

## Investigation of Major Geothermal Fields of Pakistan Using Isotope and Chemical Techniques

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### ABSTRACT

Environmental isotopes like  $^{18}\text{O}$ ,  $^2\text{H}$  &  $^3\text{H}$  of water;  $^{13}\text{C}$  of dissolved inorganic carbon;  $^{34}\text{S}$  &  $^{18}\text{O}$  of dissolved sulphates and water chemistry were used to investigate the origin, subsurface history and reservoir temperatures of major geothermal fields of Pakistan. Seven hot springs of the Murtazabad area lie along the Main Karakoram Thrust in Northern Areas and have discharge from 50 to 1200 liters per minute with the surface temperature range of 47 to 92°C. All the thermal waters are  $\text{NaHCO}_3$  type and their origin is meteoric water recharged from precipitation at higher altitude, which undergoes  $\delta^{18}\text{O}$  shift of about 1‰ due to exchange with rocks. The wide range of tritium concentrations shows that the shallow fresh groundwater is mixing with the thermal water in different proportions but the  $\delta^{18}\text{O}$ - $\delta^2\text{H}$  plot and other data indicate that the circulation time of thermal end-member is more than 50 years. Different geothermometers give reservoir temperature in the range of 185-225°C. The isochemical-mixing model based on the Na-K and quartz geothermometers estimates 227°C temperature.  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer indicates equilibrium temperatures in from 130 to 185°C. The dissolved silica vs. enthalpy plot suggests heat losses mainly through conduction.

Tatta Pani and Tato thermal springs along the Main Mantle Thrust have discharge from 30 to 2000 liters per minute with the surface temperature from 48 to 92°C. These are also  $\text{NaHCO}_3$  type. Their origin is local meteoric water and there is no mixing of shallow fresh water. Tritium data show that the residence time of thermal fluids is more than 50 years. The reservoir temperatures of Tatta Pani springs (100-120°C), determined by Na-K and quartz geothermometers, are in good agreement. The  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer indicates equilibrium temperatures around 150°C. For the Tato springs, the isotope and chemical geothermometers (except for the K-Mg) agree on an equilibrium temperature of about 175-200°C, while  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  equilibrium temperatures (170°C) is in good agreement.

Geothermal springs of Chagai are related to the youngest volcano (Koh-I-Sultan) of Pakistan. Their  $\delta^{18}\text{O}$  is very enriched (up to +4.3‰), while  $\delta^2\text{H}$  is depleted (-22 to -36‰) indicating recharge from meteoric water and very high  $^{18}\text{O}$ -shift (up to 10‰), which is due to rock-water interaction at higher temperatures. Tritium data show the age of thermal waters more than 50 years. Three springs having very high electrical conductivities (25300 to 45600  $\mu\text{S}/\text{cm}$ ) are  $\text{NaCl}$  type, while three other springs with the EC around 4000  $\mu\text{S}/\text{cm}$  are  $\text{MgSO}_4$  type. The chemical geothermometers like Na-K, K-Ca and Na-K-Ca-Mg indicate high reservoir temperature estimates mostly in the range of 200-300°C,

while the silica and  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometers are in good agreement indicating the temperature around 150°C.

### 1. INTRODUCTION

Pakistan has been experiencing shortage of electricity for the last several years. This shortage is prominent during summer season resulting in frequent power shutdown. Power is mainly generated by hydroelectric stations on rivers and thermal power plants (oil/gas fired) with some contribution of nuclear energy. Due to shortage of power supply the inhabitants of remote and under development areas face lot of problems. There are many geothermal springs in some areas having varying degree of temperature (including boiling water emanations) with significant flow-rate. If the geothermal fields have potential for power generation, this cheap source could be exploited to meet the local demands. In case of low potential the hot water can be used for warming of houses and green houses to grow vegetables especially in very cold winters.

Unfortunately, research related to geothermal waters is still in early stage. Geothermal areas were studied on a regional scale in terms of geological setting and general chemical characteristics of groundwater compositions (Todaka et al., 1988). Studies focused on the nature and evolution of geothermal water such as the origin, age, water/rock interaction or mixing between geothermal fluids and shallow groundwater, and assessment of reservoir temperature was only conducted on geothermal fields of Northern Areas (Ahmad et al., 2000; 2001; 2002). Knowledge of origin, physicochemical behavior subsurface processes, dating/replenishment and reservoir temperature is very important to assess the potential of a geothermal field. These aspects can be studied by integrating environmental isotopes along with geochemical techniques. The most commonly used isotopes are  $^2\text{H}$ ,  $^{18}\text{O}$  &  $^3\text{H}$  of water,  $^{13}\text{C}$  &  $^{14}\text{C}$  of dissolved inorganic carbon (DIC),  $^{18}\text{O}$  &  $^{34}\text{S}$  of sulphates. Such applications of isotopic and geochemical techniques for geothermal investigations were discussed by Giggenbach et al., 1983; Giggenbach, 1992; Truesdell and Hulston, 1980; Krouse, 1980 and many others. Various geochemical and isotope geothermometers applicable under different conditions established by Fournier and Truesdell, 1973; Truesdell and Fournier, 1977; Fournier, 1977; Fournier and Potter, 1979; Arnorsson, 1980; Tonani, 1980; Fouillac et al. 1981; Giggenbach et al. 1983; Kharaka and Mariner, 1989; Giggenbach and Goguel, 1989 were applied to estimate reservoir temperatures. Tatta Pani, Tato and Murtazabad in Northern Areas and Chagai (Balochistan Province) were studied.

### 2. MATERIALS AND METHODS

Water samples from hot springs were collected for chemical analysis and determination of isotopes:  $^2\text{H}$ ,  $^{18}\text{O}$  &  $^3\text{H}$  (water),  $^{18}\text{O}$  &  $^{34}\text{S}$  (sulphate), and  $^{13}\text{C}$  (TIC). Physico-chemical parameters such as temperature, pH and electrical conductivity (EC) were determined in the field. A total of six sample aliquots were collected for each hot spring site

for chemical and isotopic analyses. Where filtration was required, a 0.45  $\mu\text{m}$  pore diameter filter was used. The volume of the sample and treatment in the field for various analyses are given below.

Chemical analyses were carried out using: atomic absorption spectrophotometry for Na, K, Ca and Mg; ICP for Li; UV-visible spectrophotometry for Si and  $\text{SO}_4$ ; titrimetry for  $\text{HCO}_3$ ; and ion selective electrode for Cl (APHA, 1985). The  $\delta^{18}\text{O}$  value of the water was measured by mass spectrometer using the  $\text{CO}_2$  equilibration method (Epstein and Mayeda, 1953). For analysis of  $\delta^{18}\text{O}$  of dissolved sulphates, the sulphates were precipitated as  $\text{BaSO}_4$  in the field (Giggenbach and Goguel, 1989). The co-precipitated carbonate was removed by reacting with hydrochloric acid, and  $\text{BaSO}_4$  was obtained in powder form. The  $\text{BaSO}_4$  was reacted with graphite in a vacuum system to convert its total oxygen into  $\text{CO}_2$  (Nehring et al., 1977), which was analyzed on the mass spectrometer for  $\delta^{34}\text{S}$ .  $\delta^{18}\text{O}$  values of water and dissolved sulphate were analyzed relative to V-SMOW with a standard error of  $\pm 0.1\text{‰}$ . The tritium content of the samples was determined by liquid scintillation counting after electrolytic enrichment of the water samples with a standard error of  $\pm 1\text{ TU}$  (Hussain and Asghar, 1982).

### 3. NORTHERN AREAS

The Northern Areas having geothermal fields of Tatta Pani, Tato and Murtazabad are located between the latitudes  $35^{\circ} 20' \text{N}$  to  $36^{\circ} 30' \text{N}$  and longitudes  $74^{\circ}\text{E}$  to  $76^{\circ}\text{E}$ . These areas are characterized by steep topography and U-shaped glaciated valleys, which are drained by the rivers Indus, Gilgit and Hunza, while the rivers Shigar, Shyok, Ishkuman and Yasin form the major tributaries to these rivers. Important mountain ranges of the area are the Kailas, Rakaposhi, Masherbrum and Karakoram. Cold winters and warm and dry summers characterize the climate. June-August are the hot months during which mean maximum temperature is about  $30^{\circ}\text{C}$ . Snowfall occurs during the cold months of December-February when minimum temperature goes several degrees below the freezing point. Rainfall is scanty.

#### 3.1 Tectonic setting

The geotectonic development of the Northern Areas of Pakistan during late Cretaceous to Cenozoic involved three tectonic elements, i.e.: the Indo-Pakistan shield and its northern sedimentary cover (Indian Mass), the rocks deposited on the southern part of the Eurasian Mass, and the Kohistan Island Arc Sequence (Powell, 1979). From Archaean times, the Indian Sub-Continent was a part of Gondwanaland, which consisted of the continents of South America, Africa, Antarctica, Australia and India. A vast stretch of the Tethys Sea existed between the Indo-Australian part of Gondwanaland and the Eurasian Mass. About 130 million years ago, the Indian Ocean plate broke away from Gondwanaland and started drifting towards Eurasia with the simultaneous consumption of the Tethys Sea Plate in between (Khan et al., 1987). As a result of subduction, the Kohistan Island Arc Sequence was produced to the north of the subduction zone. The first contact of this Island Arc was with the Indo-Pakistan plate, which finally collided with the Eurasian Mass. The Kohistan Island Arc Sequence is juxtaposed between the Indo-Pakistan plate and the Eurasian plate. A major thrust fault called the Main Mantle Thrust (MMT) separates the Indian Mass from the Kohistan Island Arc Sequence while another thrust fault called the Main Karakoram Thrust (MKT) marks the boundary between the Kohistan Island Arc Sequence and the

Eurasian Mass (Tahirkheli, 1982). The geothermal manifestations under investigation lie along these faults, which are still active. A substantial amount of heat is presumably generated by frictional movement along these faults (Todaka et al., 1988). However, these faults might simply act as uprising routes of deeply circulating waters of possible meteoric origin, which become thermal because they come into contact with relatively hot rocks present at relevant depths, similar to what has been observed in the Alps (Pastorelli et al., 2000). The major tectonic features of the Northern Areas of Pakistan along with the locations of geothermal fields are shown in Fig. 1.

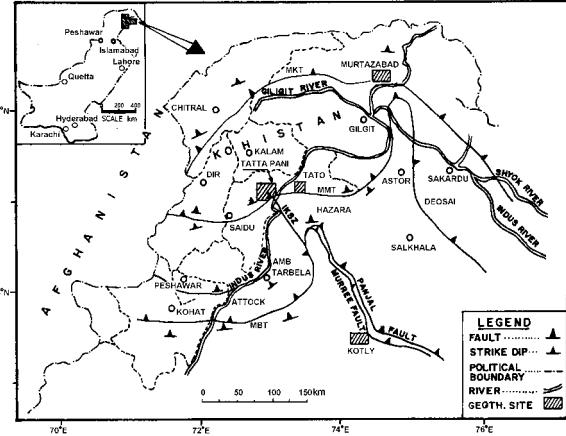


Figure 1: Map showing major tectonic features of Himalayan range and study sites

#### 3.2 Geology and Thermal Manifestations

The oldest rocks of the Indian Mass are the Salkhala Series, which are involved in the Nanga Parbat metamorphic rocks and constitute a substantial part of the massif. The main rock types are slate, phyllite, various types of schists, paragneisses, sandstone and quartzitic crystalline conglomerate, which are intruded by basic-to-acidic igneous rocks. The rocks constituting the Kohistan Island Arc Sequence consist of a thick series of calc-alkaline plutonic, volcanic and volcano-sedimentary rocks, Jurassic-Cretaceous in age (Todaka et al., 1988). The rocks of the Eurasian Mass north of MKT are late-Paleozoic metasedimentary rocks, mainly flysch (limestone- and shale-dominant), which are considered deep-sea sediments deposited by turbidity currents along the Eurasian plate margin in the northern Tethys geosyncline (Khan et al., 1987).

Tatta Pani springs flow from unconsolidated to semi-consolidated fluvial deposits or talus. Amphibolites fractured by the MMT constitute the hard rocks exposed around these geothermal manifestations. Tato spring emerges from semi-consolidated fluvial and moraine deposits. It lies about 1200 m above Tatta Pani springs. Murtazabad springs flow from a steep cliff that is made up of coarse-grained fluvial deposits. The hard rocks exposed around the manifestations are garnet-staurolite schist and lime-silicate marble of the Baltit Group, which is assigned to the lower Paleozoic to Precambrian age. The Karakoram Granodiorite Belt is located 15 km to the north of the manifestations. The manifestations at Murtazabad lie north of the MKT (Todaka et al., 1988).

#### 3.3 Results and Discussion

The discharge temperature of the hot springs of Tatta Pani varies from 48 to  $89.5^{\circ}\text{C}$  while that of the thermal waters of

Murtazabad has a range from 47 to 92°C. One spring at Murtazabad and the Tato spring discharge almost boiling water with temperatures of 92°C and 89.5°C respectively. All the thermal waters in the area are neutral to slightly alkaline. The hot springs of Tatta Pani have pH values from 7.8 to 8.9 while those of Murtazabad have pH values in the range 6.5 to 9.0 and Tato springs have pH about 9.0. The Tatta Pani hot springs have EC values in the range 860-1046  $\mu\text{S}/\text{cm}$  and Tato springs 1180-1261  $\mu\text{S}/\text{cm}$ , whereas Murtazabad hot waters are relatively more saline (EC = 1833 to 2560  $\mu\text{S}/\text{cm}$ ).

### 3.3.1 Hydrochemistry

Sodium is the dominant cation. The relative concentrations of the main anions show that these hot waters are  $\text{HCO}_3$  type except one spring, which is  $\text{SO}_4$  type. Therefore, these thermal waters are  $\text{Na}-\text{HCO}_3$  type except one sample from Murtazabad, which is  $\text{Na}-\text{SO}_4$ . These Na-rich compositions are typical of comparatively evolved waters circulating mainly in gneissic and granitic rocks (e.g., Pastorelli et al., 2000). The varying  $\text{HCO}_3/\text{SO}_4$  ratios of the Na-rich waters could be attributed to the relative importance of: (a) dissolution under oxidizing conditions of sulfide minerals, which brings about production of  $\text{H}_2\text{SO}_4$ , and subsequent neutralization of  $\text{H}_2\text{SO}_4$  by reaction with silicates, mainly feldspars, vs. (b)  $\text{H}_2\text{CO}_3$ -driven dissolution of silicates, mainly feldspars. The first process gives rise to  $\text{Na}-\text{SO}_4$  waters, whereas  $\text{Na}-\text{HCO}_3$  waters result from the second process which would be dominant in the present case. This evolution could also reflect dissolution of  $\text{CaSO}_4$  accompanied by precipitation of  $\text{CaCO}_3$ , as hypothesized for the Tekke Hmam thermal springs, near Kizildere, Turkey (Guidi et al., 1990). At Murtazabad, however, this process seems unlikely due to the absence of evaporitic rocks. As discussed below, mixing of shallow water with the thermal springs in varying proportions also changes water chemistry. Although data for the shallow groundwater are not available, mixing trends indicate that it is likely to be relatively rich in Ca, Mg and  $\text{HCO}_3$ .

At Tatta Pani geothermal field, all the thermal waters are  $\text{Na}-\text{HCO}_3$  type having Na >90% and  $\text{HCO}_3$  varying from 45 to 60% with the second dominant  $\text{SO}_4$  (20-35%). In the previous study, Ahmad et al., (2002) identified most of these springs as  $\text{Na}-\text{SO}_4$  type except for two samples that belong to the  $\text{Na}-\text{HCO}_3$  type. It indicates that transition from  $\text{HCO}_3$ -dominated water to  $\text{SO}_4$ -type is not so significant during the last few years. The thermal water of Tato spring in the nearby area also has  $\text{Na}-\text{HCO}_3$  facies. All the Tatta Pani springs are located along a straight line in a zone about 1 km wide, and have almost the same total dissolved solids and no tritium (0 TU). It seems that the same thermal water splits into different paths during movement towards the surface.

### 3.3.2 Recharge Source and Subsurface History

Isotopic data can well differentiate between the three possible types of origin of thermal water i.e. magmatic, oceanic and meteoric. Ranges of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of all the sampled geothermal manifestations of Tatta Pani are -11.3 to -10‰ and -84.7 to -62.8‰ respectively, while the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  ranges of Tato are -11.1 to -10.6 and -84.3‰ to -77.6‰ and -78‰. These data do not show the presence of any significant amount of magmatic water which generally has  $\delta^{18}\text{O}$ : +6 to +9‰ and  $\delta^2\text{H}$ : -40 to -80‰ (Pearson et al., 1980; Giggenbach, 1992). The important feature of the fluids emerging from thermal manifestations is their low salt contents. The maximum electrical conductivity (EC) is 11261  $\mu\text{S}/\text{cm}$  for Tato spring, while that of Tatta Pani ranges

from 860 to 1046  $\mu\text{S}/\text{cm}$ . The Cl content of Tatta Pani varies from 44 to 55 ppm, whereas Tato spring has relatively higher value of Cl i.e. 102-111 ppm. Normally the oceans have  $\delta^{18}\text{O}$  &  $\delta^2\text{H}$  about 0‰ (VSMOW), the salinity from 33500 to 37600 ppm and chloride about 19300 ppm (Clark and Fritz, 1997). The possibility of oceanic origin of the encountered thermal waters is ruled out by the absence of highly enriched  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , EC and Cl values. So the origin of thermal waters is obviously meteoric.

In a geothermal system,  $\delta^{34}\text{S}$  of sulphates with a magmatic origin ranges between 0 to 2‰ CDT and sulphates resulting from the dissolution of evaporites can have  $\delta^{34}\text{S}$  from +10 to +35‰ whereas  $\delta^{34}\text{S}$  of modern oceanic sulphate is about +20‰ (Krouse, 1980). The  $\delta^{34}\text{S}$  values of sulphates of hot springs of Tatta Pani fall in a small range of 11.8 to 13.5‰. It shows that the sulphate is neither of magmatic origin nor of modern oceanic origin. Such values are obtained by dissolution of evaporites, most probably Devonian to Permian  $\text{CaSO}_4$  (Clark and Fritz, 1997).

There are two most important processes affecting the isotopic and chemical concentrations during upward movement of geothermal waters viz. steam separation due to adiabatic expansion of thermal fluids with decreasing pressure and dilution/mixing with shallow fresh waters.  $^{18}\text{O}$  shift due to rock-water interaction at higher temperatures may also occur (Giggenbach et al., 1983). The isotopic and chloride signatures of the geothermal fluids have been used to identify the prevailing processes. The tritium concentration of all the thermal springs including the cold spring is zero TU. Absence of tritium indicates that there is absolutely no contribution of fresh water recharged prior to 1952 in the thermal water (Clark and Fritz, 1997). This evidence is sufficient to rule out the mixing process.

$\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  is plotted in Fig. 2 with the following local meteoric water line (LMWL) determined by Hussain et al. (1995) for the same area.

$$\delta^2\text{H} = (8 \pm 0.4) \delta^{18}\text{O} + (16.5 \pm 6) \quad (r^2 = 0.933, n = 24) \quad (1)$$

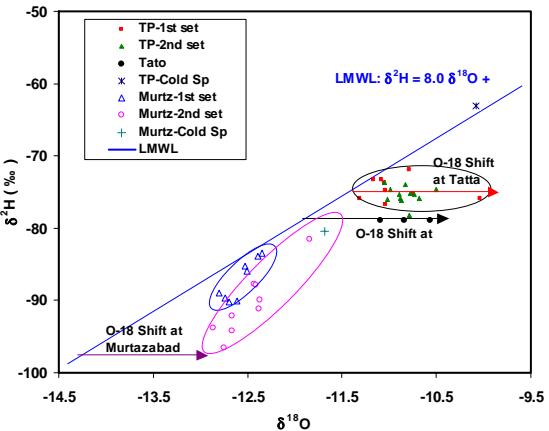
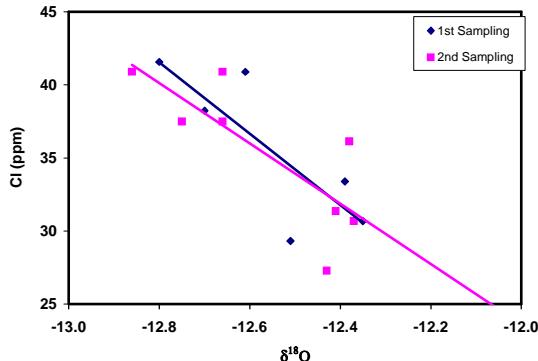


Figure 2:  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  of samples of Northern Areas

All the data points for thermal waters of Tatta Pani reflecting varying degrees of enrichment in  $^{18}\text{O}$  and  $^2\text{H}$  contents lie below and close to the LMWL. The scattered cluster seems dominantly due to  $^{18}\text{O}$ -shift but the evaporation/steam separation process might also be playing significant role. The slight change in type of water and  $\delta^{18}\text{O}-\delta^2\text{H}$  indicates that there is significant change in the subsurface processes during upward movement. The correspondence of isotopic

contents with the local meteoric water indicates a predominantly meteoric origin of geothermal discharges (Giggenbach et al., 1983). The chloride of Tatta Pani samples has very short range (44-55 ppm) and it does not have any significant correlation with temperature and  $\delta^{18}\text{O}$ , which indicate that there is no significant evaporation.



**Figure 3: Cl vs.  $\delta^{18}\text{O}$  of thermal waters of Murtazabad**

Three samples of Tato falling on the straight horizontal line indicate purely  $^{18}\text{O}$ -shift up to 1.5‰, which is more than that determined by Ahmad et al., (2000) in a previous study. Lack of tritium and high chloride contents in the water samples from Tato show that no detectable amount of fresh water is mixing with the thermal water.

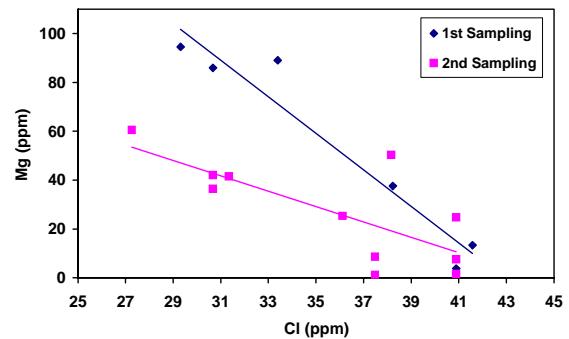
Ranges of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of all the sampled geothermal manifestations at Murtazabad are -12.9 to -11.6‰ and -98.8 to -81.5‰ respectively. These data do not show the presence of any significant amount of magmatic (Pearson and Rightmire, 1980; Giggenbach, 1992). The electrical conductivity (EC) varies from 1833 to 2560  $\mu\text{S}/\text{cm}$  while the Cl content is 27 to 42 ppm (Cl content of 192 ppm for Sample is rejected). The possibility of oceanic origin of the encountered thermal waters is ruled out by the absence of highly enriched  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and Cl values. So the origin of thermal waters is obviously meteoric.

The  $\delta^{34}\text{S}$  values of sulphates of hot springs being in the range of 4.6 to 10.7‰ shows that the sulphates are neither of magmatic origin nor of modern oceanic origin as explained in the case of Tatta Pani. Relatively low values of  $\delta^{34}\text{S}$  indicate that the major contribution of sulphates is derived from reduced sulphur compounds such as sulphide minerals and/or organic sulphides (Pearson and Rightmire, 1980). Sulphide minerals are exposed at some places along the cliff of Murtazabad terrace. Source of sulphates also confirms the origin of thermal water as meteoric which dissolves sulphide minerals during deep circulation.

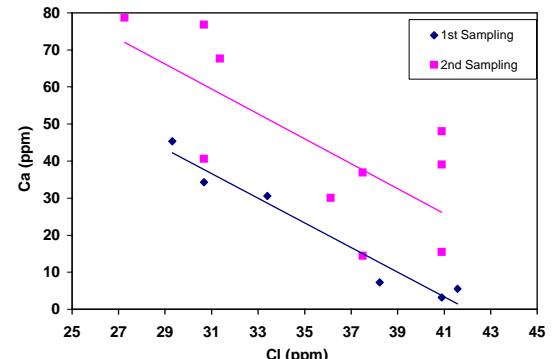
In the  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  plot (Fig. 2) all the points form a trend below the LMWL. Departure of these points from LMWL may be due to rock interaction, evaporation or mixing processes (Giggenbach et al., 1983). These plots not only confirm the mixing process but also gives insight into the history of thermal water. All the thermal waters plot below the LMWL forming the trend lines of slopes 15.6 for the first set of samples and 13.8 for the second set, which intersect the LMWL at the points having compositions of  $\delta^{18}\text{O}$ : -12.1‰,  $\delta^2\text{H}$ : -81‰ and  $\delta^{18}\text{O}$ : -11.5‰,  $\delta^2\text{H}$ : -76‰. The end-point in the second set is exactly similar to the average  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values of snow (i.e. -11.6 & -76‰) collected from Murtazabad terrace and the trend is similar to that found by Ahmad et al., (2000). Due to location at relatively low altitude the snow of the local area is

isotopically enriched as compared to general meteoric water, which originates from precipitation at high altitudes drained by rivers ( $\delta^{18}\text{O}$  = -13.8‰,  $\delta^2\text{H}$  = -94‰). The cold spring emerging from the Murtazabad terrace has isotopic indices ( $\delta^{18}\text{O}$ : -11.6‰,  $\delta^2\text{H}$ : -81‰) fall in the range of above-mentioned endpoints, therefore, it may be considered as the representative of the shallow groundwater (end-mixing component) of this area. Variation in the slopes and shifting in the mixing trends might be due to seasonal change in the isotopic values of shallow groundwater. Negative correlation of  $\delta^{18}\text{O}$  with Cl (Fig. 3) indicates mixing with shallow groundwater having low Cl content and rules out the dominance of steam separation/ evaporation process (Gonfiantini, 1986). It shows that the thermal water is getting mixed with the shallow cold water enriched in  $^{18}\text{O}$  but depleted in Cl (e.g. Giggenbach et al., 1983). The cold spring, which represents the shallow groundwater, has highest concentrations of Ca, Mg and  $\text{HCO}_3$  indicating dissolution of dolomite. Negative correlations of chloride with Mg (Fig. 4) and Ca (Fig. 5) confirm the dominance of mixing process during movement of the thermal water towards the ground surface. Different proportion of fresh water sets the different isotopic and chemical concentrations of thermal waters flowing through various paths.

Although, mixing of the thermal water with shallow groundwater is confirmed, but it does not cause significant cooling because there is no correlation of surface temperature with  $\delta^{18}\text{O}$  and chloride in both the samplings. It means that cooling of the thermal water is not mainly due to mixing of shallow cold groundwater, while the steam separation process is already ruled out. Therefore, the dominant process of cooling is conduction.



**Figure 4: Mg vs. Cl of thermal waters of Murtazabad**



**Figure 5: Ca vs. Cl of thermal waters of Murtazabad**

### 3.3.3 Chemical Geothermometry

Murtazabad thermal waters undergo mixing with the shallow groundwater, which brings about changes in water chemistry that have a remarkable influence on chemical geothermometers. The mixing process was modeled by means of the isochemical method suggested by Chiodini et al. (1996). First, the concentrations of Na, K and  $\text{SiO}_2$  involved in the geothermometers of interest were regressed with Cl and the following linear equations were obtained (excluding one sample from boiled water):

$$C_{\text{Na}} = 15.144 C_{\text{Cl}} - 206.757 \quad (2)$$

$$C_{\text{K}} = 0.432 C_{\text{Cl}} + 24.232 \quad (3)$$

$$C_{\text{Mg}} = -4.403 C_{\text{Cl}} + 193.33 \quad (4)$$

$$C_{\text{SiO}_2} = 11.768 C_{\text{Cl}} - 64.534 \quad (5)$$

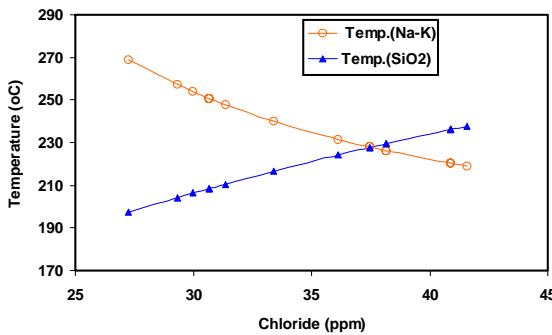
Inserting the above functions (Equations 2 to 5) in the Na-K, K-Mg, and quartz geothermometers, the following T (Cl) functions were obtained for this area:

$$T_{\text{Na-K}} = \{1217/[1.48 + \log (15.14 C_{\text{Cl}} - 206.75) - \log (0.43 C_{\text{Cl}} + 24.23)]\} - 273 \quad (6)$$

$$T_{\text{K-Mg}} = \{4410/[14.0 - 2 \log (0.43 C_{\text{Cl}} + 24.23) + \log (-4.403 C_{\text{Cl}} + 193.33)]\} - 273 \quad (7)$$

$$T_{\text{quartz}} = \{1309/[5.19 - \log (11.76 C_{\text{Cl}} - 64.53)]\} - 273 \quad (8)$$

The Na-K, K-Mg and quartz temperatures were calculated for varying Cl concentrations. Temperatures estimated by K-Mg are much lower (71-105°C) because Mg has been increased drastically by mixing of shallow groundwater. Therefore, temperatures estimated by the other two geothermometers are plotted against Cl (Fig. 6). Both the functions converge and after crossing they again diverge indicating the equilibrium temperature 227°C.

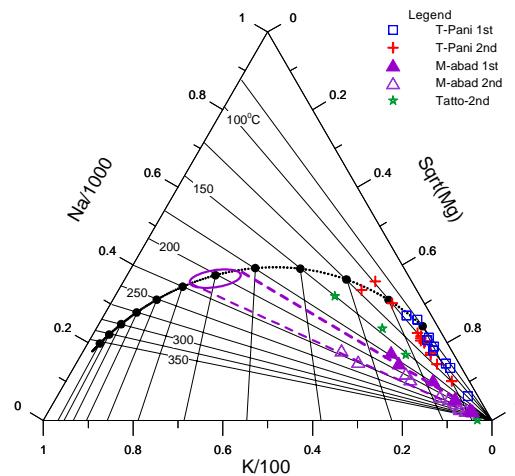


**Figure 6: Iso-chemical model temperatures of Na-K and quartz vs. Cl for thermal waters of Murtazabad area**

The geothermal reservoir temperature was also estimated using the Na-K-Mg<sup>1/2</sup> triangular diagram (Fig. 7). In this plot full equilibrium curve (FEC) is drawn using the Na-K geothermometer of Arnorsson et al., (1998) and the K-Mg geothermometers of Giggenbach (1988). This approach was adopted in order to take into account the possible uncertainties of the Na-K geothermometer. Both the sets of Murtazabad samples are spread along two alignments starting close to the Mg<sup>1/2</sup> vertex and pointing towards the full equilibrium region. As discussed above, the equilibrium of the thermal water is disturbed due to mixing of cold shallow groundwater having high Mg content, which seems to be responsible for moving the data points away from the

FEC. Assuming very low Mg content in the original thermal water component and extrapolating the trend lines towards FEC, the reservoir temperatures are estimated to 185°C (1<sup>st</sup> sampling) and 220°C (2<sup>nd</sup> sampling). This range is in close agreement with the range (185-200°C) estimated in the previous study (Ahmad et al., 2002).

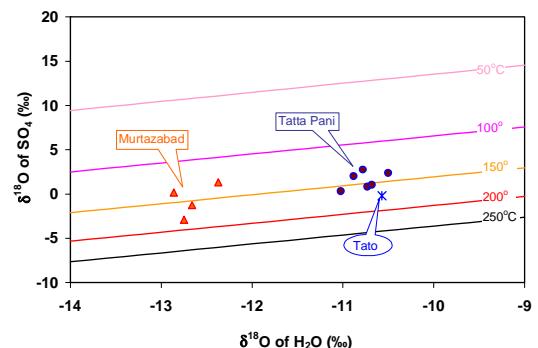
The Na-K, Na-K-Ca, Na-K-Ca-Mg and quartz geothermometers indicate equilibrium temperatures of Tatta Pani geothermal springs mostly in the range 100-150°C, while for Tato springs mostly from 170 to 200°C. As expected in the Na-K-Mg<sup>1/2</sup> triangular diagram (Fig. 7), most of the thermal waters of Tatta Pani plot between Mg<sup>1/2</sup> vertex and FEC, indicating a reservoir temperature from 75°C to 120°C. The sample from Tato plots in partial equilibrium zone along the line of 150°C temperature.



**Figure 7: Evaluation of Na-K-Mg temperatures of thermal waters of Murtazabad, Northern Areas**

### 3.3.4 Isotope Geothermometry

The results of  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer are graphically displayed in the  $\delta^{18}\text{O}(\text{SO}_4)$  vs.  $\delta^{18}\text{O}(\text{H}_2\text{O})$  correlation diagram (Fig. 8), where relevant isotherms from 100 to 250°C are also shown. Samples from Murtazabad are somewhat scattered. This scatter might be attributed, at least in part, to mixing, but the occurrence of other interfering processes cannot be ruled out. However, the isotope equilibrium temperatures range from 130-185°C.



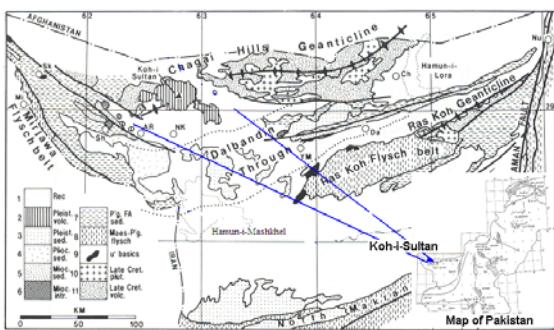
**Fig. 8.  $\delta^{18}\text{O}(\text{SO}_4)$  vs.  $\delta^{18}\text{O}(\text{H}_2\text{O})$  diagram for Northern Areas showing relevant isotherms based on the  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer of Mizutani and Rafter (1969)**

In the  $\delta^{18}\text{O}(\text{SO}_4)$  vs.  $\delta^{18}\text{O}(\text{H}_2\text{O})$  diagram (Fig. 8), the Tatta Pani samples plot around the 150°C isotherm or somewhat above it, indicating equilibrium temperatures in agreement with most of the chemical geothermometers but slightly higher than the range suggested by Na-K-Mg<sup>1/2</sup> geothermometer (75-120°C). This discrepancy might be due to the fact that the oxygen isotope (<sup>18</sup>O) exchange between dissolved SO<sub>4</sub> and H<sub>2</sub>O becomes sluggish at low temperatures and high pH values (Giggenbach et al., 1983; Chiba and Sakai, 1985). The enrichment in  $\delta^{18}\text{O}(\text{H}_2\text{O})$  due to steam separation can also cause an overestimation of equilibrium temperature. In the same figure, the Tato spring shows the  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  temperature close to 170°C, which agrees with most of the chemical geothermometers.

#### 4. CHAGAI AREA

Topography of Chagai area comprises a vast sandy plain interrupted by low hills and isolated hillocks locally called 'dik'. Miri Koh is the highest in the area with an altitude of 2332 m. The surrounding plain has an altitude ranging between 750 m and 900 m. The gradients are very gentle. Radial pattern of drainage is dominant as all the streams radiate away from the top of the volcanic cones (Todaka et al., 1988). The area can be classified as arid region since it receives scanty rainfall (about 160 mm/annum). Summers are very hot and winters are very cold. There are several hot springs in this area.

The Koh-i-Sultan volcano in Chagia area is shown in Fig. 9 (Arthurton et al., 1982). The thermal springs at Batal Kaur, Miri Kaur and Padagi Kaur are located in the close vicinity of Miri Crater. Five springs seep from the beds of rainwater-courses, which consist of lava and agglomerate of the Koh-i-Sultan Volcanic Group. The water temperature ranges from 25.6 to 34.8°C, which is lower than the ambient temperature in summer season. The acidic alteration zone is distributed to southwest of the Miri peak. Especially along Miri Kaur, leading to the Miri Camp. The rocks along the Miri Kaur are strongly silicified. Hydrogen Sulphide gas is also noted in places, and the sulphur deposits, which are formed by Hydrogen Sulphide gas are scattered in the alteration zone. The springs in the alteration zone show neutral pH i.e. 6.1-7.9.



**Figure 9: Location and geological sketch map of Chagai area**

The Chigin Dik Springs (one at Onyx Marble Quarry and one at Chigin Dik called Burbur spring) are located at about 10 km SE of Mashki Chah. Their altitudes are 830 m and 1003 m respectively. One spring originates from a more or less 100 m deep hole drilled by Pakistan Industrial Development Corporation for iron ore exploration around Mashki Chah. It discharge water intermittently like a fountain 2-3 m high and sometimes its water table goes down up to 2 m depth. Its EC is 34500  $\mu\text{S}/\text{cm}$ . The surface

rocks are recent deposits. However, the hole may penetrate the Chagai Intrusion or the Sinjrani Volcanic Group. The other spring is located in the nearby plain, which keeps on shifting the position after clogging the path due to deposition mineral salts (mostly CaCO<sub>3</sub>). It is also highly saline having EC values 44800 and 45600  $\mu\text{S}/\text{cm}$ .

#### 4.1 Geology

The Chagai volcano-intrusive complex occurs in a region constituted by three principal structural and tectonic zones. These are marked by three major physiographic units of the region, namely: Chagai Hills, Ras Koh Range and Mirjawa Range. The stratigraphic classification of the investigated area is as following (Arthurton et al., 1979; Hunting Survey corporation, 1960).

Sinjrani Volcanic Group is the oldest unit about 1000 m thick. Massive lavas dominate the volcanic pile through tuff and agglomerates, and locally thin-bedded limestone is also present, particularly in the upper part of the sequence. These volcanic rocks in general are well cemented and hard. The group has been assumed to be Cretaceous on the basis of its stratigraphic position.

Humai Formation is assigned Late Cretaceous age on the basis of fossil content. It consists of limestone, shale, sandstone, conglomerate, tuff, and subordinate lava.

Jazzak Formation is believed to be mainly Paleocene and thickness of the formation is more than 2400 m containing mainly interbedded shale, sandstone, volcanic rock, and subordinate limestone.

Koh-i-Sultan Volcanic Group consists at least three volcanic cones with central craters with many smaller, satellite cones or plugs in addition. The group is age wise divided into bassal agglomerate, top agglomerate, coarse pyroclastic deposit, tuff, lava flow, and ash flow. The group is unlikely to be older than Pleistocene.

Subrecent deposits are semi-consolidated to loosely consolidated sand, gravel and pebble deposits. Recent deposits are poorly sorted alluvial sediments consisting of sand and silt, which occur in dunes and playas. Pebbles, cobbles and boulders occur in dry washes.

Chagai Intrusions consists extensive batholiths and stocks in the Chagai Hills. The age range of these intrusions is doubtful. On the basis of fission track method, the major part of Chagai intrusions were emplaced during Oligocene and Miocene.

The area is located in the Chagai and Sultan Arcs. Initially the Chagai Arc was formed by the Cretaceous volcanic products (Sinjrani Volcanic Group) erupted on the southern margin of the Afghan block and later was covered by the sedimentary rocks (the Humai and Jazzak Formations etc.) and intruded by plutonic rocks (the Chagai Intrusions).

The Koh-i-Sultan Volcano of Pleistocene age is the youngest volcano in Pakistan. It is fairly large spreading over approximately 500 km<sup>2</sup>. It is assumed that the hot magma chamber is the heat source. Existence of high temperature magma underneath Koh-i-Sultan is inferred by the emission of hydrogen sulphide and sulphur dioxide gasses (Abid, 1975).

#### 4.2 Results and Discussion

In Chagai area the thermal waters of Padagi have relatively low EC (4940 to 8170  $\mu\text{S}/\text{cm}$ ) and they are MgSO<sub>4</sub> type.

The other three fields have very high EC values varying from 25300 to 45600  $\mu\text{S}/\text{cm}$  and they are NaCl type. EC of three water samples taken from wells in the area varies from 3150 to 4720  $\mu\text{S}/\text{cm}$ . Two of these, which are in Padagi area, belong to  $\text{MgSO}_4$  while the third one (Mashki Chah) is NaCl type.

#### 4.2.1 Origin

Isotopic data can well differentiate between the three possible types of origin of thermal water i.e. magmatic, oceanic and meteoric. Ranges of  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of all the sampled geothermal manifestations of Chagai are  $-3.7$  to  $+4.3\text{\textperthousand}$  and  $-33.4$  to  $-8.8\text{\textperthousand}$  respectively. These data do not show the presence of any significant amount of magmatic water which generally has  $\delta^{18}\text{O}$ :  $+6$  to  $+9\text{\textperthousand}$  and  $\delta^2\text{H}$ :  $-40$  to  $-80\text{\textperthousand}$  (Mizutani and Rafter, 1969; Nieve and Nieve, 1987). Normally the oceans have  $\delta^{18}\text{O}$  &  $\delta^2\text{H}$  about  $0\text{\textperthousand}$  (VSMOW). Depleted values of  $\delta^2\text{H}$  ( $-33.4$  to  $-22.3\text{\textperthousand}$  except one value of  $-8.8\text{\textperthousand}$ ) rules out any major contribution of oceanic water. These values are similar to the meteoric water of this area indicating possibility of recharge from meteoric water. Highly enriched values of  $\delta^{18}\text{O}$  can be explained by  $\delta^{18}\text{O}$ – $\delta^2\text{H}$  plot (Fig. 10).  $\delta^{18}\text{O}$  of thermal springs except one spring of Padagi Kaur follow the trend of  $^{18}\text{O}$ -shift due to exchange between water and rocks at higher temperatures. Especially, the  $^{18}\text{O}$ -shift for Batal Kaur, Miri Kaur and Chigin Dik springs is very high ( $6$  to  $8\text{\textperthousand}$ ), maybe due to rock–water interaction at high temperature (Clark and Fritz, 1997), which is very likely as the carbonate rocks are present in the area coupled with low water–rock ratio (Todaka et al., 1988). In the same plot, the thermal springs of Padagi indicate evaporation trend, which originates from the meteoric water index of Quetta area (Hussain et al., 1995). It indicates that the origin of Padagi area is meteoric water, which undergoes extensive evaporation. There is correlation between  $\delta^{18}\text{O}$  and Cl Padagi springs, which confirms the evaporation process. It seems that origin of all the geothermal springs is meteoric water recharging from the same area, most probably in the vicinity Padagi Kaur. During deep circulation, it undergoes high  $^{18}\text{O}$ -shift as a result of rock–water interaction at high temperature and there is no significant mixing or evaporation in the thermal waters.

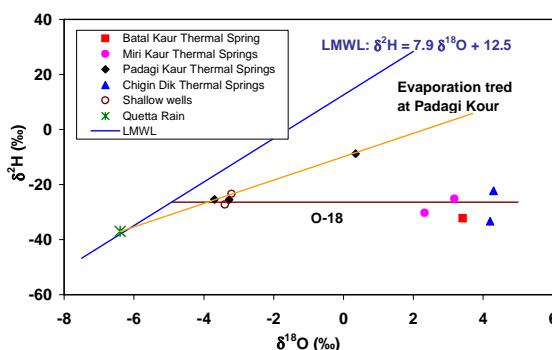


Figure 10:  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  of Chagai geothermal springs

The important feature of the fluids emerging from thermal manifestations is their high salt contents, especially in Chigin Dik (Ziarat) springs. With reference to EC, thermal springs can be divided into three groups i.e. low at Padagi Kaur ( $4940$ – $8170$   $\mu\text{S}/\text{cm}$ ), high at Batal and Miri Kaurs ( $25300$ – $26300$   $\mu\text{S}/\text{cm}$ ) and very high at Chigin Dik ( $34600$ – $45600$   $\mu\text{S}/\text{cm}$ ). The Cl and  $\text{HCO}_3$  follow the same pattern, which seems due to movement of thermal water from Padagi

Kaur towards Ziarat area and dissolution of salts. The Padagi springs have relatively low Cl ( $145$ – $409$  ppm) as compared to that of others having very high Cl ( $6560$  to  $13871$   $\mu\text{S}/\text{cm}$ ). Two springs at Chigin Dik have Cl values of  $10326$  ppm and  $13871$  ppm. Normally the oceans have the salinity from  $33500$  to  $37600$  ppm and chloride about  $19300$  ppm. Such a high Cl indicates dissolution of marine origin salts/minerals. With the increase in  $\text{HCO}_3$ ,  $\delta^{13}\text{C}$  also increases from Padagi Kaur ( $-6.2$  to  $-8.5\text{\textperthousand}$ ) towards Chigin Dik springs  $-1.4$  to  $+0.9\text{\textperthousand}$ , which is similar to that of marine carbonate (Clark and Fritz, 1997). As carbonate is dissolved,  $\delta^{13}\text{C}_{\text{DIC}}$  is evolved to more enriched values.

#### 4.2.2 Residence Time

Tritium content of the thermal waters of Chagai areas is about zero (less than detection limit i.e.  $0.8$  TU). In case of no tritium in the thermal water the exact input data of tritium is not needed for dating because, whatever the values may be, its would decay to the level of detection limit within 60 years. Hence the tritium data show that all these thermal waters were recharged before the start of nuclear weapon testing (1952) (Clark and Fritz, 1997). Tritium of the shallow open wells in Padagi Kaur area is also less than the detection limit showing residence time more than 60 years.

#### 4.2.3 Reservoir Temperature

The chemical geothermometers like Na-K and Na-K-Ca indicate high reservoir temperature estimates mostly in the range of  $200$ – $300^\circ\text{C}$ . The geothermal reservoir temperature is also estimated using the Na-K-Mg $^{1/2}$  triangular diagram (Fig. 11) (D'Amore and Arnorson, 2000). This approach was adopted in order to take into account the possible uncertainties of the Na-K geothermometer. The Chagai samples are spread along an alignment starting close to the Mg $^{1/2}$  vertex and pointing towards the full equilibrium region. Spread may be due to continuous modification of chemical concentrations at different localities. These thermal waters fall in the partial equilibrium zone and extrapolations to the full equilibrium curve indicate temperature range of  $200$ – $300^\circ\text{C}$ , while the two points nearest to the full equilibrium curve are at about  $225^\circ\text{C}$  line. Na-K-Ca-Mg gives relatively low temperature range ( $95$ – $148^\circ\text{C}$ ). In this case the estimated temperature three areas i.e. for Padagi Kaur ( $87$ – $95^\circ\text{C}$ ), Batal/Miri Kaurs ( $136$ – $138^\circ\text{C}$ ) and Chigin Dik ( $145$ – $148^\circ\text{C}$ ) follow the order of movement.

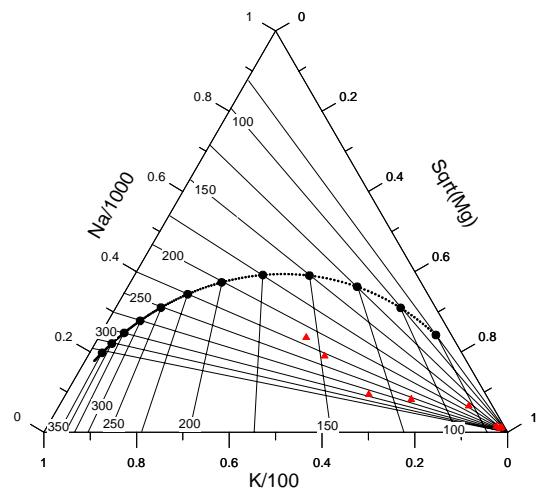
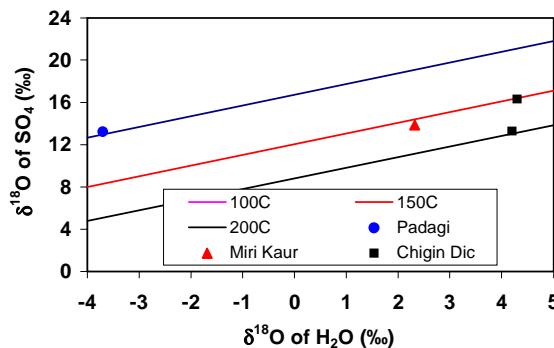


Fig. 11. Evaluation of Na-K-Mg temperatures of thermal waters of Chagai area

Silica geothermometer was applied to estimate reservoir temperature (Fournier, 1977), which ranges from 96°C for Padagi Kaur and 144°C for Miri Kaur. Two springs at Chigin Dik have 107°C and 113°C temperatures. Batal Kaur and Miri Kaur have maximum temperatures. As discussed above, the movement for thermal water is from east of Miri Crater (Padagi Kaur) to Chigin Dik. Padagi Kaur is the alteration zone, where chemical changes start. It seems that after achieving maximum temperature, the thermal water appears in Batal/Miri Kaur springs and during traveling relatively longer distance towards Chigin Dik drastic changes take place in its chemistry due to which silica concentration decreases resulting in less estimated temperature.



**Figure 12:**  $\delta^{18}\text{O}(\text{SO}_4)$  vs.  $\delta^{18}\text{O}(\text{H}_2\text{O})$  diagram for Chagai Area showing relevant isotherms based on the  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer

The results of  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer (Mizutani and Rafter, 1969) are graphically displayed in the  $\delta^{18}\text{O}(\text{SO}_4)$  vs.  $\delta^{18}\text{O}(\text{H}_2\text{O})$  correlation diagram (Fig. 12), where relevant isotherms from 100 to 200°C are also shown. Samples from Chagai are somewhat scattered. This can be attributed, at least in part,  $^{18}\text{O}$  shift and reduction of  $\text{SO}_4$ . In this case the best estimated temperature seems to be for Miri Kaur, which is slightly above 150°C. It is also in good agreement with the silica temperature.

## 5. CONCLUSIONS

The thermal waters of the Northern Areas of Pakistan are neutral-to-slightly alkaline and have low dissolved contents. Sodium is the dominant cation in all the cases. In terms of anions,  $\text{HCO}_3$  is domination. Source of recharge is meteoric water (snow-melt at higher altitude).

The thermal springs of Murtazabad area discharge mixed waters. The equilibrium temperature of the thermal end-member is in the range 185-225°C. The isochemical-mixing model based on the Na-K and quartz geothermometers estimates 227°C temperature.  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer indicates equilibrium temperatures in from 130 to 185°C. The dissolved silica vs. enthalpy plot suggests heat losses through conduction.

The thermal waters of Tatta Pani are unaffected by mixing of shallow water. The equilibrium temperatures determined by the Na-K, K-Mg and quartz geothermometers are in good agreement (100-130°C).  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometer indicates equilibrium temperatures around 150°C. For the Tato springs, the isotope and chemical geothermometers (except for the K-Mg) agree on an equilibrium temperature of about 175-200°C, while  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  equilibrium temperatures (170°C) is in good agreement.

Two springs of Padagi Kaur are  $\text{MgSO}_4$  type, while all the other springs at Batal Kaur, Miri Kaur and Chigin Dik are  $\text{NaCl}$  type. Alteration of water to  $\text{SO}_4$  type takes place by absorption of magmatic  $\text{H}_2\text{S}$  and the acidic solution is further responsible to dissolve rock salt and carbonate minerals. EC increases from Padagi springs (4940 and 8170  $\mu\text{S}/\text{cm}$ ) to Chigin Dik springs (45600  $\mu\text{S}/\text{cm}$ )

Chagai thermal manifestations receive recharge from meteoric waters in the vicinity of Padagi Kaur (east side of Miri Crater), which is heated by the hot magma chamber of Koh-i-Sultan most probably through deep circulation. Horizontal movement of thermal water is from Miri Crater towards Chigin Dik area. Residence time is more than 60 years.

The thermal waters do not have any contribution of shallow young groundwater but they have high  $^{18}\text{O}$ -shift (6 to 8‰) due to rock-water interaction.

Reservoir temperatures estimated by different chemical geothermometers like Na-K, Na-K-Ca, Na-K-Mg<sup>1/2</sup> (triangular plot) are quite high (200-300°C), while the silica and  $\delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$  geothermometers are in good agreement indicating the temperature around 150°C.

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## REFERENCES

Abid, M. S., Evaluation of geothermal resources in Pakistan.- Symposium World Energy Crisis and its implications with particular reference to the development countries, Karachi, November (1975), 1-7.

Ahmad, M., Akram, W., Tasneem, M. A., Rafiq, M., Ahmad, N., and Latif, Z.: Assessment of Reservoir Temperatures of Geothermal Springs of Northern Areas, Pakistan, *Geothermics*, **31**(5) (2002), 613-631.

Ahmad, M., Akram, W., Hussain, S. D., Sajjad, M. I., and Zafar, M. S.: Origin and subsurface history of geothermal water of Murtazabad Area, Pakistan – an isotopic evidence, *Applied Radiation and Isotopes*, **55** (2001), 731-736.

Ahmad, M., Tasneem, M. A., Akram, W., Hussain, S. D., Zafar, M. S., and Sajjad, M. I.: Isotopic investigations of Tatta Pani and Tato thermal springs: insights to their origin, age and subsurface history, *JSNM* (Nuclear Science Journal of Malaysia), **18** No. 2 (2000).

APHA (American Public Health Association): Standard Methods for the Examination of Water and Wastewater, 6<sup>th</sup> Edition, APHA, Washington D.C. (1985).

Arthurton, R.S., Farah, A., and Ahmad, W.: The late Cretaceous-Cenozoic history of western Balochistan, Pakistan, the northern margin of the Makran subduction

complex, In: Leggett, J.K. (ed): Trench Fore Arc Geology.- Geol. Soc. London, Spec. Publ. **10** (1982), 373-385

Chiba, H., and Sakai, H.: Oxygen isotope exchange rate between dissolved sulphate and water at hydrothermal temperatures, *Geochimica Cosmochimica Acta* **49**, (1985), 993-1000.

Chiodini, G., Cioni, R., Frullani, A., Guidi, M., Marini, L., Prati, F., and Raco, B.: Fluid geochemistry of Montserrat Island, West Indies, *Bulletin of Volcanology*, **58**, (1996), 380-392.

Clark, I.D., and Fritz, P.: Environmental Isotopes in Hydrogeology. Lewis Publishers, Boca Raton, New York, (1997), 253-256.

D'Amore, F., and Arnorson, S.: Geothermal manifestation and hydrothermal alteration, In: Arnorson, S. (Eds.) *Isotopic and Chemical Techniques in Geothermal Exploration, Development and Use*, IAEA, Vienna (2000).

Epstein, S., and Mayeda, T.K.: Variations of  $^{18}\text{O}$  content of water from natural sources, *Geochimica Cosmochimica Acta* **4**, (1953), 213-224.

Fouillac, C., and Michard, G., Sodium/lithium ratios in water applied to geothermometry of geothermal reservoirs, *Geothermics*, **10**, (1981), 55-70.

Fournier, R.O., and Truesdell, A.H.: An empirical Na-K-Ca geothermometer for natural waters, *Geochimica Cosmochimica Acta*, **37**, (1973) 1255-1275.

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

Fournier, R.O.: A revised equation for the Na/K geothermometer, *Geothermal Resources Council Transactions*, **5**, (1979), 1-16.

Fournier, R.O., and Potter, R.W.: Magnesium correction to the Na-K-Ca chemical geothermometer, *Geochimica Cosmochimica Acta*, **43**, (1979), 1543-1550.

Fournier, R.O., Application of water geochemistry to geothermal exploration and reservoir engineering. In: Rybach, L. and Muffler, L.J.P. (eds.) *Geothermal systems; Principles and Case Histories*, J. Willey, New York, (1981), 109-143.

Giggenbach, W. F., Gonfiantini, R., and Panichi, C.: Geothermal Systems. In: International Atomic Energy Agency, *Guidebook on Nuclear Techniques in Hydrology*, Tech. Report Series No. **91**, IAEA, Vienna, (1983), 359-379.

Giggenbach, W.F.: Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators, *Geochimica Cosmochimica Acta*, **52**, (1988), 2749-2765.

Giggenbach, W.F., and Goguel, R.L.: Collection and analysis of geothermal and volcanic water and gas discharges, Report No. CD 2401, Chemistry Division, DSIR, Petone, New Zealand (1989).

Giggenbach, W.F.: Isotope shifts in waters from geothermal and volcanic system along convergent plate boundaries and their origin, *Earth and Planetary Science Letters*, **103**, (1982), 495-510.

Guidi, M., Marini, L., and Principe, C.: Hydrogeochemistry of Kizildere geothermal system and nearby region, *Geothermal Resources Council Transactions* 14-II, (1990) 901-908.

Hunting Survey Corporation Ltd. (Hunting): Reconnaissance geology of part of west Pakistan- A Colombo plan Cooperative project, Toronto, Canada, (1960), 550.

Hussain, S.D., and Asghar, G., Programme for TI Programmable calculator for calculation of  $^{3}\text{H}$  concentration of water samples. PINSTECH/RIAD-102 (1982).

Hussain, S.D., Ahmad, M., Gonfiantini, R., Akram, W., Sajjad, M.I., and Tasneem, M.A., Isotopic and chemical studies of geothermal waters of Northern Areas of Pakistan. Proceedings of the Final Research Coordination Meeting on the Application of Isotope and Geochemical Techniques in Geothermal Exploration in the Middle East, Asia, the Pacific and Africa. Dumaguete City, Philippines. IAEA-TECDOC-788, Vienna, Austria, (1995), 127-147.

Khan, K.S.A., Khan, I.H., Leghari, A.L., and Khan, M.S.Z.: Geology along the Karakoram Highway from Hasan Abdal to Khunjerab Pass. *Geological Survey of Pakistan*, Quetta, (1987), 39-43.

Kharaka, Y.K., and Mariner, R.H., Chemical geothermometers and their application to formation waters from sedimentary basin. In: Naeser, N.D. and McCollon, T.H. (eds.) *Thermal History of Sedimentary Basins*. Springer-Verlag, New York, (1989), 99-117.

Krouse, H.R.: Sulphur isotopes in our environment, In: Fritz, P. and Fontes, J-Ch., (Eds.) *Handbook of Environmental Isotope Geochemistry*, Vol. 1, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, (1980), 227-257.

Lloyd, R.M.: Oxygen isotope behaviour in the sulphate-water system, *Journal of Geophysical Research*, **73**, (1968), 6099-6110.

Mizutani, Y., and Rafter, T.A.: Oxygen isotope composition of sulphates, oxygen isotope fractionation in bisulphite ion-water system, *N. Z. J. Sci.* **12**, (1969), 54.

Nehring, N.L., Bowen, P.A., and Truesdell, A.H.: Techniques for the conversion to carbon dioxide of oxygen from dissolved sulphates in thermal waters. *Geothermics*, **5**, (1977), 63-66.

Nieva, D., and Nieva, R.: Developments in geothermal energy in Mexico, Part 12. A cationic geothermometer for prospecting of geothermal resources, heat recovery systems and CHP 7, (1987), 243-258.

Pearson, F.J.Jr., and Rightmire, C.T.: Sulphur and oxygen isotopes in aqueous sulphur compounds, In: Fritz, P. and Fontes, J.-Ch., *Handbook of Environmental Isotope Geochemistry*, Vol. 1, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, (1980), 227-257.

Powell, C.McA.: A speculative tectonic history of Pakistan and surroundings: some constraints from the Indian Ocean. In: Abul Farah & Kees, DeJong (eds.), *Geodynamics of Pakistan*. Geological Survey of Pakistan, Quetta, (1979), 5-20.

Tahirkheli, R.A.: Geology of the Himalayas, Karakoram and Hindukush in Pakistan. *Geological Bulletin*, University of Peshawar, Special Issue, Vol. III, (1982), 18-23.

Todaka, N., Shuja, T.A., Jamiluddin, S., Khan, N.A., Pasha, M.A., and Iqbal, M.: A preliminary study for Geothermal Development Project in Pakistan. Geological Survey of Pakistan, (1988), 4-47.

Tonani, F.: Some remarks on the application of geochemical techniques in geothermal exploration. *Proceedings, Adv. Eur. Geoth. Res., Second Symp., Strasbourg, (1980)*, 428-443.

Truesdell, A.H.: Summary of section III. Geochemical techniques in exploration, second United Nations Symposium on the development and use of geothermal resources, San Francisco, (1976), 53-79.

Truesdell, A.H., and Fournier, R.O.: Procedure for estimating the temperature of a hot water component in a mixed water using a plot of dissolved silica vs. enthalpy. *U.S. Geological Survey Journal of Research* 5, (1977), 49-52.

Williams, M.D.: Stratigraphy of the Lower Indus Basin, West Pakistan, World Petroleum Cong., 5<sup>th</sup>, New York, *Proceedings., Sec. I, Paper 19*, (1959), 377-390.