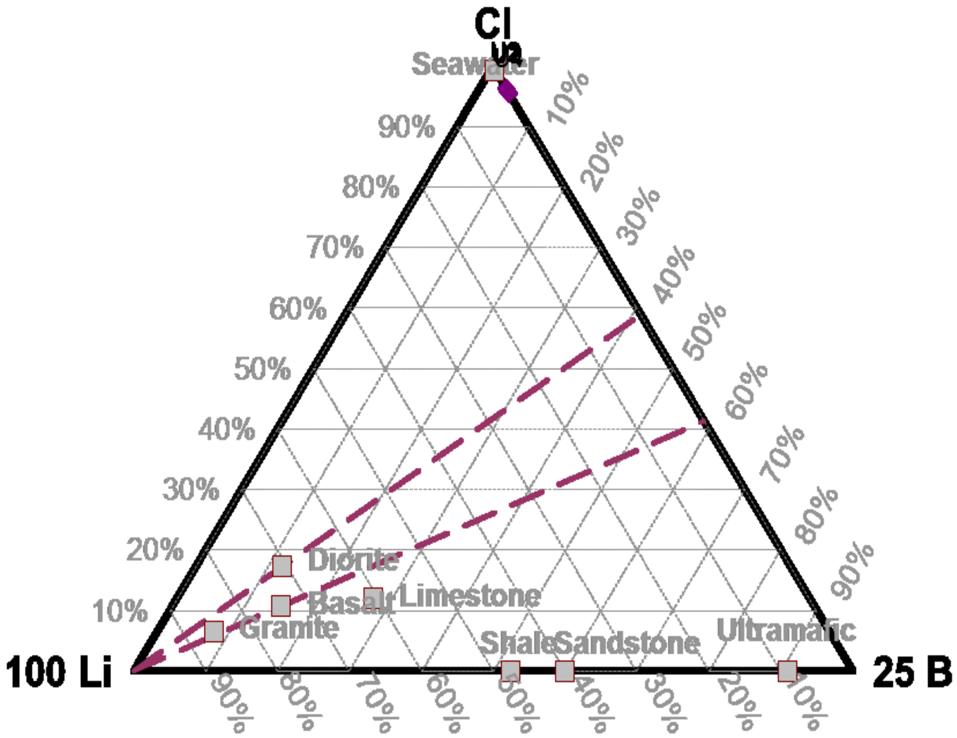


Figure 6: Tclb Plot

3.7.3 Tclb plot

The ternary of chloride, lithium and boron (Giggenbach, 1991a) is used to distinguish fluids from different sources, it reveals :

- Fractionation associated with boiling, or
- Mixing with fluids that have boiled, or
- Differentiate fluids generated by unique sources of high temperature steam (Powell and Cumming, 2010).

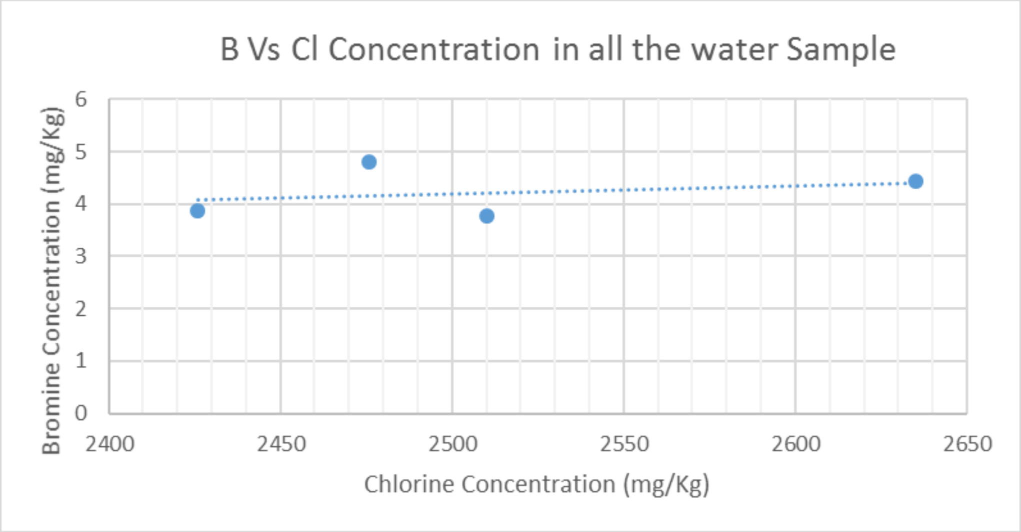


Figure 7: Plot of Cl vs. B concentrations in all thermal water samples

The ternary Tclb (Figure 6) plots Cl-Li-B results for the sampled thermal springs. Results from the plot suggest that due to negligible amount of Lithium in the samples all the points lies in the top right part of the plot which indicates water sample is more saline (high chloride content) and has been subject to possibly long term circulation of groundwater in deep source rocks and/or mixing with basin groundwater where gypsum and halite are deposits in basin fill and absorbed in solution (Love, Gootee, Cook and Spencer, 2014). Moreover, linear relationship between Chloride concentration and Bromine concentration (Figure 7) suggests mixing of very low concentration of cold water with high concentration of hot water (Witcher, 1979d). However, B/Cl ratio plot (Figure8) is almost constant for all the springs. High Cl/B ratios are attributed to seawater mixing and minimal infiltration by meteoritic recharge (DeBonne N. Wishart, 2012).

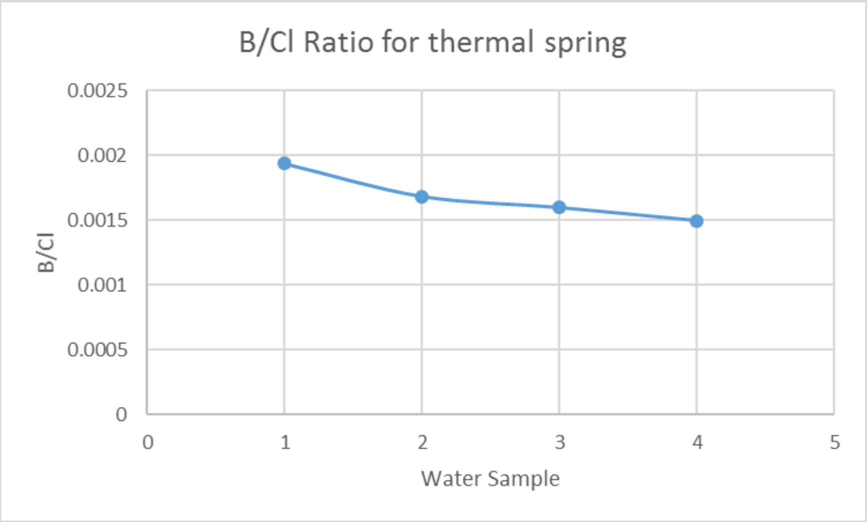


Figure 8: Plot of B/Cl ratios for the thermal springs

3.7.4 Tcfb

This ternary of Cl-F-B helps trace the water source, because, in the absence of relatively rare fluorite with which to re-equilibrate, F can be expected to be conservative (Powell and Cumming, 2010). The Tcfb ternary (Figure 9) was used to show the common source of thermal spring groundwater. Therefore, one can expect the fluoride concentrations to be similar across the samples.

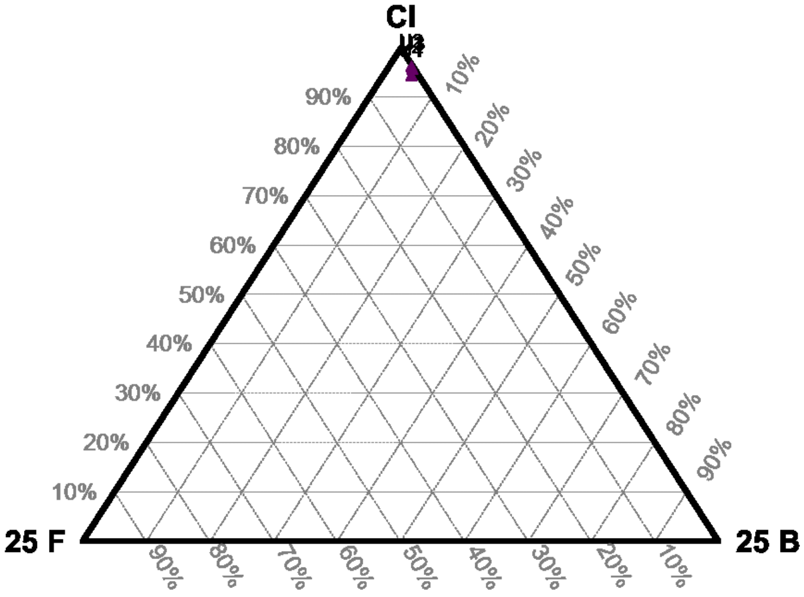


Figure 9: Tcfb Plot

3.7.5 Tnkm Plot/The Giggenbach plot/Geoindicator plot

Tnkm combines Sodium potassium (Na-K) Geothermometer with Potassium magnesium (K-Mg) Geothermometer. This is known as a "geoindicator" because it organizes the plotted data points in a manner that illustrates both the evidence that supports the interpretation of equilibrated water at high temperature and the influence of shallow processes, and possible equilibration at lower temperature (Powell and Cumming, 2010). Mariner and Janik (1995) and Maturgo et al. (2000) has shown that the extrapolations of a Geothermometer trend based on shallow samples can have excellent agreement with both Geothermometers and measured temperatures from produced wells in the reservoir.

On the ternary plot of Na-K-Mg (Figure 10), data plotted for several spring samples fall at the boundary of Partial Equilibration and immature water sector. So, it can't be defined if water is mature or falls under partial equilibrium region. However, on comparing the Tclb with Tnkm plots it can be concluded that water is in Partial equilibration and that Waters have been deeply circulated at higher temperatures having cations in 'partial equilibrium' which can be plotted on the Geothermometer grid to estimate temperatures in the geothermal reservoir. Evidently, the temperature prediction using cation Geothermometry has a different story. The temperature values estimated using cation Geothermometry has shown large variations from the expected outcome which suggests that, Cations for these samples are not in partial equilibrium, the waters are assumed to be from shallow source or mixed and temperatures are not as accurate as plotted on this Geothermometer grid.

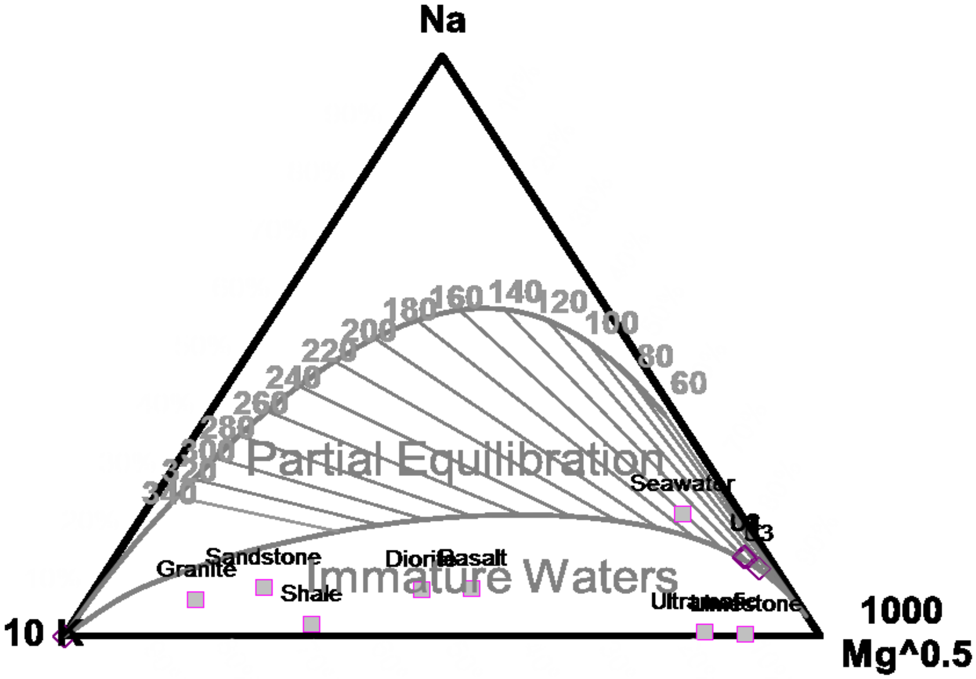


Figure 10:Tnkm Plot

3.7.6 Xkms Plot

Giggenbach and Goguel (1989) used two low temperature Geothermometers to predict the temperature of the reservoirs. By comparing two Geothermometers it increases confidence in both if they agree. The quartz Geothermometer calculations assume conductive cooling of the water after it leaves the reservoir. Disagreement between these two Geothermometers might be due to dilution, equilibration with amorphous silica, or perhaps some residual effect of an acid zone that invalidates the Geothermometry, even though the water has been neutralized (Powell and Cumming, 2010).

(Figure 11) is the cross-plot of the K-Mg Geothermometer and the quartz (conductive) Geothermometer is from Giggenbach and Goguel (1989). All the ground water sample gives the Geothermometer temperatures ranging from 60°C to 75°C. Sample 3 gives low temperature value of about 60 ^{0}C , whereas rest all the sample have almost same temperature of about 70 ^{0}C.

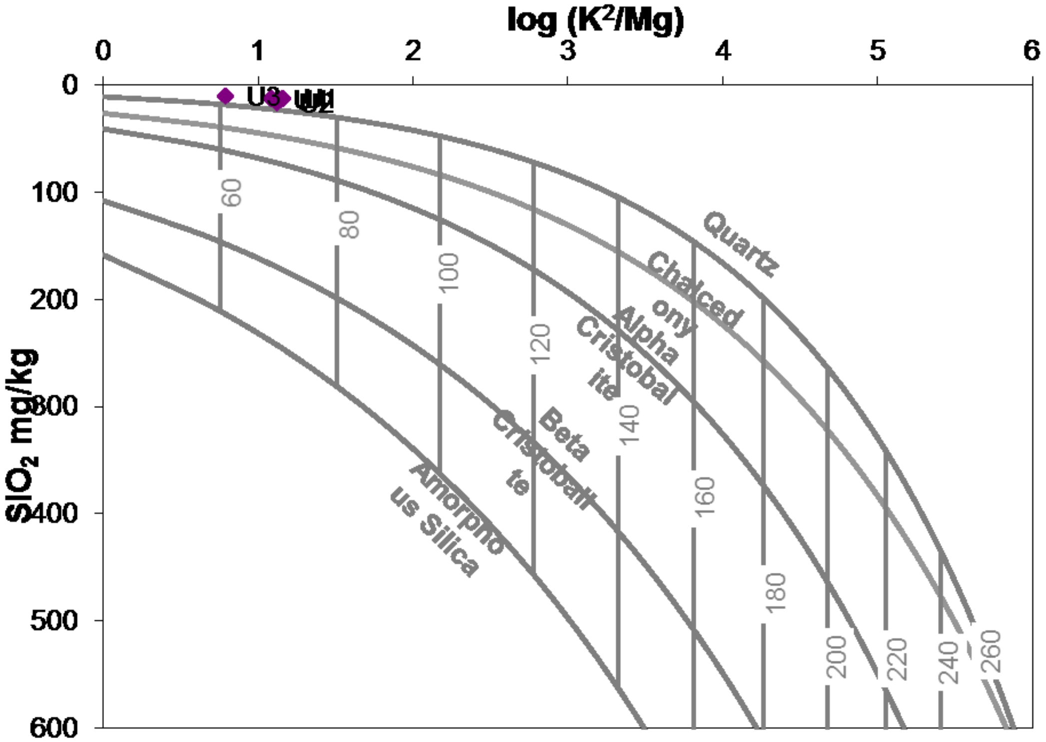


Figure 11: Xkms plot

3.7.7 Xmckn plot

It's a geoindicator plot presented by Giggenbach and Goguel (1989). It compares Na-K Geothermometer with equilibration of the system Mg-Ca. It is used to study the influence of shallow, low temperature process, which affects the Mg-Ca equilibrium. It is useful for reservoir in carbonate rocks or fluid dominated by rock chemistry rather than geothermal equilibration (Powell and Cumming, 2010).

As we can see in (Figure 12) the extent of fluid mixing shows us that all the samples plot above the 'full equilibrium' line and toward (very near to) the region of 'seawater mixing' indicating dissolution of the wall rock is because of influence of mixing with seawater (DeBonne, 2015).

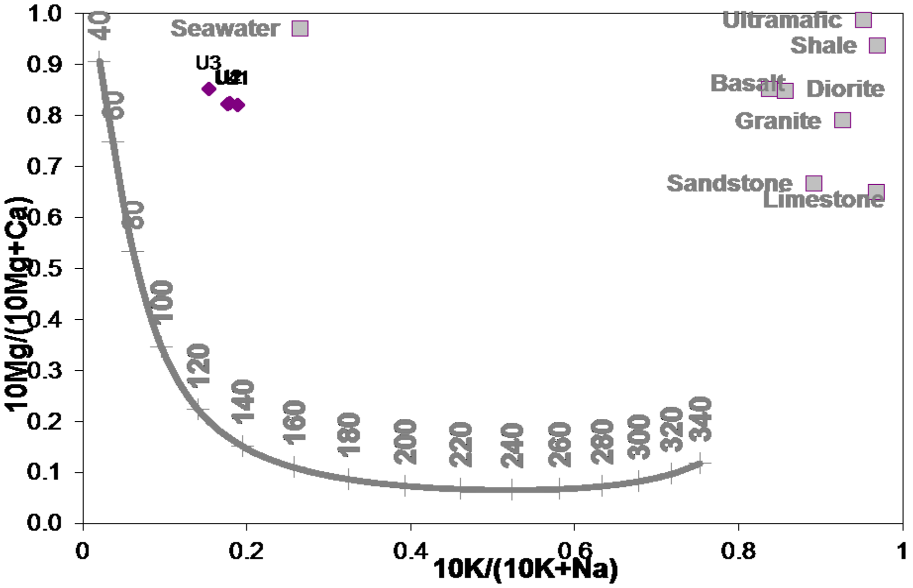


Figure 12: Xmckn Plot

3.7.8 Xkmc Plot

It is also a Geoindicator plot presented by Giggenbach and Goguel (1989). It compares the potassium-magnesium Geothermometer with a measure of the partial pressure of CO_2 based upon equilibrium between K-feldspar, calcite and K-mica on one side and dissolved Ca^{+2} and K^+ on the other (Giggenbach and Goguel, 1989).

All the cation Geothermometers are affected because of the variation of partial pressure of CO_2 being Ca^{2+} is constituent of calcite. CO_2 is likely a major component of most geothermal fluids; therefore, it is expected to contain non-equilibrium amounts and allow minor amounts of Ca^{2+}, K^+ , Mg^{2+} to adjust to the prevailing conditions of temperature and partial pressure (DeBonne,2015).

This plot helps to determine the partial pressure of CO_2 at the last temperature of water equilibration with the rock. This being the case, this plot is probably limited to assessments of whether the sampled fluid is likely to be in equilibrium with calcite in the subsurface (Powell and Cumming, 2010). Sample results that plot on Figure 13 lie within the “calcite formation” envelope and therefore likely to be in equilibrium with calcite in the subsurface, with Geothermometer temperatures between 60°C and 80°C.

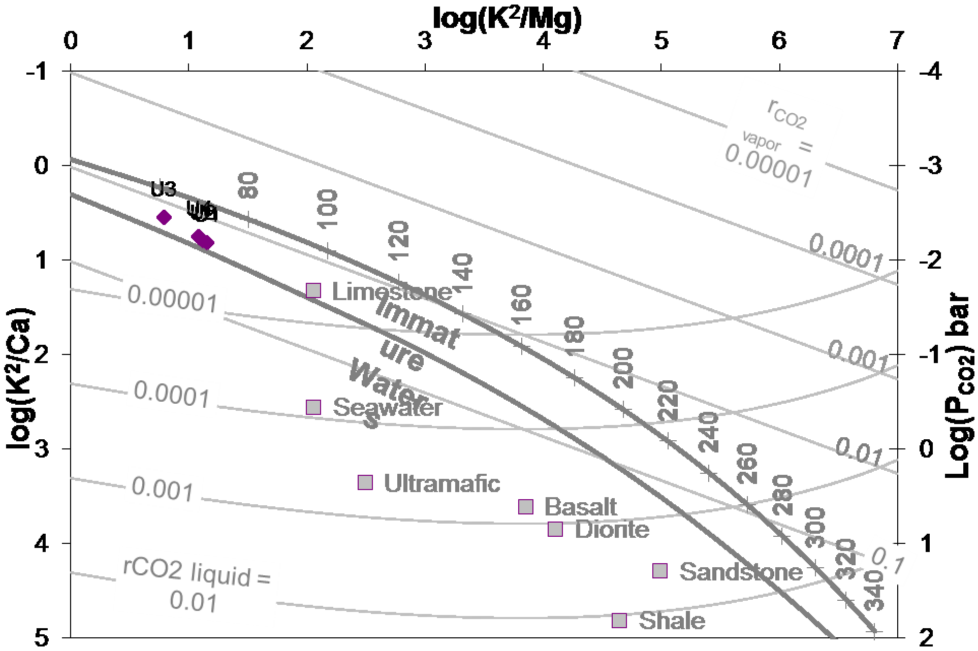


Figure 13: Xkmc plot

Geo-temperatures estimated from silica Geothermometry may be lower due to the presence of high salinity fluids that alter quartz solubility; the effects of steam separation that may precipitate silica; and the effect of pH on quartz solubility or dilution due to shallow mixing with cold meteoritic water.

4. GEOTHERMOMETRIC INTERPRETATION

As evident from the gamut of papers published in this sphere, it is possible to make predictions of subsurface temperatures based on data collected from isotopic and chemical composition of the fluids that discharge from springs and wells. The results can also help predict future developments for utilization of productive horizons. In fact it has been proved that it can also help understand the chemical state of the recharging water in the vicinity of the well as a result of boiling or heating or even depressurization. (Bruhn et al., 2010).

Most chemical reactions that may occur in geothermal systems are dependent on temperature, moreover in presence of low temperatures the kinetics of these reactions are not very fast, thus equilibrium characteristics are preserved even when the water flows to the surface and cools down. Assuming conservation of mass and heat and determining the composition it therefore possible to prognosticate subsurface temperatures. This study focused mainly on the Water or Solute Geothermometers .

4.1 Water or Solute Geothermometers

These methods focus on using concentration and ionic ratios of the components of the samples for geothermometric predictions. The most commonly used of these are the silica (chalcedony and quartz), the Na–K and the Na–K–Ca (Fournier, 1973; Fournier and Truesdell, 1973; Ellis and Mahon, 1977; D’Amore and Arnórsson, 2000). In this study the following equations were used based on their applicability for the conditions determined in surface conditions. Interpretations are made on the basis of the following geothermometers :

1) Silica

In this case temperatures are calculated using amorpohous silica, chalcedony and quartz via models that presume conductive cooling. Silica is used for the near aquifer temperature calculations; it is so because the rate at which silica reacts is higher than that of cations. The boiling hot spring formula rather than conductive cooling formula is generally used for the silica geothermometers.

2) Cations

The cation geothermometers include the empirical Na-K-Ca geothermometer (Fournier, 1981), it has been found to be consistent with measured well temperatures. Three different version of the Na/K geothermometer are presented, yielding temperature difference of 30-40ºC.

The formulae which have been utilized for deriving the results are listed below :

a) *Fournier, 1977 (Quartz):*

$$T(°C) = \frac{1309}{5.19 - logS} - 273.13$$

\- 1

b) *Fournier and Plotter, 1982 (Quartz):*

$$T(°C) = -53.5 + 0.11236S - 0.5559 \times 10^{-4}S^2 + 0.1772 \times 10^{-7}S^3 + 88.390 \log S$$

\- 2

c) *Arnórsson, 2000 (Quartz):*

$$T(°C) = -55.3 + 0.36590S - 5.3954 \times 10^{-4}S^2 + 5.5132 \times 10^{-7}S^3 + 74.360$$

\- 3

d) *Arnórsson et al., 1983 (Cation, Na-K):*

$$T(°C) = \frac{933}{0.993 + \log(\frac{Na}{K})} - 273$$

\- 4

e) *Fournier et al., 1979 (Cation, Na-K)*

$$T(°C) = \frac{1217}{0.993 + \log(\frac{Na}{K})} - 273.15$$

\- 5

\

f) *Giggenbach et al., 1988 (Cation, Na-K)*

$$T(°C) = \frac{1390}{1.75 + \log(\frac{Na}{K})} - 273.15$$

\- 6

g) *Fournier and Truesdell, 1973 (Cation, Na-K-Ca):*

$$T(°C) = \frac{1647}{\log\frac{Na}{K} + \beta\left[log\left(\frac{\sqrt{Ca}}{Na}\right) + 2.06\right] + 2.47} - 273.13$$

\- 7

Where S represents Silica Concentration in mg/l .

The following Table (4) was obtained by the empirical calculation of temperature using the formulae for Chemical Geothermometers that have been listed above.

	Silica Geothermometry					**Cation Geothermometry**			
	Quartz			**Chalcedony**		**Na-K**			**Na-K-Ca**
Sample Name	**Fournier & Plotter - 1982 (^{o}C)**	**Fournier (1977) (^{o}C)**	**Arnórsson et al. – 2000 (^{o}C)**	**Fournier et al. – 1977 (^{o}C)**	**Arnórsson et al. – 2000 (^{o}C)**	**Arnórsson et al. - 1983 (^{o}C)**	**Fournier et al. -1979 (^{o}C)**	**Giggenbach et al. -1988 (^{o}C)**	**Fournier & Truesdell- 1973 (^{o}C)**
Uthan-S1	44.275	46.1659	30.2249	13.56530536	17.99602229	82.1056	123.102	137.6942	127.6449
Uthan- S2	52.6413	52.966	37.5232	20.54004037	24.66124209	32.5409	74.8524	91.7654	94.2031
Temple- S1	57.044	57.122	41.925	24.82308187	28.74498056	78.4645	119.624	134.418	125.4557
Temple- S2	50.0554	50.5497	34.9446	18.05690882	22.29044286	39.2976	81.5467	98.1999	101.7292
Bhaliyad- S1	37.6079	39.1957	22.5939	6.458913711	11.18574982	68.1409	109.7063	125.0465	116.5891
Bhaliyad- S2	57.3819	57.443	42.2634	25.1545998	29.06077959	37.5083	79.7775	96.5014	99.1874
Dholera- S1	46.6943	47.4374	31.5998	14.86638702	19.24078317	77.2858	118.4958	133.3542	124.2266
Dholera- S2	55.0774	55.2593	39.957	22.90149772	26.91368118	35.8795	78.1649	94.9518	98.3081

Table 4 : Temperatures obtained from the Geochemical Analysis results

4.2 Result Analysis

As can be seen from the results presented above, using the Silica as well as Cation Geothermometry various temperature estimates have been made.

However the estimation using quartz Geothermometry are very different from each other. This flaw in the calculation is due to the difficulty in preserving ionic concentrations for Silica. The temperature that has been estimated using the following shows the ambient temperature rather than the sub surface well temperature. The probable reason being that, all geochemical data accumulated in field studies directed at the determination of spatial variation in rock bodies contain error due to both sampling and analysis. Sampling error associated with a rock specimen is the compositional difference between the specimen and the part of the rock body that the specimen is intended to represent. No sampling or analytical procedure gives results that are perfectly precise, or reproducible; some imprecision is present in all observational data. This may be due to the time lag between the actual analysis and sample collection , specifically for silica concentrations. Onsite measurement was precluded due to the non-availability of on-site sampling tools.

However the Cation Geothermometry data is more representative of the downhole temperatures. In fact a lot of studies tend to reinforce the fact that cationic geothermometry tend to be more representative if sample on being properly preserved which is much simpler as it requires just reducing pH to ensure precipitation doesn't occur. Using these results it's evident that the temperatures lie in the range of 60-80 ^{o}C. The above results have been in fact reinforced by the implementation of a heat pump system in the area.

5. CONCLUSION

The study proved that the geothermal waters in this region are Sodium, Potassium Chloride and Sulphate Rich Mature waters. The Cationic Geothermometer predictions were found to be reasonably accurate and applicable in this environment. The constituents are at equilibrium when they are produced but Silica undergoes rapid precipitation which makes temperature predictions using silica geothermometers tough. The temperatures

The study conducted provided a lot of insight about the how prospective the region would be for implementing a pilot geothermal project. The temperatures estimated from the cross-plots and the Geothermometric analyses did show that the springs were a part of low enthalpy geothermal reservoir system. This helped increase the confidence in implementing a greenfield project in this area for a district heating and cooling system in the future as the area is a part of the Delhi-Mumbai Economic Corridor and the Smart City project of the government. Dholera has been declared a Special Investment Region and the presence of these potential reservoirs helps increasing the chances of implementing projects with lesser carbon footprints when economic activity starts. Also it is evident that there is significant mixing of the geothermal waters being produced with the deep seated circulation system even though the region is located in a sedimentary area.

It also helped verify results that had been obtained using exploration work done using MT survey, Gravity- Magnetic and Remote Sensing in the area.

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