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Geochemical Evolution and Isotopic Characteristics of Thermal Waters from Gujarat Region, India

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ABSTRACT

India is making a significant stride towards the development and utilisation of clean energy. At present, sincere efforts are put to develop the geothermal and solar energy resources across the country. The Indian state of Gujarat has a lot of geothermal potentials, which is manifested in the form of a number of thermal springs distributed across the state. In the present study, an attempt has been made to evaluate the chemistry of the thermal spring water and its isotope characteristics. For this purpose, 11 thermal water samples have been collected from the active discharging thermal springs located in five thermal clusters. Additionally, 3 hot groundwater samples (av. temp. 30^0C) from non-discharging thermal springs and 3 groundwater samples (av. temp. 22^0C) from tube wells were collected. These water samples were analysed for various major and trace elements and also for the stable isotope ratios of oxygen and hydrogen. Thermal springs water and hot groundwater samples show different physical and chemical characteristics as compared to groundwater. The pH and the temperature of thermal spring water range from 7.1-8.5 and 40°-73°C, respectively. The thermal water shows Na-Cl characteristics and falls in the mature field of anion variation diagram, thus indicating intense rock-water interaction and also their suitability for application of chemical geothermometry to calculate the reservoir temperature. Chemical geothermometers indicate a reservoir temperature ranging from 70° C to 150°C. The stable isotope ratio indicates meteoric origin of thermal spring water with varying degrees of evaporation. The area has been tectonically active in the past and is intersected by a number of deep-seated faults. The deeper circulation of meteoric water through these fractures leads to the heating up of the water.

1. INTRODUCTION

Modern society demands a lot of energy to fulfil its requirements. Due to the increase in pollution and improvements in the stands of living, the energy demand is increasing exponentially. India is the third largest energy-consuming country in the world, and the current energy demand is expected to grow four times by the end of 2050 (IEA, 2019). Presently 70% of India's energy depends on conventional, non-renewable energy resources and thus causes significant CO2 emission. In line with the Paris Agreement, the countries have pledged to countdown the CO2 emission. Continuous efforts are being made in this direction throughout the globe. The countries, including the USA, New Zealand, Japan, Italy, France, Mexico, China, and Iceland, have already made significant progress and developed their geothermal resources significantly. India also has a vast geothermal potential, and its existence is manifested in the form of more than 400 hot springs distributed across the country. To realise India's geothermal potential, the Ministry of New and Renewable Energy, Govt. of India has made a policy to exploit the geothermal resources and has set up an ambitious goal of achieving 500 GW of energy by the end of 2030 from renewable energy resources. This is 40% of its total installed power capacity and is probably one of the world's greatest renewable energy expansion plans (Goswami S. et al., 2022).

The geothermal springs of India are grouped into 10 geothermal provinces, namely Himalayan Geothermal Province; Naga Lushai Geothermal Province; Andaman– Nicobar Islands Province; West Coast Geothermal Province; Cambay Geothermal Province; Aravalli Province; Son-Narmada-Tapti (SONATA) Geothermal Province; Godavari Geothermal Province; Mahanadi Geothermal Province and South Indian Cratonic Province (Fig. 1a) (Zimik et al., 2017). The chemistry of the thermal water, its origin and the source of heat varies from one province to the other. Literature archives show that Cambay geothermal province has a few numbers of hot spring clusters, and a limited attempt has been made to study them. In the present study, an attempt has been made to fill this gap in the scientific knowledge. The present study is conducted with the aim to (i) evaluate the chemistry of the thermal spring water, (ii) determine the origin of thermal water, and (iii) calculate the temperature of the geothermal reservoir.

2. STUDY AREA

The study area falls in the Indian state of Gujarat, which has an area of about 1,96,024 km² and lies along the western margin of India. It is situated between latitude 20°06' - 24°42' N and longitude 68°10' - 74°28' E. All the thermal springs belong to Cambay geothermal province (CGP), which are cretaceous to recent in age. The geothermal activity is due to non-orogenic activity and is associated with the tectonism of the area (Thussu, 2002).

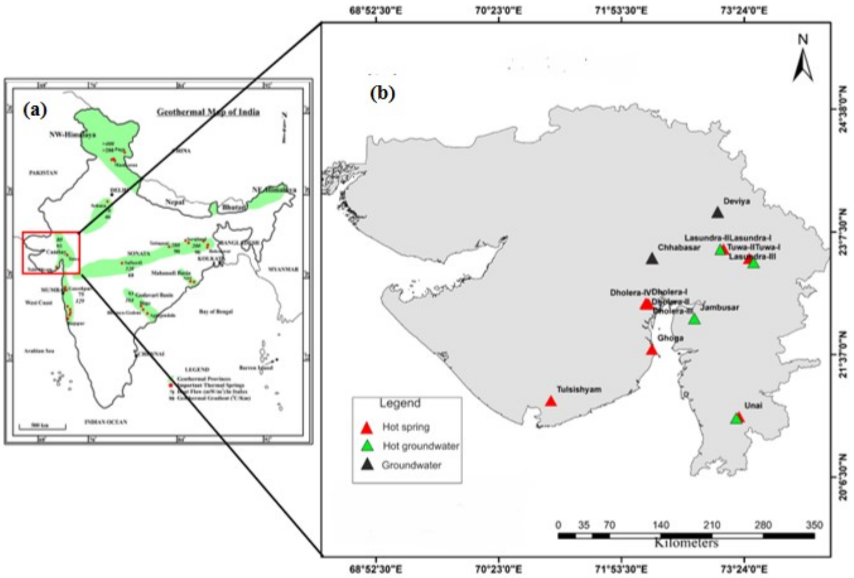

Figure 1: (a) Map of India showing geothermal provinces (Chandrasekharam 2005, Zimik et al. 2017), (b) Map of Gujarat showing sample collection sites.

2.1 Geological Setting:

The state of Gujarat has three distinct physiographic domains, namely Mainland Gujarat, Saurashtra Peninsula, and Kutch Peninsula, which are developed as a result of the interaction of geologic, tectonic, and climatic factors (Biswas S.K., 1987). Three significant marginal rift basins: the Kutch, Cambay, and Narmada, are located nearby one another. The Cambay basin is mostly a Tertiary basin, in contrast to the Mesozoic Kutch and Narmada basins. It began in the Mesozoic but started to disappear more quickly in the Tertiary. The Saurashtra Peninsula has been dominated by three tectonic trends: the Delhi trend (NE-SW), the Son-Narmada-Tapti (SONATA) trend (ENE-WSW), and the Dharwar trend (NNW–SSE). The lithology of the region varies from the Archean to the Quaternary period. The main Cambay basin structure, which gave rise to the recent tectonic framework, is bounded on the W-SW by the Saurashtra peninsula, which is covered entirely by the Deccan Traps, on the E-NE by the Deccan lavas and Archaean and Precambrian formations. Palaeogene- Quaternary sediments in the centre of the basin attain a maximum thickness of about 4000 m and lie directly over the Deccan flows (Raju et. al., 1970). Rocks are exposed from Archean to Quaternary, and Cambay basin is its main tectonic structure. The two major fault systems bordering the Cambay basin, supposed to extend to mantle depths (Kaila et al., 1981), are the foci of major alkaline magmatism that occurred before and after the main Deccan volcanic event (Sheth and Chandrasekharam,1997). Geophysical studies across the basin revealed that the 1250°C isotherm is present at a depth of about 18 km (near Unai), and thus gives evidence of a thin continental crust in this region (Panday and Negi, 1995).

The active hot springs are distributed throughout the state of Gujarat and show different geological, structural and tectonic conditions. The Dholera and Tulshishyam thermal springs are part of the Saurashtra peninsula. Dholera 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. Tulsishyam is located on a horst structure in the very SW part of the Saurashtra peninsula (Mesozoic to Cenozoic) that has undergone multiple tectonic movements. Thermal clusters of Lasundra and Tuwa are a part of Mainland Gujarat and North Gujarat- Cambay region, which comprise ~500-m thick multi-layered sedimentary sequence of fluvially transported Quaternary alluvium deposited in the Cambay Graben and on its flanks (Merh, 1995). The Unai hot spring is located near the Narmada-Son Lineament, a mid-continental rift system surrounded by multiple faults and lineaments. The tectonic framework and location of the active thermal springs are given in Fig. 2.

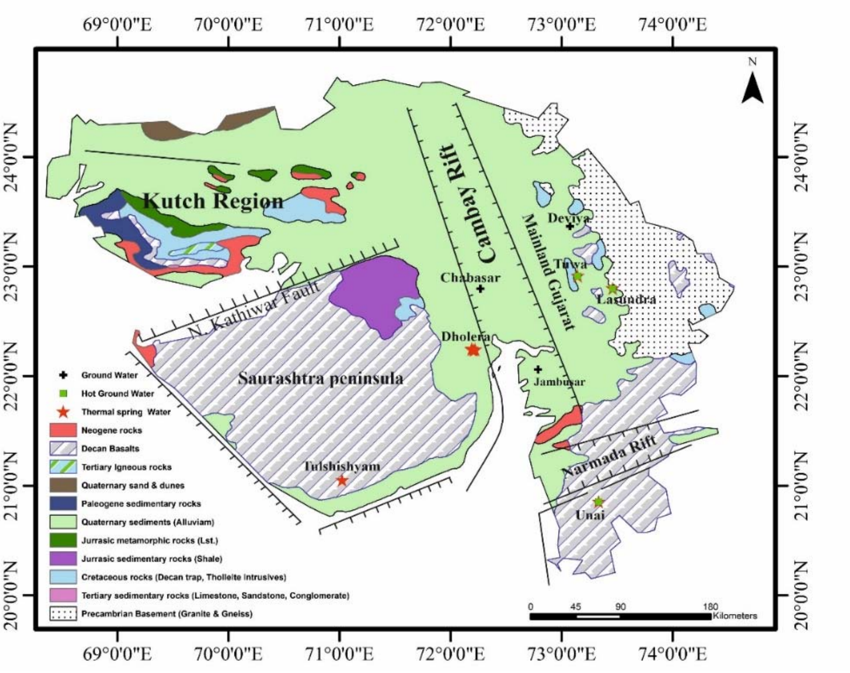

Figure 2: Tectonic framework map of Gujarat with lithology of different areas and location of the thermal springs in different geological settings

3. SAMPLE COLLECTION AND METHODOLOGY

To collect the water, sample a field campaign was conducted in May 2022. In total 17 numbers of water samples were collected of which 11 were from active discharging thermal springs located in five thermal clusters (namely Dholera, Unai, Tulshishyam, Lasundra, Tuwa). At 3 places, the thermal springs are not discharging anymore but the groundwater in those areas surrounding the thermal spring has shown elevated temperatures (i.e., av. temp. 30^0C). The groundwater from these locations were also collected and onwards referenced as hot groundwater. Also, 3 normal groundwater (av. temp. 22^0C) were collected. The sample collection locations were collected from various locations as shown in Fig. 1(b). All the water samples were collected in pre-washed 250 ml high-density polyethylene (HDPE) bottles following the standard scientific protocol (APHA 2012).

From each sampling location, three sets of samples were collected, one to be used for the determination of cations and trace elements, one for anion analysis and the third for water stable isotope analysis. At the time of collection, each sample was filtered with a 0.45 µm cellulose nitrate filter and stored at a low temperature in airtight bottles until further analysis. The samples to be utilised for cation analysis were acidified with 5 ml of 14 M ultrapure HNO_3/L, while for anion and water stable isotopes remained unacidified. All the water bottles were filled completely with water to ensure that no air bubbles to remain trapped within in the bottle. Each sampling site was geo-referenced using a Garmin Global Positioning System (etrex 20) instrument. The groundwater samples were collected from active tube wells. The tube wells were pumped for at least 5 minutes to remove the standing casing water before the sample collection.

3.1 Analytical Techniques

Physio-chemical parameters (pH, temperature, electric conductivity etc.) were directly measured in the field at the time of sample collection. The pH value was measured with Orion 261S portable pH meter with a combination electrode (pH C2401–7). Temperature of water samples was measured by a celsius thermometer, while EC and TDS were measured by a conductivity meter (Orion 250A+). Major cations and trace elements in the water samples were analysed by ICP-OES (Thermo iCAP 7000 plus). The major anion concentration was measured by an Ion chromatography system (Dionex IonPac AS with 4A column). The Isotopic ratios of oxygen and hydrogen were determined using Liquid Water Isotope Analyzer (model LWIA-24d). The percentage error in the analysis was calculated and was found to be within the range of ± 5%.

3.2 Geothermometry

Generally, the fluids in the geothermal reservoir stay for a longer time and continuously interact with the reservoir rocks until they attain equilibrium. The chemistry of such geothermal fluids can be utilised to determine the sub-surface geothermal reservoir temperature. Through special care needs to be taken to ensure that the chemistry of the thermal water is not altered during its ascend by mixing with the shallow groundwater. By utilising the reaction kinetics and the concentration of various non-conservatives, a number of geothermometers have been developed. These chemical geothermometers are widely used to estimate the temperature of the geothermal reservoir. In the present study, the following chemical geothermometers are used to estimate the reservoir temperature.

A. Na/K Geothermometer (Fournier, 1979)

$$\text{Temperature (°C)} = \frac{1217}{Log\left(\frac{Na}{K}\right)+1.483} - 273.15 \tag{1}$$

B. Na/K Geothermometer (Giggenbach, 1988)

$$\text{Temperature (°C)} = \frac{1390}{\text{Log}\left(\frac{\text{Na}}{\text{K}}\right)+1.75} - 273.15 \tag{2}$$

C. Na-K-Ca Geothermometer (Fournier and Truesdell, 1973)

$$\text{Temperature (°C)} = \frac{1647}{Log\left(\frac{Na}{K}\right)+\beta\left(Log\frac{\sqrt{Ca}}{Na}+2.06\right)+2.47} - 273.15 \tag{3}$$

Here, Na, K and Ca are the concentration of that element in the water in mg/l. In the above equation (3), the value of β is 4/3 when $\log(\frac{\sqrt{ca}}{Na})$ + 2.06 is positive. If the calculated temperature remains <100 °C, the temperature is considered as valid, and its think to be the actual reservoir temperature. But if the of $\log(\frac{\sqrt{ca}}{Na})$ + 2.06 is negative or estimated reservoir temperature is >100 °C then the β value considered to be =1/3. The Na-K-Ca geothermometers are more reliable where Ca concentration is relatively high, and the temperature of the reservoir is low.

3.3 Stable Isotopes

Stable isotope ratios of hydrogen (δD) and oxygen (δO^{18}) have widely been utilised to trace the origin of thermal waters, as their ratios are modified by various processes such as mixing of shallow groundwater with thermal water and steam separation. The relative enrichment or deficient in oxygen or hydrogen isotope ratios in a particular water sample measured with reference to an international standard V-SMOW (Vienna- Standard Mean Ocean Water) as given in the equation below-

$$\delta = \left(\frac{R_{sample}}{R_{V-SMOW}} - 1\right) \times 10^3 \tag{4}$$

where, R is the ratio of ^{18}O and ^{16}O for $\delta^{18}O$ and D/H for δD.

A number of studies involving the determination of δD and $\delta^{18}O$ values in precipitation have found that δD values are empirically related to the $\delta^{18}O$ values. The empirical equation showing this relationship as given below defines the global meteoric water line (GMWL).

$$\delta D = 8 \times \delta^{18}O + 10 \tag{5}$$

Direct derivatives of rain water or unaltered groundwater are expected to satisfy this equation. However, various processes such as rock-water interaction, evaporation, moisture recirculation etc., may lead to a noticeable shift in the isotopic ratios with respect to the GMWL in place to place. Thus, there is a need to define local meteoric water lines (LMWLs) for more accurate regional studies (Rozanski et al., 1993, Kumar et al., 2011). In the present study, to compute the LMWL for the Gujarat region's last 12 years, rain event data was used (Deshpande et al., 2010; Oza H. et al., 2020). A total 329 precipitation events from Ahmedabad station are taken into consideration, and the LMWL is defined as:

$$\delta D = 7.7 \times \delta^{18}O + 7.8 \tag{6}$$

4. RESULTS AND DISCUSSION

4.1. Chemical Evaluation of Water Samples

The pH of the thermal water, hot groundwater and groundwater varies within a narrow range of 7.0 – 8.5. No specific trend has been observed in pH. The temperature of the thermal water varied between 38.6 to 73˚C, while for hot groundwater, it ranges between 32-35˚C. The normal groundwater temperature in the area remains within a range of 22-24˚C. Though there is no significant change in the physicochemical parameter, however, the chemical characteristics of the thermal water and the hot groundwater are drastically different from the normal groundwater.

The concentration of various cations (Na, K, Ca, Mg) and anions (Cl^-, HCO_3^-, SO_4^{2-}) in the thermal water and hot groundwater were found to be quite similar but much higher than the normal groundwater. The chemical composition of water, when plotted in the Piper diagram, shows that the thermal and hot groundwater represents the Na-Cl water facies. In contrast, the normal groundwater falls in the Ca-HCO_3 field (Fig. 3).

The Na-Cl water facies reflect the mixing or circulation of seawater as the thermal spring water. However, in such cases, the Na-Cl water is coupled with high TDS content (≈35,000 mg/l) (Gemici and Feliz 2001). In the present study, the maximum TDS value reported is 10,500 mg/l from Lasundra hot spring. Though the TDS values are high, the faraway location of the thermal spring from the coast negates any such possibility of mixing or circulation of seawater into the thermal spring water. The study area was tectonically unstable in the geological past and had many deep-seated faults. The water percolating through these fractures may go much deeper and have a longer residence time. Such conditions are ideal for rock-water interaction and increase the TDS content of the thermal waters. The ascending thermal water when intersected by another set of fractures, leads to its subsurface spread and mixing with the groundwater. Such a scenario causes elevated groundwater temperature and higher TDS values.

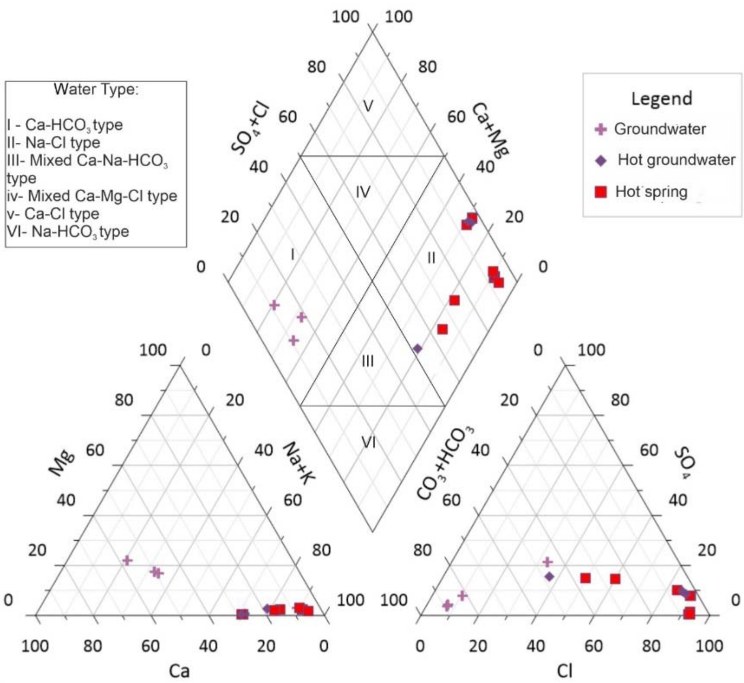

Figure 3: Piper diagram showing the chemistry of thermal spring water

5.2 Chemical geothermometry

The chemical signatures of thermal water can be utilised to determine the reservoir temperature and interpret other important subsurface processes provided that they fulfil some primary requirements such as defining a mineral solute reaction, the reaction must be temperature dependent, there must be sufficient supply of the mineral to dissolve etc. (Zimik et al., 2017). An anion variation diagram is an easy and quick way to determine whether the thermal water fulfils these criteria or not. The thermal waters that fall in the mature field of the anion various diagram fulfils all the requirements and can be used to determine the reservoir temperature by application of chemical geothermometers. In the present study, most of the thermal water and hot groundwater samples fall in the mature water field (Fig. 4) and thus are fully equilibrated with the reservoir rock. Only two thermal water samples (Unai, and Tulshishyam) fall close to the mature water field, indicating their partial equilibration. The fully equilibrated thermal water samples give the accurate geothermal reservoir temperature, while partially equilibrated thermal waters can provide only a rough estimate of the reservoir temperature. The normal groundwater samples and one of the hot groundwater samples that falls in the peripheral water field indicate limited rock-water interaction. The anion variation diagram clearly indicates that for most of the thermal water samples (except Unai and Tulshishyam), chemical geothermometers can be applied.

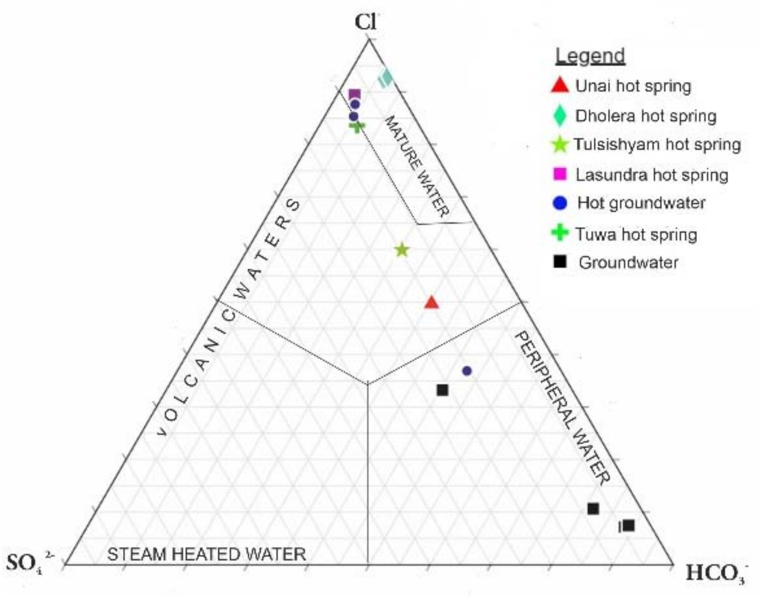

Figure 4: Anion variation diagram showing the distribution of thermal water samples into different water fields

The reservoir temperature calculated by applying various chemical geothermometers on mature and partially mature water samples indicates that the temperature of the geothermal reservoir ranges from 65-166°C (Na/K geothermometer) and 87-185°C (Na- K geothermometer). The Na-K-Ca geothermometer gives slightly lower reservoir temperatures (81-121°C). The reservoir temperature calculated from individual thermal water is given in Table 1.

Table 1: Calculated reservoir temperatures from chemical geothermometers (all values are in °C)

Hot springs	Na-K Fournier (1979)	Na-K Giggenbach (1988)	Na -K- Ca Fournier& Truesdell(1973)
Unai	124.5	144.6	81
Dholera	70.9	92.2	94
Tulshishyam	166.9	185.2	102
Lasundra	154.7	173.6	119
Tuwa	145.2	164.5	101

5.3 Stable Isotope Systematic

The isotopic composition of thermal and non-thermal waters showed signification variation in terms of δD and $\delta^{18}O$ values. The most depleted thermal waters were from Dholera (-22.5 and -3.09 for δD and $\delta^{18}O$, respectively), while the thermal spring of Tulshishyam shows a higher enrichment (-10.0 and -1.09 for δD and $\delta^{18}O$ respectively). The hot groundwater samples don't have much variation in isotopic composition. The isotopic ratios were plotted with reference to GMWL and a Local Meteoric Water Line (LMWL). The LMWL closely follows the GMWL. The plots for various thermal clusters are given in Fig. 5 (a), (b), (c), (d) and (e). The thermal water samples collected from the Dholera region show a prominent $\delta^{18}O$ shift, which indicates an intense rock-water interaction (Fig. 5a). Such an interaction leads to the enrichment of ^{18}O in the geothermal fluids. As Dholera is situated in the vicinity of the west marginal fault of the Cambay rift, it allows quick percolation and restricts substantial evaporation. The thermal water and hot groundwater samples from Lasundra (Fig. 5b) fall on the evaporation line; however, a different degree of evaporation has been noticed where the thermal water has gone through a lesser degree of evaporation compared to the hot groundwater. Tuwa region follows the same trend as Lasundra and shows different degrees of evaporation (Fig. 5c). However, the thermal water sample from the Unai region exactly falls on the LMWL, implying a negligible amount of evaporation where the hot groundwater samples show some degree of evaporation and are slightly heavier (Fig. 5e).

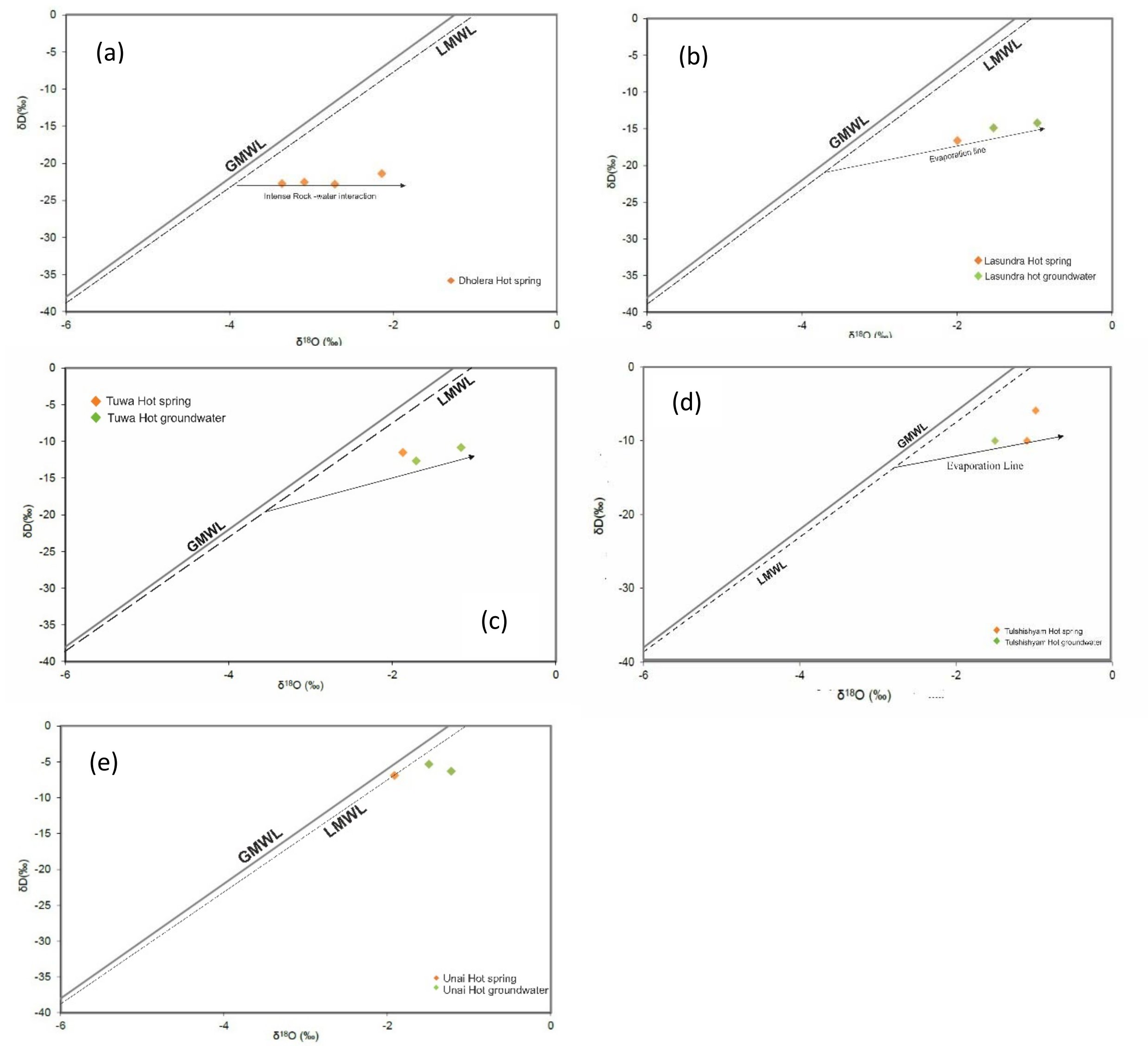

Figure 5 (a-e): Plots showing the position of hot springs and hot groundwater from different locations (a: Dholera, b: Lasundra, c: Tuwa, d: Tulshushyam e: Unai) w.r.t the GMWL & LMWL

6. CONCLUSIONS

The study provides a comprehensive understanding of the geothermal systems of the Indian state of Gujarat. The pH of thermal water shows a neutral to alkaline character. The hydrogeochemical investigation indicates that hot springs belong to the Na-Cl type water type. The hot groundwater surrounding these thermal springs also has similar chemical characteristics. The elevated temperatures and closely matching chemical characteristics of groundwater with the thermal water indicate the subsurface seepage of the thermal water and mixing with the local groundwater in the nearby areas. All the thermal spring water falls in the mature field of anion variation diagram. Chemical geothermometers indicate that the reservoir temperate ranges between 65.6 – 185.2°C, thus confirming the existence of a low enthalpy geothermal system. The isotope fingerprints confirm that the thermal and hot groundwaters are of meteoric origin and are derived from local precipitation. Rock-water interaction and evaporation have been identified as the main processes controlling the chemistry and isotope ratios of thermal waters, respectively. Further, different thermal springs have shown different degrees of evaporation. The tectonic history of the area and isotope composition suggests a deeper circulation of meteoric water through deep-seated faults. The geothermal resources of the area can be utilised either for direct purposes or for power generation through the organic rankine cycle (ORC) technique by setting up a binary power plant.

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