

**ISOTOPE AND CHEMICAL INVESTIGATION OF GEOTHERMAL SPRINGS AND
THERMAL WATER PRODUCED BY OIL WELLS IN POTWAR AREA, PAKISTAN**

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Abstract:

Isotopes and geochemical techniques were applied to investigate the origin, subsurface history and reservoir temperatures of geothermal springs in Potwar. Two sets of water samples were collected. Surface temperatures of geothermal springs ranges from 52 to 68.3°C. Waters produced by oil wells in Potwar area were also investigated. Geothermal springs of Potwar area are Na-HCO₃ type, while the waters produced by oil wells are Na-Cl and Ca-Cl types. Source of both the categories of water is meteoric water recharged from the outcrops of the formations in the Himalayan foothills. These waters undergo very high ¹⁸O-shift (up to 18‰) due to rock-water interaction at higher temperatures. High salinity of the oilfield waters is due to dissolution of marine evaporites. Reservoir temperatures of thermal springs determined by the Na-K geothermometers are in the range of 56–91°C, while Na-K-Ca, Na-K-Mg, Na-K-Ca-Mg and quartz geothermometers give higher temperatures up to 177°C. Reservoir temperature determined by $\Delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$ geothermometer ranges from 112 to 138°C. There is wide variation in reservoir temperatures (54–297°C) of oilfields estimated by different chemical geothermometers. Na-K geothermometer seems more reliable which gives close estimates to real temperature (about 100°C) determined during drilling of oil wells.

ISOTOPE AND CHEMICAL INVESTIGATION OF GEOTHERMAL SPRINGS AND THERMAL WATER PRODUCED BY OIL WELLS IN POTWAR AREA, PAKISTAN

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 on earth 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 cold winters. Most of the high enthalpy geothermal resources of the world are within seismic belts associated with zones of crustal weakness such as plate margins and centers of volcanic activity. This geotectonic framework suggests that Pakistan should not be lacking in commercially exploitable sources of geothermal energy. This view is further strengthened by the fairly extensive development of alteration zones and fumaroles in many regions of Pakistan, presence of a fairly large number of hot springs in different parts of the country, and indications of Quaternary volcanism.

There are many geothermal sites in Pakistan having low to high temperature (boiling water). Preliminary research related to most of the sites like Murtazabad and Tatta Pani in Northern Areas, Chagai (Balochistan Province), Karachi etc. was carried out [Ahmad et al., 2000; 2001; 2002; Todaka et al., 1988] but there is no information about some geothermal springs present in Potwar Plateau, perhaps they were never studied. A comprehensive study on 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 conducted in Potwar area (Fig. 1) by Pakistan Institute of Nuclear Science and Technology (PINSTECH) under IAEA/RCA Project RAS/8/092 "Investigating the Environment and Water Resources in Geothermal Areas", which is reported in this paper.

The isotopes ^2H , ^{18}O & ^3H of water, ^{13}C & ^{14}C of dissolved inorganic carbon (DIC), ^{18}O & ^{34}S of sulphates were used in the study. Such applications of isotopic and geochemical

techniques for geothermal investigations were discussed by many scientists [Giggenbach et al., 1983; Fournier, 1977; Truesdell and Hulston, 1980]. Various established geochemical and isotope geothermometers applicable under different conditions were used to estimate reservoir temperatures [Fournier and Truesdell, 1973; Fournier, 1977; Fournier and Potter, 1979; Arnorsson, 1983; Tonani, 1980; Fouillac and Michard, 1981; Giggenbach et al., 1983; Kharaka and Mariner, 1989; Giggenbach and Goguel, 1989].

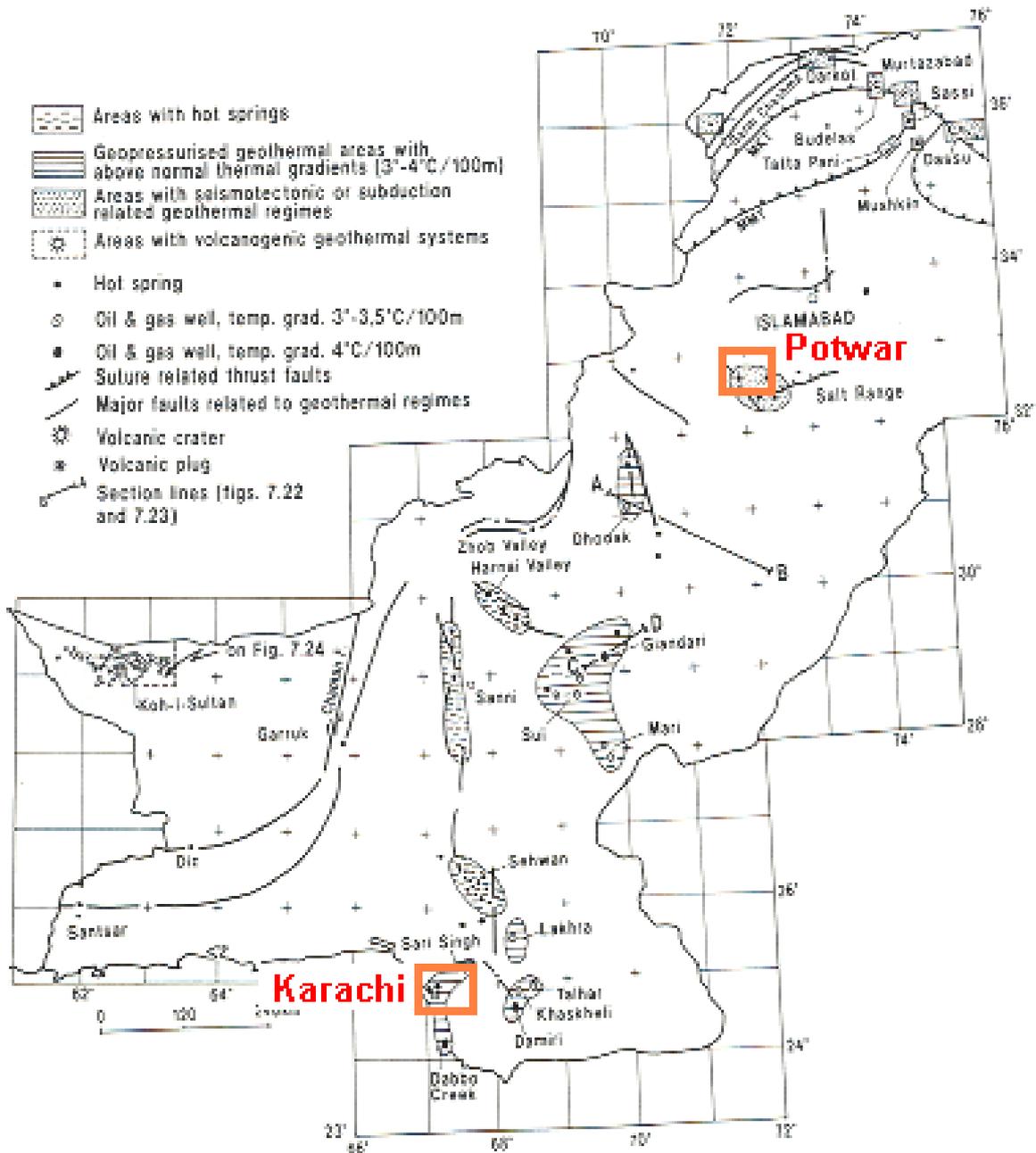


Fig.1. Map showing geothermal areas in Pakistan

2. DESCRIPTION OF STUDY AREAS

Figure 1 shows a view of geothermal areas in Pakistan. In Potwar area three hot springs at Balkassar, Fimkassar and Pindori were sampled. There are many oilfields in this area, which are producing water with oil from various formations. As the temperature of these formations are known which can be used to verify the results of geothermometers. Therefore, water samples were also taken from a dozen of oil wells.

2.1. *Geology*

The study area is in the famous plateau of Potwar, which falls in the Indus Basin between the Himalayan foothills and the Indus plains. The rocks are sedimentary and range from Paleocene to Recent in age. A generalized stratigraphic sequence of rocks in the area consists of the following formations [Bender and Raza, 1995].

Nagri Formation: The formation is widely distributed in the Indus Basin. A maximum thickness is recorded in the west of Dhulian and around Meyal-Jhammat area. Generally speaking, its thickness ranges from 300 m to as much as 2000 m. The formation consists of sandstone with subordinate clay and conglomerate. The sandstone is greenish grey, medium to coarse grained, grass bedded and massive. In places, the sandstone is bluish grey, dull red with “salt and pepper” pattern, calcareous, and moderately to poorly cemented. The clay is sandy or silty, chocolate brown or reddish grey and pale orange and proportion varies from section to section.

Chinji Formation: The formation is widely distributed in the Kohat-Potwar province. It is only confined to the southern half of eastern Sulaiman range and is not developed in the rest of the lower Indus Basin. The formation is 750 m thick in the type area (Chinji village in Attock District). Thickness varies from 1800 m in the Shinghar Range and 150 m thick in the Zindapir area of the Eastern Sulaiman range. Chinji formation of Pilgrim (1913) consists of red clay with subordinate ash grey or brownish grey sandstone. The sandstone is fine to medium grained, occasionally gritty, cross-bedded and soft.

Kamlial Formation: Kamlial formation is widely distributed in the Kohat and Potwar areas. It is 90 m thick at Kamlial (the type section), 580 m at Khaur, 650 m at Soan Gorge and 60 m at Ling River near Rawalpindi. In the subsurface, it is about 100 m at Balkassar, 150 m at Pamal Domeli, 180 m at Jhatla and varies between 120 and 300 m in the Western Potwar. The formation overlies the Murree formation conformably with a broadly transitional contact but in places it is unconformably overlying the Sakessar Limestone and the contact is marked by a Basal conglomerate with derived fossils. The formation is conformably overlain by the Chinji formation of the Siwalik group. The formation consist of purple-grey and dark brick-red sandstone which is medium to coarse grained and contains interbeds of hard purple shale and yellow and purple intraformational conglomerate. It is distinguished from underlying Murree formation by its usually spheroidal weathering and heavy mineral contents in which tourmaline dominates over epidote.

Murree Formation: The formation is widely developed in the Kohat-Potwar areas. It has also been recognized in Kashmir. The formation ranges in thickness between 180 and 600 m in the northern salt range. Throughout its extent, the formation unconformably overlies various formations of Eocene age. Its upper contact is broadly transitional with the Kamlial formation. The main body of the formation is poorly fossiliferous. The fauna indicates an early Miocene age for the formation. The formation is composed of a monotonous sequence of dark red and purple clay and purple grey and greenish grey sandstone with subordinate intraformational conglomerate. The basal strata of the formation consist of light greenish grey calcareous sandstone and conglomerate with abundant derived Eocene larger foraminifers. This horizon has been designated as Fatehjang Member. In the Kohat area, the formation has a higher percentage of sandstone, which is brown, greenish grey, in places purple and is medium to coarse grained. The interbeds of hard siltstone, lenses of conglomerate and purple to reddish brown shale are frequent.

Chorgali Formation: The formation is distributed in the eastern Salt Range, Kala-Chitta Range, Khair-e-Murat range (type section), and in the Hazara area. Its thickness varies from 150 m at Chorgali pass and 15 m at Bahadur Khel. In the Salt Range, the formation conformably overlies the Sakessar Limestone and at other places Margalla Hill Limestone. In the Salt Range, it is unconformably overlain by the Murree Formation while conformably in other areas by the Kuldana Formation. The formation is composed of shale and limestone. In

Khair-e-Murat Range, it is divisible into two distinct units. The lower unit comprises dolomitic limestone and shale. The dolomitic limestone is white to light grey and yellowish grey and medium-bedded, while the shale is grey to greenish grey. The upper part of the formation is composed predominately of shale with one thick bed of dark grey limestone and a bed of nodular argillaceous limestone near the top.

Sakessar Limestone: The unit consists dominantly of limestone with subordinate marl. Limestone, throughout its extent, is cream colored to light grey, nodular, and usually massive, with considerable development of chert in the upper part. The formation is widely distributed in the salt range and Sughar range. In the salt range its thickness varies between 70 m and 150 meter. It is 220 m at Chichali pass and about 300 m in other parts of Sughar range.

3. Materials and methods

Two sets of water samples from hot springs, oil wells and shallow groundwater were collected from Potwar area in June 2002 and March 2004. Physico-chemical parameters such as temperature, pH and electrical conductivity (EC) were determined in the field. A total of seven (7) sample aliquots were collected for each hot spring site for chemical and isotopic analyses. Where filtration was required, a 0.45 μm pore diameter filter was used. The volume of the sample and treatment in the field for various analyses are given below.

Table I. Required volume and treatment of water samples for chemical analysis and isotopes

Analysis	Volume	Treatment
Anions (Cl, HCO ₃ , SO ₄)	1L	Unfiltered, unpreserved
Cations (Na, K, Ca, Mg,)	250 mL	Filtered, acidified with HNO ₃
Silica	100 mL	Filtered, diluted with deionized water (1:1)
Stable isotopes: (¹⁸ O, ² H)	500 mL	Unfiltered, unpreserved
¹³ C (DIC)	100 mL	Filtered and poisoned
¹⁸ O, ³⁴ S (Sulphate)	1L	Filtered
Tritium (³ H)	1L	Unfiltered, unpreserved
Carbon-14 (¹⁴ C)	60 L	

Chemical analyses were carried out using: atomic absorption spectrophotometry for Na, K, Ca and Mg; UV–visible spectrophotometry for Si and SO₄; titrimetry for HCO₃; and ion selective electrode for Cl [APHA, 1985]. The $\delta^{18}\text{O}$ value of the water was measured by

mass spectrometer using the CO₂ equilibration method [Epstein and Mayeda, 1953]. For analysis of $\delta^{18}\text{O}$ of dissolved sulphates, the sulphates were precipitated as BaSO₄ in the field [Giggenbach and Goguel, 1989]. The co-precipitated carbonate was removed by reacting with hydrochloric acid, and BaSO₄ was obtained in powder form. The BaSO₄ was reacted with graphite in a vacuum system to convert its total oxygen into CO₂ [Nehring et al., 1977], while it was reacted with V₂O₅ to convert in to SO₂ [Yanagisawa et al., 1983]. CO₂ and SO₂ were analyzed on the mass spectrometer for ^{18}O and ^{34}S relative to VSMOW. $\delta^{13}\text{C}$ was analyzed against PDB by reacting water samples directly with phosphoric acid to convert inorganic carbon into CO₂ and subsequent measurement on mass spectrometer [Clark and Fritz, 1997]. Measurement uncertainty for $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ is about $\pm 0.1\%$ while that of $\delta^2\text{H}$ is $\pm 1.0\%$. The tritium content of the samples was determined by liquid scintillation counting after electrolytic enrichment of the water samples with a standard error of ± 1 TU [Hussain and Asghar, 1982]. For analysis of ^{14}C , inorganic carbon was precipitated as BaCO₃ in the field [Giggenbach et al., 1989] and direct CO₂ absorption method in conjunction with liquid scintillation counting was used [Qureshi, et al., 1989].

4. Results and discussion

Surface temperature of Balkassar, Fimkassar and Pindori hot springs are 65°C, 68.3°C and 52°C respectively. Temperature of the water produced with oil wells could not be measured as it changes in the separators. EC of the thermal springs varies from 2780 to 3690 $\mu\text{S}/\text{cm}$. The water samples collected from oil wells have very high salinity (EC: 6940–154900 $\mu\text{S}/\text{cm}$) except two samples of Miyal-12 and Dhulian-39 having EC of 875 $\mu\text{S}/\text{cm}$ and 560 $\mu\text{S}/\text{cm}$, which might result from condensation of water vapours. In the second sampling EC of Miyal-12 is significantly high (21400 $\mu\text{S}/\text{cm}$), which is the actual water produced from the formation. The pH ranges from 6.3 to 8.

The triangular plots of cations and anions (Fig. 2 and Fig. 3) show the chemical types of these waters. Thermal springs of Balkassar, Pindori and Fimkassar are Na–Cl–HCO₃, Na–HCO₃–Cl and Na–HCO₃–SO₄ types. The cold spring is Ca–HCO₃ type. The waters produced by oil wells are NaCl type except two samples of Pindori-3 and Pindori-4, which are Ca–Cl type. The shallow groundwater samples are Na–Cl and Na–HCO₃.

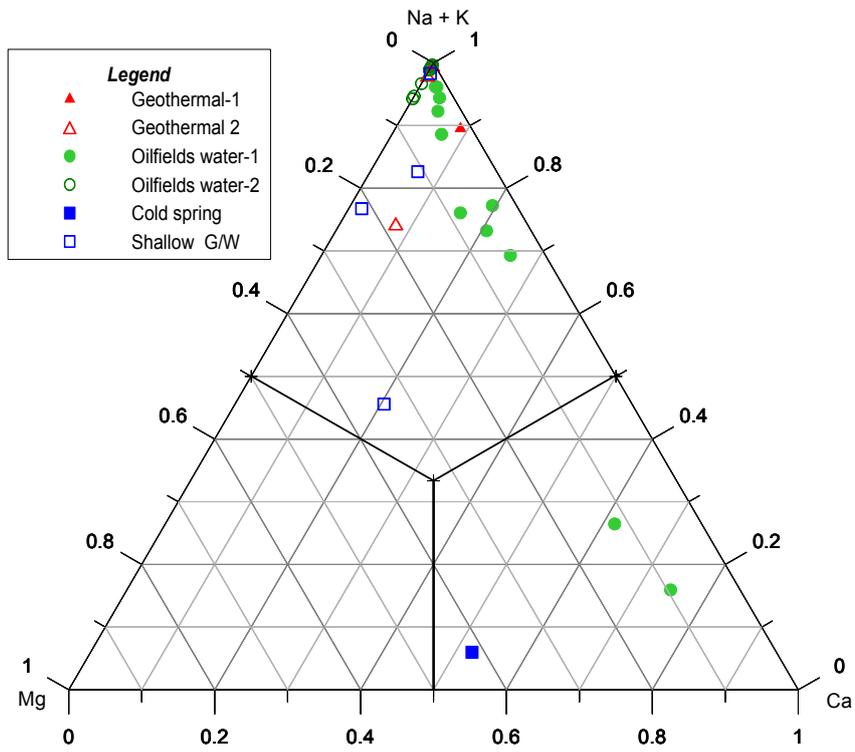


Fig. 2. Triangular plot of cations of Potwar area

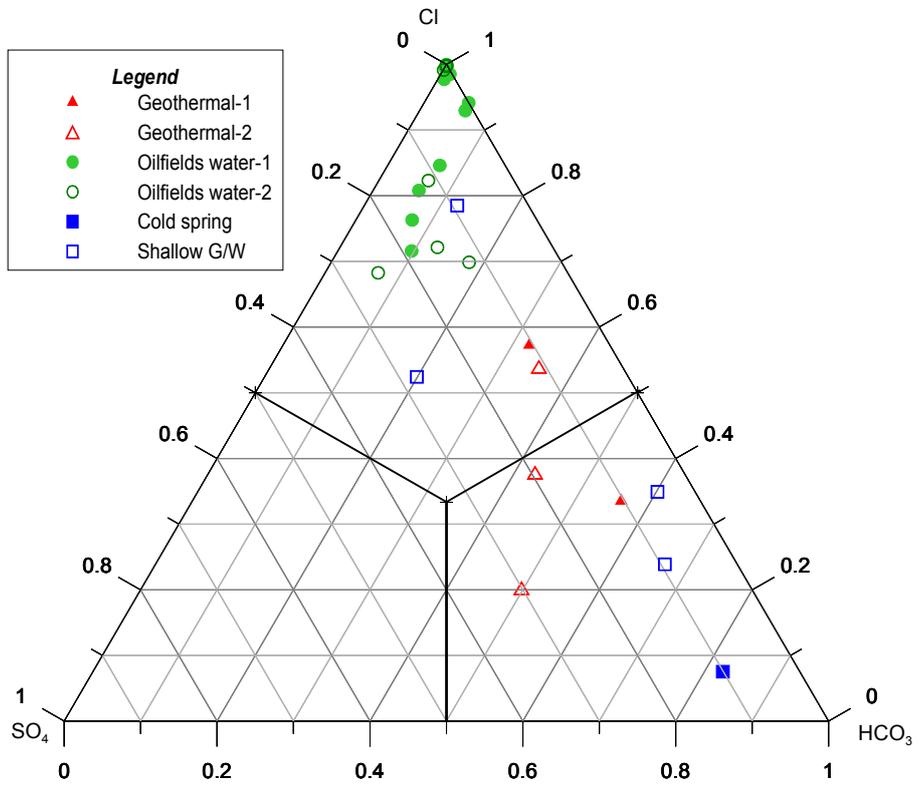


Fig. 3. Triangular plot of anions of Potwar area

4.1 Origin and subsurface processes

The $\delta^{18}\text{O}$ of the geothermal springs ranges from -4.3‰ to -2.2‰ (VSMOW), while the $\delta^2\text{H}$ ranges from -75 to -70‰ (VSMOW) in the two sets of samples. $\delta^{18}\text{O}$ of the first set of water samples collected from oilfields is highly enriched (-0.99 to $+3.3\text{‰}$) except Parivali-1 (-6.4‰). $\delta^2\text{H}$ of all these samples is quite depleted and falls in the range of -81 to -65‰ . In the second set of samples, $\delta^{18}\text{O}$ is even more enriched (up to $+7.8\text{‰}$). The possibility of oceanic origin of the encountered geothermal springs and water produced by oil wells is ruled out as $\delta^2\text{H}$ contents are much depleted. $\delta^2\text{H}$ of both types of the samples is similar to that of magmatic water generally having $\delta^{18}\text{O}$: $+6$ to $+9\text{‰}$ and $\delta^2\text{H}$: -40 to -80‰ [Clark and Fritz, 1997]. $\delta^{18}\text{O}$ also seems to be affected by mixing of magmatic water. The $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ of both data sets with the local meteoric water line (LMWL) for nearby area (Islamabad) are plotted in Fig. 4 and Fig. 5.

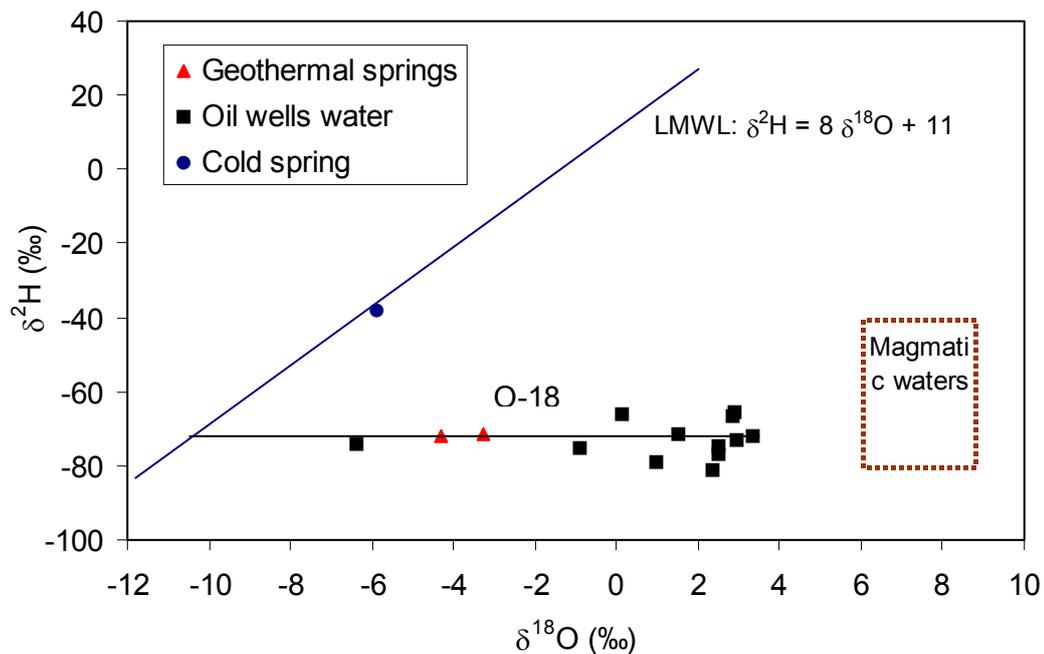


Fig. 4. $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot of first set of samples of Potwar area

The data points pertaining to the thermal springs and all the oilfield water samples plot around a horizontal line starting from the LMWL and extending up to the range of magmatic water. These trends indicate two possibilities: (a) mixing of meteoric water recharged in the high temperature zones with magmatic water, and (b) the positive ^{18}O -shift due to exchange with rocks at high temperature. The geology of the area does not support the possibility of magmatic water mixing as the area is underlain by sedimentary rocks with out

any magmatic activity. Hence, contribution of any magmatic water does not seem possible. These formations have outcrops in the foothills of Himalayas (Northern Areas) where precipitation is depleted in heavy isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). Most probably, the meteoric water recharged from the outcrops gets enriched in ^{18}O due to exchange with carbonate rocks having very high $\delta^{18}\text{O}$ value, while the $\delta^2\text{H}$ does not show any significant effect. Therefore, the horizontal trends show ^{18}O -shifts, which is 6 to 8‰ for the thermal waters and up to 18‰ for the water samples of oil wells. This ^{18}O -shift is similar to some of the highest degree ^{18}O -shift found at Salton Sea, California [Craig, 1966] and Lanzarote [Arana and Panichi, 1974]. In a carbonate reservoir at high temperature, the degree of disequilibrium for meteoric waters is extreme. Carbonate minerals are highly enriched in ^{18}O , with values close to +29‰ VSMOW. During the formation of marine carbonates at ambient temperature, $\varepsilon^{18}\text{O}_{\text{CaCO}_3\text{-H}_2\text{O}} = +29\text{‰}$, whereas, it is reduced to +17‰ at 100°C and 8‰ at 250°C [Clark and Fritz 1997]. As the exchange process proceeds, $\delta^{18}\text{O}$ of water becomes enriched while the carbonate rocks become depleted. Large ^{18}O -shift from exchange with carbonate rocks can also occur at temperatures as low as 10°C in oilfield formation water, where water/rock ratios are extremely low and contact times are very long [Clayton et al., 1966]. Therefore, ^{18}O -shift of 18‰ can be expected even at reservoir temperatures less than 100°C.

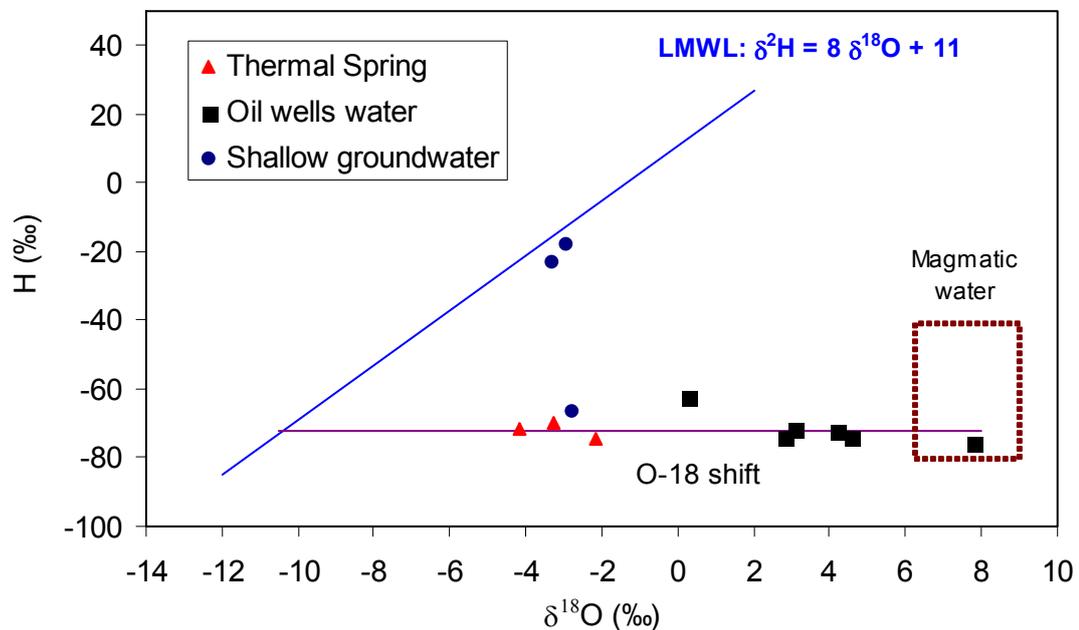


Fig. 5. $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot of second set of samples of Potwar area

$\delta^{13}\text{C}$ of the thermal springs is -8.0 ‰ and -8.5 ‰. Such values may evolve due to dissolution of calcite under closed system conditions, when carbonic acid resulting from soil

CO₂ is consumed by limestone dissolution. As discussed above the origin of the thermal water seems to be the meteoric water recharged from the outcrops in the Northern Areas, where δ¹³C of soil CO₂ was measured in the range of -19 to -17‰. Therefore, the δ¹³C of the thermal water is due to mixing of soil CO₂ derived ¹³C with limestone (δ¹³C: 0‰ PDB) in the ratio of 1:1. The oilfield water samples have δ¹³C in the range of -4.2 to +2.3‰. The δ¹³C more enriched than -1‰ is generally complete derivation from carbonate rocks. Direct correlation between δ¹³C and δ¹⁸O (Fig. 6) shows that with the higher ¹⁸O-shift, ¹³C also gets enriched. May be, the ¹⁸O-shift in water due to longer contact or strong interaction with carbonate rocks at higher temperature is accompanied by precipitation and re-dissolution of carbonate, which results in enriched values of δ¹³C.

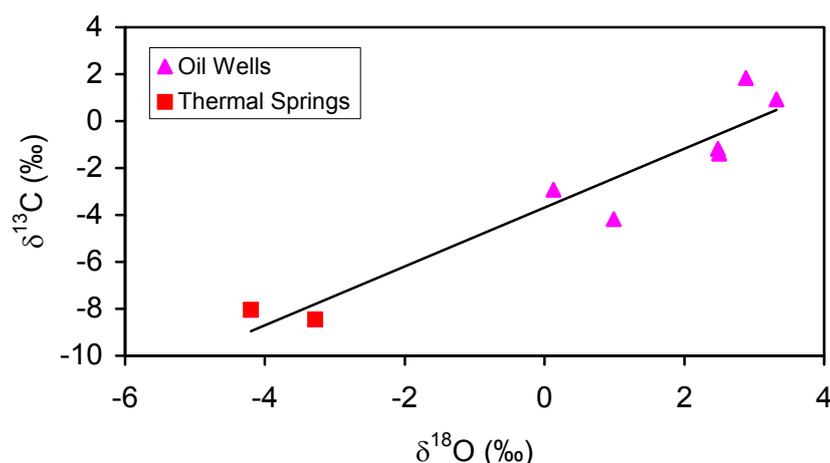


Fig. 6. δ¹³C (DIC) vs. δ¹⁸O (water) of geothermal springs and oil wells in Potwar

The waters produced by oil wells have very high salinity (EC up to 154.9 mS/cm) as compared to geothermal springs (2.95–3.69 mS/cm) and shallow groundwater (1.68–6.04 mS/cm). The high salinity is mainly due to Na and Cl contents. Plots of EC vs. Na and Cl (Fig. 7a & 7b) indicate positive correlations of EC with Cl and Na. Cl and Na are also positively correlated as shown in Fig. 8a and Fig. 8b. They are linearly correlated for relatively low concentrations (<8000 ppm), while at higher concentrations, increase in Na is less as compared to the increase in Cl following non-linear correlation. It is noted that for higher EC and Cl concentrations, other major cations (K, Mg and Ca) are also high. Therefore, dissolution of NaCl causes high salinity in most of the cases and chloride of other cations is additional sources in some cases. Geology of the area is also favourable as there are huge deposits of rock salt in the nearby Salt Range.

The δ³⁴S of dissolved sulphate of the geothermal springs of Balkassar (P2) and Pindori-5 is 1‰ and 7.6‰ CDT, while the δ¹⁸O is 8.8‰ and 13.2‰ VSMOW respectively. These combinations indicate that the source of sulphates is atmospheric (IHP, 2000). As discussed above, the source of the thermal waters is meteoric water recharged from the outcrops of sedimentary formations in the foothills of the Himalayas. These areas being clean and away from sea, do not have significant atmospheric sulphur contributions in the form of wet precipitation (H₂SO₄), atmospheric dry deposition (SO₂) and sea spray aerosols, therefore the high sulphate contents (196 ppm and 341 ppm) might result from mineral dissolution. Enrichment of ³⁴S and ¹⁸O in sulphates with the increase of SO₄ content shows mixing of sulphates of different origin like terrestrial evaporites and marine evaporates.

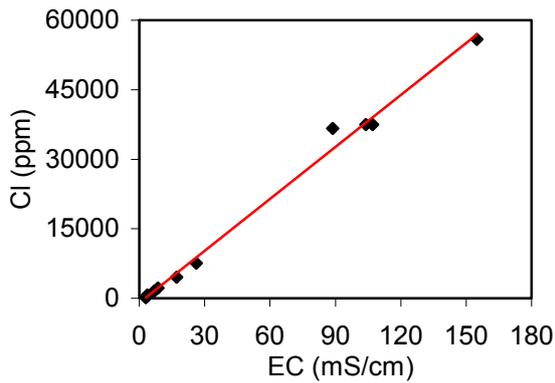


Fig. 7a. EC vs. Cl of geothermal springs and oil wells

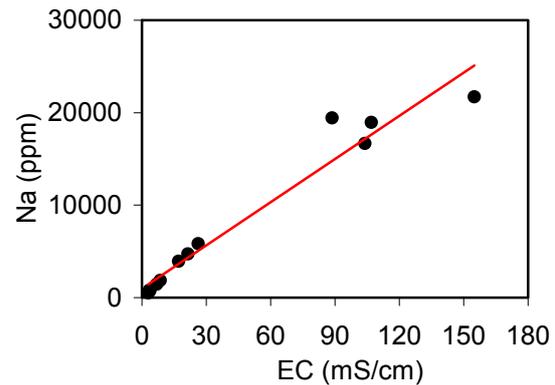


Fig. 7b. Na vs. EC of geothermal springs and oil wells

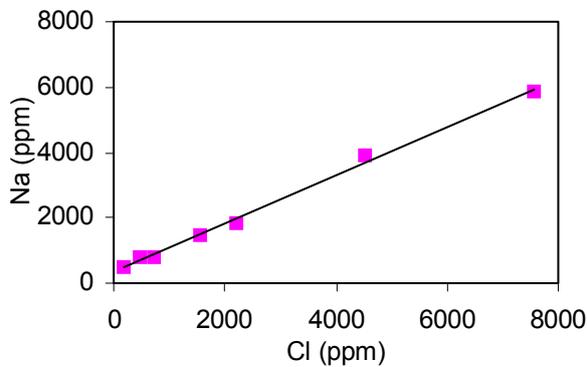


Fig. 8a. Na vs. Cl of geothermal springs and oil wells in Potwar (samples with low concentrations)

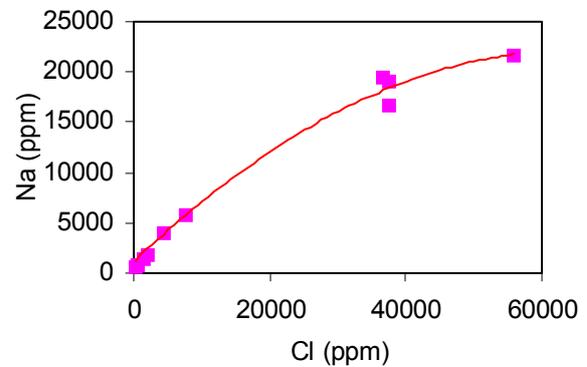


Fig. 8b. Na vs. Cl of geothermal springs and oil wells in Potwar (all the samples)

4.2. Circulation time

Tritium content of the thermal springs and water samples collected from oil wells in Potwar areas is about zero (less than detection limit i.e. 1TU). The tritium data show that all these waters were recharged before the start of nuclear weapon testing in 1952 [Clark and Fritz, 1997].

Two samples collected from Fimkassar and Balkassar have ^{14}C values 17.2 PMC and 10.5 PMC respectively. ^{14}C dating was done using $\delta^{13}\text{C}$ Mixing Model for dilution correction. $\delta^{13}\text{C}$ of soil CO_2 (about -18‰) determined in the possible recharge area and 0 ‰ carbonate were used [Clark and Fritz, 1997]. The age of both the samples comes out to be 3297 ± 1210 years and 3913 ± 1590 years.

4.3. Chemical Geothermometry

Various chemical geothermometers like Na–K [Fournier, 1979; Arnorsson et al. 1983; Nieva and Nieva, 1987; Giggenbach, 1988] K–Mg [Giggenbach, 1988], Na–K–Ca [Fournier & Truesdell, 1973], Na–K–Ca–Mg and quartz [Fournier, 1977] were used to estimate reservoir temperatures of thermal springs and the oilfields. The results are shown in Table II. Temperatures of thermal springs determined by the Na–K geothermometers are in the range of 56–91°C, while Na–K–Ca, Na–K–Mg, Na–K–Ca–Mg and quartz geothermometers give higher temperature ranges (74–179°C, 175–177°C, 89–121°C and 147–173°C respectively).

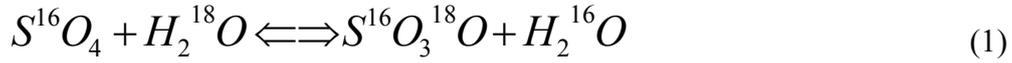
There is wide variation in reservoir temperatures (54–297°C) of oilfields estimated by different chemical geothermometers. Temperature of most of the oilfield waters estimated by Na–K and Na–K–Ca–Mg geothermometers is generally around 100°C except Parivali-1, Pindori 3, Pindori 4 and Turkwal 1, which have higher Na–K temperatures. Na–K–Ca, Na–K–Ca–Mg and SiO₂ geothermometers give higher temperatures for the oilfields mostly in the range of 150–200°C. One of the main reasons of high variation is the improper sampling of water which might have undergone significant changes in chemical concentrations during separation process. According to the temperature data of oilfields, the actual reservoir temperature in most of the oilfields is about 100°C. In this case Na–K geothermometer seems more reliable.

Table II. Reservoir temperatures estimated by geochemical thermometers for Potwar area

Sample / Oil well	Na-K-Ca	Na-K	Na-K	Na-K	Na-K	Na-K-Ca- Mg	Na-K- Mg	SiO ₂	$\Delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$
	Fournier & Truesdell, 1973	Fournier, 1979	Arnorsson et al., 1983	Nieva and Nieva, 1987	Giggenbach, 1988		Giggenbach and Goguel, 1989	Fournier, 1977	Fournier, 1977
Balkasar-P2 (Th. Sp.)	179	65	73	56	87	121	177	147	138
Pindori-5 (Th. Sp.)	74	69	77	60	91	89	175	173	112
Parivali-1 (Oil Well)	248	165	167	153	183	138	297		
Parivali-2 (Oil Well)	148	89	95	79	110	110	217		
Meyal-8 (Oil Well)	136	85	91	74	106	108	209		
Meyal-12 (Oil Well)		127	132	116	147	59	190		
Balkasar-A3 (Oil Well)	140	79	86	69	100	114	193		
Balkasar-H2 (Oil Well)	154	82	89	72	103	116	203		
Balkasar-P2 (Oil Well)	176	80	87	70	102	123	204		
Fimkasar-1 (Oil Well)	124	95	91	74	106	108	196	169	
Fimkasar-2 (Oil Well)	150	63	71	54	85	117	182	204	
Pindori-3 (Oil Well)	55	146	150	135	165	82	224		
Pindori-4 (Oil Well)	89	210	209	197	226	93	291		
Turkwal-1 (Oil Well)	122	124	129	113	144	105	233		

4.4. Isotope Geothermometry

The $\Delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$ is often the most useful isotope geothermometer because isotope equilibrium can be attained in a reasonable lapse of time depending on temperature and pH [29, 30]. The geothermometer is based on the oxygen isotope exchange reaction between dissolved sulphates and water.



The reservoir temperatures are calculated using the relationship of [McKenzie and Trues dell 1977].

$$1000 \ln \alpha_{\text{SO}_4\text{-H}_2\text{O}} = 2.88 \times 10^6 T^{-2} - 4.1 \quad (2)$$

where

$$\alpha = \frac{[1000 + \delta^{18}\text{O}(\text{SO}_4)]}{[1000 + \delta^{18}\text{O}(\text{H}_2\text{O})]}$$

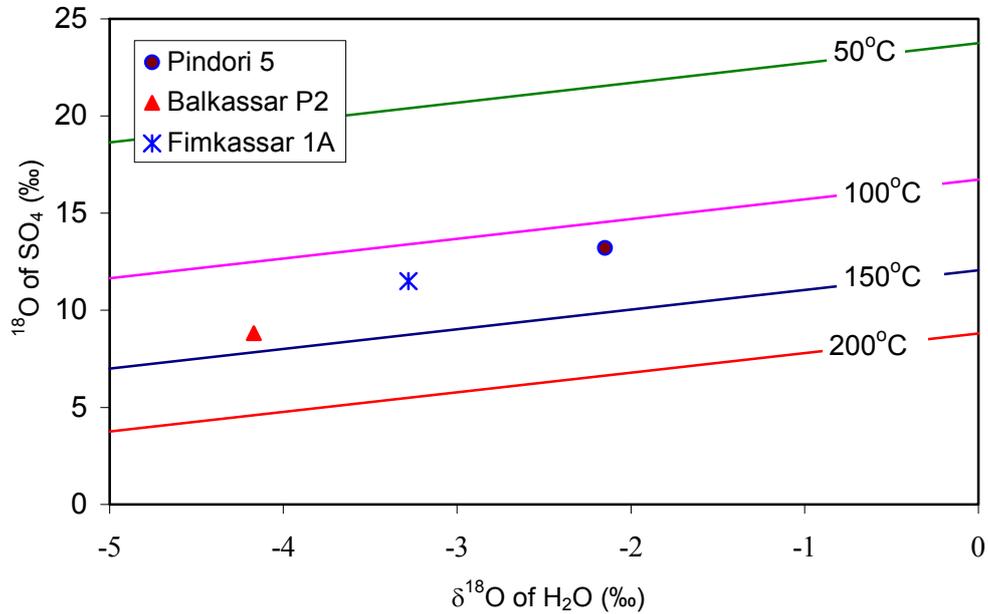


Fig. 9. $\delta^{18}\text{O}(\text{SO}_4)$ vs. $\delta^{18}\text{O}(\text{H}_2\text{O})$ diagram for thermal springs of Potwar area with relevant isotherms based on the $\Delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$ geothermometer

The results of $\Delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$ geothermometer are graphically displayed in the $\delta^{18}\text{O}(\text{SO}_4)$ vs. $\delta^{18}\text{O}(\text{H}_2\text{O})$ diagram (Fig. 9) along with relevant isotherms from 50°C to 200°C. Data points of the thermal spring samples are somewhat scattered. This might be due to various degrees of ^{18}O shift and dissolution of different types of sulphates at different location. Estimated temperatures for the geothermal springs using $\Delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$ geothermometer are in the range of 112–138°C, which is in between the low range estimated by Na–K and high ranges estimated by other chemical geothermometers.

5. Conclusions

Geothermal springs of Potwar area are Na–HCO₃ and Na–Cl type, while the water produced by oil wells is Na–Cl except two samples which are Ca–Cl type. Source of thermal springs and water produced from oilfields is meteoric water recharged from the outcrops of the formations in the Himalayan foothills. Both the categories of water undergo ^{18}O -shift which is very high (up to 18‰) in case of oilfields waters. High salinity of the oilfield waters is due to dissolution of marine evaporates.

Reservoir temperatures of thermal springs determined by the Na–K geothermometers are in the range of 56–91°C, while Na–K–Ca, Na–K–Mg, Na–K–Ca–Mg and quartz geothermometers give higher temperatures up to 177°C. Reservoir temperature determined by $\Delta^{18}\text{O}(\text{SO}_4\text{-H}_2\text{O})$ geothermometer ranges from 112 to 138°C. There is wide variation in reservoir temperatures (54–297°C) of oilfields estimated by different chemical geothermometers. Na–K geothermometer seems more reliable which gives close estimates to real temperature (about 100°C).

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