Turnover time of Tural and Rajvadi hot spring waters, Maharashtra, India

D. V. Reddy*, P. Nagabhushanam and G. Ramesh

CSIR-National Geophysical Research Institute, Uppal Road, Hyderabad 500 007, India

Sixty hot springs are spread over 18 regions in the west coast of Maharashtra, India. The area is covered by Deccan Basalts. Periodic water sampling was done for more than 5 years from Tural and Rajvadi hot springs along with waters from other deep wells for hydrochemical and isotopic analyses to study the relation between seismicity and hydrochemistry. Residence time of hot spring waters was estimated using the ^{14}C dating. Though the studied hot springs are located in an active seismic region, their hydrochemical, isotopic and temperature signatures did not indicate any major change during the period of the experiment. A comparison with the data collected by GSI three and a half decades ago indicates no long-term change in the hydrochemistry and temperature. Lack of long-term change in hydrochemistry reveals no major effect of seismicity on these geothermal waters. Radiocarbon dating of these two hot spring waters indicates relatively more turnover time for Tural spring (3080 ± 40 years BP) than the Rajvadi (1720 ± 45 years BP). The trace element characteristics of the spring waters are close to those measured on waters of granitic terrains, thus indicating the circulation of meteoric water through the granitic basement, before its discharge in the form of thermal springs in the Deccan Trap terrain.

Keywords: Hot springs, radiocarbon dating, turnover time, water sampling.

GEOTHERMAL springs in India located in different geological environments are broadly distributed into seven provinces: Himalaya, Sohana, Cambay, West Coast, Son–Narmada–Tapi (SONATA), Godavari and Mahanadi[1]. A group of 18 hot spring areas is spread over the west coast of Maharashtra, which is occupied by thick basaltic lava flows[2]. The hot springs are located in a tract 30 km long and 20 km wide, which is characterized by deep faults trending NNW–SSE parallel to the west coast of India and between north of Mumbai and south of Ratnagiri (Figure 1, inset). In fact, the 18 areas together contain 60 hot springs[2]. Detailed geological, hydrogeological, geochemical and geophysical studies were carried out in the west coast geothermal field by the Geological Survey of India (GSI) in the 1975 and 1976 field seasons to assess the deep geothermal aquifers[3,4]. The stable isotope (deuterium, ^{2}H and Oxygen-18, ^{18}O) and radioactive tritium (^{3}H) studies of these hot springs were carried out by Giggenbach[5] and Gonfiantini[6] under UNDP Project to explore the linkage between the meteoric and geothermal waters.

The study region has been seismically active since the last 45 years. The region experienced 21 earthquakes $M > 5$ (including one M 6.3), ~170 of M 4 to 5 and several $M < 4$ earthquakes during the last 45 years[7,8] and all these earthquakes have a focal depth of < 10 km.

The present study is aimed at understanding the source of hot spring water, its turn-over time and the type of geothermal reservoir from which the water is being circulated. An attempt is also made to look for long-term temporal variation in hydrochemistry, if any, with reference to local seismicity.

The two studied hot springs, i.e. Tural and Rajvadi are located close to the Mumbai–Goa highway, ~ 8 km north of Sangameshwar town and west of the Western Ghats hill range (Tural: 17°15′N; 73°33′E and Rajvadi: 17°14′N; 73°33′E). The Western Ghat hill range, more than a kilometer high above the mean sea level (amsl) runs in the north-south direction, parallel to the sea coast and to the east of the springs. There is a sudden drop in the topographic height of the Western Ghats hill range by about 800 m with step escarpment on the western side. The hot springs are located at elevations less than 40 m amsl. Tural spring is located adjacent to National Highway-17 (NH-17) and Rajvadi spring is located a little interior, about 1.5 km SSE of Tural spring and few meters lower elevation than it. Another hot spring, Arvalli is located along the road (NH-17) and ~ 8 km north of Tural. A cold spring at Nivle is located 30 km SE of Tural within the Western Ghats hill range (Figure 1).

The present study is mainly focused on Tural and Rajvadi hot springs. Supporting evidences have been taken from the Arvalli hot spring, Nivle cold spring and deep groundwater from the basaltic and granitic regions. Periodic sampling for more than 5 years was done from Tural and Rajvadi and limited sampling from Arvalli hot spring (Figure 1) to characterize their waters chemically and isotopically. Radiocarbon dating was done in 2008 on Tural and Rajvadi hot spring waters to estimate their turnover time. Trace element analysis was done (one time) on the two hot spring waters and compared with the granitic and basaltic waters to understand the probable medium of hot water circulation.

Major ion composition of the hot spring waters is determined using the Dionex Ion Chromatograph; the stable isotope ratios (δD and $\delta^{18}O$) are measured using a Dual Inlet Stable Isotope Ratio Mass Spectrometer at the National Geophysical Research Institute (NGRI), Hyderabad. Trace element composition was determined (one time) using the Inductively Coupled Plasma Mass Spectrometer (ICP-MS), model ELAN DRC II, Perkin-Elmer Sciex® Instrument, USA, also at NGRI.

*For correspondence. (e-mail: dvreddy.ngri@gmail.com)

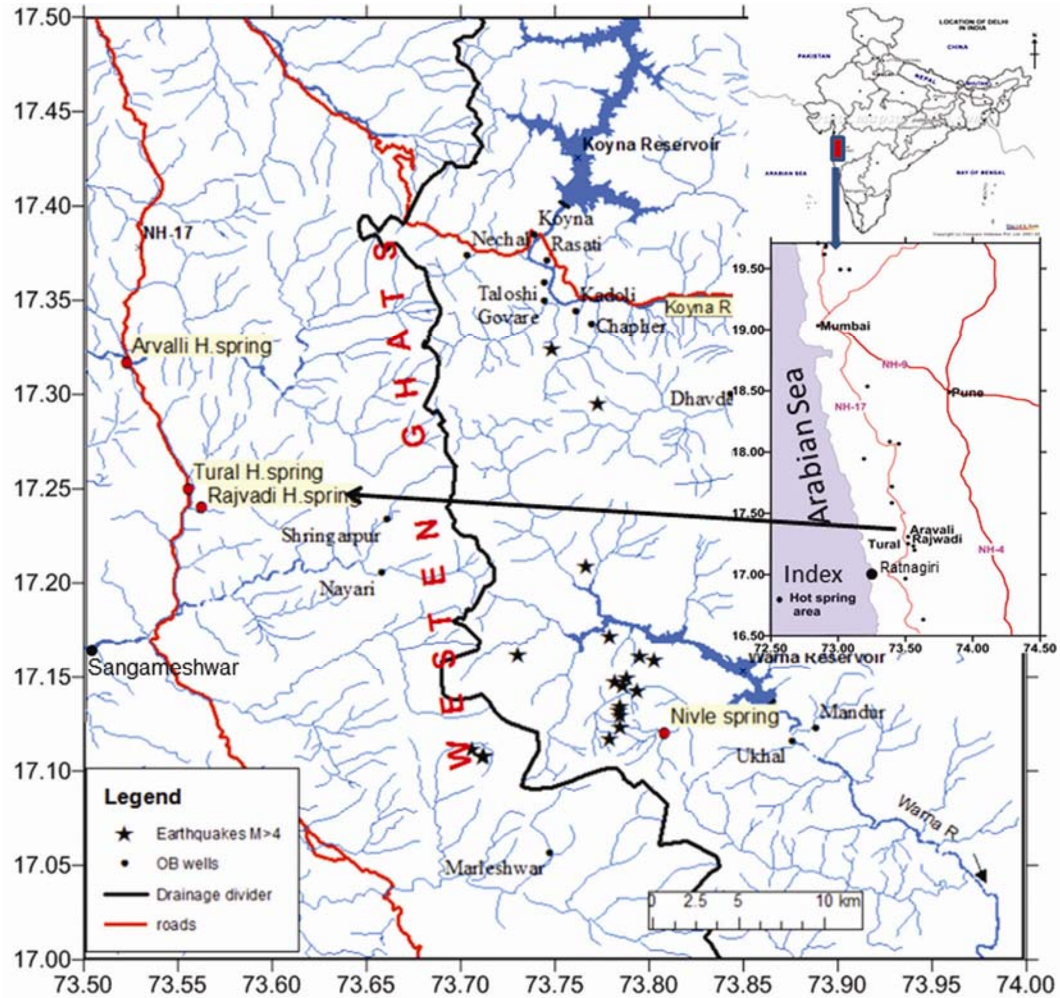

Figure 1. Location map of the studied hot springs and active seismic belt of Koyna–Warna region. (Inset) Eighteen hot spring areas in the west coast of Maharashtra.

The radiocarbon chronology was done using the Accelerator Mass Spectrometer (AMS) at the Australian National University, Canberra, Australia, adopting the procedure described in Gupta and Polach[9].

The temperature of Tural and Rajvadi hot waters was recorded as 62°C and 58°C respectively, using a temperature sensor at the time of water sampling. At Tural, the temperature sensor was placed in the orifice for about 4 months from where the hot water is bubbling out. The recorded data indicated a temperature of 61.5 ± 0.5°C. Temperature of Arvalli spring water is 42°C.

Statistical distribution of major ions and stable isotope (δ^{18}O and δD) composition of the studied hot spring waters during 2006–2011 is shown in Table 1. These waters are slightly 'alkaline' with an average pH of 7.66 for Tural, 7.92 for Rajvadi and > 8 for Arvalli hot springs. Average total dissolved solids (TDS) for Tural and Rajvadi springs are ~ 775 mg/l and for Arvalli spring it is only 425 mg/l. The concentrations of cations in the Tural and Rajvadi hot springs are as follows: sodium (Na) 206–318 mg/l, followed by calcium (Ca) 45–84 mg/l, potassium (K) 6.7–10 mg/l and magnesium (Mg) 0.4–2.2 mg/l. Similarly, anion concentration is Cl > SO_4 > HCO_3 [chloride (Cl) 334–431 mg/l, sulphate (SO_4) 89–119 mg/l, bicarbonate (HCO_3) 34–79 mg/l]. Similar to TDS value, all other ions in Arvalli hot spring water are slightly more than half the concentration of the respective chemical values of Tural and Rajvadi waters, and also display their hierarchy (Table 1). The hydrochemical measurements on one cold spring water (Nivle) were carried out 16 times during the period January 2006–April 2008. pH of this water varies between 5.3 and 7.4, with an average of 6.1, indicating that it is acidic like rainwater. Among the dominating cations, Na and Ca concentrations are almost same (range: 2.1–3.7 mg/l with an average of 2.7 mg/l and 1.6–2.9 mg/l with an average 2.1 mg/l respectively) and HCO_3 dominates over other anions with a range 6–15 mg/l and average 9 mg/l (Table 1). Figure 2 shows the respective ion variations in Tural and Rajvadi hot spring and Nivle cold spring waters.

Table 1. Hydrochemical parameters and stable isotope values (average, minimum, maximum and standard deviation) from hot spring and cold spring waters and a shallow groundwater sample

Location		pH	Eh (mV)	EC µS/cm	TDS	Na	K	Mg	Ca mg/l	Cl	SO_4	HCO_3	F	Br	$\delta^{18}O$‰	δD‰
Tural	Average	7.66	–65	1444	769	259	7.8	1.1	61	380	103	53	2.5	0.7	–2.09	–3.94
Hot	Minimum	7.23	–83	1300	690	210	6.7	0.8	45	334	89	37	1.8	0.0	–2.59	–7.22
Spring	Maximum	8.02	0	1570	840	283	8.9	1.7	76	431	116	79	3.3	2.2	–1.71	–1.03
	Std.*	0.23	13	72	39	15	0.5	0.2	8	24	7	10	0.3	0.7	0.19	1.46
Rajvadi	Average	7.92	–77	1491	794	273	8.0	0.7	63	392	107	47	2.6	0.9	–1.89	–3.24
Hot	Minimum	7.43	–96	1380	740	206	6.9	0.4	48	366	92	34	2.1	0.0	–2.14	–7.85
Spring	Maximum	8.41	0	1560	830	318	10.0	2.2	84	414	119	61	4.0	5.2	–1.62	–1.46
	Std.*	0.25	20	36	18	20	0.7	0.3	8	13	5	7	0.4	1.1	0.14	1.41
Arvalli	Average	8.05	–90	797	424	173.0	4.4	0.2	13.2	188.6	87.5	52.7	0.9	0.0	–1.96	–3.60
Hot	Minimum	6.92	–115	658	350	142.4	4.1	0.1	11.6	181.5	84.9	42.7	0.0	0.0	–2.06	–4.88
Spring	Maximum	8.45	–30	847	451	189.0	4.9	0.3	14.1	201.4	90.9	64.1	6.0	0.2	–1.58	–2.85
	Std.*	0.57	31	63	34	14.5	0.3	0.1	1.0	6.6	2.1	7.6	2.3	0.1	0.17	0.69
Nivle	Average	6.09	30	28	14	2.7	0.4	0.7	2.1	4.0	0.9	9	0.0	0.0	–2.02	–4.18
Cold	Minimum	5.30	–29	22	0	2.1	0.1	0.0	1.6	3.4	0.6	6	0.0	0.0	–2.49	–8.20
Spring	Maximum	7.42	104	33	18	3.7	1.3	1.2	2.9	4.7	1.2	15	0.2	0.0	–1.68	1.77
	Std.*	0.45	32	3	4	0.4	0.4	0.2	0.5	0.4	0.2	3	0.1	0.0	0.21	2.89
Tural HP, June 2009	Single collection	7.02	–20	1230	660	62.1	1.0	20	102	276	66	73.2	0.0	0.0	–2.05	–1.75

*Std., Standard deviation.

Table 2. Trace element concentration (ppb) of studied hot spring waters and groundwaters from basaltic and granitic regions

Sample	1 Li	2 Be	3 B	6 Al	7 Si	10 V	11 Cr	12 Mn	13 Fe	14 Ni	15 Co	16 Cu	17 Zn	18 As	19 Se	20 Rb	21 Sr	22 Mo	23 Ag	24 Cd	25 Sb	26 Ba	27 Pb
Rajvadi-hot spring	102	0.04	263	20	45	16	8.12	24.74	177	6.25	0.20	8.02	221	3.09	6.40	57.3	585	5.39	0.15	0.38	0.09	102	0.21
Tural hot spring	97	0.04	256	9.3	42	12	7.10	3.32	166	5.59	0.13	7.63	183	2.51	5.79	64.0	718	4.70	0.12	0.25	0.09	39	0.48
Average values of basaltic groundwater	0.38	0.01	60	34	19	28	2.12	0.87	26	0.97	0.06	6.20	10	1.22	0.48	1.00	16	48.9	0.04	0.17	0.56	14	0.24
Average values of granitic groundwater	7.41	0.34	337	1.7	30	159	10.54	58.34	627	47.2	3.82	142	3200	11.86	10.54	8.27	1461	8.50	1.81	1.75	0.58	307	84.6

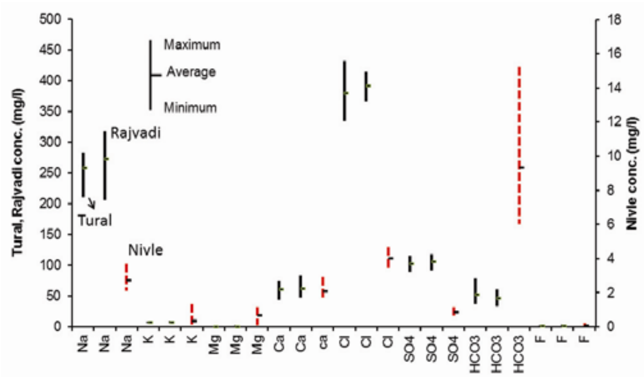

Figure 2. Average major ion concentration in Tural and Rajvadi hot spring and Nivle cold spring waters.

The stable isotope (δ^{18}O and δD) content of thermal and cold spring waters showed close average values (Table 1). The average values of δ^{18}O of Rajvadi and Tural hot spring waters are –1.89‰ and –2.09‰, and δD values are –3.24‰ and –3.94‰ respectively. The average δ^{18}O value (from seven measurements) of Arvalli hot spring water is –1.96‰ and δD is –3.6‰. The average δ^{18}O and δD values of Nivle spring water is –2.02‰ and –4.18‰ respectively. The single shallow groundwater sample close to Tural spring has δ^{18}O value of –2.05‰.

The radiocarbon chronology (AMS ^{14}C data) of Rajvadi water is 1720 ± 45 years BP, whereas for Tural water, it is 3080 ± 40 years BP (BP stands for Before Present with respect to AD 1950). The Arvalli hot spring water is not ^{14}C dated.

Trace element concentration of the hot spring waters, and groundwater of basalt and granite environments are used to identify the probable medium of interaction of hot waters. Trace element concentration (measured one time) of Tural and Rajvadi spring waters along with the average concentration of groundwater collected from ~15 deep wells (110–250 m) penetrating basalts from the same area, and 25 groundwater samples collected from granitic region are shown in Figure 3 and Table 2. The trace element concentrations in both the hot springs are almost the same. There is a large difference in the trace element concentrations between basaltic and granitic groundwaters. However, the trace element concentration of hot spring waters is much higher than the average basaltic water, except Al, V and Mo. On the other hand, some of the elements, viz. B, Si, Cr, Se, Mo of these hot waters show concentration close to that of granitic waters and the elements Mn, Fe, Ni, Co, Cu, As, Zn, Sr, Ba and Pb have concentration less than granitic groundwaters.

If physico-chemical changes occur temporally at great depths and at relatively high temperatures either naturally or induced by seismicity, then the chemical changes can be best appreciated through long-term analysis of hot water chemistry. Similarly, if shallow water mixing occurs with the upwelling hot water, then also chemical changes can be expected. Though the present study spans over a period of 5 years (a set of 40 samples for each hot spring), the hydrochemical data of the two studied hot spring waters remained almost constant (within the statistical limits), thus highlighting that minimal or no physico-chemical changes occurred during the experimental period in the geothermal regime.

The measured temperature, hydrochemical and isotopic values of the present study are compared with data from the published literature[10]. There is not much change in temperature, chemical composition and isotope values over a period of three and a half decades even after high seismicity in the region. For example, the average Cl concentration reported by earlier studies[10] for Rajvadi and Tural hot spring waters was ~375 mg/l, whereas from the present study the average values are ~392 mg/l (Rajvadi) and ~380 mg/l (Tural). Tural spring water had almost the same value, whereas the Rajvadi chloride signature deviated slightly (difference of 15 mg/l) from the earlier measurements. Similar variation is evident between the reported Na values of Tural and Rajvadi waters (230–240 mg/l) and the present Na values (259–273 mg/l). SO_4 content is almost same as that of the reported (100 mg/l) and present values (103 and 107 mg/l for Tural and Rajvadi waters respectively). Minor variation can be attributed to the difference in the measurement technique and the error percentage.

The stable isotope data of the two hot spring waters reveal almost the same isotopic composition. Average δ^{18}O is –1.89‰ for Rajvadi hot spring and –2.09‰ for Tural, whereas δD is –3.24‰ and –3.94‰ respectively for these waters. Previous studies under the UNDP project[5,6] reported stable isotope data for Tural hot spring: –1.55 and –2.9‰ for δ^{18}O and δD respectively[2]. The Tural water isotope values of the present study show depletion (δ^{18}O: –0.54‰ and δD: –1.04‰) compared to the previous study. The difference could have arisen from long duration of the present study (5 years) in comparison to the earlier short-duration measurements and also from instrument calibration and measurement differences. Local shallow water tapped by hand pump (adjacent to the Tural hot spring, Table 1) showed a δ^{18}O value of –2.05‰ (6/2009 sample collection), which is almost same as that (–2.09‰) of Tural hot spring water. Thus, with the δ^{18}O data of the two hot spring waters, cold spring water and the shallow groundwater being almost the same, the isotopic evidence suggests meteoric origin of their waters[11]. Similar observation was also made on geothermal and non-geothermal waters in Sri Lanka[12].

The Konkan area, where the hot springs exist, is covered by about 500 m thick, massive basaltic flows resting directly on the Archaean basement[13]. Based on the available information on the thickness of the basalts, a schematic circulation model is drawn using the actual (real) topographic cross-section from west to east across the two studied hot spring areas (Figure 4) to visualize the

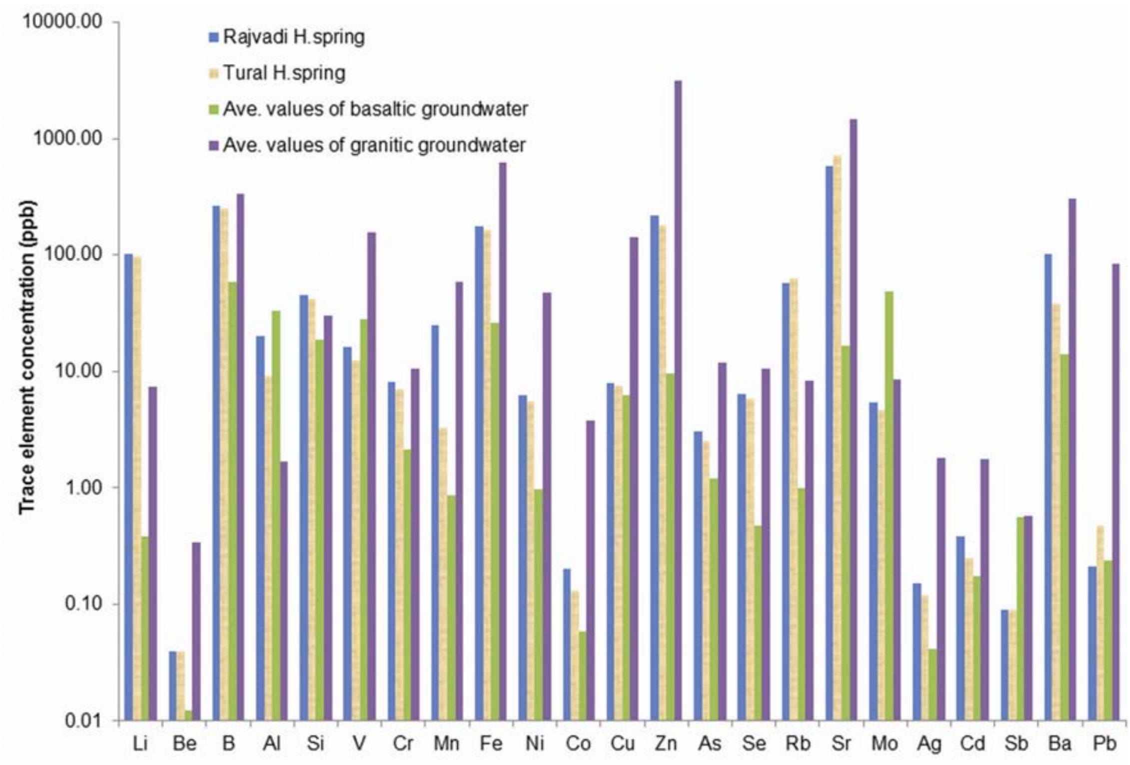

Figure 3. Average trace element concentration in Tural and Rajvadi hot spring waters in comparison with the respective average values of basaltic and granitic waters.

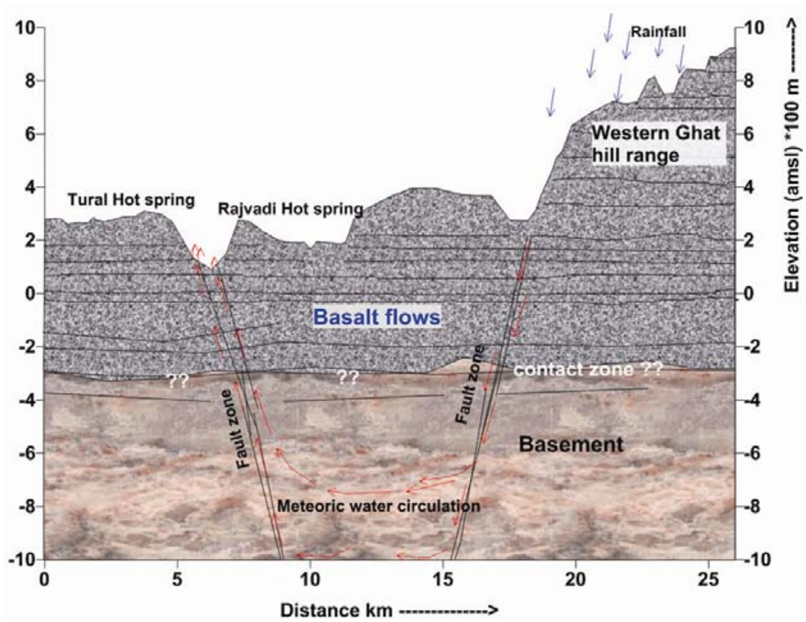

Figure 4. Hypothesized geological cross-section (west–east) associated with real topographic section indicating the possible mechanism of origin of hot springs with different circulation paths.

groundwater circulation system, their chemical changes and long residence time.

These two hot springs showed almost the same average chemical concentration of the measured major ions (excepting Mg), and also the average values of δ^{18}O and δD. But the turnover time of these waters differs by a ratio of 1 : 1.8 (Rajvadi : Tural ages). Generally, the composition of the recharging rainwater undergoes changes in the vadose zone, and further chemical species evolution takes place in the groundwater flow regime[14]. In the present case, the chemistry of the recharging meteoric water may not undergo much change in the vadose zone as there is very little weathered zone, but the change can be expected due to geochemical interaction of water during deep circulation at elevated temperatures. Hence the chemistry of the hot spring waters is different from the Nivle spring, which has limited circulation. On the other hand, high chloride content in shallow groundwater may be due to the influence of hot spring in the adjacent area. However, the stable isotope contents of all these waters retained their original characters, including hot spring waters even after deep circulation. If the mixing of magmatic water (δ^{18}O: +5.5 to +10‰)[15] with the geothermal system takes place, it manifests in the form of enriched δ^{18}O in hot spring waters. This kind of manifestation is lacking in the hot waters; rather the δ^{18}O content of cold and hot spring waters is almost the same. Even the mixing of sea water as a major component of geothermal water is ruled out on the basis of lack of relationship between δ^{18}O and chloride content of geothermal waters of the west coast[11].

The radiocarbon content of recharged groundwater diminishes with time due to radioactive decay. However, dilution of ^{14}C content can be expected through contribution of ^{14}C-depleted carbon to the groundwater by carbonaceous rocks via geochemical processes and/or mixing of waters of magmatic and sea origin. In this geological set up, presence of carbonaceous rocks and their contribution of dead carbon to the geothermal waters is unlikely. Recent deep drilling by NGRI up to 1500 m in the Koyna region indicated no intertrappean sediments[16]. Thus, the ^{14}C chronology of these two hot springs, while negating the mixing possibilities, is rather depicting the recharge episodes and circulation time. Earlier studies[4] observed high helium concentration and low tritium (radioactive hydrogen isotope, ^{3}H) values in some of the geothermal waters of the west coast, inferring long residence time of groundwaters at great depths. Thus the present ^{14}C chronology of Tural and Rajvadi hot spring waters proves the hypothesis made earlier with regard to long residence time of geothermal waters. The differences in turnover time and also temperature of these two hot spring waters can arise due to different aquifers having various recharge episodes and feeding the hot springs.

The trace element concentration of hot spring waters, which is more than the basaltic water and close to or less than granitic groundwaters[12] (Figure 3), supports the schematic circulation model where the meteoric water is being circulated through granitic rocks.

The thermal waters of Rajvadi and Tural in the west coast geothermal field of Maharashtra have a temperature difference of 4°C. They contain almost the same major ion and trace element chemical signatures and have not changed their chemical signatures since the last 35 years, even after increased seismic activity in the region. The observed ionic species enrichment may be related to geochemical evolution at greater temperature. The stable isotope content concurred with that of local shallow groundwater and cold spring water, thus depicting their meteoric origin. The observed difference in the radiocarbon dates of the two geothermal waters arises from different palaeo-recharge (turnover time) episodes.

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