Characteristics of Chemical weathering and water-rock interaction in Lake Nyos dam (Cameroon): Implications for vulnerability to failure and re-enforcement

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Abstract

For the first time, comprehensive study of hydrogeochemistry of water seeps, role of chemical weathering on dam failure, estimation of minimum width of dam to resist failure and simulation of changes in dissolved ions and secondary mineral was conducted on the Lake Nyos dam. The salient results and conclusions were; the dam spring water represented a mixture of 60 - 70 % rainwater and 30 - 40 % Lake water (from 0 - -40 m). The chemistry of the observed waters was Ca-HCO₃ for rainwater, Ca-Mg-HCO₃ in boreholes, and Mg-Ca-HCO₃ for spring water. The relative rate at which ions dissolved in water was HCO₃⁻ > Mg²⁺ > Ca²⁺ > Na⁺ > SiO₂ > K⁺ > NO₃⁻ > SO₄²⁻ > Cl⁻. Weathering of rocks resulted in the formation of clay minerals such as kaolinite and smectite. Relative mobility of elements compared to Alumina (Al₂O₃) indicated that in monzonites there was a loss of CaO, Na₂O, K₂O, P₂O₅ and gain of SiO₂, Fe₂O₃, TiO₂, MnO and MgO, while in basalts there was a loss of SiO₂, Fe₂O₃, Ca₂O, NaO, MgO and gain of TiO₂, K₂O and P₂O₅. Values of chemical alteration index that ranged from 49 to 82 suggest a weak to intermediate categories of chemical weathering that occurred at a rate of 5.7 mm/year. Paired to that rate, which suggests that the dam is not vulnerable to failure at the previously thought time scale, some other processes (physical weathering, secondary mineral formation and lake overflow) can cause instant failure. Hydrostatic pressure of 1.6 GN generated by Lake water can be supported only when the width of the dam is greater than 19 m. PHREEQC-based simulation for 10 years indicates decoupling of Ca and Mg, and Na and Mg. Multidisciplinary monitoring of the dam is advocated.

Keywords: Chemical weathering. Water-rock interaction. Dam failure. Simulation. Temporal monitoring. Lake Nyos dam (Cameroon).

36 1. Introduction

37 In 1986, Lake Nyos in the north western region of Cameroon released a mixture of water and carbon
 38 dioxide gas that killed over 1750 people and 3000 cattle in valleys to the north of the Lake (e.g., Kling et al.,
 39 1987; Kusakabe et al., 1989; Sigurdsson et al., 1987; Sigvaldson, 1989). Scientific visits to the lake in the
 40 aftermath of the gas disaster revealed the presence of a natural dam in its northern border (Fig. 1). Besides the
 41 hazard's direct relation to the extremely high recharge rate of magmatic CO₂ from the Lake bottom (e.g., Kling
 42 et al., 2004; Kusakabe et al., 2008), a second risk must be considered for Lake Nyos, where the natural dam that
 43 impounds the lake water is described as weak (Lockwood et al., 1988; Lockwood and Schuster, 1991; Tassi and
 44 Rouwet, 2014). Although the recent findings of Aka and Yokoyama (2013) suggest that a potential flood
 45 disaster from the failure of the dam is not as eminent and alarming as previously thought, the reports of previous
 46 researchers based on physical erosion recognized that the dam is back eroding at a geologically alarming rate,
 47 and that the dam is likely to fail in the near future (Lockwood and Schuster, 1991; Tchindjang and Konfor,
 48 2001), and to fail 'within the next 5 years' (UNEP/OCHA, 2005). Failure of the dam will release about 60
 49 million cubic meters of lake water that could cause a devastating flood in the northern part of the lake, affecting
 50 about 10000 people in Cameroon and northeastern Nigeria (Lockwood et al., 1988). If the dam happens to fail
 51 when the bottom of the Lake is still enrich in CO₂ gas, then the lowering of the Lake by ca. 40 m will drastically
 52 decrease the hydrostatic pressure at the bottom layers of the Lake, thus triggering another gas burst. The
 53 argument for a possible collapse of the dam is based on the following: 1) It is bisected by several fractures
 54 (Lockwood et al., 1988; Tchindjang and Konfor, 2001) that caused rock blocks of about 3 m in diameter to fall
 55 off (rock fall) it upper unit unto its downstream face; 2) the falling off of the blocks has caused the width of the
 56 dam to reduce from 285 m to 45 m (Freeth and Rex, 2000) after 400 years (Lockwood and Rubin, 1989), 5000
 57 years (Aka et al., 2008), 8000 years (Aka and Yokoyama, 2013), 100,000 years (Freeth, 1988; Freeth and Rex,
 58 2000); 3) Lake Nyos water permanently seeps from 3 lithological contacts on the dam's face (Lockwood and
 59 Rubin, 1989).

60 All of those findings on the dam were based on the domains of geochronology and physical weathering only and
 61 constitute the basis for deciding to re-enforce the dam with concrete. Such a decision was good, but to argue for
 62 a long term safety of the dam, scientific constraints from other disciplines such as upliftment, landslide, volcanic
 63 activity, (Aka and Yokoyama, 2013), and chemical weathering that will infinitely continue to occur on the dam
 64 and may contribute to understanding the vulnerability of the dam to failure remain unclear.

65 Although a European Union-supported operation is going on to strengthen the dam, Evans et al. (2012), reported
 66 that such strengthening will only reduce the danger of the dam to fail, thus the use of other disciplines such as
 67 the rate of chemical weathering, hydrogeochemistry, formation of secondary minerals, mechanical properties of
 68 rocks in the dam, and volume of Lake overflow to assess the vulnerability of the dam is imperative. The rate of
 69 chemical weathering of rocks depends among others on the chemistry of water in the area of interest, major
 70 element composition in fresh and altered rocks, and annual discharge of surface flows (Vuai and Tokuyama,
 71 2007; Faure, 1991; Boeglin and Probst, 1998; Goldberg and Humayun, 2010; Shao et al., 2012; Gurumurthy et
 72 al., 2012). In addition, the effect (evolution of chemical components, and primary and secondary minerals) of

time on chemical weathering has been successfully demonstrated by kinetic simulation in the domain of hydrogeochemistry (e.g., Parkhurst and Appelo, 1999). Although previous studies (e.g., Aka and Yokoyama, 2013) suggest that water that leaks from the Lake Nyos dam is entirely lake water, Lockwood et al. (1988) suggest that the dam spring water is a mixture of Lake Nyos water and local precipitation. Although the differences in mixing may depend on when spring water is sampled, the different views may also be an indicator that not only a comprehensive data on the origin and chemical characteristics of the water remain unknown, but also the chemical evolution and mixing proportions need more clarification based on the not yet availability of comprehensive data on representative water samples from the dam.

Against these backdrops, this study focuses on the disciplines of chemical weathering and hydrogeochemistry of the lake Nyos dam. The intention to assess chemical weathering of the dam is buttress by the observation of Issa (*personal communication*) that spatial distribution of CO₂ on the surface of Lake Nyos is high in the Northern part of the lake, which is in direct contact with the dam material (Fig. 2 ESM Only), thus favouring incongruent dissolution of silicates (e.g., Garrels and Makenzie, 1967; Faure, 1991, and references there-in), which can over time reduce the height, width, or length of the dam to a critical dimension that cannot resist hydrostatic pressure from the Lake (White, 2005). Likewise, the success of tracing the origin of spring water has also been demonstrated in various studies such as those of Fantong et al. (2010) in northern Cameroon, Asai et al. (2009) in central Japan, Goni (2006) in Chad basin, and Kazahaya and Yasuhara (1994) in Japan.

Accordingly the objectives of this study are; 1) to trace the origin and assess the chemical characteristics of the springs that are leaking from the dam, 2) assess characteristics (rate, intensity) of chemical weathering and solute generation on the Lake Nyos dam, 3) simulate hydrogeochemical evolution on the dam for a period of 10 years, and 4) estimate the critical (minimum threshold) width of the dam that can resist hydrostatic pressure from the 40 m layer of the Lake water.

The data of this study will contribute in understanding the role of chemical weathering on the vulnerability of the dam to failure on a temporal scale. Multidisciplinary understanding of the dam's vulnerability to failure will also contribute to a more effective prevention and control of the potential hazard, thus Cameroon and Nigeria can continue to secure the friendly geo-political relationship that could be questioned (affected), should the dam collapse (Tassi an Rowet, 2014; Adedeji and Olukorede, 2010).

2. Study area

The Lake Nyos dam is located in the Northern border of Lake Nyos and along latitude 06°26'45"N and Longitude 10°17'45"E as seen in Figure 1. Its length, width, and height are 100, 45, and 40 m, respectively. Those dimensions give it a volume of about ca.180,000 m³. Lithological loggings from 3 boreholes (Fig. 3a) on the dam reveal that the 40 m thick material is made up from bottom to top of ca. 2 m thick altered monzonite (acidic rock), ca. 28 m thick volcanic ash (basic rock), and ca. 12 m thick pyroclastic (basic rock). The overlying pyroclastic deposit is bisected by several fractures trending N40E, which are widened to form potholes of almost 1 m deep on the spillway on the dam (Lockwood et al., 1988). The basic materials on the dam contain ultramafic and granitic xenoliths from gravelly to cobble size. Annual mean humidity, atmospheric temperature, and rainfall depths in the area are 70%, 20°C, and 2000 mm, respectively. Rainwater falls in the

area during the rainy season, when the moisture-laden SE monsoon air blows over the area from March to October, while the dry season lasts from November to May, during which time the NE harmattan air mass blows over the area. The rainwater infiltrates the dam materials as they possess permeability of 10^{-5} m/s (for pyroclastics) and 10^{-7} m/s for compacted ash as reported in Kamtchueng et al. (2014). Interplay of the lithological characteristics of the dam, a preferential flow plane (a lithological unconformity between the overlying pyroclastic basic surges and granitic monzonite) at ca. 40 m, vertical fractures into the pyroclastic materials occupying the first 10 m of the dam, climatic regime around Lake Nyos, and the hydrology of the Lake Nyos catchment, causes water to seep permanently through the lower unit of the dam where there is a contact between the basic (basaltic) and the granitic (monzonite) rocks. During the rainy season ephemeral springs seep from entire cliff surface of the dam.

3. Materials and methods

3.1. Desk study and field work

A total of 17 water samples, 1 altered basaltic rock, 1 fresh monzonite, and 1 altered monzonite were considered for this study. Of the 17 water samples, 10 were collected during this study and data on 7 samples were gotten from literature (Tanyileke, 1994; Tuttle et al., 1987; Kusakabe et al., 2008). Collection of samples was done in March of 2012 and 2013. The sites of location of the water samples that were collected during this study and co-opted from literature are shown in Figure 3b, which also shows that the distribution of collected samples of water and rocks are representative of the lake Nyos dam. Samples from the 3 boreholes were collected at different depths with a borehole sampling device.

From all the water sources, the water to be sampled was initially collected into a bucket that was thoroughly rinsed. Water from the collector was then filled into four sets of new 100 ml capacity plastic bottles after three times of rinsing with the samples. A set of bottles that contained water samples for isotopes (^{18}O , ^2H) analyses were cocked tightly to avoid evaporation that may cause evaporative enrichment of the isotope prior to analyses. Nitric acid (HNO_3) was added to a second set of bottles that contained water samples for major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) analyses. A third set of bottles that contained no nitric acid were filled with water samples for major anions (Cl^- , SO_4^{2-} , NO_3^-) analyses, and the fourth set of bottles were filled with water samples that was used for determining alkalinity (HCO_3^-). Temperature, electrical conductivity (EC), and pH were measured in the field using a portable electrical conductivity meter (pH/EC water proof HANNA, Dist 5) and a portable pH meter (Shindengen, ISFET pH meter KS723). The pH meter was calibrated with pH 4.0 and 6.8 buffer solutions. Dissolved oxygen (DO) was measured using a FUSO DO-5509 dissolve oxygen meter, and ambient temperature was measured using a custom CT-45⁰WR thermometer. Each sample was collected after EC, pH, and temperature values stabilized. The water samples that were collected for analyses of the various parameters

except alkalinity were filtered through a 0.45 μm cellulose filter. During the dry season months of the years 2012 and 2013, monthly discharge measurements of the spring that drains the dam was done using the bucket and stop watch approach (e.g., Fantong et al., 2013).

Rock samples were collected from classified boreholes logs of the Lake Nyos dam (Fig. 3a), which were provided by the Institute of Mining and Geological Research (IRGM) - Yaounde. Fresh basalt was sampled from the cliff of the dam, while altered basalt, altered monzonite, and fresh monzonite were sampled from 0-12 m, 36-40 m, and 50 -54 m of the logs as shown in Figure 3a. The sample collection sites for water samples (springs, boreholes, and Lake) are shown in Figure 3b.

3.2. Analytical method

The measurement of alkalinity for each water sample was performed within 8 – 10 hours after sample collection. During alkalinity measurement, 50 g of water sample was titrated with 0.02N HCl to an end point pH of 4.8. The measurement procedure was done three times for each sample and the average of at least two similar values of the three runs were used for obtaining the alkalinity. The HCO_3^- concentration for each sample was calculated from the titration parameters as explained in Fantong et al. (2009).

Both the water and rock samples were analysed in the laboratory of the Department of Environmental Biology and Chemistry, University of Toyama, Japan. The cations were analyzed with an ion chromatograph (Metrohm 861compact IC) and anions were also analyzed using ion chromatograph (Metrohm 761 compact IC). The reliability of analytical technique was examined using charge balance between cation and anion. The data which is presented in Table 1 plot close to 1:1 line (Fig. 4 ESM Only) with slope of correlation line of 0.93. Dissolved silica was analysed with a UV-VIS spectrophotometer (SHIMADZU UV mini-1240). Hydrogen isotope ratio (D/H) was measured using an on-line chromium reduction technique with a conventional isotope ratio mass spectrometer (PRISM, VG Isotech, UK) as described in Itai and Kusakabe (2004). Oxygen isotopic analysis was done using the automated $\text{H}_2\text{O}-\text{CO}_2$ equilibrium method (Epstein and Mayeda, 1953). The stable isotope ratios were given in conventional delta expression (δ , ‰). The isotopic standards for δD and $\delta^{18}\text{O}$ were VSMOW2 and analytical precisions were $\pm 1\text{‰}$ for δD , $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$.

Weight % oxide of major elements (Si, Al, Ti, Mn, Na, Ca, Mg, K, P) were measured with SHIMADZU EDX (Energy Dispersive X-Ray Spectrophotometer) – 700 HS from 4 gram of rock powder. The detection limits (in wt. %) are 0.9 for SiO_2 , 0.7 for TiO_2 , 0.5 for Al_2O_3 , 0.3 for Fe_2O_3 , 0.05 for MnO, 0.6 for MgO, 0.6 for P_2O_5 .

4. Results and interpretations

4.1. Variation of EC, pH, dissolved silica, water composition, and stable environmental isotopes in sample water

Table 1 presents the chemical compositions and stable environmental isotope (δD and $\delta^{18}O$) ratios of water samples at different depths from three boreholes on the dam, two springs seeping from the dam, Lake Nyos water from 3 depths (0, 30, and 40 m) that are in direct contact with the dam, and rainwater from the Lake Nyos catchment. The EC (in $\mu S/cm$) varied from 19.4-19.9 in the dam spring, 160-250 in the boreholes and 126-134 in the Lake water. The pH values varied from 8.0-8.9 in dam springs, 6.6-7.2 in boreholes, and 7.0-7.3 in lake water. Concentration of dissolved silica (in mg/L) ranged from 15.0-16.3 in dam springs, 9.6-16.8 in Lake water, 9.6-14.9 in boreholes, and 0.49 in rainwater. The obtained concentration of major ions were plotted on Stiff diagrams (Fig. 5), whose shapes showed that sample water from rain and shallow (0-36 m) depths in boreholes were $Ca-HCO_3$ type, sample water from deep (36-45 m) levels of boreholes, dam springs, and Lake water were $Mg-Ca-HCO_3$ type. The variation in the sizes of the Stiff diagram also indicates that rainwater had the lowest mineralization (smallest size), followed by higher mineralization (intermediate sizes) of water in the shallow levels of the boreholes, and highest mineralization (largest sizes) of water from the deepest levels of the boreholes and the dam springs. The discharge of the dam spring was measured in the months of January, February, March, April, May, June, and December, when the lake water does not overflow the spillway of the dam. The observed values of discharge ranged from 4 to 6 litres/second. Using a median (modal) discharge of 5 litres/second for the spring, an annual discharge of ca. 1.6×10^8 litres was obtained.

Hydrogen and oxygen isotope ratios in the sample waters are also shown in Table 1. The $\delta^{18}O$ values ranged from -1.9 ‰ to -1.8 ‰ in the dam springs, -2.6 ‰ to -1.9 ‰ in boreholes, -2.8 ‰ to -1.6 ‰ in rainwater, and -2.7 ‰ to -1.9 ‰ in lake water. The δD values ranged from -9.0 ‰ to -8.0 ‰ in the dam springs, -10.1 ‰ to -4.7 ‰ in boreholes, -12.0 ‰ to -5.7 ‰ in rain, and -15.2 ‰ to -7.5 ‰ in lake water. The observed δ -values are graphically presented in Figure 6 (ESM Only). The distribution of sample points on the delta space showed that about 60 percent of the observed samples plot below and parallel to the Global Meteoric Water Line (GMWL) of Craig (1961) and Nyos Meteoric Water Line (NMWL) of (Kamtchueng, *personal communication*), and 40 percent plot along the GMWL. By considering all the data points, the diagram showed similar isotopic ratio for water from Lake Nyos (from depth range of 0-40 m), the Nyos dam springs and boreholes, suggesting that the dam springs have a remarkable contribution from the Lake water. As the dam springs showed an isotopic similarity with the 1986 Lake water, this indicates that the spring may have a residence time of about 26 years. The estimated residence time was confirmed using CFCs-based data on the spring water which suggests that the spring was recharged between 1987 and 1992 (Kamtchueng, *personal communication*). If the median year of 1990 is considered as the recharge year, then the spring had a residence time of 24 years, which is close to the age of 26 years for the 1986 Lake water at shallow depths that showed similar isotopic values with the dam spring waters, but differed from the other samples (Fig. 6 (ESM only)) due probably to mixing immediately after the eruption. However, waters from the Nyos dam springs and boreholes are also found to be sandwiched between the Nyos rain water and the 2006 Lake water as two end members. Considering a binary mixture the dam spring may represent a mixture of about 30-40 % 2006 lake water and 60-70 % rain water. Such a mixture agrees with the findings of Tuttle et al. (1992) and Lockwood et al. (1988).

4.2. Variation of major oxides (in weight %) in observed rock samples

Table 2a, 2b, and 2c present the major-element oxide (in weight %) in basalt (fresh and altered), Lake Nyos catchment clay, and monzonite (fresh and altered), respectively. Relative variation of the major oxides in the rocks observed is graphically presented in Figure 7 (ESM Only). Both rocks (fresh monzonite and basalt) were compared to their altered equivalents and to the Lake Nyos Catchment Clay (LNCC), which is considered to represent the most altered phase in the vicinity of the study area. The remarkable variations of the major-element oxides in the observed rocks were as follows: From fresh basalt to LNCC (Fig. 7a (ESM Only)), weight percent increase was observed in Al_2O_3 , and TiO_2 , and decrease in CaO , MgO , Na_2O , and SiO_2 . From fresh monzonite to LNCC (Fig. 7b (ESM Only)), weight percent increase was observed in Al_2O_3 , Fe_2O_3 and TiO_2 , and decrease in CaO , MgO . The decreasing pattern in CaO and MgO could explain the observed dominance of Mg and Ca cations in the observed water samples. While the increasing pattern of Al_2O_3 , Fe_2O_3 suggests that they make up the secondary minerals (clay) after incongruent dissolution.

5. Discussions

5.1. Origin and hydrochemical evolution of water seeping from the dam

To assess the origin and hydrochemical process of the Lake Nyos dam spring water, a combination of Piper's diagram (Piper, 1944), Chadha diagram (Chadha, 1999) (Fig. 8a and 8b) and the delta-space diagram shown in Figure 6 were used. From the Piper's and Chadha's diagrams, the waters can be described as fresh and recharging Ca-Mg- HCO_3 waters, which lies along the mixing line of two end members consisting of local rainwater and Lake Nyos epilimnion water. The observation that the spring water origin is a combination of rainwater and Lake Nyos water is confirmed by the isotope plots in Figure 6, which has shown a mixing proportion of about 30-40 % 2006 lake water and 60-70 % rain water. From the recharge to the discharge of the springs, the water evolved from low mineralized Ca- HCO_3 type rainwater to more mineralized Ca-Mg- HCO_3 borehole water due to inputs from either the Mg rich Lake water or incongruent dissolution of ultramafic minerals that constitute the essential minerals in the basic rocks of the dam, or both. The Ca-Mg- HCO_3 water finally discharges as Mg-Ca- HCO_3 water due probably to more input from Lake Nyos water that seeps across the contact (that occur at ca. 40 m depth below the spillway of the dam) between the overlying basaltic rocks and the basement granitic monzonite rock.

5.2. Solute flux

In order to assess the relative flux of the dissolved ions in the dam spring, the solute flux was calculated (e.g., Vuai and Takuyama, 2007). The solute flux (Q_i) for an individual component (i) was calculated by using the following procedure:

$$Q_i (\text{mol km}^{-2}\text{y}^{-1}) = C_i V_t / A \quad (1)$$

Where C_i is annual weighted mean concentration (mol L^{-1}) of spring water in Table 3. V_t is annual average water discharge (L) in Table 1. For the spring that drains the entire Lake Nyos dam, the average discharge for 2 years (2012 and 2013) was used. A is average drainage area of the dam (km^2). The obtained annual flux of chemical species through the dam spring (Table 1) follows the trend $\text{HCO}_3^- > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{SiO}_2 > \text{K}^+ > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$.

The annual flux in chemical species indicates that chemical weathering, which we characterized by determining the degree and type of rock weathering through the calculation of molecular ratio $Re ((SiO_2)/(Al_2O_3))$ (e.g., Ruxton, 1968; Boeglin and Probst, 1998; Gurumurthy et al., 2012; Tardy 1971) in altered monzonite and basalt from the dam. The obtained results were used to characterize the weathering process according to the classification of Pedro (1966): if $Re = 0$, the dominant weathering process is the genesis of gibbsite (called ‘allitization’), if $Re = 2$, kaolinite is essentially formed (‘monosiallitization’), if $Re = 4$, the weathering products are mainly smectites (‘bisiallitization’). Such a weathering index can be calculated for the Nyos dam because the spring that drains from the dam is continuously seeping from the contact between granitic basement rock (monzonite) and basaltic pyroclastic deposit that contains xenolithic blocks of granitic rock. The mean annual Re calculated from the data in Table 2 for the period 2012 and 2013 were 3.35 for altered basalt on the dam, and 5.10 for altered monzonite are presented in Table 3. These values are close to the values of 2 and 4, which correspond to the chemical weathering processes of monosiallitization (formation of kaolinite) and bisiallitization (formation of smectite), respectively, which formed the secondary clay minerals through incongruent dissolution of silicates minerals such as albite, anorthite, forsterite, K-feldspars, and micas that constitute essential minerals in rocks of the study area. Equation 3 represents the typical reaction that occurs during incongruent dissolution of albite in the rocks.

In order to confirm the thermodynamic stability of such secondary minerals coexistent with specific waters, stability diagrams of cation-Si plot (Tardy, 1971; Faure, 1991) were drawn. The diagrams (Fig. 9 (a)-(c)) show that the chemical behaviour of water samples in the area of study is similar to shallow spring waters (Garrels and Mackenzie, 1967), in which the water dissolves plagioclase to form kaolinite (Garrels, 1967). Since the meteoric water contains very little silica and cations, the sample is situated in the far-left corner of the diagrams, where gibbsite [$r-Al(OH)_3$] is the stable mineral. On the other hand, the spring, borehole and lake waters with higher cation/Si ratio than the host rock coexist with kaolinite. The diagrams showed that monosiallitization phase (kaolinite) which was suggested by the classification of chemical weathering above, is coexisting stably with waters in the thermodynamic point of view. In this way, the incongruent dissolution, which controls the cation/Si ratio, was supported by chemical weathering and stoichiometry.

With the occurrence of incongruent dissolution, its effect on the chemical composition of rocks is readily apparent by comparing the concentrations of major-element oxides in fresh and weather samples of a rock (e.g., Faure, 1991). However, such direct comparisons may be misleading because of the ‘close table effect,’ which is the property of chemical analyses, expressed in weight percent, of having to add up to 100. Thus the procedure for identifying changes in chemical composition (real gains and losses of elements) as a result of chemical weathering is based on the assumption that one of the major-element oxide has remained constant in amount even though its concentration may appear to have changed. The constituent chosen most often for this purpose is Al_2O_3 , consistent with the limited solubility of $Al(OH)_3$ at pH values between 6 and 8 (e.g., Eggleston et al., 1987; Claridge and Campbell, 1984). In order to demonstrate the effects of weathering on the chemical composition of rocks, the data in Table 2 was examined for samples of fresh monzonite and basalt, and for samples of altered monzonite and basalt from the Lake Nyos dam. In the case at hand, Al_2O_3 (with its concentration apparently increasing from 71.77 % to 73.22 %, and from 53.03 % to 55.05 % as a result of

weathering of the monzonite and basalt, respectively), was selected as the constant immobile oxide to normalize mobile elements and assessing the effect of leaching. The concentration of a constituent expressed in weight percent is equivalent to an amount in grams per 100 g of rock. Therefore, 100 g of monzonite originally contained 14.3 g Al_2O_3 (Table 2b). If we assume that the amount of Al_2O_3 remained constant, the apparent increase in the concentration of Al_2O_3 must be caused by a reduction in the weight of the rock from 100 g to some smaller amount derivable from the relation

$$\text{Weight of constituent/weight of rock} \times 100 = \% \text{ concentration} \dots\dots\dots (3)$$

In the case under consideration, the weight of the rock is $(14.3/14.36) \times 100 = 99.6$ g, which implies that 0.4 g of rock was removed by weathering from each 100 g of monzonite. The amounts of the other oxide constituents remaining in the altered monzonite were calculated by multiplying their percent concentrations in the monzonite by the weight loss factor (W) derived from the ratio of the concentrations of the constant oxide in the fresh and weathered rock.

$$W = (\text{Al}_2\text{O}_3)_{\text{fresh}} / (\text{Al}_2\text{O}_3)_{\text{weath.}} = 14.3/14.36 = 0.996 \dots\dots\dots (4)$$

where the parenthesis signify concentrations in weight percent of the selected oxide in the fresh and weathered rock, respectively. For, example, the amount of SiO_2 remaining after weathering is $73.22 \times 0.996 = 72.91$ g. All the concentrations of the oxide components of the weathered monzonite in Table 2b were multiplied similarly by the weight-loss factor (W) and the remaining amount that are listed in column 4. These amounts sum to 98.5 g, which indicates that $100 - 98.5 = 1.5$ g of material was lost as a result of weathering per 100 g of original monzonite. The actual gains and losses of each component was then determined by the comparing the data in column 4 (amount remaining) to the analyses of monzonite in column 2 of Table 2b. For SiO_2 we had a real gain of $72.91 - 71.77 = 1.14$ g. The gain or loss of all the element-oxide during chemical weathering is shown on column 5 of Table 2b, which indicate that relative to conservative component (Al_2O_3) chemical weathering caused real losses of CaO , Na_2O , K_2O , P_2O_5 , and gains of SiO_2 , Fe_2O_3 , TiO_2 , MnO , and MgO for monzonite. On the other hand, chemical weathering caused real losses of SiO_2 , Fe_2O_3 , Ca_2O , NaO , MgO , and gains of TiO_2 , K_2O , and P_2O_5 for basalt as shown in Table 2a.

The final step in the evaluation of the obtained element-oxide data is to rank the oxide components in terms of the magnitude of the losses and gains that occurred. For this purposes we express the losses and gains in terms of percent of the amount originally present in the monzonite. For example during the alteration of monzonite, it gained $(1.14/71.77) \times 100 = 1.6\%$ of SiO_2 . The greatest losses in decreasing order occurred for $\text{P}_2\text{O}_5 > \text{Na}_2\text{O} > \text{K}_2\text{O} > \text{CaO}$, while the gains occurred for $\text{TiO}_2 > \text{MnO} > \text{Fe}_2\text{O}_3 > \text{MgO} > \text{SiO}_2$. For incongruent dissolution of basalt the losses occurred for $\text{CaO} > \text{Fe}_2\text{O}_3 > \text{Na}_2\text{O} > \text{MgO} > \text{SiO}_2 > \text{MnO}$, and the gains occurred for $\text{K}_2\text{O} > \text{TiO}_2 > \text{P}_2\text{O}_5$. By calculating the losses and gains between the fresh basalt and a clay sample (Table 2c) that was collected within the Lake Nyos catchment, but away from the dam, the results showed that losses occurred as follows: $\text{CaO} > \text{MgO} > \text{MnO} > \text{P}_2\text{O}_5 > \text{SiO}_2 > \text{Na}_2\text{O} > \text{K}_2\text{O}$, while gains occurred as follows: $\text{Fe}_2\text{O}_3 > \text{TiO}_2$. Evidently, chemical weathering of monzonite and basalt in Lake Nyos dam led to the formation of altered equivalent that is composed of Al_2O_3 , SiO_2 , Fe_2O_3 , and K_2O , while the aqueous phase was enriched in the

component (MgO, CaO) with high losses in the rocks, rendering the water chemistry to be dominated by Mg and Ca cations as seen in Figure 8.

The magnitude of occurrence of losses and gains during chemical weathering depends on intensity of weathering. In this study the weathering index of Parker (PI) (Parker, 1970), which is defined as

$$PI = \left[\frac{2Na_2O}{0.35} + \frac{MgO}{0.90} + \frac{2K_2O}{0.25} + \frac{CaO}{0.70} \right] \dots\dots\dots (5)$$

And the chemical alteration index, CIA (e.g., Nesbit and Young, 1989; Kim and Park, 2003), which is defined as

$$CIA = \frac{Al_2O_3 \times 100}{Al_2O_3 + CaO + Na_2O + K_2O} \dots\dots\dots (6)$$

The calculated CIA and PI values for the observed rock are presented in Table 3. Those values were plotted (Fig. 10) to evaluate the intensity of chemical weathering in the study area. Considering the CIA-based classification of intensity of chemical weathering (e.g., Shao et al., 2012), Figure 10 indicates that in the study area the intensity of chemical weathering vary from weak (50 - 60 CIA unit), to intermediate (65 - 85 CIA unit), and to strong (> 85 CIA unit) in altered basalt, altered monzonite, and Nyos catchment clay, respectively. The weak and intermediate intensities observed on the rocks constituting the dam may be an indicator that the rate of chemical weathering of the dam is slow.

5.3. Rate of chemical weathering and its role on temporal vulnerability of dam to failure

For the estimation of the duration that chemical weathering would take to erode the dam, the rate of chemical weathering was calculated. Chemical weathering rate of silicates (WRch) was calculated from the flux of dissolved silica in spring water (QSiO₂ (kg m⁻²)) presented in Table 3. If the chemical composition of silica in parent rock (So) and of the alteration facies (Ss) are known, then WRch can be estimated using the formula reported by Vuai et al. (2007), and Boeglin and Probst (1998).

$$WRch = QSiO_2 / (So - Ss) \dots\dots\dots (7)$$

The chemical composition of silica (weight %) in the sample rocks from the dam are 71.77 in fresh monzonite, 73.22 in altered monzonite, 53.03 in fresh basalt, and 55.05 in altered basalt and density was taken as 2.6, 1.6, 2.9, and 1.4 ton m⁻³ for fresh monzonite, altered monzonite, fresh basalt, and altered basalt, respectively (Dalai et al., 2002; Vuai and Tokuyama, 2007; Boeglin and Probst, 1998). These give the values of So and Ss equal to 1867 kg/m³, 1172 kg/m³, 1538 kg/m³, and 771 kg/m³ for fresh monzonite, altered monzonite, fresh basalt, and altered basalt, respectively. The specific flux of SiO₂ (QSiO₂) for the dam spring is 4195 kg/km²y. For the Lake Nyos dam materials, the calculations gave the weathering rates of 6 and 5.4 mm/y for monzonite and basalt, respectively as shown in Table 2. For comparison, the results are higher than those for crystalline rock (0.0085, 0.078, 0.063, and 0.048 mm/y) presented by Nkounkou and Probst (1987), but agree with the findings of Boeglin and Probst (1998) in the Niger basin, which includes the Lake Nyos catchment.

Considering that the dam has a total volume of $180,000 \text{ m}^3$ ($100_{\text{length}} \times 40_{\text{thickness}} \times 45_{\text{width}}$) and it is chemically eroded at a rate of 5.7 mm/y ($((6 + 5.4)/2)$), then based on chemical weathering, the estimated time for the dam to be completely eroded is ca. 7000 years.

Assuming that 1) the original length (presently the 45 m width) of the dam was 285 meters (Freeth and Rex, 2000), 2) the thickness was the same as the actual 40 m, and 3) chemical weathering would erode the 45 m wide dam in 7000 year, chemical weathering would reduce the original dam's width from 285 to 45 m in ca. 37000 years. This number of years is higher than the geochronological-base years of 400 (Lockwood and Rubin, 1989), ca. 5000 (Aka et al., 2008), and ca. 8900 (Aka and Yokoyama, 2013). Thus, based on the rate of chemical weathering, the remaining 45 m wide Lake Nyos dam may not be vulnerable to failure within the next 7 millennia. This agrees with the reiteration of Aka and Yokoyama (2013) that the collapse of the dam and the attendant potential flood disaster are not eminent and alarming as previously thought to have occurred by the year 2010 after 5 years from 2005 (UNEP/OCHA, 2005). However, considering that potential dam failure triggers such as physical and chemical weathering of dam failure are natural processes that forever continue to erode the dam, another question of the dam vulnerability to failure, which needs verification is that, what is the threshold width of the dam that can hold back the lake water? In other words, if the $40 \times 1500 \text{ m}$ water lake mass pushes a wall, how much pressure can it generate and what is the minimum width of the wall that can resist the hydrostatic pressure before breaking? These questions are pertinent for assessing the vulnerability of the dam because, it is not the full 45 m width of the dam that needs to erode away before breaking occurs. Thus the question was addressed in 2 steps:

1. Interacting forces on the dam

Considering that the dam has a length (L), height (H) and width (x), the dam is subjected to external interacting forces such as:

- The resultant hydrostatic force ($\vec{F}$) is applied at the centre of the pressurized surface (C) that is located under the centre (O) of the wetted face of the dam. The distance between O and C is equal to $H/6$ (White 2001);
- The weight of the dam ($\vec{P}$) that is applied at a centre of gravity (G);
- The reaction of the ground ($\vec{R}$) that is applied on the face of the dam that is on the opposite of the lake, and at the center of the intersection (B) between the dam and the ground. This reaction generates a normal component ($\vec{N}$) and a tangential component ($\vec{T}$).

The module of the resultant hydrostatic force is given by

$$F = \frac{1}{2} \rho_e g L H^2$$

Where ρ_e is the water density and g is the acceleration of gravity.

In this case, the pressure from the Lake Nyos water (F) was estimated to be = 1.568 GN.

While the module of the weight is gotten by

$$P = \rho_s g L H x$$

Were, ρ_s is the solid density of altered basalt and altered monzonite which is almost equal to $1.5 \text{ ton} / \text{m}^3$. With the measured width (x) of = 45 m, the weight of the dam (P) is = 1.764 GN.

2. Condition of dam's stability

In this case it is assumed that the width of the dam is unknown and the minimum width that can render the dam to be unstable is calculated. From the physical equilibrium of the dam, we obtain that $T = F$, $N = P$,

$$\frac{FH}{3} - \frac{1}{2} \rho_s g L H x^2 = 0$$

Therefore, the minimum width (x) of the dam that can resist the calculated hydrostatic pressure of 1.6 GN and still be stable is

$$x = H \sqrt{\frac{\rho_e}{3\rho_s}}, \text{ thus } x = 19 \text{ m.}$$

The obtained values indicate that the pressure generated by 40 m depth of water at Lake Nyos is about 1.6 GN, and after considering both rotational and translational motions the minimum width of the Lake Nyos dam that is expected to resist the obtained hydrostatic pressure without failing is about 19 m, thus if the width of the dam reduce to less than 19 m, then the dam will collapse as a function of hydrostatic pressure.

Although Evans et al. (2012) stated that the re-enforcement of the natural dam by the Cameroon Government and the European Union shall only reduce the possibility of the dam to collapse, the findings of this study suggest that the dam is not vulnerable to failure so soon based on the rate of chemical weathering. However, some other processes inevitably occur which weaken the dam and can cause instant failure: (1) physical weathering (rock fall), (2) changes in hydraulic and rock mechanical properties, (3) secondary mineral formation, and (4) lake overflow.

Considering that the reaction between CO_2 -water- and concrete that is used to re-enforce the dam may alter the natural signature of chemical weathering, a temporal monitoring of both physical and chemical weathering is advocated after the artificial re-enforcement of the dam. Hence, simulation was done in order to have a pre-knowledge of hydrogeochemical evolution on a time scale in the study area.

5.4. Simulation of water-rock interaction

To assess the role of the chemical weathering on the evolution of the dissolved components and production of secondary minerals (kaolinite, brucite, hematite, and calcite) with time, we simulated the evolution of the hydrochemistry and secondary mineral assemblages in the Lake Nyos dam system using the initial composition of the spring (in Table 1) that drains water from the dam. The primary and secondary phases in the study area

were selected from literature (Aka et al., 2008) and determined petrographically from (Fantong, unpublished data). While the chemical composition of quartz, albite, anorthite, clinocllore, apatite, muscovite, phlogopite, calcite, zircon were taken from the data base of Lawrence Livermore Natural Laboratory (LLNL.DAT) because it is a huge database with many mineral phases and temperature dependent equilibrium constants. The evolution of hydrochemistry and solid phases were simulated for a duration of 10 years and assuming a temperature of 25°C, using the kinetic reactions of PHREEQC (version 2) (Parkhurst and Appelo 1999). The results of the simulation are show in Fig. 11 indicates a single rise from acidic pH of 6.3 to a slight dropping circum-neutral pH with time (Fig. 11a), which may be reflecting the drop and in CO₂, over time as shown in Table 4. As the pH varies within the acidic to circum neutral range, the water remains aggressive and scavenges more cations and silica from the silicates. Finally, interaction between the dissolved cations and the newly formed secondary minerals (clay) shall enhance cation exchange that may cause observed decoupling of Ca and Mg, and Na and Mg as shown in Figure 11b. Figure 11b also shows that in present time the relative pattern (in decreasing order) of the dissolved ions is Mg > Ca > Na, reflecting the pattern observed during his study, but after 10 years (the duration considered for this simulation), the pattern (in decreasing order) of dissolved ions could be Ca > Na > Mg. Dissolved Fe, Si, and Al are also shown to have an increasing pattern over time (Fig. 11c), suggesting that the water may remain under saturated with respect to iron phases, and clay minerals as shown in Table 4, thus favouring the continuous formation of secondary phases such as kaolinite and brucite , although the iron phase (hematite) remains unchanged as shown in Figure 11d.

The above simulation also indicates that when water-rock interaction progresses, Ca²⁺ is emitted into solution and Mg²⁺ is absorbed into the ion exchangeable clay minerals, such as smectites (Garrels and Christ, 1965), by the following reaction

To test the validity of the results of the simulation, we propose that although the dam is undergoing re-enforcement based on the effect of physical erosion, temporal monitoring should continue on the dam for chemical weathering and water/ rock interaction, which shall continue to occur indefinitely.

6. Conclusions and recommendation

- The origin of the spring water is a mixture of about 60 - 70 % rainwater and 30 - 40 % Lake Nyos water with chemistry that evolves from Ca-HCO₃ type in rainwater to Ca-Mg-HCO₃ in borehole water and finally to Mg-Ca-HCO₃⁻ spring water.
- The annual flux of chemical species through springs follows the following trend HCO₃⁻ > Mg²⁺ > Ca²⁺ > Na⁺ > SiO₂ > K⁺ > NO₃⁻ > SO₄²⁻ > Cl⁻ for the Lake Nyos dam.
- The mean annual degree of rock weathering calculated from the molecular ratio (Re) for the period 2012 and 2013 are 3.35 for altered basalt, and 5.10 for altered monzonite, which correspond to the incongruent dissolution of monosiallitization (formation of kaolinite) and bisiallitization (formation of smectites).

- The Chemical Intensity of Alteration index (CIA) values of 50 - 60 in altered basalts, 65 - 85 in altered monzonite, and > 85 in Nyos catchment clay, indicate that the intensity of chemical weathering vary from weak to intermediate in the dam, and vary from weak to strong in the Lake Nyos catchment.
- Alumina (Al_2O_3) normalized mass balance calculations showed depletion of CaO, Na_2O , K_2O , P_2O_5 and enrichment of SiO_2 , Fe_2O_3 , TiO_2 , MnO and MgO in monzonite, and depletion of SiO_2 , Fe_2O_3 , Ca_2O , NaO, MgO and enrichment of TiO_2 , K_2O and P_2O_5 in basalt.
- The weathering rates were estimated at 6 and 5.4 mm/y for monzonite and basalt, respectively. If an average rate of 5.7 mm/y is considered, then based on chemical weathering, it would take about 7000 years for the dam to be completely eroded. Paired to the calculated rate (5.7 mm/year) of chemical weathering, which indicates that the dam is not vulnerable to failure at the previously thought time scale, some other processes inevitably occur which weaken the dam and can cause instant failure: (1) physical weathering (rock fall), (2) changes in hydraulic and rock mechanical properties, (3) secondary mineral formation, (4) lake overflow.
- The pressure generated by the 40 m depth of water at Lake Nyos is about 1.6 GN, and after considering both rotational and translational motions the minimum width of the Lake Nyos dam that is expected to resist the obtained hydrostatic pressure without failing is about 19 m.
- The observed trends of the 10 years simulation of hydrogeochemistry of the dam showed that: a) cation exchange may eventually cause decoupling of Ca and Mg, and Na and Mg; b) At present time the relative pattern (in decreasing order) of the dissolved ions in the observed water is $\text{Mg} > \text{Ca} > \text{Na}$, but after 10 years the pattern (in decreasing order) could be $\text{Ca} > \text{Na} > \text{Mg}$; c) Dissolved Fe, Si, and Al increase over time, thus favouring the continuous formation of secondary phases such as kaolinite and brucite; d) as water-rock interaction progresses, Ca^{2+} is emitted into solution and Mg^{2+} is absorbed into the ion exchangeable clay minerals, such as smectites; e) pH varies within the acidic to circum-neutral range, thus the water remains aggressive and scavenges more cations and silica from the silicates.
- Chemical weathering would reduce the original (285 m) to actual (45 m) width in ca. 37000 years, which is higher than the geochronological-base years of 400, 5000 and 8900, thus, based on the rate of chemical weathering, the Lake Nyos dam is not vulnerable to failure as soon as purported and the attendant potential flood disaster may not be eminent and alarming as previously thought.
- Considering that the reaction between CO_2 -water- and concrete that is used to re-enforce the dam may alter the natural signature of chemical weathering, a temporal monitoring of both physical and chemical weathering is advocated after the artificial re-enforcement of the dam. That way the dam-based geopolitical constraints between Cameroon and Nigeria could be transformed into a win-win multidisciplinary scientific collaboration in the near future.

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Figure captions

Fig. 1: Location of Lake Nyos dam in Cameroon. The locations of three boreholes where water samples and boring logs were collected are also shown.

Fig. 2 (ESM-Only): Spatial distribution of CO₂ concentration (efflux) in shallow water of Lake Nyos. The distribution shows that the highest efflux occurs in water that is in direct contact with the dam.

Fig. 3a: Downstream cliff face of Lake Nyos dam, and litholog variation from the three boreholes on the dam. The boring core of 54 m thick from borehole 1 is shown. The digits (1, 2, and 3) represent sample collection sites: The altered basaltic material (volcanic ash) was collected from core that was extracted at 211 m. The altered monzonite and fresh monzonite were collected from 42 and 53 m, respectively. Msp represents the main spring that drains the dam.

Fig. 3b. Location of sample collection sites in the study area. Discontinuous circle represents dam spring sample sites. Full circle represents sample sites from boreholes. Full diamonds represents sites (0, -30, and - 40 m) of samples that were considered from Lake Nyos.

Fig. 4 (ESM-Only). Reliability of analytical technique measured by charge balance between total cation and anion.

Fig. 5. Stiff diagrams showing relative concentration of dissolved ions in observed samples. Their shapes show that sample water from rain and shallow (0-36 m) depths in boreholes were Ca-HCO₃ type, sample water from deep (36-45 m) levels of boreholes, dam springs, and Lake water were Mg-Ca-HCO₃ type.

Fig. 6 (ESM Only). The delta-space plot δ -values of δD ‰ and $\delta^{18}O$ ‰. The distribution of sample points on the delta space showed that about 60 percent of the observed samples plot below and parallel to the Global Meteoric Water Line (GMWL) of Craig (1961) and Nyos Meteoric Water Line (NMWL) of (Kamtchueng, Unpublished data), and 40 percent plot along the GMWL.

Fig. 7 (ESM-Only). Variation of major-element oxide (weight %) in (a) fresh basalt, altered basalt and Lake Nyos catchment clay (LNCC), (b) fresh monzonite, altered monzonite, and LNCC.

Fig. 8. A. Piper diagram describing the chemical composition of water samples for Lake Nyos dam. B. Chadha diagram describing geochemical classification of different hydrochemical processes in the water samples. Units in X and Y ordinates are in milliequivalent percentages.

Fig. 9. Stability diagrams at 25°C. (a) Albite system, (b) Anorthite system, (c) Microcline system.

Fig. 10. Correlation between the CIA and PI in fresh basalt, altered basalt, fresh monzonite, altered monzonite, and LNCC.

Fig. 11. Kinetic simulation for 10 years on the evolution of (a) pH, (b) Na, Mg, and Ca (c) Fe, Al, and Si, and (d) Secondary mineral phases (kaolinite, brucite, and hematite).

Table captions

Table 1. Chemical and isotopic composition of sample waters and flux of dissolved ions from water (dam spring) that drains the entire dam.

Table 2a. Comparison of chemical analyses (Major element-weight %) of basalt and its altered equivalent from lake Nyos dam.

Table 2b. Comparison of chemical analyses (Major element-weight %) of monzonite and its altered equivalent from lake Nyos dam.

Table 2c. Comparison of chemical analyses (Major element-weight %) of basalt and weathering product (LNCC) from lake Nyos dam.

Table 3. CIA, PI, Re, and WRch of rocks from the Lake Nyos dam.

Table 4a. PHREEQC simulated values of pH, and chemical components, over a period of ten years.

678 Table 4b. PHREEQC simulated values of secondary minerals and si (saturation indices) with respect to selected
679 phases over a period of ten years.

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681

682

Table 1.

Sample name	pH	Te mp.	EC	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	HCO ₃ ⁻	TA	TC	Si	Al ³⁺	Disch.	δD	δ ¹⁸ O	Source
		°C	μS/cm	mg/l								meq/l		mg/l	μg/l	L/S	‰		
Nr1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nc	nc	nm	nm	nm	-5.7	-1.6	a
Nr2	6.8	nm	11	1.99	0.40	0.99	bd	1.42	0.97	1.24	4.0	0.09	0.10	0.49	nm	nm	-12	-2.8	TS
Bh1(-14)	7.01	23.0	26.4	31.35	25.29	8.86	3.85	4.61	0.85	11.28	123.8	2.35	2.30	9.62	nm	nm	-4.7	-1.9	TS
Bh1(-26)	6.74	23.1	230	30.86	22.61	8.70	4.69	3.89	0.73	8.62	126.9	2.33	2.20	10.09	nm	nm	nm	nm	TS
Bh1(-44)	6.50	23.4	250	31.97	22.31	7.50	2.98	1.15	0.82	0.92	120.0	2.12	2.10	14.96	nm	nm	-	-2.6	TS
																	10.1		
Bh2(-12)	7.25	23.2	14.8	25.49	19.96	5.79	3.12	1.42	1.64	6.82	95.8	1.73	1.79	9.57	nm	nm	nm	nm	TS
Bh2(-34)	7.11	22.2	189	32.06	19.69	6.63	3.18	0.50	0.71	1.17	116.5	1.95	1.98	13.35	nm	nm	-7.1	-2.3	TS
Bh3(-18)	6.60	23.1	17.1	27.81	16.40	6.25	3.15	0.52	0.63	0.95	126.9	1.80	1.72	12.27	nm	nm	-7.4	-2.1	TS
Bh3(-40)	6.90	22.8	160	28.78	16.78	6.05	2.95	0.26	0.59	0.92	103.1	1.71	1.74	14.86	nm	nm	-6.8	-2.2	TS
LN (0)*	7.27	25.5	140	24.05	7.78	5.72	3.00	0.71	1.94	2.91	56.1	1.00	1.24	9.63	nm	nm	-	-2.0	a, b
																	10.4		
LN (-30)*	5.90	21.9	278	39.99	50.01	9.06	4.00	1.06	0.97	3.11	209.3	3.52	3.55	9.57	nm	nm	-9.7	-1.9	a, b
LN (-40)*	5.44	21.9	512	51.99	63.21	11.95	5.00	0.68	0.97	0.01	302.0	4.97	4.54	16.79	nm	nm	-7.5	-2.0	a, b
LN (0)†	nd	23.5	126	12.82	16.04	4.38	1.95	0.85	0.59	0.74	73.2	1.24	1.21	nd	nm	nm	-15	-3.0	c
LN (-30)†	nd	22.0	130	12.82	15.54	3.87	1.90	0.28	0.97	0.62	73.2	1.22	1.17	nd	nm	nm	-15	-2.4	c
LN (-40)†	nd	21.9	134	12.82	15.06	4.10	1.95	0.38	0.81	0.75	73.2	1.23	1.16	nd	nm	nm	-15	-2.7	c
Dam sp 1	8.91	19.9	19.4	42.49	25.50	7.42	5.05	0.52	8.17	0.94	147.1	2.52	2.56	16.25	nm	nm	-9	-1.9	TS
Dam sp 2	8.03	20.2	19.9	41.72	25.62	8.57	6.30	0.41	3.88	2.65	144.0	2.45	2.63	15.01	25.2	5	-8	-1.8	TS
Flux of ion				13982	13984	5173	2796	140	559	560	32159			4195					

Flux of ion in kg/km²y⁻¹. Temp.= water temperature. EC = electrical conductivity. TA = Total anion. TC =Total cation. Disch. = Discharge. Nm = not measured. Nd = not data. Bd = below detection. Nd = not detected. L/S = Liters/second. Nr = Nyos rain. Bh = borehole. LN = Lake Nyos. Sp = spring. a = Tanyileke (1994). B =Tuttle et al. (1987). C = Kusakabe et al. (2008). TS = This study. The bracketed values under the SN column represent depths (in meters) to water collection point. † = data generated in 2006 (after commencement of degassing at Lake Nyos). * = data was generated in 1986 and 1994 (before degassing of Lake Nyos commenced). The ionic flux was calculated for *Dam Sp 2* only, because it drains the entire dam.

Table 2a

	Fresh basalt (%)	Altered basalt (%)	Amount remaining (g)	Gain (+) or loss (-) (g)	Gain (+) or loss (-) (%)
SiO₂	53.03	55.05	47.38	-5.65	-10.66
Al₂O₃	14.14	16.43	14.14	0.00	0.00
CaO	14.04	10.53	9.06	-4.98	-35.45
MgO	0.22	0.25	0.22	0.00	-2.20
Na₂O	1.7	2.53	2.18	0.48	28.08
K₂O	6.68	4.56	3.92	-2.76	-41.25
Fe₂O₃	4.08	3.76	3.24	-0.84	-20.69
MnO	4.61	4.22	3.63	-0.98	-21.22
TiO₂	0.38	1.37	1.18	0.80	210.28
P₂O₃	0.27	0.33	0.28	0.01	5.19
Sum	99.15	99.03	85.23		

Table 2b

	Fresh monzonite (%)	Altered monzonite (%)	Amount remaining (g)	Gain (+) or loss (-) (g)	Gain (+) or loss (-) (%)
SiO₂	71.77	73.22	72.91	1.14	1.59
Al₂O₃	14.3	14.36	14.30	0.00	0.00
CaO	2.49	4.2	4.18	1.69	67.97
MgO	0.04	0.08	0.08	0.04	99.16
Na₂O	0.32	0.98	0.98	0.66	204.97
K₂O	1.48	1.2	1.19	-0.29	-19.26
Fe₂O₃	0.48	0.72	0.72	0.24	49.37
MnO	2.77	1.18	1.18	-1.59	-57.58
TiO₂	6.25	2.95	2.94	-3.31	-53.00
P₂O₃	0.11	0.04	0.04	-0.07	-63.79
Sum	100.01	98.93	98.52		

Table 2c

	Fresh basalt (%)	LNC clay (%)	Amount remaining (g)	Gain (+) or loss (-) (g)	Gain (+) or loss (-) (%)
SiO₂	53.03	35.1	28.92	-24.11	-45.46
Al₂O₃	14.14	40.35	33.25	19.11	135.12
CaO	14.04	17.04	14.04	0.00	0.00
MgO	0.22	0.08	0.07	-0.15	-70.04
Na₂O	1.7	2.98	2.46	0.76	44.43
K₂O	6.68	0.09	0.07	-6.61	-98.89
Fe₂O₃	4.08	0.26	0.21	-3.87	-94.75
MnO	4.61	3.41	2.81	-1.80	-39.05
TiO₂	0.38	0.37	0.30	-0.08	-19.77
P₂O₃	0.27	0.12	0.10	-0.17	-63.38
Sum	99.15	99.8	82.23		

LNC: Lake Nyos catchment

Table 3

	CIA (%)	PI	RE	WRch (mm/year)
Fresh basalt to altered basalt	72	-	-	5.4
Fresh basalt to Lake Nyos catchment clay	92	-	-	-
Fresh monzonite to altered monzonite	46			6
Altered basalt	55	44	3.4	-
Nyos catchment clay	91	23	1	-
Altered monzonite	73	21	5.1	-

CIA: Chemical Index of alteration, PI: Parker Index, Re: Weathering Index, WRch: Rate of chemical weathering.

Table 4a.

Time	pH	pe	Na	K	Mg	Ca	Fe	Si	Al
(Second)			(mol/L)						
3.00E+00	6.35	12.13	3.74E-04	1.61E-04	1.05E-03	8.48E-04	1.80E-12	2.49E-04	2.54E-09
3.00E+02	6.55	12.11	3.74E-04	1.61E-04	1.05E-03	8.32E-04	1.80E-12	2.50E-04	2.59E-09
3.00E+03	6.67	11.98	3.76E-04	1.61E-04	1.06E-03	6.82E-04	1.78E-12	2.61E-04	3.14E-09
3.00E+04	7	9.33	4.29E-04	1.61E-04	8.12E-04	1.53E-05	5.54E-12	4.04E-04	6.42E-07
3.00E+05	7.55	7.39	6.96E-04	1.61E-04	4.21E-07	1.72E-03	1.65E-10	1.16E-03	2.07E-04
3.00E+06	7.53	7.40	6.96E-04	1.61E-04	4.32E-07	1.76E-03	1.64E-10	1.30E-03	1.81E-04
3.00E+07	7.51	7.44	6.96E-04	1.61E-04	5.15E-07	2.10E-03	1.52E-10	2.22E-03	9.13E-05
3.00E+08	7.5	7.46	6.96E-04	1.61E-04	5.68E-07	2.31E-03	1.46E-10	2.76E-03	6.79E-05

Table 4b.

Time (Second)	pH	kaolinite	Brucite	Hematite	si_Siderite	si_kaolinite	si_Brucite	si_Goethite	si_Hematite	si_Smectite	si_Quartz
		(mol/L-water)									
3.00E+00	6.35	6.89E-07	0.00E+00	2.76E-07	-1.62E+01	0.00E+00	- 4.62E+00	-4.84E-01	0.00E+00	-5.27E+00	5.20E-01
3.00E+02	6.55	2.28E-05	0.00E+00	2.76E-07	-1.62E+01	0.00E+00	- 4.60E+00	-4.84E-01	0.00E+00	-5.24E+00	5.22E-01
3.00E+03	6.67	2.24E-04	0.00E+00	2.76E-07	-1.64E+01	0.00E+00	- 4.37E+00	-4.84E-01	0.00E+00	-4.94E+00	5.40E-01
3.00E+04	7	2.25E-03	3.02E-04	2.76E-07	-1.89E+01	0.00E+00	0.00E+00	-4.84E-01	0.00E+00	-2.63E-01	4.51E-01
3.00E+05	7.55	5.27E-03	1.11E-03	2.76E-07	-2.38E+01	0.00E+00	0.00E+00	-4.84E-01	0.00E+00	-1.68E+00	-4.31E-01
3.00E+06	7.53	5.33E-03	1.11E-03	2.76E-07	-2.38E+01	0.00E+00	0.00E+00	-4.84E-01	0.00E+00	-1.55E+00	-3.77E-01
3.00E+07	7.51	5.71E-03	1.11E-03	2.76E-07	-2.38E+01	0.00E+00	0.00E+00	-4.84E-01	0.00E+00	-8.99E-01	-1.12E-01
3.00E+08	7.5	5.93E-03	1.11E-03	2.76E-07	-2.38E+01	0.00E+00	0.00E+00	-4.84E-01	0.00E+00	-6.29E-01	0.00E+00

Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 4

Figure 5

Figure 6

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Figure 9a

Figure 9b

Figure 9c

Figure 10

Figure 11a

Figure 11b

Figure 11c

Figure 11d