Chapter

Hydrogeochemistry of the Pidong Crater Lake, Jos Plateau Volcanic Province, Nigeria: Constraints on Chemical Elements Sources

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Abstract

The occurrence and recurrence of floating 'mat' vegetation around the Pidong Crater Lake and intermittent change in the color of the lake water from natural blue to brown-yellowish color call for a better understanding of the factors controlling these biological and physico-chemical changes. As a result of these changes, a hydrogeochemical monitoring regime was employed where the lake water samples were collected and analyzed on a monthly basis over a period spanning for 3 years. The hydrogeochemical results for the lake water when plotted in the piper trilinear diagram display predominantly Mg-Ca-HCO_3 type with minor water types of Na-K-HCO_3, Na-K-Cl and Na-K-SO_4 types ($\leq 20\%$), suggesting a derivation from water-rock interaction processes (hydrolysis). The visible dominance of the alkali earth metals ($Mg^{2+} + Ca^{2+}$) over the alkali metals ($Na^+ + K^+$) is expected from a basaltic host rock aquifer due to the dissolution of its constituent ferromagnesian minerals and plagioclase respectively. The general depletion of LILE (Ba, Rb, Sr) (1–10 x Chondrite) and that of High Strength Elements (HSE) (Nb-Yb) (0.001 to <1 Chondrite values) suggest that these elements are from sources (basaltic rocks) highly depleted in these elements. Study of Oxygen-18 ($\delta\ ^{18}O$) and Deuterium (δ^2H) study of the lake water shows that it is of meteoric origin and of relatively recent age (230 ± 30 yrs. before present). The increase in PCO_2 in the lake water triggers the increase in Fe concentration (335 ppb to 429 ppb) which is manifested by the sporadic color change and increased acidity in the lake from pH 7.35 to pH < 6.71.

Keywords: Pidong Crater Lake, Jos Plateau, hydrogeochemistry, water color changes, fumaroles (CO_2), meteoric water

1. Introduction

The volcanoes of the Jos Plateau are aligned in four specific volcanic lines-namely Miango, Kassa, Panyam (Sura) and Gu volcanic lines [1]. There is no record of any actual activity in the Nigerian volcanic provinces in the recent past [2–5]. Recent K-Ar dating the volcanoes of the Kassa volcanic line revealed recent eruption during the Pleistocene ages [6].

Recently, biological and physico-chemical changes were observed within the Jos Plateau Volcanic Province within and around the Pidong Lake which is characterized by the occurrence and recurrence of floating ‘mat’ vegetation (Plate I & II). The physical changes are dominated by the intermittent color changes from its natural bluish to yellow brownish color and these activities call for a comprehensive study of these phenomena. In light of the intermittent activities in the lake, this study seeks to determine- (1) the hydrogeochemical characteristics of the lake, (2) constraint the origin and source (s) of the lake water and its chemical elements (3) to ascertain the factors responsible for the observed color change in the lake.

2. Location and geography

The Jos Plateau is located in the Northcentral area of Nigeria. It is the second largest volcanic province in Nigeria after the Biu Plateau [4, 7] and consists of about 22 volcanoes [3, 8]. The Panyam Volcanic Line is the second Southwest end member of the Jos Plateau volcanic region. The Pidong volcano is the southernmost of a series of 7 volcanoes of the Panyam Volcanic Line located in the southwestern segment of the Jos Plateau. The Pidong volcanic crater lake is located on the summit of the Pidong volcano within the southernmost of the 3 crater and lies on longitude $9^0$12′20”-$9^0$12′40” and latitude $9^0$18′50″- $9^0$19′10” at an altitude of 1300 m. The lake’s morphological and bathymetric data shows that the lake has a length of 160 m with maximum depth of 6 m [9, 10].

2.1 Geology of the Pidong maar

The Pidong volcano is hosted by medium to coarse grained granite gneiss rocks of PreCambrian age [11]. The volcano extrudes through three craters arranged in a N-S direction with the southernmost breached by water. The Pidong maar is bounded to the south and southeast by granite gneiss rocks and to the west, north and northeast by pyroclastic surge deposits explosively ejected during formation (**Figure 1**). The volcanic ejecta consists mainly of pyroclastic materials, scoria, basaltic lava, pulverized granite materials, and volcanic ash [3, 9, 12]. Beside the lake’s crater rim to the extreme south-east are characterized by deposits of large boulders of granite rocks and this is evident of the high explosion that characterized the eruption of the Pidong Maar/Lake [9].

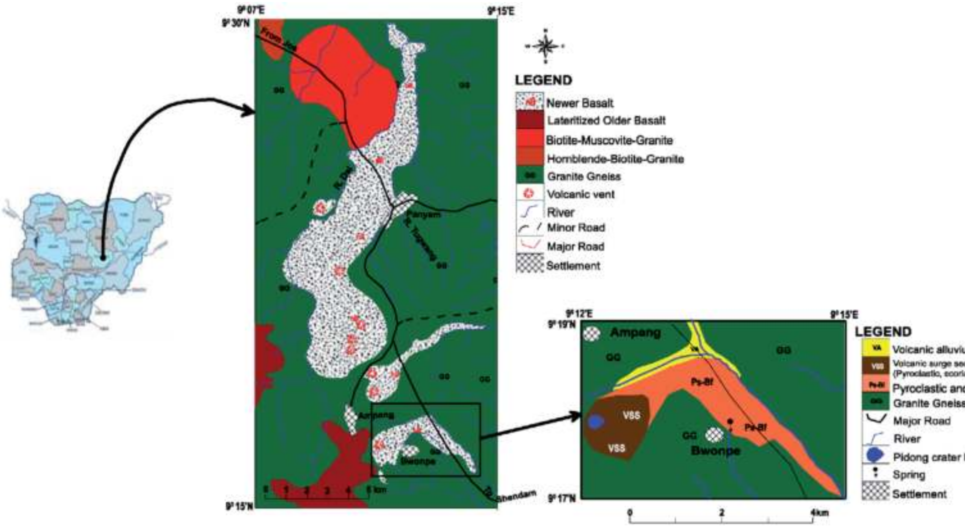

Figure 1.
Location and geological map of Panyam Volcanic Province and Pidong crater Lake area.

3. Methodology

3.1 Water sampling and hydrogeochemical analysis

A hydrogeochemical monitoring regime of the Pidong Crater Lake was carried out by sampling the water on a monthly basis to determine any hydrogeochemical changes over the 2 to 3 year study period. The physical parameters of Temperature, pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS) were carried out directly in the field using an MT 806/pH/EC/TDS/Temperature portable meter. The major, trace and rare earth elements analysis (Mg, Ca, Na, K, Cr, Ni, Co, Sc, V, Cu, Pb, Zn, Bi, Cd, Sn, W, Mo, AS, Sb, Rb, Cs, Ba, Sr., Ga, Li, Ta, Nb, Hf, Zr, Y, Th, U, B, Fe, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were carried out using ICP-MS method. The anions (SO_4, Cl, HCO_3, NO_3, F, Br and PO_4) concentrations were determined using colorimetric method at Bureau Veritas Minerals Laboratory Ltd., Canada. The oxygen and hydrogen isotopes analyses of the lake, local rainfall and volcanic spring water was carried out at Activation Laboratory Ontario Canada using cavity ring down spectroscopy with V-SMOW as standard and reported in per mill notation ($_{0/00}$).

The Carbon-14 dating of the lake water was determined by single stage accelerator mass spectroscopy (Source: Activation Laboratories, Canada).

4. Results

4.1 Hydrogeochemical analysis of the crater lake

4.1.1 Physico-chemical parameters

The physico-chemical analyses of the lake water are presented in **Table 1**. The physico-chemical characteristics show slight variability over the 2 to 3 year monitoring period. The pH values for the lake water range from 6.20 to 7.7. The pH is more acidic (< 7) during the dry season (March–June) and becomes more alkaline (rises to >7) during October–December period. Temperatures are highest during the month of March–April (27^0-30°C) and correlates well with highest EC (340-390 μs/cm) and TDS (150-170 mg/l) values. In general, there is a gradual decrease in temperature from 30°C in March to 20°C in December each year.

4.1.2 Major cations

The major cations (Mg, Ca, Na and K) concentrations are in the order of-Mg > Ca > K > Na. The highest concentration of Mg range from 30 mg/l to 40 mg/l, Ca from 21 mg/l to 25 mg/l, Na from 8 to 11 mg/l and K from 5.38 to 15 mg/l and are observed during the dry season (January to April) while the lowest concentration of Mg (16 to ≥25 mg/l), Ca (10 to 15 mg/l), Na (3 to 5.25 mg/l) were observed during the rainy season (August to October) (**Table 2**). Comparative analysis of Fe concentration with Patterson 1986 [9] show that the Fe concentration have increased from 0.27 to 0.612 mg/l over the last 29 yrs. It is observed that Fe concentration progressively increased from 0.332 mg/l in October, 2014 to 3.249 mg/l within the period of lake color change activities from November 2014 to February 2015. From the physico-chemical concentrations of the lake over the study period shows that it is seasonally dependent. However, a comparison of the pH values in the present study with that reported by Patterson [9] showed a decrease in pH from 9.35 to ≤7 with corresponding decrease in alkalinity ($CaCO_3$) from 335 mg/l to 187 mg/l.

Date	pH	Temp.°C	EC (ms/ cm)	TDS (ppm)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)	SO_4 (mg/l)	Cl (mg/l)	F (mg/l)	Br (mg/l)	HCO_3 (mg/l)	PO_4 (mg/l)	NO_3 (mg/l)
25/05/13	7.08	27.4	0.49	240	41.85	23.66	8.80	14.52	3.67	6.2	—	0.018	200	0.0117	<2.0
27/06/13	7.70	28.0	0.39	140	41.53	25.35	9.23	15.27	<0.50	11	—	0.017	185	0.0116	<2.0
22/07/13	6.99	26.6	0.23	110	—	—	—	—	—	—	—	—	—	—	—
30/08/13	6.94	26.5	0.031	160	31.16	19.03	7.52	11.84	1.54	6.3	—	0.019	210	0.0220	<2.0
27/09/13	7.09	24.6	0.23	110	23.23	16.53	4.97	9.00	<0.50	0.53	—	<0.01	110	0.0452	< 2.0
28/10/13	7.1	24.4	0.31	150	30.40	19.23	7.62	12.26	1.19	8.7	—	0.022	220	0.0152	—
27/11/13	7.42	26.5	0.29	150	32.29	18.75	5.96	10.80	0.51	5.2	—	0.015	147	0.0175	<2.0
18/12/13	7.66	20.3	0.36	190	32.82	19.39	6.03	10.93	0.55	5.2	—	0.016	143	0.0311	<2.0
30/01/14	7.19	23.1	0.26	130	33.74	17.63	7.08	11.30	<0.5	5.3	0.290	—	200	0.0906	<2.0
14/03/14	7.18	27.6	0.37	180	38.05	22.24	7.69	13.35	<0.5	5.8	0.320	—	190	0.0163	<2.0
28/03/14	6.86	28.2	0.38	190	39.17	25.71	7.84	13.73	<0.5	5.9	0.330	—	180	0.0321	<2.0
24/04/14	6.89	28.9	0.39	190	39.11	23.37	8.54	14.26	<0.5	8.6	0.320	<0.10	215	0.0161	0.035
24/5/14	7.06	26.2	0.35	170	35.36	21.29	7.18	13.07	<0.50	7.0	0.290		240	0.0081	<0.020
28/6/14	7.16	28.5	0.33	160	31.85	19.53	6.67	12.19	<0.50	5.8	0.28	0.018	218	<0.05	<0.02
29/7/14	7.0	24.9	0.29	140	29.13	18.45	5.84	10.55	<0.50	5.2	0.250	0.016	200	0.0086	0.023
14/8/14	6.9	25.8	0.28	140	25.74	17.48	5.15	9.80	<0.50	4.9	0.240	0.017	185	<0.005	<0.02
30/9/14	6.95	25.5	0.22	110	16.47	10.86	3.01	5.34	<0.5	2.1	0.140	0.011	103	<0.05	<2.0
29/10/14	7.37	27.8	0.24	110	23.72	15.92	4.26	7.42	4.38	1.4	0.118	—	—	—	<2.0
28/11/14	6.71	26.3	0.25	120	25.22	16.31	4.78	8.10	<0.5	4.0	0.200	0.020	174	0.0117	<2.0
17/12/14	6.86	22.6	0.25	120	25.64	18.94	6.21	8.74	0.53	4.1	0.200	0.021	169	0.0157	<2.0
29/01/15	6.96	22.1	0.28	140	19.68	16.15	11.5	4.87	4.13	5.3	0.180	0.011	138	0.0644	2.11
26/02/15	7.0	24.3	0.32	160	31.54	21.15	6.17	19.52	<0.5	7.1	0.270	0.022	211	0.165	0.629

Date	pH	Temp.°C	EC (ms/cm)	TDS (ppm)	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)	SO_4 (mg/l)	Cl (mg/l)	F (mg/l)	Br (mg/l)	HCO_3 (mg/l)	PO_4 (mg/l)	NO_3 (mg/l)
18/03/15	7.10	24.1	0.30	150	30.26	25.35	9.08	11.69	<0.5	7.8	0.270	0.023	211	0.0439	0.778
23/04/15	7.08	30.5	0.34	170	34.22	22.69	7.04	12.73	<0.5	6.3	0.290	0.022	225	0.0193	0.205
27/05/15	7.15	28.01	0.24	170											
21/06/15	7.04	25.3	0.211	165											
22/07/15	6.96	24.7	0.24	163											
31/08/15	7.05	25.2	0.23	168											
24/09/15	7.15	24.9	0.21	170											
25/10/15	6.83	25.4	0.22	110											
23/11/15	6.93	24.8	0.24	120											
23/12/15	6.99	25.1	0.23	130											
27/01/16	7.13	23.4	0.24	140											
28/02/16	7.18	24.8	0.211	150											
29/03/16	7.08	27.3	0.21	160											
30/04/16	6.97	27.4	0.211	170											
24/09/16	6.2	25.9	0.22	173											

Table 1.
Physico-chemical parameters of the Pidong volcanic crater Lake (may 2013–April 2015).

Period	pH	Temperature ^{0}C	EC µs/m	Mg (mg/l)	Ca (mg/l)	Na (mg/l)	K (mg/l)	Zn (mg/l)	Fe (mg/l)	Cu (mg/l)	Al (mg/l)	SO_4 (mg/l)	Cl (mg/l)	Alkalinity ($CaCO_3$) (mg/l)	F (mg/l)
Patterson (1986) report	9.35	28.50	410	36.40	13.65	12.80	25.80	0.065	0.270	< 0.004	—	< 0.33	2.50	335.0	—
Present study (2013–2015)	7.17	26.10	299	29.680	39.670	6.890	11.390	0.064	0.612	0.004	0.456	1.030	5.607	141.500	0.249

Table 2.
Comparative hydrogeochemical data of 1986 and present study (after Lar [12]).

4.1.3 Trace elements concentrations

Some of the trace elements (Cu & Zn) show wide variability in concentration varying from 13.4 mg/l, 0.003 to 0.088 mg/l respectively (**Table 2**). The spider graphs (**Figures 2** and **3**) of the Light Ion Lithophile Elements (LILE) (Ba, Rb, Sr) normalized to chondrite values show enrichment (1–10 X chondrite values) while Nd to Yb are impoverished (0.001 to <1 X chondrite). These elements display variations in concentration over the study period.

4.1.4 Rare earth elements concentrations

The REE concentrations displayed in the spidergraph (**Figure 4**) show slight variability during the study period and are rarely depended on the seasons (**Table 3**). The concentration variations for La, Ca, Pr, Nd, and Sm is 0.01 to 0.5 ppb, 0.06 to 1.09 ppb, < 0.01 to 0.12 ppb, and < 0.02 to 0.08 ppb respectively. However, Gd-Lu concentration range between ≤0.01 and with few deviations >0.01 ppb which is not dependent on season. The sum average concentration for the REE (La to Lu) is 0.54 ppb and varies between <0.01 and 1.09 ppb. The REE are impoverished relative to chondrite values (< 1 X chondrite). There are significant variations (0.03 to 0.18 X chondrite) for La-Sm in the LREE concentration relative to HREE (Gd to Lu). An important characteristic of the variations is the relative similarities in the geochemical spectra indicating similar source.

4.1.5 Anion concentrations

The major anions of the lake water are HCO_3^-, Cl^-, SO_4, and NO_3 with average concentration of 141.4 mg/l, 5.65 mg/l, 0.845 mg/l. The minor anions are F, Br and PO_4 with average concentration of 0.24 mg/l, 0.017 mg/l, 0.03 mg/l respectively. Generally, the highest (193.675 mg/l) and the lowest (186.5 mg/l) sum of the major anions concentrations are observed during the dry and wet seasons respectively.

A comparative hydrochemical concentration of the anions of chloride (Cl^-) and sulphate (So_4^{-2}) in the present study with Patterson [9] values (**Table 1**) showed Cl and SO_4 have increased from 2.5 mg/l to 5.67 mg/l and < 0.33 mg/l to 1.03 mg/l respectively.

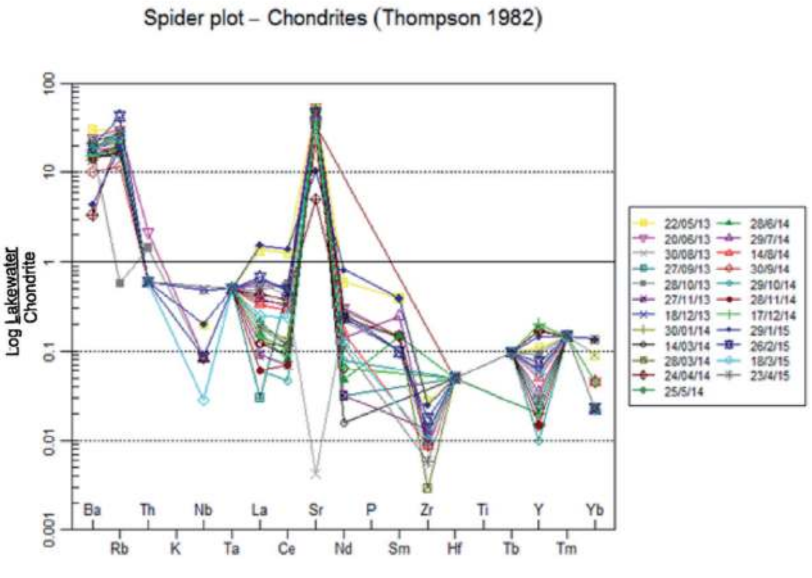

Figure 2.
Spidergraph of incompatible trace element concentrations of Pidong crater Lake normalized to chondrite.

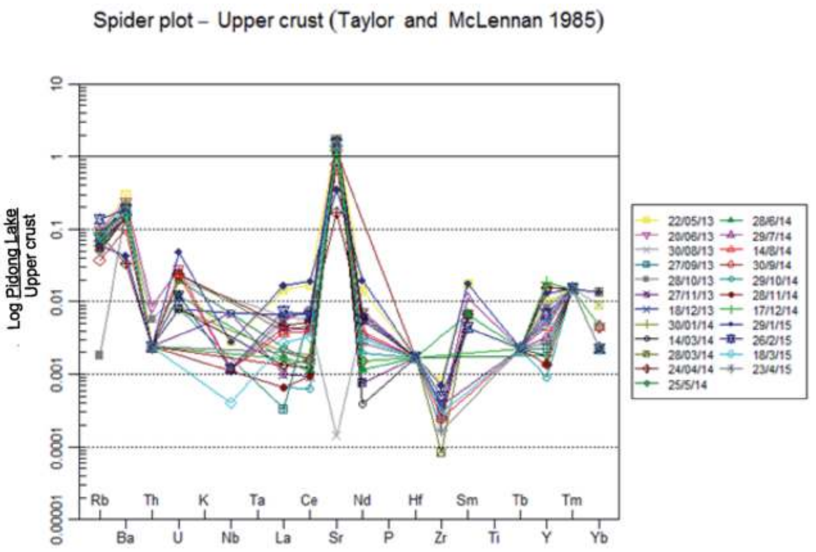

Figure 3.
Spidergraph of incompatible trace element concentrations of Pidong crater Lake normalized to upper crust abundance.

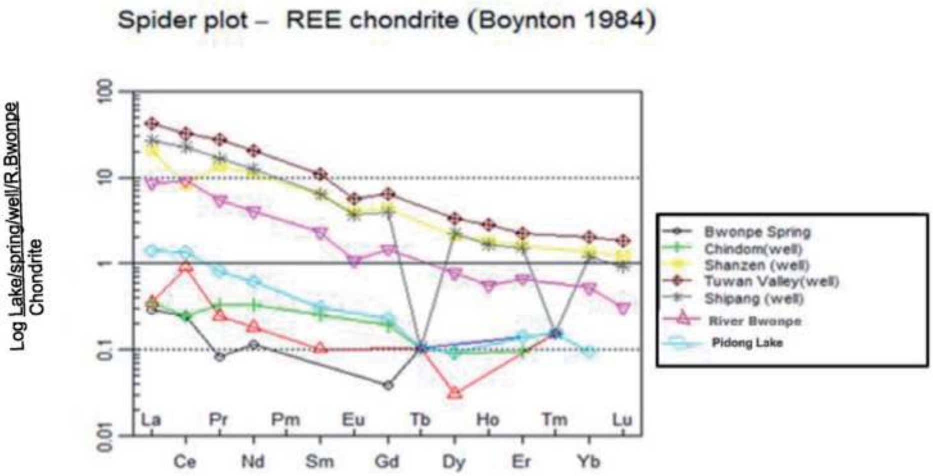

Figure 4.
Spidergraph of REE of Pidong crater Lake, Bwonpe volcanic spring, wells and river Bwonpe normalized to chondrite.

4.2 Oxygen, hydrogen and carbon isotopes

The Pidong Crater Lake isotope composition of oxygen-18 and deuterium are $-4.9_{0/00}$ and $-25_{0/00}$ respectively and that of the rainfall within the upper River Ndai basin are $\delta^{18}O$ ($-4.75_{0/00}$) and $\delta^{2}H$ ($-31_{0/00}$) (**Table 4**). The plot of the $\delta^{18}O$ versus $\delta^{2}H$ falls close to Standard Meteoric Water Line (**Figure 5**). The hydrocarbon age of the lake water is 230 ± 30Bp (**Figure 6**).

4.3 Lake color change activities

The Pidong Crater Lake intermittently display color changes from its natural bluish color to brown-yellowish color (**Figure 7**). The lake color change activities were observed in November 2014, October 2015 and September 2016. During

Date	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE
22/05/13	0.44	1.09	0.10	0.37	0.08	<0.01	0.06	<0.01	0.03	<0.01	0.03	<0.01	0.02	<0.01	2.22
20/06/13	0.18	0.46	0.05	0.19	0.03	<0.01	0.03	<0.01	0.03	<0.01	0.02	<0.01	0.01	<0.01	1.0
22/07/13	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
30/08/13	0.19	0.36	0.04	0.14	0.02	<0.01	0.02	<0.01	0.02	<0.01	0.01	<0.01	0.02	<0.01	0.82
27/09/13	0.01	0.44	<0.01	0.02	<0.02	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.49
28/10/13	0.16	0.49	0.03	0.14	0.03	<0.01	0.02	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.88
27/11/13	0.03	0.06	<0.01	0.02	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.11
18/12/13	0.20	0.44	0.04	0.17	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.87
30/01/14	0.06	0.12	0.01	0.04	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.23
14/03/14	0.04	0.08	0.01	0.01	<0.02	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.15
28/03/14	0.12	0.30	0.03	0.18	0.03	<0.01	0.05	<0.01	0.05	<0.01	0.03	<0.01	0.03	<0.01	0.82
24/04/14	0.14	0.33	0.04	0.15	0.03	<0.01	0.06	<0.01	0.05	<0.01	0.04	<0.01	0.01	<0.01	0.85
24/05/14	0.07	0.10	0.01	0.04	<0.02	<0.01	<0.01	<0.01??	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.22
28/06/14	0.05	0.07	0.02	0.03	0.03	0.02	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.29
29/07/14	0.13	0.27	0.03	0.09	0.05	0.02	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.62
14/08/14	0.11	0.25	0.03	0.10	<0.02	<0.01	<0.01	<0.01	0.02	<0.01	0.01	<0.01	0.01	<0.01	0.53
30/09/14	0.04	0.10	<0.01	0.04	<0.02	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.2
29/10/14	0.02	0.04	<0.01	0.05	<0.02	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.12
29/11/14	0.02	0.06	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	0.1
17/12/14	0.05	0.09	<0.01	0.04	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.19
29/01/15	0.5	1.21	0.12	0.51	0.08	0.01	0.07	<0.01	0.05	<0.01	<0.01	<0.01	0.03	<0.01	0.258
26/02/15	0.22	0.41	0.04	0.15	0.02	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.87

Date	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REE
18/03/15	0.08	0.21	0.01	0.08	<0.02	<0.01	0.02	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.41
23/04/15	0.06	0.10	<0.01	0.07	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.23

**Element concentration in ppb.*

Table 3.
REE (Rare earth elements) concentration in Pidong volcanic crater Lake (may 2013–April 2015). NB- All element concentration in parts per billion.

lake color change activities pH were observed to have decrease from 7.39 to 6.71, 7.15 to 6.83 and 7.18 to 6.20 in November 2014, October 2015, and September 2016 respectively.

Location/source	**Date of sampling**	**Analyte**		
		$\delta^{18}O_{H2O}$ (‰)	**$\delta^{2}H_{H2O}$ (‰)**	**$\delta^{3}H_{H2O}$ (‰)**
Pidong Crater Lake	June, 2014	−4.8	−25.0	17.0
Bwonpe Volcanic Spring	June, 2014	−4.7	−26.0	34.0
Rainfall	June, 2014	−4.9	−31.0	12.0

Table 4.
Oxygen and hydrogen isotope composition of Pidong crater Lake, Bwonpe volcanic spring and rainfall.

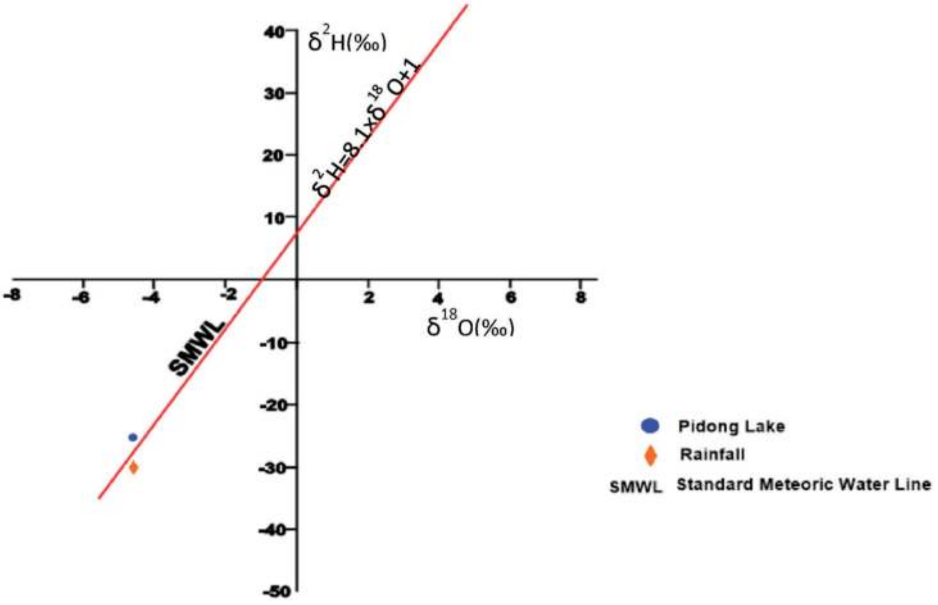

Figure 5.
δ2H versus δ18O diagram for Pidong crater Lake, Bwonpe volcanic spring, rainfall and standard mean ocean water (SMOW).

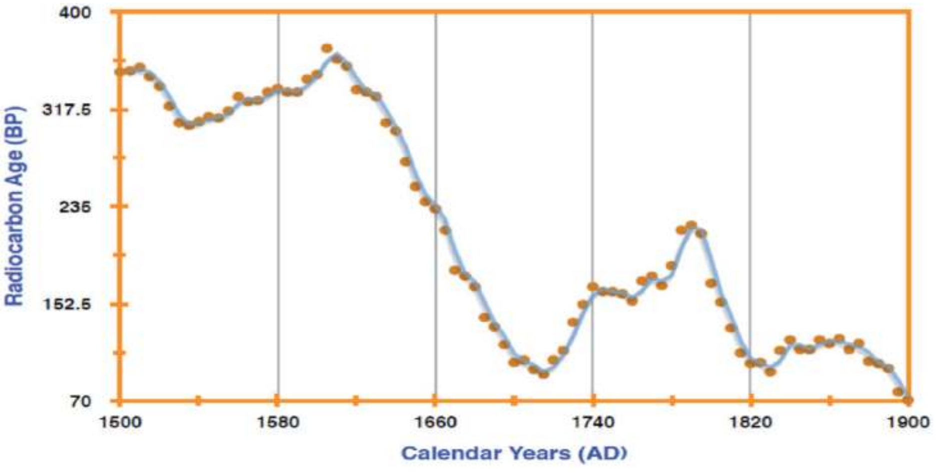

Figure 6.
Radio carbon (^{14}C) age of Pidong crater Lake.

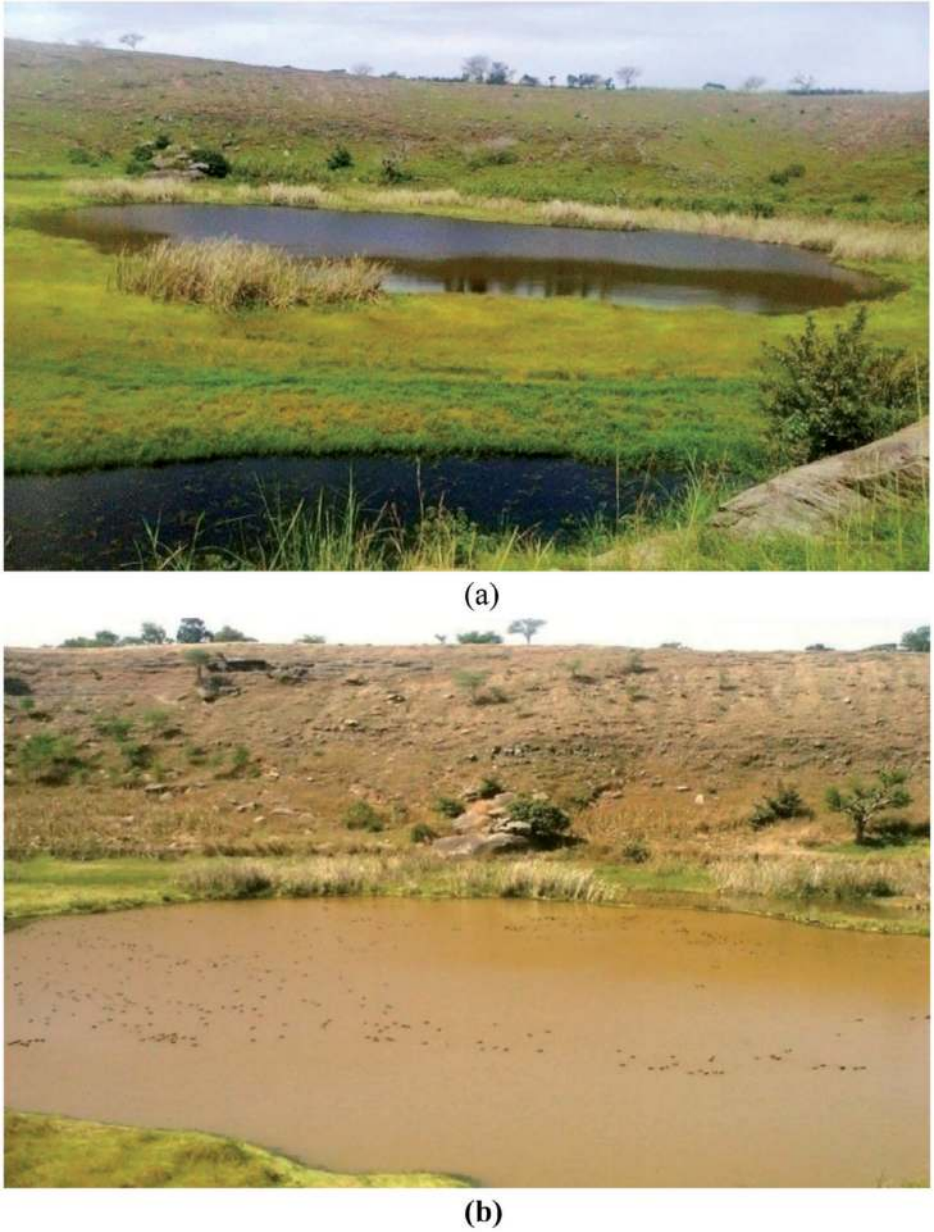

Figure 7.
(a) Natural bluish water color of Pidong crater Lake; (b) Pidong crater Lake water color change activities in November 2014, October 2015 and September 2016.

4.4 Lake water types and sources of major ions

The Piper Trilinear diagram (**Figure 8**) for the lake water plots predominantly in the Mg-Ca-HCO_3 segment. The minor water types which constitutes only about 10–20% and include Na-K-Cl and Na-K-SO_4 water types.

The major element concentration abundance of the lake is in the order of $Mg^{2+} > Ca^{2+} > K^{+} > Na^{+}$. Similarly, the major element oxide distribution order for the volcanic ejecta materials (Basalts, pyroclastic, ash) for the Pidong volcanic rocks is in order of $MgO > CaO > Na_2O > K_2O$ [12, 13]. The major cation concentration order

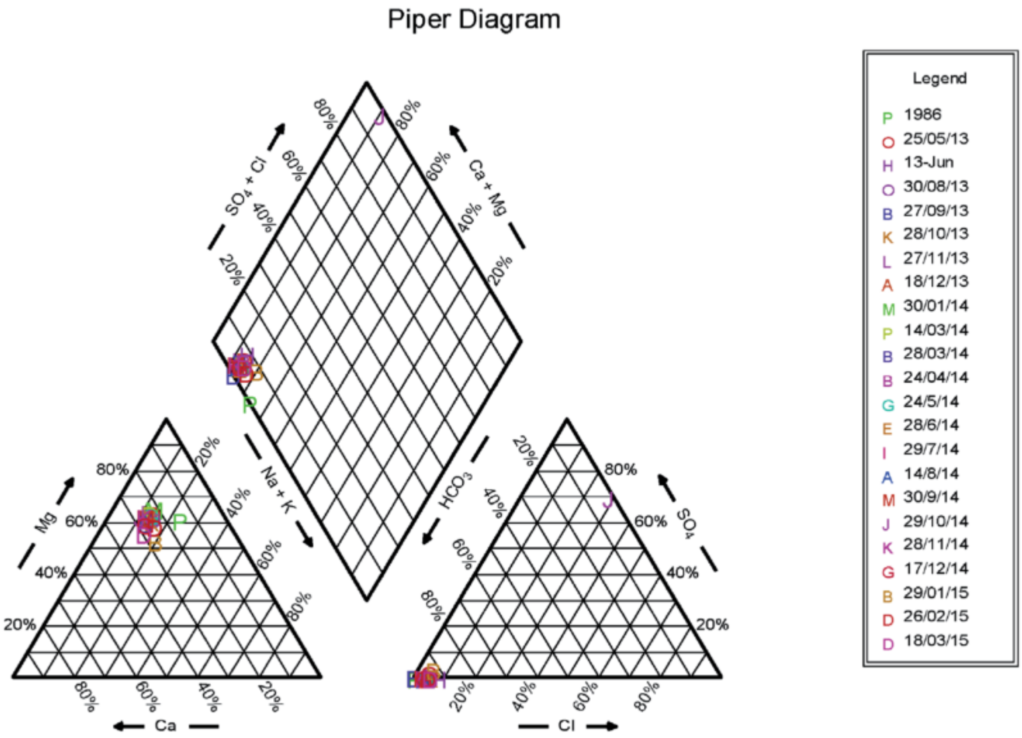

Figure 8.
Piper trilinear diagram for Pidong crater Lake.

of the lake water and that major oxides of the Pidong volcanic rocks show similarity in the concentration abundance.

The Gibbs diagram is an illustration of the mechanism controlling the chemistry of groundwater samples in crystalline aquifers. The plot is that of the ratios of $\frac{Na^+}{Na+Ca^+}$ vs. Total Dissolved Solids and $\frac{Cl^-}{Cl^- + HCO_3}$ vs. Total Dissolved Solids. The Gibbs diagrammatic plot for the Pidong Crater Lake water shows it is controlled predominantly by water-rock dominance processes (**Figure 9**).

4.5 Partial carbon dioxide pressure (PCO_2)

Partial carbon dioxide pressure of crater lake water is the partial pressure of carbon dioxide in equilibrium with lake and saturated atmospheric pressure. PCO_2 is based on the equilibria of carbon specie in solution. The PCO_2 plot for the two year observation for the Pidong Lake shows zit is constantly and several orders of magnitude higher than air saturated water pressure except June, 2013 (**Figure 10**). The highest PCO_2 of 4.5 X 10^{-2} and 2.5 X 10^{-2} bars were observed in March and November, 2014 respectively and correlate with highest decreases in pH from 7.38 to 6.71 in November 2014. The lowest decreases in pH were observed during lake watercolor change activities (**Table 2**). Generally, increases in pH and PCO_2 were observed to be linked with decrease in pH and lake color change activities.

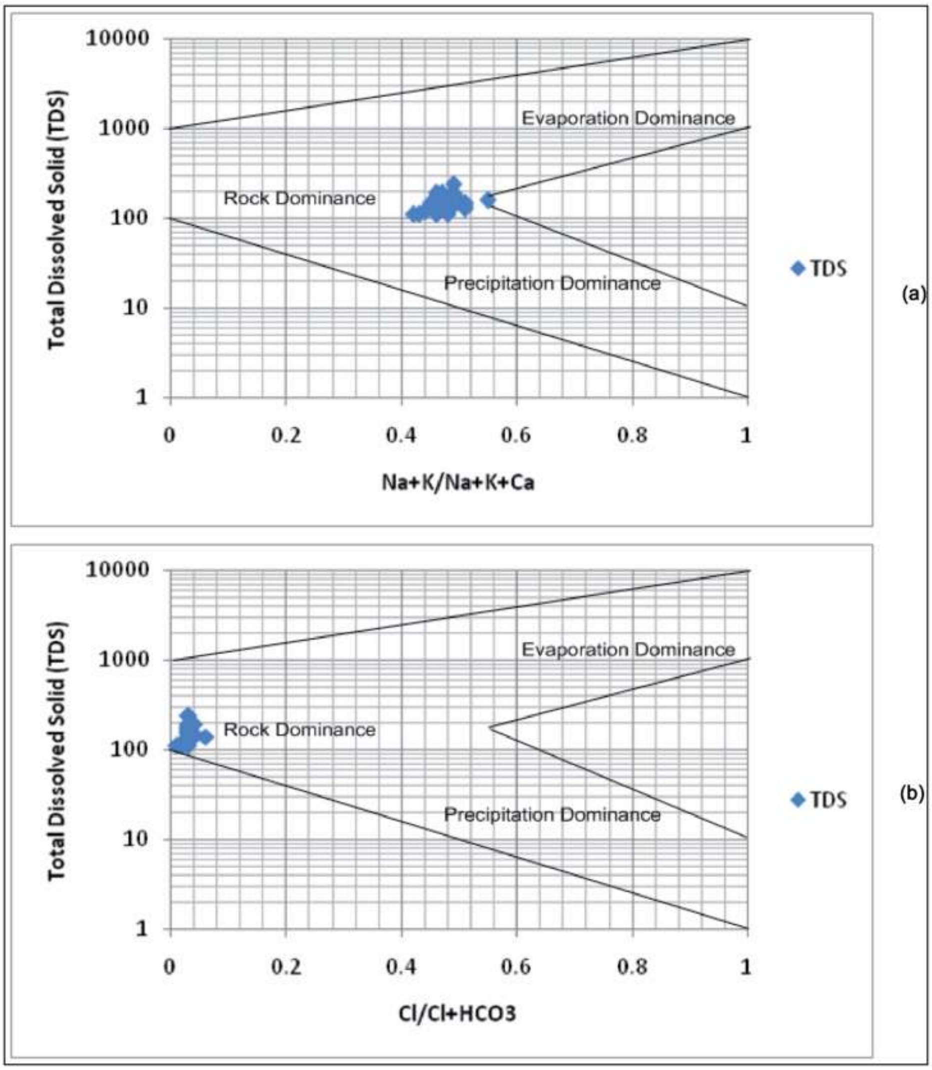

Figure 9.
Gibbs diagram for Pidong crater Lake.

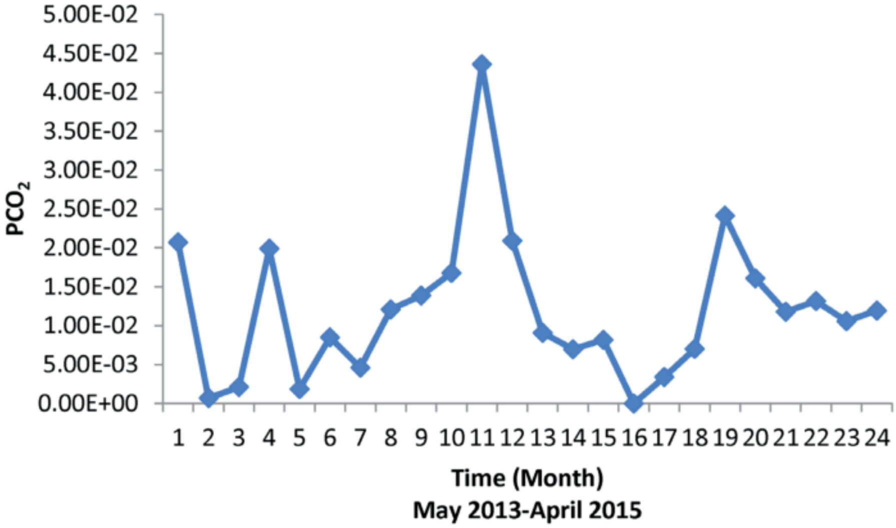

Figure 10.
PCO2 versus time for Pidong crater Lake.

5. Discussion

5.1 Sources of major ions

The Gibbs diagram for the Pidong Crater Lake shows that the lake water is characterized mainly by water-rock interaction processes [14]. The hydrogeochemical abundance order of the lake ($Mg^{2+} > Ca^{2+} > Na^+ > K^+$) and that of the host rock ($MgO > CaO > NaO > K_2O$) show similarity and may suggests derivation from the overlaying volcanic rocks. Similarities in hydrogeochemical spectral patterns of lake and host volcanic rocks are indicators of sources of derivation [4, 15, 16]. The major cations of groundwater are derived mainly from chemical weathering [17]. Generally, the silicate minerals present in the basalts, pyroclastic materials, ash and pulverized granite get weathered by hydrolysis producing mainly Mg-HCO_3 and Na^+ and K^+ depleted groundwater. Groundwater containing CO_2^{2-} can easily react with orthoclase to release Magnesium ion, Calcium bicarbonate ions (Mg^{2+}, Ca^{2+}, HCO_3^-) [18]. The Na^+ and K^+ alkali appear to originate from hydrolysis of plagioclase in the basalt and granite rocks. In water-rock interaction processes the following chemical reaction of volcanic rocks may occur and hence the chemical sources are derivable from these processes.

1. Hydrolysis of plagioclase minerals

$$CaAl_2SiO_8 + HCO_2 + \tfrac{1}{2}\,O_{2\rightarrow}\ Al_2Si_2 4(OH) + CO_3^{\,2-} \qquad (1)$$

2. Oxidation (chemical weathering) for ferromagnesium minerals (Pyroxene)

$$(Mg,Fe,Ca)SiO_3 9H_2CO_3 \rightarrow \left(Mg^{2+},Fe^{2+},Ca^{2+}\right) + 4HCO_3^{\,-} + HCO_3 + H_4SO_4 \qquad (2)$$

5.2 Trace elements concentration

It is observed that Fe concentration have significant increase by 200% from 0.27 mg/l in 1986 to 0.612 mg/l in present study [12]. Lake water, Fe concentration gradually increases from 423 ppb in November, 2014 to 3249 ppb in March 2015 during the lake color change activities. This phenomenon is similar to the Lake Nyos CO_2 gas disaster episode of 1986 [19, 20]. The lake color change phenomenon was attributed to upliftment of deep anoxic water carried upwards to shallow lake level where oxidation of ferrous iron precipitates to form murky water.

The spider plot for the LILE normalized to upper crustal values (UC) (**Figure 2**) displays strong positive anomalies in Sr. (>1x UC values), Ba (>0.1x UC values) and enrichment in Rb (0.1x UC values). There is a visible negative anomaly in Zr (0.0001 x UC values), all together suggesting that these elements are originally from a source that is highly depleted in these elements (probably deep mantle source) [21]. The dominant rock types that comprise of the crater lake/maar are basalts, pyroclastics and volcanic ash. Generally, hydrogeochemical constituents of any groundwater are signatures of the background rock types the water precolates through [17, 22].

5.3 Rare earth elements concentrations

Generally, REE spidergraph of the Pidong lake water normalized to chondrite values show high impoverishment or depletion (< 0.01 to <1 X chondrite) (**Figure 4**). The slight enrichment in the LREE (La-Sm) is suggestive of influence by crustal rocks materials (host granitic basement rock) rich in these elements (**Figure 4**).

There is high similarity in the REE patterns in the well waters compared to that of the lake and the spring water. The well waters generally exhibit higher REE concentrations (. > 1x Chondrites) but maintain similar LREE enrichment relative to HREE suggestive of significant influence from the surrounding basement complex host rocks. The impoverishment in REE in the lake and spring water suggests a derivation from a mantle source depleted in these elements [4, 15, 16, 22].

5.4 Anion concentrations

The concentration of the SO_4, Cl and F are generally influenced by the water-rock interaction processes between rainfall and host volcanic/granitic rocks. Generally, HCO_3^- is derived from dissolution of silicate minerals of orthoclase, plagioclase, hornblende, diopsite, olivine and biotite of country rock by carbonic acid [18, 23–25]. A comparative analysis of the hydrogeochemical anion concentrations of the lake in this study with that of Patterson [9] show that there is significant increase in Cl, SO_4 and Fe and corresponding decrease in alkalinity and pH over the last 29 years. These increases have been attributed to intermittent CO_2 degassing (fumaroles) into the lake from the subsurface hydrothermal system [12].

5.5 Origin and age of water

The $\delta^{18}O$ and $\delta^{2}H$ compositional values for the lake (**Table 2**) falls within meteoric water composition values [12, 26] and this is further affirmed by the plot (**Figure 5**) of the SMOW line in the $\delta^{18}O$ and $\delta^{2}H$ correlation diagram [26–28]. The hydrocarbon-14 (^{14}C) age of the lake water is calculated to be 230 ± 30 yrs. and this affirm, that the lake water is relatively young and suggests constant replenishment by precipitation.

5.6 Lake color and hydrogeochemical changes

The Pidong Lake color change activities are characterized by decrease in pH values 7.39 to 6.71, 7.15 to 6.83 and 7.18 to 6.20 as observed in November 2014, October 2015 and September 2016 respectively. The intermittent lake color changes associated with CO_2 degassing into the lake and its dissolution forming weak acid. The HCO_3^- specie increases over time and resulting in decrease in pH from 9.35 to neutral or slightly acidic as seen in the comparative study (**Table 1**). This process can be explained as follows:

$CO_{2\,(gas)}$, $CO_{2\,(aq)}$, HCO_3, CO_3^{2-}, specie are related to pH and temperature of fluid [28]. When $CO_{2\,(gas)}$ undergoes hydration and ionization, hydration of CO_2 forms $H_2^-CO_3^{2-}$, CO_2 gas dominated sub aqueous relevant with the lake

$$2H_2O + 2CO_2 \rightarrow 2H_2CO_3 \tag{3}$$

$$\text{Ionization process, } 2H_2CO_3 \rightarrow 2H_2{}^{+}{}_{+}\, CO_3{}^{2-} + CO_3{}^{2-}. \tag{4}$$

It is observed that the highest ionization correlates with the lowest pH (6.71) during the period of lake color change. This result suggests a magmatic gas/fumaroles (CO_2) connecting upwards below the lake from shallow mantle and mixing with shallow groundwater and controlled by meteoric recharge. This similar phenomenon was observed in Popocapetl volcanic springs [28]. The intermittent CO_2 gas and associated gas input into the lake during color change activities over time is suggestive of the cause of the decrease in pH from 9.35 to neutral or near acidic as well as alkalinity from 330 mg/l to 147 mg/l [9] as compared with present study.

5.7 Partial carbon dioxide pressure (PCO_2)

Generally, the PCO_2 versus saturated atmospheric pressure for the lake is above equilibrium for the study period. However, several peaks ($4.5 X 10^{-2}$ and $2.5 X 10^{-2}$ bar) were observed during the lake color change in November 2014 etc. with corresponding pH decreases (6.71). Similarly, these characteristics where increases in PCO_2 are characterized by decrease in pH were observed in Popocapetl volcanic activities [28]. The increased PCO_2 and decreased in pH characterized by lake water color change activities suggest low pressure CO_2 gas influx or bubbling degassing input and its ionization to form weak carbonic acid.

6. Conclusion

The Pidong Crater Lake water is majorly meteoric origin probably coming from percolating meteoric waters of relatively young age (230 ± 30 years before present). The chemical element composition of the Lake is dominantly of Mg-HCO_3 water type, influenced mainly by the interaction between meteoric water and basaltic rocks with surrounding granitic host rock from relatively deeper aquifers. In addition, the chemical composition of the lake water is further influenced by minor CO_2 degassing, attributable to minor intermittent fumaroles activities possibly from deep mantle source.

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