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ORIGINAL ARTICLE

Geochemistry and Utilization of Water from Thermal Springs of Tawang and West Kameng Districts, Arunachal Pradesh

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ABSTRACT

The hydrogeochemical studies provide insights about reservoir conditions of geothermal springs along with utilization of thermal waters for domestic, livestock and irrigation purposes. Most of the hot springs of Tawang and West Kameng districts of Arunachal Pradesh emanated through garnet bearing high grade gneiss-migmatite-schist-quartzite sequence of the Se La Group, except for Dirang hot springs which emanate from river terrace deposits lying on the footwall of deformed quartzite-phyllite. The thermal waters are of mixed Na-Ca-HCO_3-SO_4-Cl type, meteoric in origin and at the same time immature in nature, moving sluggishly towards mineral-fluid equilibration zone with slow rock-water interactions. Chemical geothermometry showed wide variation in estimation of sub-surface reservoir temperature and quartz geothermometry model fits prominently to provide the most reliable reservoir temperature varying within 90±40°C. The studies recorded highest reservoir temperature of Thingbu hot spring with 133°C with very high fluoride concentration in all the hot springs except Bishum and Phudung as per BIS (2012) IS: 10500 specifications. High fluoride and sulfate concentration in thermal spring waters make it unsuitable for drinking purpose. The applicability of thermal waters for irrigation is predicted through sodium adsorption ratio (SAR) calculations which showed that waters of Dirang-2, Sorbe and Kitpi-1&2 are not suitable for irrigation purpose due to high salinity and SAR values.

INTRODUCTION

Geothermal water chemistry provides important evidences about the geology of host rocks in association with indications of recharge, discharge and storage of geothermal waters. The alteration in geochemical parameters, either by geological formations or by anthropogenic activities, can directly influence geothermal water quality. This quality of water justifies its applications in health, environmental issues, and irrigation purposes in connection with extraction of thermal waters from reservoirs. Emission of greenhouse gases, like carbon dioxide, methane, etc., from geothermal sprouts, aggravates global warming (Appelo, 2004; Singh, 2016). The waters from geothermal springs, sometime, contain fluoride, sulfate, arsenic, cadmium, and other heavy metals, etc. beyond the maximum permissible limits as prescribed by safety guidelines of WHO or BIS for drinking water. The consequences become catastrophic when these harmful geothermal fluids containing these harmful contents gets mixed with ground water causing contamination and long-term damage to occupational health and environment. The geothermal waters with enhanced salinity (high sodium content) causes agglomeration of soils and hence makes it flabby for agriculture and irrigation purposes. The hydrogeological studies of geothermal springs expose the origin and type of water by analysing the isotopic ratio and major cations and anions present in water (Giggenbach, 1986). Depending on extent of rock-water interaction at different temperature and pressure, geochemical equilibrium is disturbed and thus variation of aquatic geochemistry occurs. High temperature shifts the geochemical equilibria in that direction where water gets concentrated due to leaching of many trace elements from surfaces of minerals/rocks along with precipitation thereby altering its geochemistry.

The geological mapping of Arunachal Himalaya was carried out early by Bakliwal and Das (1971) along Bhalukpong-Sela pass who sub-divided the rocks into Sela Group, Bomdila Group, Tenga Formation, Bichom Group, Gondwanas and Siwaliks. The Bomdila granite is coarse grained and porphyritic in nature, comprising of microcline, plagioclase, quartz, biotite, muscovite, tourmaline and epidote (Bhattacharjee and Nandy, 2007; Bhattacharjee and Nandy, 2017). The geochemical parameters of two hot springs, one in Dirang and another one in Kitpi, were earlier reported by Bora et al., (2006). The geothermal springs are well-known for balneotherapy which have traditional medicinal aspect of curing various skin diseases and provide relief from stress. The study of physicochemical properties of hot springs of Braksar, Thingbu, Tsachu and Dirang were reported initially by Taye and Chutia (2016), however, detailed geochemical analysis of geothermal fluids of Arunachal Pradesh were missing in the literature. Taye and Chutia (2016) predicted that geothermal waters are of meteoric in origin with minor rock-water interaction.

Keeping all these in mind, and in the quest of detailed understanding of geochemistry of hot springs of Arunachal, eleven hot springs and five cold springs were monitored and water samples collected from West Kameng and Tawang districts of Arunachal Pradesh and evaluated their utilization in agriculture/irrigation and drinking purposes as per specifications of Bureau of Indian Standards (BIS 2012 IS: 10500). The geo-hydrological and geochemical studies of hot springs have been carried out to find the major ionic and elemental constituents present in water and to elucidate the nature and origin of thermal waters. Chemical geothermometry is used to predict the sub-surface reservoir temperatures of hot springs of the study areas. Geochemistry of gases emanating from thermal springs could provide an idea pertaining to the signature of presence of radioactivity or fossil fuels underneath.

GEOLOGICAL SETTING OF THE AREA

Eleven hot springs are located in the north and south vicinity of the Main Central Thrust (MCT) in parts of the high reaches of West Kameng and Tawang districts of Arunachal Pradesh, India. Almost all hot springs emanate through garnet bearing high grade gneiss-migmatite-schist-quartzite sequence of the Se La Group, except Dirang hot springs which emanates through river terrace deposits lying on the footwall of deformed quartzite-phyllite (now mylonitised) sequence along the MCT zone near north Dirang town. The medium to high metamorphic grade rocks of the Se La Group has derived its name from the Se La pass (Bakliwal and Das, 1971). Se La Group of rocks predominantly comprise of migmatite, higher grade schist and gneisses with profuse intrusions of tourmaline granite. The Dirang Formation comprises of low grade metamorphites like phyllite, mica schist, sericite-micaceous quartzite, calc-silicate and actinolite-tremolite marble (Fig. 1).

Out of these, Dirang-1, Dirang-2, Monkemp, Kitpi-1 & 2, Sorbe, Tsachu-1 and 2, Thingbu, Bishum and Phudung hot springs are issuing hot waters (17°C-72°C, where average ambient atmospheric temperature ranges between 14°C-15°C), just above stream water levels along the tributary streams like Tsachu, Mago Chu, Jang Chu streams of Tawang Chu river and Dirang Chu/Khouma/Khyamin Ro, Timkong

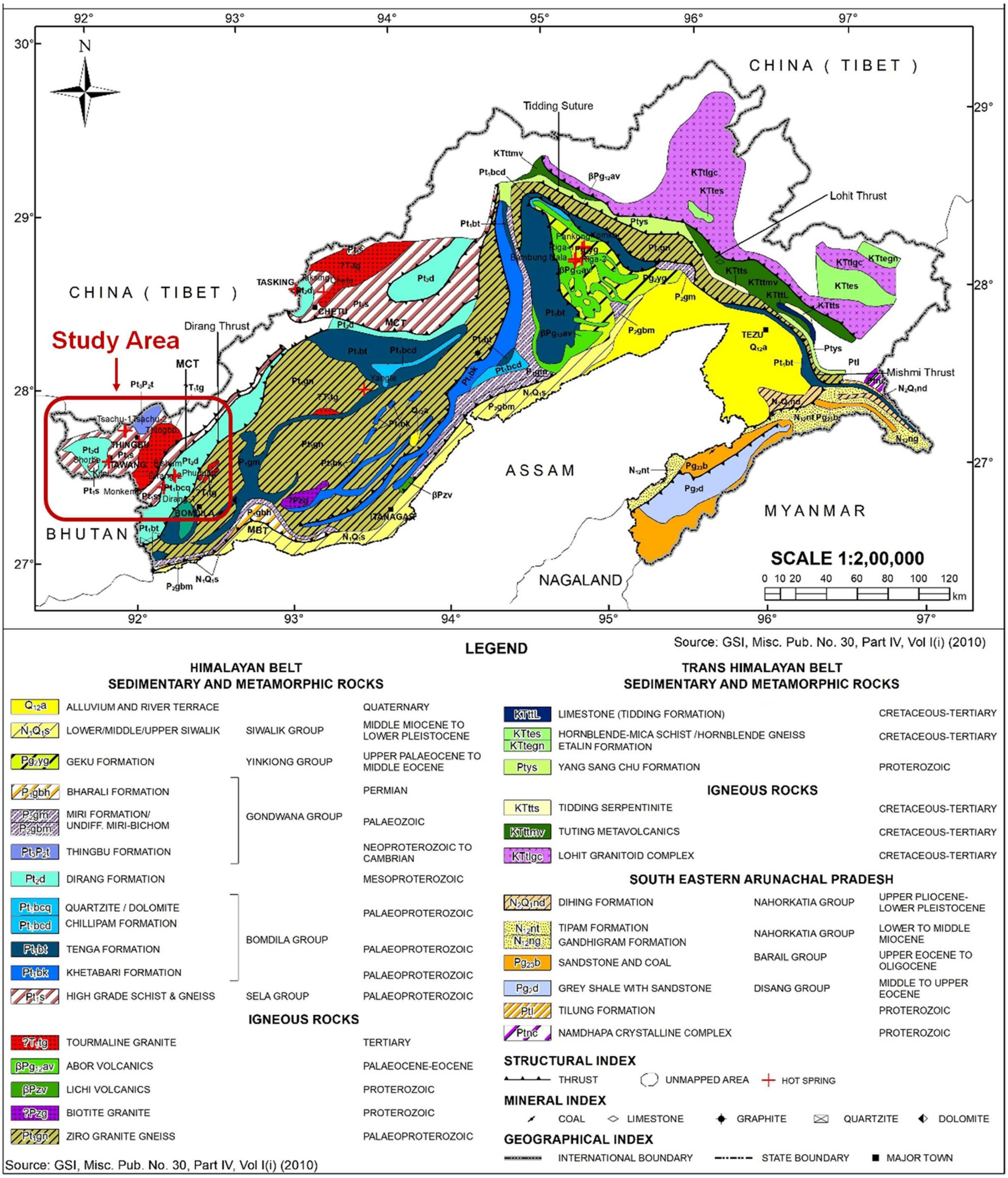

Fig.1. Location Map of the hot springs areas in Tawang and West Kameng districts, Arunachal Pradesh. (Source: GSI, Misc. Pub. No. 30, Part IV, Vol I(i) 2010).

Rong/Chutsang Rong of Kameng river valleys. Besides regional MCT zone, many PGRS interpreted cross faults and seismic incidences are also reported around these river valleys of the northwestern Arunachal Himalaya. These river valleys are easily approachable from Itanagar. Tawang town is situated at height of 2669 m above mean sea level and connected with Itanagar town by NH 13 road and can be approached via Tezpur-Kalaktang/Bhalukpong-Bomdila-Dirang-Se La Pass and Jang towns. The Thingbu geothermal field (at about 60 km from Tawang via Jang and New Milling) located along a tributary of Mago-Chu River emanates through migmatised gneiss of the Se La Group and shows highest surface water temperature (72°C) among all hot springs of Tawang Chu river valley. Dirang and Monkemp hot springs are located at about 3 km and 20 km north of Dirang town respectively along Dirang Chu at Dirang-Tawang road section. Phudung hot spring is located at about 22 km east of Dirang town along Dirang-Phudung road section lying at the bank of Sangti and Gouri rivers, the tributaries of Dirang river while Bishum hot spring is located at about 3 km from Phudung village in the forest area. The thermal springs located at Kitpi and Sorbe villages are about 34 km from Tawang on Jang-Tawang road. Two hot springs are located along the banks of Tsachu river at high reaches of Arunachal Himalaya, at a distance of about 102 km from Tawang via Lhou, Jangdha, Broksar and LGG.

METHODOLOGY

The surface temperatures of sixteen thermal springs, collected from several hot spring locations of West Kameng and Tawang districts of Arunachal Pradesh, are given in tabular representation along with their chemical composition (Table 1 and Fig. 1). High-density polyethylene (HDPE) bottles were used for sample collection following Standard protocols of American Public Health Association (APHA 2006) to ensure data excellence and constancy. In order to avoid exposure of the samples to air, water was filled up to the brim and labelling of samples were done systematically. The complete analyses of water and gas samples were done in Chemical Laboratory of Geological Survey of India (GSI), Northern Region, Lucknow. The physical parameters pH, electrical conductivity (EC) and total dissolved solids (TDS) are measured by using Systronics µ pH system 361, Systronics Conductivity Meter with cell constant 1.0 ± 10%, Systronics water analyser 371, respectively, and the major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{2-}, SO_4^{2-}, F^{-}, Cl^{-}, SiO_2, PO_4^{3-}, Li^{+}, B) are analysed using standard operating procedures. The sodium and potassium ions are quantified using Systronics Flame Photometer instrument 128; calcium, magnesium, bicarbonate, carbonate and chloride are estimated by standard titrimetric methods; Sulfates are estimated by turbidimetry; fluoride is measured by thermo scientific ion selective electrode (ISE) instrument; SiO_2, PO_4^{3-}, and B are measured by Thermo (type UV330) UV spectrophotometer instrument. The analysis of gas samples emanated from various hot springs are performed in VARIAN 450 GC gas chromatograph instrument.

RESULTS

The analytical results of all thermal spring waters collected from Tawang and West Kameng districts are evaluated in Table 1.

pH of Thermal Waters

The pH value of water provides valuable information about its nature, whether acidic (pH<7) or alkaline (pH>7), which plays vast information about the chemical equilibrium of the thermodynamic system. Depending on this geochemical equilibrium, rock-water interaction occurs in the geothermal springs which manifests acidic or alkaline nature of water. As per BIS (2012) IS: 10500 specifications, the maximum desirable limit of pH suitable for drinking purpose is 6.5 to 8.5. The pH value of most of the hot spring water samples in the study area varies from 6.7 to 9.3 while for cold spring water samples, the value ranges from 7.3 to 8.1. The values clearly indicate that the water from hot and cold springs are feebly alkaline in nature except the hot spring water sample of Monkemp where water is highly alkaline in nature with pH of 9.35. The high pH value of hot spring water sample in Monkemp is attributed to alkalinity due to both bicarbonate and carbonate while for other hot springs, the alkalinity is primarily contributed by bicarbonate.

Electrical Conductivity (EC) and Total Dissolved Solids (TDS) of Thermal Waters

EC can be classically defined as the degree of movement of ions in aqueous solution under the influence of electrical gradient. The hot spring water samples have EC values ranging from 204 µS/cm to 3600 µS/cm and cold spring water samples have EC values ranging from 38 µS/cm to 144 µS/cm. The enhanced conductivity of water is the signature of greater enrichment of salts in water of geothermal springs. It also implicitly indicates an approximate index of the total dissolved substances (TDS) in water. As per Hem et al. (1985), depending on enrichment of water with the concentration of salts, EC is classified in three different categories: EC-Type 1 with conductance value <1500 µS/cm, EC-Type 2 with conductance value 1500-3000 µS/cm and EC-Type 3 with conductance value >3000 µS/cm (Hem, 1985). In our geochemical study it has been found that 50% of geothermal springs are of EC-Type 1, 37% of geothermal springs are of EC-Type 2 and 13% of geothermal springs are of EC-Type 3. As per BIS (2012) specifications, the maximum desirable limit of TDS in drinking water is 500 ppm and maximum permissible limit is 2000 ppm (ppm: parts per million). In our geochemical study it has been found that 44% of geothermal springs have TDS value <500 ppm, 43% of geothermal springs have TDS value between 500-2000 ppm (within BIS-2012 specifications) and 13% of geothermal springs have TDS value >2000 ppm. The observed value of TDS of hot and cold springs ranges from 21-2700 ppm. For all the hot springs, except Dirang-2 (HS/02/19), TDS values are within the prescribed limits of BIS (2012) specifications. Higher TDS of HS/02/19 is also depicted with its maximum EC value which makes it unsuitable for drinking/irrigation purpose. The higher concentration of TDS in geothermal hot springs is due to leaching of salts from rocks/soil resulting in enhanced salinity of water or percolation of domestic sewage due to anthropogenic activities.

Hydro-geochemical Studies of Geothermal Waters

Amongst various types of alkali and alkaline earth metal ions, sodium, potassium, calcium and magnesium are the major cations present in water while sulfate and chloride are the major anions. Alkalinity and pH of water are determined by chemical equilibrium between carbonate and bicarbonate which is dependent on temperature and pressure of the thermodynamic system. As per Fig. 2, for hot spring samples from (HS/01-03/19), amongst all the cations, concentrations of Na^{+} and K^{+} ions are comparatively higher than Ca^{2+} and Mg^{2+} ions in the geothermal water samples. However, Mg^{2+} concentration in water is not negligible and kinetic equilibration exists between the ions. The higher concentration of these alkali metal ions reveals that these ions leach from adjacent rocks due to greater extent of interaction with water compared to alkaline earth metal ions. The hot spring water sample of Kitpi-1 (HS/04/19) and Sorbe (HS/05/19) with surface temperature 40° and 35°C respectively, have predominantly Na^{+} and K^{+} ions concentrations; Thingbu (HS/08/19) hot spring with temperature 72°C (which is the highest recorded temperature among the thermal springs of Arunachal Pradesh) has all the cations like sodium, potassium, calcium, magnesium and anions like chloride and sulfate. In all the geothermal springs, except Bishum, sodium ion is more predominant compared to calcium which is further predominant than potassium. For Bishum hot spring, calcium is more predominant

Table 1. Chemical composition of thermal discharges of West Kameng (WK) and Tawang (TG) districts, Arunachal Pradesh.

Field Sample ID	Locality	Temp (°)	pH	Sp. Cond. at 25°(µS/cm)	TDS (ppm)	HCO_3^- (ppm)	CO_3^{2-} (ppm)	Cl^- (ppm)	NO_3^- (ppm)	SO_4^{2-} (ppm)	Ca^{2+} (ppm)	Mg^{2+} (ppm)	Na^+ (ppm)	K^+ (ppm)	Li^+ (ppm)	B (ppm)	SiO_2 (ppm)	F^- (ppm)	PO_4^{3-} (ppb)
HS/01/19	Dirang-1 (WK)	35	6.74	1530	918	358	NIL	152	2	423	95	10	224	40	0.4	5	27	1.4	375
HS/02/19	Dirang-2 (WK)	30	6.93	3600	2700	719	NIL	700	9	309	63	18	615	71	1	19	26	7.5	430
HS/03/19	Monkemp (WK)	25	9.35	204	150	61	6	6	<1	12	6	3	38	<1	<0.2	1	25	17.5	390
HS/04/19	Kitpi-1 (TG)	40	7.55	2130	1600	299	NIL	304	6	457	55	2	398	20	<0.2	12	30	12.5	487
HS/05/19	Sorbe (TG)	35	7.62	3100	2015	732	NIL	504	51	307	40	3	579	47	<0.2	26	40	12.5	715
HS/06/19	Tsachu -1 (TG)	56	7.21	2090	1260	311	NIL	88	1	906	203	22	236	17	<0.2	7	73	1.8	2225
HS/07/19	Tsachu -2 (TG)	57	7.2	2050	1230	306	NIL	95	<1	909	226	14	230	18	<0.2	8	70	2	630
HS/08/19	Thingbu (TG)	72	8.14	1060	742	139	NIL	27	<1	330	30	14	144	1	<0.2	5	92	2	597
HS/11/19	Kitpi-2 (TG)	41	8.19	2760	1794	444	NIL	268	5	512	68	7	405	16	0.4	14	25	7	132
HS/12/19	Bishum (WK)	23	7.82	2090	1254	58	NIL	30	<1	1269	478	36	7	2	<0.2	<1	24	1	<50
HS/13/19	Phudung (WK)	17	8.05	269	167	139	NIL	6	1	29	30	11	5	1	<0.2	<1	10	<0.2	<50
CS/01/19	Dirang-1 (WK)	17	7.31	38	21	20	NIL	5	<1	<5	2	1	6	1	<0.2	<1	19	0.4	347
CS/02/19	Kitpi (TG)	18	7.61	136	81	90	NIL	6	<1	10	17	5	10	<1	<0.2	<1	34	<0.2	395
CS/03/19	Tsachu (TG)	18	8.1	144	85	90	NIL	5	<1	5	29	2	2	2	<0.2	<1	13	<0.2	242
CS/04/19	Thingbu (TG)	16	7.69	68	41	39	NIL	5	<1	9	11	2	4	2	<0.2	<1	11	<0.2	260
CS/08/19	Phudung (WK)	7	7.72	76	46	17	NIL	8	1	12	14	1	2	<1	<0.2	<1	4	<0.2	<50

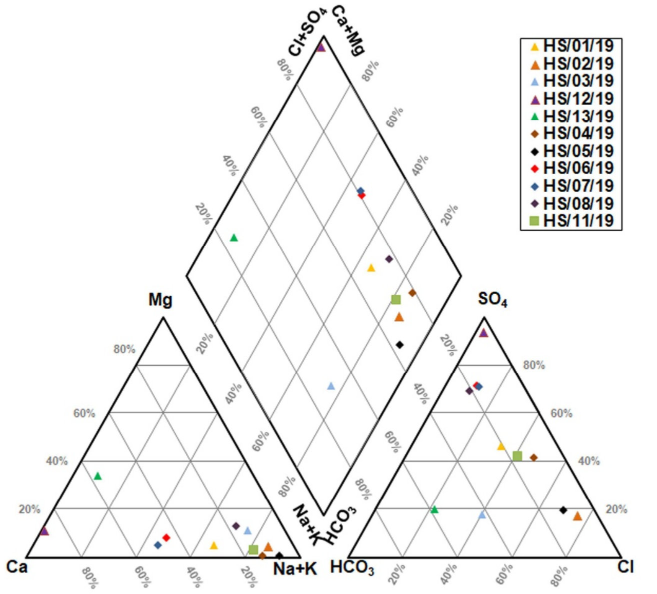

Fig.2. Piper diagram of hot spring water samples of West Kameng and Tawang districts, Arunachal Pradesh (Piper et al., 1944).

than sodium along-with greater concentration of sulfate too which clearly indicates that the rocks type surrounding Bishum hot spring have calcium and sulfate prevalence in association with other mineral forming elements.

The *Na-K-Mg* ternary diagram has an important application in estimating sub-surface reservoir temperature by Na-K-Mg geothermometer. The Na-K-Mg diagram is used to classify waters into fully equilibrated, partially equilibrated and immature waters. The diagram recognizes type of water which has attained equilibrium with the host lithology and demarcates fully equilibrated water over partially and non-equilibrated water (obtained either by dilution or mixing or near-surface reactions) in estimating reservoir temperature. As per Fig. 3a and 3b, in Na-K-Mg ternary diagram of hot spring and cold spring water samples, respectively, most of the points are shifted on the magnesium vertex. The type of water is immature or dilute in nature suggesting minor water-rock interaction where content of alkaline earth metal is possibly affected by the absorption of dissolved rock. The geothermal waters of Kitpi-1 (HS/04/19) and Sorbe (HS/05/19) lie along the partial equilibration zone of mature and immature water which suggests that dynamic equilibration in these water systems depending upon reservoir pressure and temperature. The water of Kitpi-2 (HS/11/19) lies just along the boundary of immature water and partially equilibrated water which suggests that immature water is actively dissolving rock-forming minerals in it and moving slowly towards partially equilibrated zone. The waters of hot springs of Dirang area also lies closer to partially equilibrated zone suggesting onset of rock-water interactions.

The ternary plot is consisted of *Cl-SO_4-HCO_3* indicates the type of natural water or geothermal fluids existing in the system: (a) immature or peripheral water, (b) mature water, (c) steam-heated water, and (d) volcanic water (Giggenbach, 1988). The thermal fluids are assumed to achieve geochemical equilibrium due to prolonged water-host rock interactions at an elevated temperature and pressure in the reservoir. These thermal fluids, however, carry traces of deep thermal processes as they ascent as thermal outlets/springs, varying in chemical constituents due to various en route physicochemical changes. These fast ascent geothermal fluids are hence very important to ascertain reservoir behaviour (Giggenbach, 1988; Singh, 2020; Dávalos-Elizondo, 2021). From Fig. 3c and 3d it can be illustrated that, the geothermal waters of Dirang-2, Monkemp, and Phudung of

West Kameng district and Sorbe of Tawang district are mostly of peripheral type with bicarbonate predominance. The hot spring water samples of Dirang-1, Kitpi-1 and Kitpi-2 lie nearly along the common boundary of steam-heated water and peripheral water which indicate that waters are of mixed nature. The equal concentration of chloride and bicarbonate (~700 ppm) with less quantity of sulfate in hot spring water sample of Dirang-2, justifies its water with Cl-HCO_3 type. The geothermal waters of Tsachu and Thingbu of Tawang district are mostly of steam heated type of water with predominance of sulfate content. The hot spring water of Kitpi-1 of Tawang district is of mixed character, lying around boundary of peripheral water, volcanic water and mature water with higher sulfate content while for Kitpi-2, the hot spring water is also peripheral in nature with predominance of bicarbonate and sulfate ion compare to chloride ion. The hot spring water sample of Bishum has very high sulfate content with predominance of calcium ion which indicates water-type is Ca-Mg-SO_4. All the cold spring water samples show bicarbonate predominance. The waters of cold spring are mainly peripheral in nature with poor rock-water interactions. The cold spring water sample of Phudung has slight higher concentration of sulfate over bicarbonate and water, though peripheral in nature, is dissolving rock-forming minerals in it through various chemical forces and gradually moving towards mature water zone [Table S1 of ESI].

Chemical Geothermometry

The geothermometers are used to assess sub-surface reservoir temperature of the thermal systems by monitoring temperature-dependent water-rock reactions. Quartz geothermometry (proportional to logarithmic concentration of SiO_2) is more reliable than other geothermometers for estimating sub-surface reservoir temperature of geothermal systems with lower enthalpy like in Arunachal (Apollaro et al., 2016). The reservoir temperature values as evaluated from chalcedony conductive geothermometer and K/Mg Giggenbach (1986) geothermometer do not furnish logical and acceptable values [Table S3 of ESI]. The quartz conductive geothermometer predicts that the reservoir temperature of thermal springs varies from 52-133°C. As most of the thermal waters are immature in nature, except Kitpi-1 and Sorbe, cation geothermometry can hardly estimate reservoir temperature of hot springs. However, cation geothermometry can be used with reduced accuracy to predict reservoir temperature of thermal springs in Kitpi and Sorbe. The thermal springs of Arunachal being low enthalpic with sub-surface temperature much less than 90°C, the concentration of silica is primarily controlled by quartz over chalcedony (a polymorph of quartz). Hence, chalcedony geothermometry cannot be used to furnish reservoir temperatures of hot springs with confidence Fournier (1979b).

Geochemistry of Gases Emanated from Hot Springs

The concentration of gases emanating from hot springs is an important factor to access potential geothermal resources in the area. Although the predominant gases associated with geothermal steam from both hot water and steam producing areas are CO_2 and H_2S,

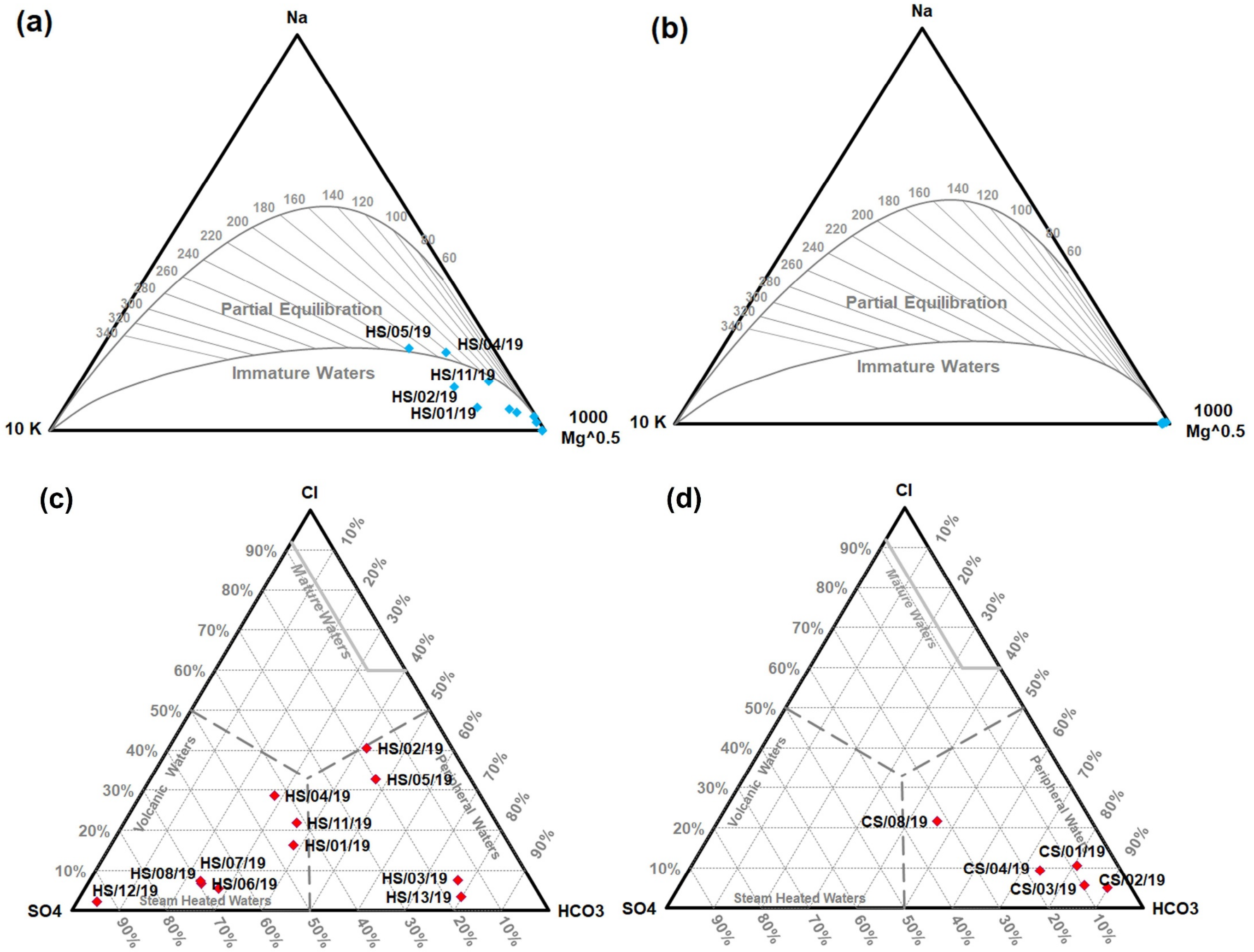

Fig. 3. (a) and **(b)** *Na-K-Mg* triangular diagram, and **(c)** and **(d)** *Cl-SO_4-HCO_3* ternary diagram of hot and cold spring water samples respectively, of West Kameng and Tawang Districts (Giggenbach et al., 1986).

however, in the circulating meteoric water, gas is mainly nitrogen. The oxygen is presumably lost within the rocks through oxidation process. The primary gases present in the hot springs are CO_2, H_2S, CH_4, H_2 and N_2 (Ármannsson et al., 2005). The analysis of gas samples indicate that the gas sample collected from Kitpi hot spring in Tawang district (temperature of thermal spring ~40°C) has minor concentration of Helium gas (279.64 ppm). Helium gas is a kind of indicator of radioactive minerals buried underneath as its charge is similar to charge of an alfa particle emitted from radioactive elements. Thus signature of radiogenic helium may be a fingerprint of radioactive source present in very low concentrations in thermal springs probably contributed from surrounding gneisses and pegmatites of Sela Group. Hydrogen gas is not observed in any gas samples. Methane is known as "Marsh Gas" as it is found basically in wetlands due to decomposition of organic or biological materials under the influence of microorganisms by the phenomenon called methanogenesis. The presence of very low amount of methane in all the gas samples is a signature of decomposition of organic materials inside the geothermal springs. Carbon dioxide is not detected in any of the samples. It is present in the form of soluble bicarbonate ion whose dissociation to carbonate ion is governed by the pH of water. The gas mixtures show good concentration of nitrogen (~90%) which gas plays the role of carrier gas for other emanating gases [Table S2 of ESI]. Though feeble sulfurous odour is detected from some thermal springs, but, detectable hydrogen sulfide gas is not observed in any gas samples. Though sulfate is observed in most of the hot spring water samples, hydrogen sulfide gas is not detected owing to greater solubility of H_2S in water. The solubility of gases follows the following trend: $N_2<O_2<H_2<CH_4<CO_2<H_2S<NH_3$. Hence, H_2S was not physically quantified by instrument unless it is present in significant amount in thermal springs.

DISCUSSIONS

Hydrochemistry and Origin of Geothermal Waters

The order of cationic abundance in geothermal waters are $Na^+>Ca^{2+}>K^+>Mg^{2+}$ and for anionic abundance is $HCO_3^->SO_4^{2-}>Cl^->F^->CO_3^{2-}$. The main expression from diamond plot of Piper diagram is most of the type of thermal waters in study areas are (sodium chloride) Na–Cl type, except the waters of Bishum and Phudung hot springs which are (calcium chloride sulfate) Ca-Cl-SO_4 type and (Magnesium bicarbonate) Mg–HCO_3 type, respectively. Among all the thermal waters, NaCl type of water represents 82% of the hot spring waters, while both $CaClSO_4$ type and Mg-HCO_3 type represents total 18% of the hot spring waters of study areas. The greater predominance of alkalis over alkaline earth metals furnishes plagioclase feldspar having compositions $NaAlSi_3O_8$ to $CaAl_2Si_2O_8$ of the country rocks which may contribute sodium and calcium atoms where both can substitute for each other in the mineral's crystal lattice structure. It is also further confirmed by the observation of huge white deposits calcium sulfate (or impure gypsum) surrounding Bishum hot spring. In the cold springs, there is a general abundance of bicarbonate ions. It has been observed that a dynamic chemical equilibrium exists between bicarbonate and carbonate ions where bicarbonate ion dissociates in carbonate ion followed by a release of proton. This dynamic equilibrium is reliant on temperature and pressure. At high temperature, bicarbonate dissociates to carbonate and proton by absorbing heat from its neighbour and thus the process is an endothermic reaction process. Due to low temperature of cold springs, bicarbonate ion remains undissipated and it is in correlation with our observation. The predominance of calcium ion over sodium in the waters of cold springs depicts that the springs are less "soda" springs. Deposits of travertine (terrestrial sedimentary rock, $CaCO_3$) can be observed around bicarbonate predominant cold springs formed by prolonged temperature dependent decomposition and precipitation of bicarbonate.

Generally, the greater enrichment of salts implies higher TDS and EC of water samples. The intrusion of salts into the geothermal springs due to weathering and diagenesis processes result in higher values of TDS which can together contribute in altering pH of water (Appelo, 2004). The anthropogenic activities like disposal of sewages and use of chemical fertilizers in nearby agricultural areas of Dirang and Tawang Chu river valleys could be a plausible reason behind meagre alkalinity of water. The enhanced effect of saline level intrusion due to prolonged rock-water interaction in the sub-surface reservoir along with some anthropogenic activities, could be some of the contributing factors behind higher EC values of waters of hot springs.

From triangular plot of major cations, the area of partial equilibrium indicates that there could be some mineral like plagioclase feldspar, amphiboles, etc. that have been dissolved, though have not attained equilibrium or geothermal water may have been diluted with ground water and is yet to achieve equilibrium. The analyses of mineral contents in hot spring deposits by powder X-ray diffractometer also confirm the presence of minor and trace quantities of orthoclase, anorthite, amphibole, and clinochlore, respectively. The microscopic studies of rock samples collected from Kitpi and Sorbe hot springs (HS/04/19, HS/05/19, and HS/11/19) showed the presence of coarse grained plagioclase feldspar with lamellar twinning in association with biotite mica flakes and quartz (Fig. S1 of ESI) (Kaura and Basu Roy, 1982; Kesari, 2010). For those points which plots are close to Mg corner, indicate relatively very high proportion of cold groundwater mixed in the hot water system. For cold spring water samples, all points are shifted towards magnesium vertex and the water type is immature and no partial equilibrium exists between mature and immature waters. The shifting of all points of geothermal springs towards magnesium vertex along the zone of immature water clearly indicates that although the rock-water interaction is minute, leaching of magnesium in water is pertinent from minerals in rocks than sodium or potassium. The higher charge density of magnesium allow it to interact electrostatically with electronegative oxygen atom of water molecule, rendering its enhanced leaching from surrounding Mg-rich mafic rocks. The triangular plot of major anions reveals that thermal waters of study areas are mainly peripheral and steam-heated for hot springs and only peripheral for cold springs. These peripheral-bicarbonate predominant water occurs at relatively shallow depths at some distance from the geothermal field and are meteoric in nature. The unprompted mixing of cold groundwater or meteoric water with hot water could be a probable reason behind peripheral nature of most of the thermal waters.

It is suggested that quartz conductive geothermometer provides best results for estimating reservoir temperatures of low-enthalpic thermal springs whose waters are immature in nature with high cold water admixture as revealed from cation triangular diagram. The equivalent concentrations of silica in two hot springs of Dirang suggest nearly equal reservoir temperature indicating that hot springs are recharged from same source with multiple outlets. Very high silica concentrations have been observed in hot springs of Tsachu and Thingbu which suggest their high sub-surface temperature (>115°). Lower and nearly comparable silica content of hot springs in Kitpi also suggests similar reservoir temperature of two springs, confirming identical rock-water interactions in two springs. The quartz geothermometry predicts reservoir temperature of hot springs of Arunachal to vary from 90±40°C, suggesting low enthalpic hot springs. The reservoir temperatures obtained from K/Mg Giggenbach (1986) geothermometer for thermal springs of Kitpi-1 and Sorbe are 105°C and 125°C, respectively, while quartz conductive geothermometry predicts comparatively lower reservoir temperature value of 84°C and 94°C, respectively. The relatively low temperature obtained from quartz geothermometry compared to K/Mg Giggenbach (1986) geothermometer probably due to the fact that quartz geothermometry is dependent on absolute concentration of silica that is affected significantly through cold water mixing or dilution over cation geothermometry which depends on relative ionic ratio of K and Mg. The significant incongruity between quartz and K/Mg Giggenbach (1986) geothermometers points out that all the thermal waters are mixed and immature in nature with significant ground water or meteoric water intrusions that have not achieved chemical equilibrium after mixing (Fournier, 1979b).

Utilization of Geothermal Waters

The hot water quality has been analysed in the light of approved Bureau of Indian Standards (BIS-2012) limits for each parameter. According to BIS standards the desirable limits of Ca^{2+} and Mg^{2+} in drinking water are 75 ppm and 30 ppm respectively while maximum permissible limits are 200 ppm and 100 ppm respectively. In study areas, two samples collected from Tsachu have high calcium content with values 203 ppm and 226 ppm which is beyond the maximum permissible limit of calcium as per BIS specification. In case of magnesium concentration, all the hot spring samples have values within maximum desirable limit. Calcium is maximum for Bishum hot spring (478 ppm); calcium is the source of formation of calculi in human body and hence water will be eligible for drinking after proper purification procedure. The deficiency of fluoride ion can cause dental fluorosis and osteoporosis (increase in fragility of bones and decreasing bone density) while excess in fluoride ion concentration causes skeletal fluorosis which can be genetically transmitted too in some extreme cases. As per BIS-2012 norms, in hot water, maximum desirable limit of fluoride ion is 1.0 ppm while highest permissible limit is 1.5 ppm. Fluoride values are above permissible limit in approximately all the hot spring water samples of West Kameng and Tawang districts. The highest concentration of fluoride is observed for Monkemp with 17.5 ppm followed by Kitpi-1 and Sorbe with 12.5 ppm and 12.5 ppm, respectively. For Tsachu, Thingbu and Dirang study areas, the fluoride concentration is a bit lower than Monkemp, Kitpi and Sorbe areas, but, the values are still higher than the highest permissible limit of fluoride as per BIS norms, thereby making all the hot spring water unfit for drinking purpose. All the water samples have chloride concentration below highest permissible limit with average concentration of 110 ppm. Sulfate is used as cleansing agent in domestic purpose. Sulfur is the common element present in hot spring samples and on areal oxidation, it produces various oxides of sulfur which though are not generally detected by gas chromatograph instrument but detection of H_2S in the instrument can be identified as a fingerprint of sulphur. Because of the high solubility of SO_2 in water, and its low *pKa*, it is unlikely that environmentally significant quantities are volatilized from geothermal systems of the low-temperature type characteristic of hot springs of Arunachal Pradesh. As per BIS specifications, maximum desirable limit of sulfate in water must be 200 ppm while highest permissible limit is 400 ppm. In study areas, except in Bishum, Kitpi-2, and Tsachu, all the thermal springs have sulfate content less than highest permissible limit. Monkemp hot spring have very low sulfate content while Tsachu, Bishum and Kitpi-2 have very high sulfate content of around 900 ppm, 1269 ppm, and 512 ppm respectively. High sulfate and fluoride content in hot spring water of Kitpi-2 make it unfit for drinking and commercial utilization purpose [Table S4 of ESI]. In category of toxic elements, the elements like arsenic, cadmium, molybdenum, and lead are considered. Here, all these heavy toxic elements are present in concentration lower than maximum desirable limits as per BIS specifications.

Sodium Adsorption Ratio (SAR)

The concentration of sodium ion is very vital to measure the applicability of geothermal waters in agriculture and irrigation purposes. Higher sodium concentration in soil (*i.e.* higher soil salinity) detoriate soil quality by replacing calcium and magnesium from it, thus forming agglomeration. Hence, soils with lower sodium adsorption ratio (SAR) values are fit for agricultural purposes. As per Todd et al. (1980), SAR can be expressed by following mathematical formula:

$$\mathrm{SAR} = \frac{\mathrm{Na}}{\sqrt{(\mathrm{Ca} + \mathrm{Mg})/2}} \qquad (1)$$

Where the concentrations of Na, Ca and Mg in equation-1 are measured in milli-equivalents per litre (meq/l). The calculated values of SAR in the study areas vary from 0.198 to 23.74 [Table S5 and Fig. S2 of ESI]. The waters with SAR value lying within 0 to 4 are best for irrigation management while SAR values greater than 10 are considered to be highly unsuitable for irrigation and water can cause soil agglomeration and enhance salinity. The waters of Dirang-2, Sorbe and Kitpi-1/2 are not suitable for irrigation purpose before proper salinity management due to their high SAR and EC values. Higher EC provides check on crop productivity, causing less water availability for plants: a condition biologically called “physiological drought” (Joshi et al., 2009). Other thermal waters are suitable pertaining to irrigation purpose and can be used directly.

CONCLUSION

The chemical analysis of thermal waters of Tawang and West Kameng Districts of Arunachal Pradesh revealed that waters are mildly acidic to feebly alkaline in nature with EC values ranging from 269 to 3600 μScm^{-1} for hot spring samples. Na is the principal dominant cation in all the thermal springs, except for Bishum and Phudung hot springs, amongst all the major cations while HCO_3^- is the dominant anion amongst all anions followed by sulfate and chloride. The thermal waters are predominantly mixed Na-Ca-HCO_3-SO_4-Cl types, as evident from Piper diagram. The thermal waters are meteoric in origin, with minor rock-water interaction, which percolate through faults and fractures on surface of country rocks and emerge as warm water either due to internal pressure or geothermal gradient. The waters are suitable for drinking purposes as per BIS norms, except Monkemp, Kitpi, Tsachu, Sorbe, Thingbu, Bishum and Dirang-2, for their high fluoride and sulfate content. The quartz geothermometry predicts that the sub-surface temperature of hot springs varies between 90±40°, depending on absolute concentrations of silica. Higher SAR values of some thermal springs indicate unsuitability of thermal waters for irrigation purpose. Recurrent water sampling on pre-and post-monsoon basis is recommended for better understanding of aquatic chemistry of geothermal waters of Arunachal.

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