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Trace Element and REE Concentrations in the Thermal Waters, West Coast Geothermal Province, India

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ABSTRACT

Extensive work has been carried out in the past on the major ion and isotope chemistry of the thermal waters along the west coast of Maharashtra. However, trace element and rare earth element (REE) study was never attempted. This is the first time such a project has been taken up with the aim of understanding the evolution and circulation pattern of these thermal springs. The concentration of trace elements viz., B, Ba, Br, Cs, F, Li, Rb, Si, Sr and REE's in the thermal springs, ground-waters and surface waters have been determined. The thermal waters had temperatures ranging from 42 to 71 °C, pH from 7.7 to 8.8 and total dissolved solids between 337and 2534 ppm. Most of the thermal waters were Na-Ca-Cl type except one which was of Na-Ca-HCO_3 type. The thermal waters contained low concentration of some elements such as < 0.1 ppb of Ag and Cd, 1-3 ppb of Cr, Zn, Co, Cu, Pb and Ni, whereas elements like Li (25-177 ppb), B (47 – 374 ppb), Sr (16-5548 ppb), Rb (13-221 ppb), Cs (3-28 ppb) and Ba (3- 2077 ppb) were much higher in concentration. The chondrite normalized pattern for REE's exhibits a positive Eu anomaly. In the light of the present study, it appears that there could be different sources of rocks playing a part in the evolution of these thermal springs in contrast to the earlier belief that all the springs are issuing through a similar geological set-up of the Deccan Flood Basalts.

1. INTRODUCTION

The west coast of Maharashtra which is a part of the Deccan trap territory hosts an array of thermal springs along the west coast fault line with temperatures ranging from 42 to 71 °C. Sixty thermal springs occur at eighteen locations in the West Coast hot spring belt. The springs fall in straight line along the coast with an average distance of about 50 km from the shore and are flanked by the western Ghats on the east. The northernmost Koknere hot spring and the southern-most Rajapur hot spring are approximately 350 km apart (Figure 1).

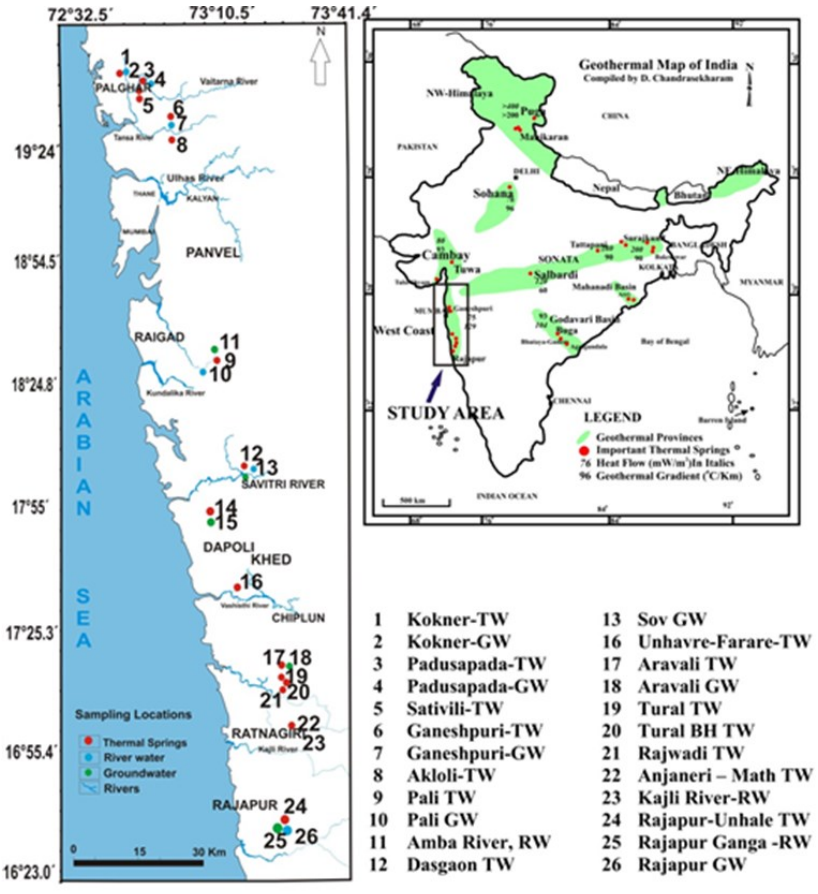

Figure 1: Sampling locations along the west coast of Maharashtra; Inset: Geothermal provinces of India (modified after Chandrasekharam, 2000) TW-Thermal springs/water; GW- Groundwater; RW- River water

The circulation of these springs is through several faults and graben structures which were formed during the attenuation and foundering of the continental crust prior to the outpouring of the large volume of lavas along the coast (Chandrasekharam and Parthasarathy, 1978; 1985). All the tectonic structures in the Konkan coastal tract are oriented in the NS and NNW-SSE directions and developed during the break-up of the Gondwanaland. All thermal springs discharge along such structures (Minnisale et. al, 2000). The hot springs also show a linear N-S trend.

Though extensive work has been done on the major ion and isotope chemistry of the thermal waters of the study area (Chandrasekharam, et. al, 1992, Ramanathan, A. and Chandrasekharam, D., 1997, Minnisale et al, 2000); trace element and REE study has not been attempted on any of the hot springs either in the present study area or any other thermal springs in India. Recently, many studies have been taken up to investigate the dissolved trace and REE concentrations in geothermal waters (Möller, 2000; Wood, S.A., 2006; Taran, et. al., 2008; H. Kaasalainen and A. Stefánsson, 2012) in an attempt to understand the origin of fluids, nature of water-rock interaction, their circulation pattern, and as a potential aid in exploration for and exploitation of geothermal fields of economic importance.

In view of the same, the present investigation has been taken up to establish baseline concentrations of trace elements and REE's in the thermal springs, ground water and surface waters along the west coast of Maharashtra. An attempt has been made to understand the reservoir characteristics based on their concentrations and inter-elemental relationships. In this paper, we present the data of selective seven thermal springs spread over the entire stretch along with two groundwater and two surface water samples.

2. GEOLOGY OF THE STUDY AREA

The Deccan volcanic province which hosts all the thermal springs located along the west coast, covers a total exposed area of 500 000 km^2 featuring numerous faults and dykes swarms (Hooper, 1990 and Chandrasekharam, 1985). The major tectonic feature along the coast is the West coast Fault, which runs parallel to the coast for a length of about 500-600 km. This structure was formed during the melting of the continental crust prior to the volcanism, and was reactivated after the Deccan volcanism (Chandrasekharam, 1985). All the thermal springs are aligned along this fault. The thickness of the basaltic lavas runs from around 2500 – 3000 m along the coast but for the Rajapur area where the thickness of the basalt flows is approximately 600 m (Figure 2, Subbarao et al. 1994). Sporadic exposure of granitic rocks can be observed towards the southern end of the study area near Rajapur.

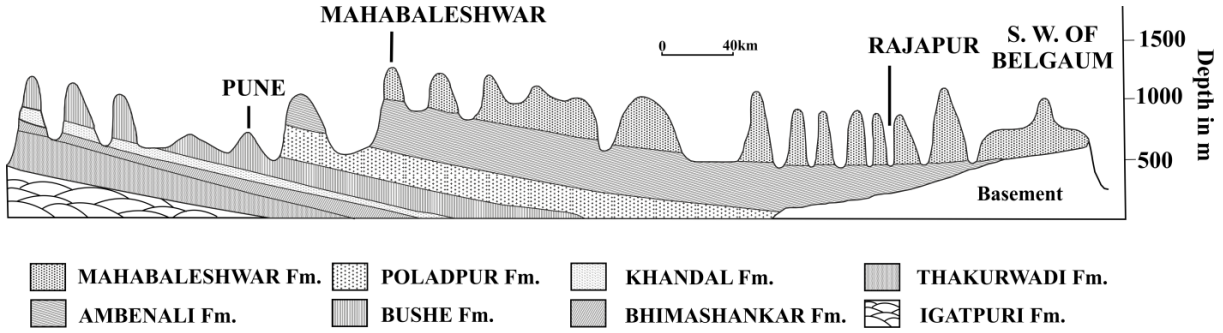

Figure 2: North-south cross section of the Western Ghats (Subbarao et al., 1994)

3. SAMPLING AND ANALYTICAL METHOD

Samples for trace and REE elements were collected in one liter High Density Polyethylene (HDPE) bottles which were cleaned by soaking overnight in 5% nitric acid followed by soaking in deionized (DI) water. Two sets of samples (1 liter each) were collected at each location. One set of unfiltered samples was acidified in the field to estimate the REE's associated with particulate matter (van Middlesworth and Wood, 1998). The second set of samples was filtered using 0.45µ Polysulfone filter membrane and then acidified with high purity HNO_3. Samples for anion estimation were collected separately (500 ml). Temperature, pH, and conductivity were measured in the field. Alkalinity and other anions (F^-, Cl^-, Br^- and SO_4^{2-}) were measured in the laboratory within a week of sample collection.

Trace elements (Al, Ag, As, B, Ba, Cd, Co, Cr, Cs, Cu, F, Fe, Li, Ga, Mn, Mo, Ni, Pb, Rb, Zn, Sb, Si, Sr, Tl, W and Zr were estimated using ICP-MS facility at PRL Ahmedabad after appropriate dilution. For the ICP-MS analysis, standards were prepared using commercial mixed, NIST-traceable standards available, which were diluted appropriately as instrument calibration standards using ultrapure grade acids. The Fe $(OH)_3$ co-precipitation technique (Shannon and Wood, 2005) was used as a pre-concentration step for determination of REE's. Dummy samples with known amount of REE's were prepared and the Fe-hydroxide pre-concentration method was tested for recovery of REE which was >95%. Ru and Rh were used as internal standards to compensate for changes in analytical signals during the operation.

4. RESULT AND DISCUSSION

4.1 Major ion chemistry

The hot springs were near neutral to alkaline in nature with pH varying from 7.7 (Rajapur, #24) to 8.8 (Sativili, #5). The temperatures of the thermal springs ranged from 42 to 71 °C with Unhavre–Farare (#16) recording the highest temperature while the conductivity values varied from 526 µS/cm to 3960 µS/cm The groundwater and surface water temperatures were between 30-31 °C. The springs show very high value of calcium (25 ppm-420 ppm) but negligible magnesium content which can be attributed to the dilute sea-water basalt interactions at elevated temperatures (Muthuraman and Mathur, 1981).

The chloride concentration in the thermal waters was highest at station #8 (1410 ppm) and station # 16 (1325 ppm), while Rajapur TW (#24) recorded the lowest concentration with 6 ppm chloride. A general trend of increase in Cl with respect to sodium can be seen in Figure 3. It is apparent from figure 3 that the salinity in thermal waters is controlled by the sea water. Around 1-5 % of saline component has been experimentally determined in the past by sea-water basalt interactions at elevated temperatures (Muthuraman,, K., 1986)

Bromine is linearly correlated to chloride suggesting similar source, probably marine in origin. Sulphate values in Rajapur (7 ppm) were the lowest and closer to the ground water values while other springs had sulpahte values between 92-275 ppm. Tural (# 19) recorded highest silica content (95 ppm, Table 1) compared to other springs where average SiO_2 is around 60 ppm. Rajapur has the lowest value at 26 ppm.

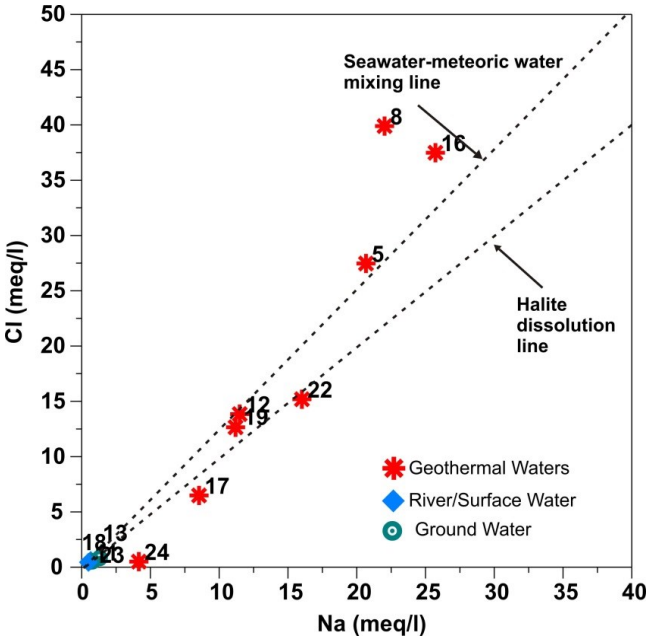

Figure 3: Na-Cl diagram of the West coast thermal and surface waters. The diagram indicates seawater mixing and halite dissolution lines.

The classification of waters using Piper diagram (Piper, 1944; Fig. 4) indicates that most of the thermal springs are either Na-Ca-Cl type except the Rajapur thermal spring which is Na-HCO_3 type. The groundwater and surface waters belong to Ca-HCO_3 type and fall close to each other indicating meteoric origin. The Rajapur thermal springs (#24) have entirely different chemistry compared to other springs indicating that they belong to an entirely different reservoir, presumably interacting with the Puttur granites or the Precambrian granites underlying the Deccan Basalts (Ramanathan et. al, 1997 and Singh et al. 2014). The current data very well matches with the earlier studies conducted by Ramanathan et al, 1997 and Minissale et al, 2000 indicating a well-organized geothermal system operating in the west coast geothermal province.

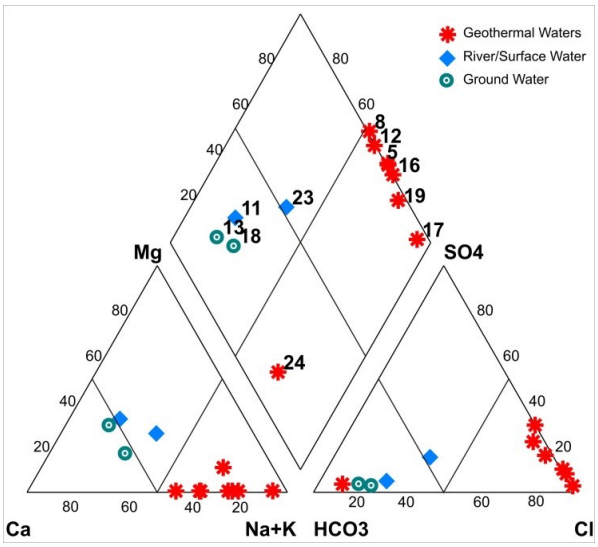

Figure 4: Piper diagram indicating classification of water samples (Piper, 1944)

4.2 Trace Element Compositions

Except for a few trace elements (Minissale et. al., 2000), investigation of the trace elements concentration in the thermal waters of west Coast of India is lacking. A systematic study has been undertaken to analyze the concentration of trace elements in the west coast thermal waters in order to understand the evolution of the thermal waters and reservoir characteristics. The data is presented in Table 2.

A few elements like Ag, Cd, In, Tl, Th and U were analyzed but were found below the detection limit of the instrument and hence not reported in the Table 2. Trace elements like Li, B, Co, Ni, Ga, Rb, Cs, Sr and Ba remain unaffected in the thermal waters due to secondary processes (Giggenbach, 1991) and hence play a significant role in understating the evolution of the thermal waters.

The alkali metals such as Li, Rb and Cs, which are useful in understanding the deep processes (Giggenbach, 1991), are plotted in the trilinear diagram (Fig. 5). Li and Cs were highest in sample # 16 which also had highest emergence temperature. It is interesting to note that sample # 16, 17 and 19 and #8, 5 and 12 may be belonging to similar reservoir, while sample #24 which has a different chemistry altogether indicates uptake of Cs in zeolites at temperatures lower than 300 °C.

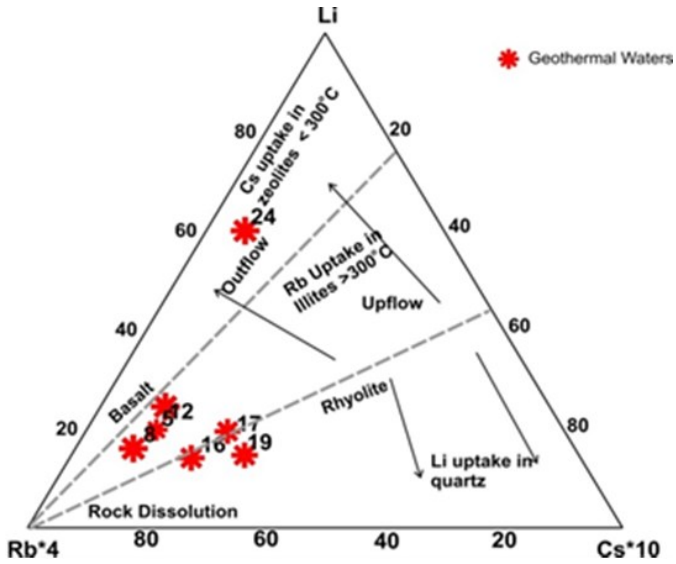

Figure 5: Li-Rb-Cs ternary diagram, (Giggenbach, 1991)

Boron concentration in the water samples varied from 47-374 ppb for thermal waters and 4-11 ppb for groundwater. In most of the thermal waters, enrichment of B over Li, Rb and Cs may be due to preferential release of B from the host rock (Goguel, 1983) and also due to the incorporation of the alkali elements into secondary minerals as discussed in Figure 5.

Rajapur thermal spring (#24) recorded highest concentration of B (374 ppb). Earlier studies on the gravity anomaly have predicted that the main heat source for the Rajapur thermal springs is the granitic batholith, which extends from Gugi in Karnataka to the Rajapur (Singh, et.al, 2014). The circulation of Rajapur waters through these granites may be greatly affecting the chemistry of these springs. This trend is clearly depicted in the B- Li- F ternary diagram (Fig. 6) where Rajapur spring (#24) falls in a B field indicating its circulation through granitic source.

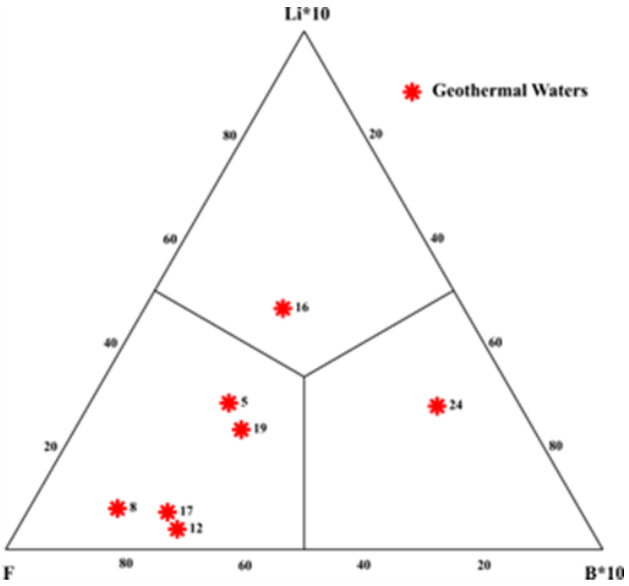

Figure 6: Ternary B(10x) - Li(10x) – F diagram for thermal waters

The Ba concentrations in the thermal springs range from 5-2000 ppb, although the average concentration was approximately 35 ppb. The Rajapur (#24, Table 2) thermal springs recorded the highest Ba content of 2000 ppb. Ba and Sr are known to form sulfate and carbonate minerals as well as being incorporated into carbonates, sulphates and aluminium silicates where they substitute for Ca (Nemee, 1975). The Ca-Ba and Ca-Sr relationships are shown in Figure 7. The Rajapur thermal springs are $NaHCO_3$ type and are depleted in Ca as against other springs at the west coast. As discussed in the previous sections, the major ions composition of the Rajapur springs depicts a circulation through Precambrian granites high in Ba concentrations. This supports our earlier observation that Rajapur thermal waters are circulating through granite basement rocks even though the springs are issuing through Deccan basalt flows (Chandrasekharam et al., 1992, Ramanathan and Chandrasekharam, 1997 and Singh et al. 2014).

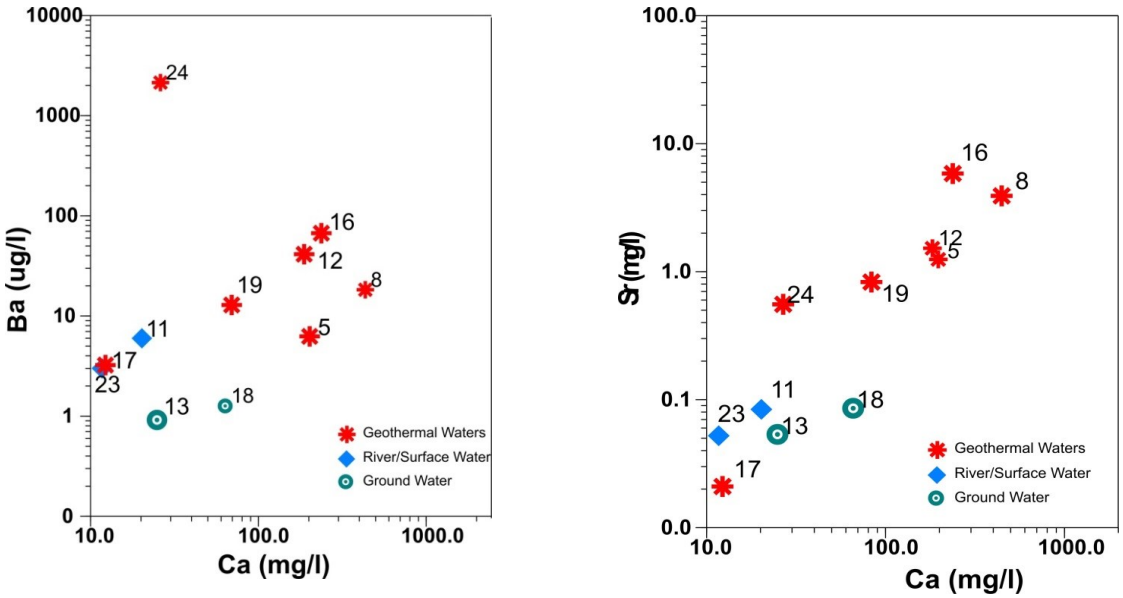

Figure 7: Ca/Ba and Ca/Sr relationship in the geothermal and surface waters of west coast.

4.3 Rare Earth Elements

The studies on REE composition in geothermal waters has gained momentum in a past few years owing to its probable application in tracing the origin of fluids, which is fundamental in understanding any fluid-rock system. The suite of REE's enables us to study the source of fluids, the state of equilibrium in water-rock interaction, and changes of fluid composition by both precipitation and scale formation during ascent. Most of these studies are limited to high enthalpy resources with acidic brines as they contain considerable amount of REE as compared to alkaline waters.

In the present study, REE content of low enthalpy alkaline waters is investigated. The ∑REE content in the unfiltered thermal waters was very low ranging from 11-700 ppt (ng/L) and ranges from ~10^{-6} to 10^{-5} times chondrite content. The chondrite normalized patterns exhibit an overall negative slope indicating LREE (light rare earth elements with atomic number 57-64) enrichment.

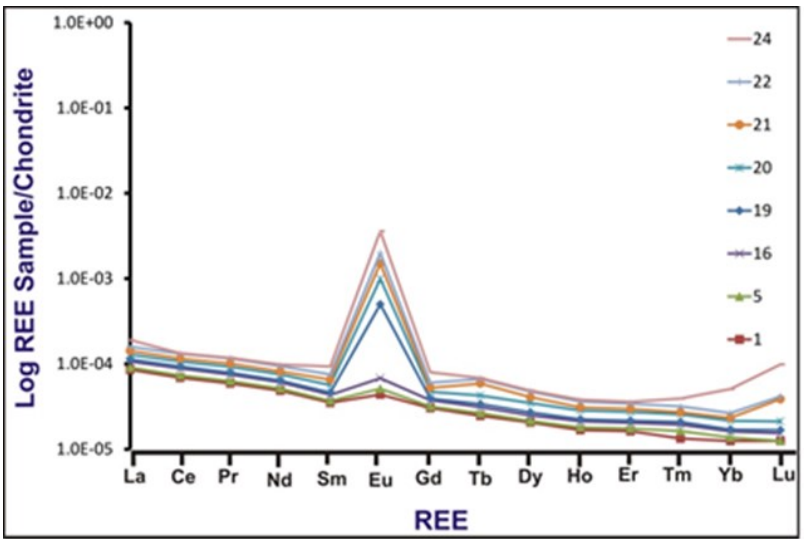

Figure 8: Log-Chondrite normalized REE pattern in unfiltered samples of thermal waters from west coast.

A pronounced positive Eu anomaly can be seen in all the chondrite normalized water samples (Fig. 8). Strongly positive Eu anomaly occurs at temperatures above 250°C (Moller, 2000). At higher temperatures Eu occurs as Eu (II) as there are reducing

conditions, but in alteration reactions and at low temperatures, Eu is in Eu (III) state and this process rejects Eu (II), which gets sorbed on to mineral surfaces. This can give rise to an inherited Eu anomaly. This can particularly happen in alteration of feldspar particularly plagioclase. Thus alteration of feldspar seems to be a source of such prominent positive Eu anomaly as most of the thermal springs in the west coast circulate through the Deccan Basalts.

5. CONCLUSION

The West coast of Maharashtra in India hosts several thermal springs which are aligned along a major tectonic feature, the West Coast Fault. The temperatures of these springs varied from 42 to 71°C while groundwater temperatures were around 30°C. The chemistry of thermal waters deciphered using Piper diagram indicates that the thermal waters are mostly Na-Ca-Cl or Ca-Na-Cl type with exception of Rajapur which is of $NaHCO_3$ type.

Trace elements namely; Al, Ag, As, B, Ba, Cd, Co, Cr, Cs, Cu, F, Fe, Li, Ga, Mn, Mo, Ni, Pb, Rb, Zn, Sb, Si, Sr, Tl, W and Zr were estimated in Thermal Springs, Ground waters and surface waters for filtered and unfiltered samples. Elements like Li, Rb, Cs, and B remain in the dissolved form and are hence play a significant role in understating the evolution of the thermal waters. In the Li, Rb and Cs plot, samples from the northern part # 5 and 8 and samples # 16, 17 and 19 cluster together indicating two separate reservoirs or processes controlling these springs. Incorporation into Feldspars and clays at temperature less than 250 °C was seen in Rajapur thermal spring (#24). Sample number #24, the most southern sampling point, seems to be controlled by a complete different geological set-up.

The thermal waters showed enrichment in LREE with positive Eu anomaly, which may be an inherited anomaly due to the alteration of plagioclase rich basalts.

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REFERENCES

Chandrasekharam, D. and Parthasarathy, A.: Geochemical and tectonic studies on the coastal and inland Deccan Trap volcanics and a model for the evolution of Deccan Trap volcanism. N. Jb. Min. Abh. **132**, (1978), 214-229

Chandrasekharam, D. and Parthasarathy, A.: Tectonic aspects of Deccan Traps., Geological Survey of India, Sp. Pub., **14**, (1985). pp 20-24

Chandrasekharam, D., Ramanathan, A., and Selvakumar, R. L.,: Thermal springs in the Puttur crystallines of the western continental margin of India—field and experimental results in water-rock interaction :, Kharaka, K. and S. Maest (eds.), (1992) AA Balkema, Netherlands, 1272–1274

Chandrasekharam, D.: Geochemistry, oxygen and hydrogen isotope ratios of thermal springs of western continental margin of India, *Proceedings,* 28th International Geothermal Congress, Washington. D.C. (Abs). (1989).

Chandrasekharam, D.: Geothermal Energy Resources of India: Country Update, *Proceedings,* World Geothermal Congress, Kyushu-Tohoku, Japan, (2000) 133-144.

Chandrasekharam, D.: Structure and evolution of the western continental margin of India deduced from the gravity, seismic, geomagnetic and geochronological studies, *Phys. Earth Planet. Int.* 41, (1985),186-198.

Giggenbach, W. F.:"Chemical techniques in geothermal exploration,": in Applications of Geochemistry in Geothermal Reservoir Development, UNITAR-UNDP (ed. F. D'Amore), (1991), 119-144.

Goguel R.L.: The rare alkalies in hydrothermal alteration at Wairakei and Broadlands geothermal fields, NZ, *Geochimica. Cosmochica Acta*, **47**, (1983), 429-437.

Gunnlaugsson, E., Arnórsson, S.: The chemistry of iron in geothermal systems in Iceland. *Journal of Volcanology and Geothermal Research*, **14**, (1982), 281–299.

Hooper, P.R.: The timing crustal extension and the eruption of continental flood basalts, *Nature,* **349**, (1990), 246-249.

Kaasalainen, H and Stefánsson, A.: The chemistry of trace elements in surface geothermal waters and steam, Iceland, *Chemical Geology*, **330–331**, (2012), 60–85.

Minissale, A., Vaselli, O., Chandrasekharam, D., Magro, G., Tassi, F. and Csiglia, A.: Origin and evolution of 'intracratonic' thermal fluids from central-western peninsular India, *Earth and Planetary Science Letters*, 181, (2000), 377-394.

Möller, P.: Rare earth elements and yttrium as geochemical indicators of the source of mineral and thermal waters. In Stober. I. and Bucher. K. (eds): Hydrology of crystalline rocks, Kluwer Acad. Press, (2000), 227-246.

Muthuraman, K. and Mathur, P. K.: Experimental water/rock interaction studies and the thermal waters of the West Coast of Maharashtra, India. Journal of Geological Society of India, **22**, (1981), 69-77.

Muthuraman, K.: Sea Water-Basalt Interactions And Genesis Of The Coastal Thermal Waters Of Maharashtra, India, *Geothermics,* **15**, (1986), 689-703

Nemee, D.: Barium in K-Feldspar Megacrysts from Granitic and Syenitic Rocks of the Bohemian Massif, Tschermaks Min. Petr. Mitt., **22**, (1975), 109--116

Piper, A.M.: A graphic procedure in the geochemical interpretation of water-analyses. Transactions, American Geophysical Union **25**, (1944), 914-923

Ramanathan, A. and Chandrasekharam, D.: Geochemistry of Rajapur and Puttur thermal springs, west coast of India, *Journal of geological society of India*, **49**, (1997), 559-565.

Shannon, W. M. & Wood, S.A.: The Analysis of Picogram Quantities of Rare Earth Elements in Natural Waters. In: Johannesson, K. H (ed.): Rare Earth Elements in Groundwater Flow Systems, Springer, (2005), 1-38.

Singh,H. K., Yadvendra K., Chandrasekharam, D., Trupti G. and Singh, B.,: High-heat-producing granites of East Dharwar Craton around Gugi, Karnataka, and their possible influence on the evolution of Rajapur thermal springs, Deccan Volcanic Province, India, *Geothermal Energy,* **2**:2, (2014)

Subbarao K.V, Chandrasekharam ,D., Navneethakrishnan P and Hooper P.R., Stratigraphy and structure of parts of the Central Deccan Basalt Province: eruptive models. In: Subbarao KV (ed) Volcanism. Wiley, New Delhi, (1994), 321–332.

Stefánsson, A. and Arnórsson,S.: The Geochemistry of As, Mo, Sb, and W in Natural Geothermal Waters, Iceland, *Proceedings*, World Geothermal Congress, (2005)

Taran, Y., Rouwet, D., Inguaggiato, S., Aiuppa, A.: Major and trace element geochemistry of neutral and acidic thermal springs at El Chichón volcano, Mexico: implications for monitoring of the volcanic activity. *Journal of Volcanology and Geothermal Research*, **178**, (2008), 224–236.

Van Middlesworth, P. E. and Wood, S. A.: The aqueous geochemistry of the rare earth elements and yttrium. Part 7. REE, Th and U contents in thermal springs associated with the Idaho Batholith, *Applied Geochemistry*, **13**, (1998), 861-884.

Wood, S. A.: Rare earth element systematics of acidic geothermal waters from the Taupo Volcanic Zone, New Zealand, *Journal of Geochemical Exploration,* **89,** (2006), 424–427.

Table 1. Major ions in a few selected samples (All values in mg/Kg unless specified)

S. No	Water type	Location	Latitude	Longitude	Temp (°C)	pH	Cond (µS/cm)	Na	K	Ca	Mg	Cl	HCO_3	SO_4	F^-	Br^-	SiO_2
5	TW	Sativali	19° 37' 51.6"	72° 54' 32"	57	8.78	2941	471	7.99	199	0.00	970	15	129	1.84	2.56	61.0
8	TW	Akloli-	19° 29' 44.02"	73° 2' 6.3"	48	8.53	3960	502	8.6	420	0.00	1410	10	160	2.50	3.52	60.3
11	RW	Amba, Pali	18° 32' 40.9"	73° 12' 57"	30	7.83	171.5	8.10	0.75	19.2	7.59	12.4	60	3.08	0.15	0.11	23.5
12	TW	Dasgaon	18° 5' 5.10"	73° 23' 6.7"	43	8.4	1870	260	3.65	177	0.00	486.5	15	275	3.40	2.48	48.4
13	GW	Sov	18° 04' 46.0"	73° 24' 27"	30	7.04	212.6	8.06	0.18	23.6	7.71	9.2	85	2.79	0.18	0.09	58.4
16	TW	Unhavre-Farare (V)	17° 36' 11.3"	73° 19' 10"	71	8.14	3590	587	17.9	224	0.00	1325	15	137	1.29	4.59	66.7
17	TW	Aravali	17° 18' 58.5"	73° 31' 19"	44	8.64	875	192	4.59	11.6	0.00	226	30	92.3	3.37	0.57	82.9
18	GW	Aravali	17° 18' 39.1"	73° 31' 32"	30	7.28	415	28.3	2.69	62.5	10.09	26.1	170	4.66	0.20	0.036	19.7
19	TW	Tural	17° 14' 57.2"	73° 33' 16"	63	7.8	1446	257	7.94	65.5	0.35	447	40	110	2.31	0.00	94.2
23	RW	Kajli River	16° 56' 2.50"	73° 29' 50"	30	7.25	160.4	11.8	0.46	11.1	4.49	17.5	40	9.79	0.20	0.00	26.2
24	TW	Rajapur-Unhale	16° 38' 44.2"	73° 31' 52"	42	7.7	526	91.4	13.1	25.3	7.91	14.6	255	7.19	0.91	0.00	26.7

TW – Thermal Springs; GW- Groundwater, RW- River/Surface water

Table 2. Trace Element concentration in the water samples (in µg/L)

Sample. No.	Li	B	Rb	Cs	Ba	Sr
5-A	106	86.7	93.2	5.99	5.87	1178
5-B	107	70.3	96.6	6.23	5.96	1175
8-A	25.3	46.6	28.1	1.48	17.9	3715
8-B	26.7	49.3	29.9	1.60	18.7	3738
11-A	0.02	2.45	0.89	0.01	5.63	75
11-B	0.02	5.95	1.09	0.01	7.43	65
12-A	18.9	130	13.4	0.75	38.8	1488
12-B	17.7	120	13.0	0.72	37.2	1536
13-A	0.18	3.87	0.26	0.05	0.84	51
13-B	0.16	2.44	0.23	0.03	0.66	44
16-A	196	97.1	221	27.5	63.0	5548
16-B	193	93.4	218	27.2	61.2	5472
17-A	34.6	113	26.4	4.48	3.04	16
17-B	34.8	113	27.3	4.70	2.95	18
18-A	0.40	11.1	0.97	0.04	1.24	80
18-B	0.40	10.0	0.89	0.02	1.90	86
19-A	108	130	103	20.2	12.1	629
19-B	104	124	102	19.9	11.7	618
23-A	4.04	20.3	1.46	0.40	2.82	53
23-B	3.97	16.7	1.73	0.56	3.08	45
24-A	177	374	24.7	1.69	2077	527
24-B	173	358	24.2	1.65	1989	546

< - below detection limit or < 0.01 ppb; A : Filtered acidified sample; B: Unfiltered acidified sample