

# The evolution of thermal structure and water chemistry in Lake Nyos

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## Abstract

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We collected a time series of physical and chemical data to gain a better understanding of the dynamics of Lake Nyos. Measurements of water and gas chemistry, and temperature made during January, March, and May 1987 are compared to data taken in September 1986 just after the initial CO<sub>2</sub> gas release. There is no pattern of change in overall heat content of the lake, although heat input to bottom waters (185-208 m) has occurred at a rate of 1600 mW m<sup>-2</sup>. This increase in heat content translates to a change from 23.38 to 24.12°C at 200 m and can be explained by geothermal heat flow and addition of thermal spring water. Concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Fe<sup>2+</sup> and alkalinity have increased only in bottom waters. In situ lake processes such as sulfate and iron reduction are unable to account for the changes in alkalinity. Observed chemical changes are consistent with a scenario where slightly thermal soda water is being input to the bottom of the lake. Measurements of pCO<sub>2</sub> at depth ranged from 18 to 28% of saturation and exhibited horizontal variability. Overall recharge of CO<sub>2</sub> in bottom waters is negligible. Mainly because of increasing ion concentrations in bottom water, total stability of the water column increased 33% from 48,800 J m<sup>-2</sup> in September 1986 to 64,700 J m<sup>-2</sup> in May 1987. As long as CO<sub>2</sub> concentrations remain the same, this level of stability is higher than could be disrupted by common limnologic or meteorologic processes. There is thermal and chemical evidence that a buildup of dissolved iron and CO<sub>2</sub> in bottom waters must have preceded the August 1986 gas release. In addition, a survey of all crater lakes in Cameroon indicates that only Lakes Nyos and Monoun contain high concentrations of dissolved iron and CO<sub>2</sub>. Thus there is a low probability of any other Cameroonian lake releasing a substantial volume of CO<sub>2</sub>.

## Introduction

On August 26, 1986 an enormous volume of CO<sub>2</sub> was released from Lake Nyos that killed about 1700 people (see papers in this volume). Two possible explanations for this event center around a limnologic hypothesis (Kling et al., 1987) and a volcanic eruption hypothesis (Tazieff et al., 1987). This rare natural disaster is complex, little understood, and difficult to

study. By characterizing basic properties and processes in this system, we hope to resolve questions about the state of the pre-event lake, the mechanism of gas release, and any future dangers.

As a form of introduction, we summarize the analyses and conclusions made by the American Scientific Team studying the event (Kling et al., 1987; Tuttle et al., 1987). On the basis of <sup>14</sup>C, He and δ<sup>13</sup>C-CO<sub>2</sub> data from dissolved gas

in the lake it is apparent that most of the CO<sub>2</sub> released during the event was magmatic in origin. However, undisturbed sediment and clear water at depth, low water temperatures, absence of acid gases, and the low sulfur nature of the system indicate that no major volcanic eruption occurred. Much if not all of the CO<sub>2</sub> released was stored in the lake prior to the event. Accumulation of CO<sub>2</sub> in the lake starts when CO<sub>2</sub>-rich gas of magmatic origin rises to the Earth's surface and contacts groundwater. Oxygen and hydrogen isotope data plus the relative proportions of solutes in surrounding springs suggest a common origin for ground and lake water. This common origin is consistent with the hypothesis of groundwater transfer of dissolved CO<sub>2</sub> into the lake. In addition, measured values of <sup>18</sup>O and <sup>2</sup>H indicate that evaporative concentration is not responsible for the greater concentrations of major ions in Lake Nyos relative to other Cameroonian crater lakes. Post-event depth profiles of major ions imply that stable stratification existed before the release, and that only partial mixing of lake waters occurred during the release.

The trigger mechanism responsible for the gas release from the lake is unknown but has received much speculation. We know of no data that require as an explanation a single, specific trigger mechanism. In fact, if *p*CO<sub>2</sub> levels were near saturation prior to the event, almost any physical process common in lakes could have moved water vertically enough to cause local oversaturation and thus initiate the release.

Pathological studies indicated that victims rapidly lost consciousness and died of CO<sub>2</sub> asphyxiation. There was no evidence for chemical burns on victims or survivors as would be expected from volcanic sulfur gases, and Kusakabe et al. (1989, this issue) provide further chemical evidence against the possibility of such burns. The skin lesions were attributable to some combination of the following: (1) exposure to a direct heat source such as a cooking fire; (2) pressure sores from prolonged lying in a fixed position; (3) post mortem decomposi-

tion; and (4) sores that predated the event. Observed skin blisters were associated with extended unconsciousness, similar to symptoms found in comatose drug overdose patients (Baxter and Kapila, 1989, this issue).

One intriguing aspect of the Lake Nyos gas release and a similar but smaller release of CO<sub>2</sub> from Lake Monoun (Sigurdsson et al., 1987) is that both events occurred in August and were only two years apart. There are recent trends of decreasing air temperature and insolation relative to long-term means in this region of Cameroon. These trends suggest that weakening of lake stratification, coupled with a predictable yearly interval of reduced lake stability during August, may be responsible for the timing of these events (Kling, 1987a).

The purpose of this paper is to describe the evolution of thermal structure and water chemistry in Lake Nyos. From this we hope to better define the location of gas before the release, the possible triggers and the mechanism of gas release, and the potential for future releases of CO<sub>2</sub>. Site descriptions of Lake Nyos and the surrounding area are given in Kling et al. (1987) and papers in this volume.

## Methods

Temperature was measured with a recently calibrated thermistor ohm-meter combination interconnected by 4-conductor cable (Sass et al., 1981; accuracy=0.1°C, precision=0.001°C). Water samples were collected with a PVC Niskin or van Dorn bottle and filtered through 0.1 μm filters in the field. Conductivity, pH, and alkalinity by potentiometric titration were also measured in the field. Non-carbonate alkalinity was measured on selected samples and was always <2% of total alkalinity. The pH values of deep water samples were affected strongly by CO<sub>2</sub> degassing. In these samples pH was calculated using measured HCO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> concentrations and was always higher than 5.10. Water for oxygen analysis was fixed immediately with Winkler reagents and

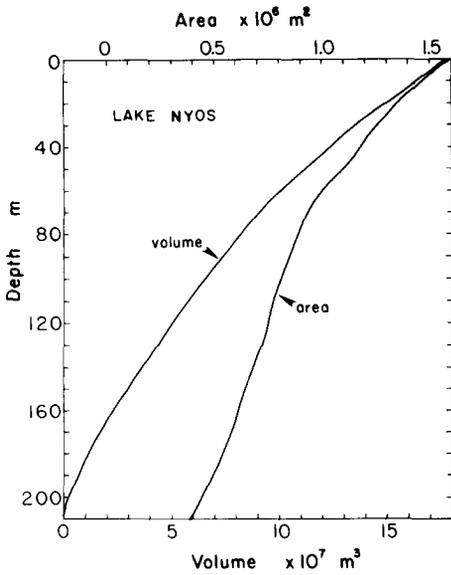


Fig. 1. Hypsographic curve and depth-volume relationship for Lake Nyos.

titrated with phenylarsine oxide within six hours of collection. Dissolved gases were collected in situ using evacuated stainless steel cylinders. The cylinders were depressurized in the lab and gases collected and analyzed using procedures similar to those used by Evans et al. (1988). Collection of dissolved gases in pressurized cylinders, as opposed to collection of bubbles from samplers brought to the surface, eliminates errors caused by differing gas solubilities. Major anions were analyzed by ion chromatography. Water samples for major cations were acidified in the field using HCl and analyzed by atomic absorption or induction-coupled plasma spectrophotometry. Major ions in water collected in the pressurized cylinders were analyzed similarly. Ammonium was determined by specific ion electrode in the field. Values for  $\delta^{13}\text{C}-\Sigma\text{CO}_2$  and  $\delta^{13}\text{C}-\text{CH}_4$  were determined on a Finigan MAT 251 mass spectrometer.

Ion and solid phase chemical equilibria were calculated using the computer program PHREEQE (Parkhurst et al., 1980). Calculations involving water masses were made using the hypsographic curve and depth-volume rela-

tionship presented in Figure 1. Water density, lake stability, and  $\text{CO}_2$  fugacity were determined using methods detailed in Appendix 1.

## Results and discussion

### Temperature and heat content

All temperature profiles taken since the event are similar in overall character to the May 1987 profile presented in Figure 2. Temperatures decrease with depth until they reach a subsurface minimum, and then they steadily increase with depth to the bottom. In September 1986 the thermocline was weak and poorly defined. Water temperature began to increase slightly at a depth of  $\sim 5$  m and the water was anoxic below 10 m. By January 1987 a thermocline had developed at 7 m and below 11 m water temperature began to increase. In May 1987 a thermal structure more typical of an undisturbed lake existed. The thermocline had deepened to 11 m and a distinct upper mixed layer (epilimnion) had developed. At this time increases in water temperature began at 22 m and dissolved oxygen was present to 15 m.

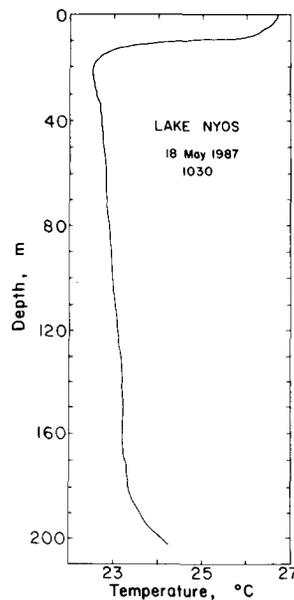


Fig. 2. Temperature versus depth for Lake Nyos.

The phenomenon of increasing water temperature with depth in Lake Nyos exists due to controls on water density by chemical stratification. Heat accumulates in bottom waters (hypolimnion) because geothermal heat flux to the surface is slowed by strong density gradients and low eddy diffusion (see Turner, 1973). At present in Lake Nyos, calculated Brunt-Väisälä frequencies (a measure of stratification strength) approach  $\approx 10^{-3} \text{ s}^{-1}$  across the density boundary between depths of  $\sim 5\text{--}15$  m. These frequencies correspond to low eddy diffusion rates compared to rates in other stratified lakes (Quay et al., 1980). Before the event, density gradients would have been even stronger between dilute surface water (conductivity =  $40.5 \mu\text{S cm}^{-1}$ ; Kling 1987b) overlying a hypolimnion close to saturation with  $\text{CO}_2$ . In Lake Nyos dissolved  $\text{CO}_2$  accounts for most of the increase in water density with depth. In such a situation of stable stratification, a geothermal heat flow similar to a global average of about  $50 \text{ mW m}^{-2}$  (Čermák et al., 1984) would take 100 years to accumulate the excess heat found below 55 m after the event, compared to the heat content of an isothermal temperature profile. This time value assumes no heat loss by vertical diffusivity, but also ignores any heat input from thermal springs. It shows that it is quite possible for the observed temperature profile to develop once strong chemical stratification was established. Thus the inverse temperature stratification in Lake Nyos argues for stable stratification and accumulation of  $\text{CO}_2$  well before the August 1986 gas release.

Changes in thermal structure from September 1986 to May 1987 have been small except near the surface and close to the lake bottom. Surface waters followed the general pattern of seasonal change in temperatures in this region (Kling, 1987a) by cooling from September to January and then warming from January to May. Mean temperature values at the middle depths (65–175 m) deviated little between dates (Table 1). However, temperature below  $\approx 185$  m has increased steadily since September 1986.

TABLE 1

Lake Nyos water temperature at selected depths in September 1986, January 1987 and May 1987

Depth (m)	Temperature ( $^{\circ}\text{C}$ )		
	September $N=2$	January $N=3$	May $N=4$
55	22.875	22.796(0.003)	22.770(0.058)
65	22.875	22.817(0.004)	22.793(0.057)
75	22.900	22.850(0.001)	22.830(0.060)
85	22.925	22.880(0.004)	22.870(0.056)
95	22.950	22.921(0.005)	22.915(0.053)
105	23.125	22.960(0.004)	22.959(0.053)
115	23.400	23.020(0.010)	23.021(0.057)
125	23.113	23.070(0.009)	23.078(0.054)
135	23.163	23.122(0.003)	23.133(0.053)
145	23.188	23.182(0.005)	23.172(0.054)
155	23.225	23.197(0.003)	23.184(0.056)
165	23.225	23.202(0.001)	23.190(0.053)
175	23.275	23.210(0.001)	23.210(0.055)
185	23.275	23.270(0.021)	23.358(0.060)
190	23.325	23.312(0.029)	23.468(0.039)
195	23.338	23.486(0.042)	23.698(0.055)
200	23.375	23.689(0.149)	24.121(0.042)
204	23.438	23.936(0.077)	24.158(0.052)

Standard deviation of the mean given in parentheses.

The corresponding mean increase in heat content of the 185–208 m layer was calculated using temperature profiles taken in various parts of the lake. Heat content increased from  $236.7 \text{ kJ cm}^{-2}$  (mean of two measurements) in September to  $238.2 \text{ kJ cm}^{-2}$  ( $N=3$ ,  $\text{S.D.}=0.45$ ) in January and finally to  $240.3 \text{ kJ cm}^{-2}$  ( $N=4$ ,  $\text{S.D.}=0.52$ ) in May. A regression equation describing this change over 256 days is significant at the  $P<0.0001$  level and is given by  $\text{HEAT} (\text{kJ cm}^{-2}) = 236.5 + (14.14 \cdot \text{DAY})$ ,  $r^2=0.91$ . Thus the heat flow into the lake required to account for these significant changes in heat content must be about  $1600 \text{ mW m}^{-2}$ . The magnitude of geothermal heat flow below Lake Nyos is unknown; this value of  $1600 \text{ mW m}^{-2}$  is higher than the range of  $20\text{--}130 \text{ mW m}^{-2}$  found in various settings worldwide (Čermák et al., 1984; Beck, 1985).

A second potential source of this heat is from advection of thermal groundwater. Thermal soda springs in Cameroon can reach tempera-

tures of 74 °C (Marechal, 1976). In May 1987 we sampled the Ahoy Ekenzu spring (number 94 in Marechal, 1976), which had a chemistry similar to that of Lake Nyos bottom water (spring conductivity = 1530  $\mu\text{S cm}^{-1}$ ,  $\text{HCO}_3^- = 19.0 \text{ mM}$ ). It discharged free plus dissolved  $\text{CO}_2$  at an estimated 500  $\text{L min}^{-1}$ , and was slightly thermal at 27 °C. Assuming an input of water similar to this spring at 27 °C into the bottom of Lake Nyos, the flow required to account for the heat changes observed in the 185–208 m layer since September is only 7  $\text{L s}^{-1}$ . This flow rate over 256 days amounts to about 1.3% of the volume of water below 185 m. An analogous system is that of Lake Kivu in East Africa, which is heated from below by thermal springs (Degens et al., 1973; Tietze, 1978). In Lake Kivu the upward heat flux of 710–1600  $\text{mW m}^{-2}$  (Newman, 1976) is similar to the 1600  $\text{mW m}^{-2}$  value calculated for Lake Nyos. On the basis of temperature measurements alone, however, the relative heat contributions of geothermal flux versus groundwater advection in Lake Nyos are difficult to separate.

Rates of temperature increase in bottom waters are constrained by buoyancy effects. On the basis of measured water density at 204 m in May 1987 (Appendix 1), water temperatures would need to reach 35 °C in order to ascend buoyantly. This upward mixing would redistribute heat in the water column and thus set a maximum attainable temperature of bottom waters. In the last nine months, however, the mean increase in water density at 204 m caused by solute input (+0.00034  $\text{g cm}^{-3}$ ) has roughly matched the decrease in density caused by rising temperatures (–0.00027  $\text{g cm}^{-3}$ ). Such a stable system inhibits the turbulent movement of water and limits, to the process of eddy diffusion, exchange of mass and heat from the bottom to upper water levels. It will be interesting to follow these density changes through time, although at present the short run of data places projected temperature increases in the realm of speculation.

It has been argued that the high surface water

temperatures measured in Lake Nyos just after the August 1986 gas release (Barberi et al., 1989, this issue) prove that significant heat was associated with the gas release and that it was volcanic in nature (see Sigvaldason, 1987). An equally viable explanation for these temperature measurements is solar heating of the surface water. For example, enhanced rates of heating are commonly observed in lakes when particulate concentrations are high (Schreiner, 1984). Such heating rates can be modeled in any water by a modified version of the equation presented in Zaneveld et al. (1981) as follows:

$$\frac{\partial T}{\partial t} = [(Q_s/pC_p D) (1 - e^{-kD})] - (B/pC_p D)$$

where  $T$  is temperature in °C,  $t$  is time,  $Q_s$  is short wave radiation incident at the lake surface,  $p$  is water density,  $C_p$  is specific heat of water,  $D$  is depth of mixed layer,  $k$  is extinction coefficient, and  $B$  is surface heat loss (long wave radiation + evaporation + sensible heat transfer). This equation was applied to Lake Nyos for September 1986, just after the event when particulates (mainly iron minerals) were high in surface waters. Values of  $Q_s = 880 \text{ W m}^{-2}$  and  $B = 225 \text{ W m}^{-2}$  were estimated from values in the Smithsonian Tables and values for nearby lakes (Kling, 1987b) assuming cloudless conditions and winds  $< 1 \text{ m s}^{-1}$ . An extinction coefficient of  $1.7 \text{ m}^{-1}$  was calculated from measured secchi depth and an empirical relation between  $k$  and secchi depth ( $\log[k] = 0.1952 - (0.9959) (\log[\text{secchi}])$ ,  $r^2 = 0.84$ ; raw data in Kling, 1988). Taking a 1-m mixed layer depth, the theoretical rate of heating in Lake Nyos on 3 September is  $0.43 \text{ }^\circ\text{C h}^{-1}$ . This is a mean temperature increase integrated over the chosen mixed layer, and the heating rate near the surface or in specific subsurface particulate layers could be higher. The calculated rate is similar to differential rates of heating observed by Schindler et al. (1981) that were up to  $0.5 \text{ }^\circ\text{C h}^{-1}$  in particulate layers at a depth of 2 m. Heating at such rates accumulated over several days could account for much of the anoma-

lously high surface temperatures recorded by Barberi (Sigvaldason, 1987).

As a test of this theoretical model of heating rates an actual balance of surface energy was calculated for Lake Nyos on May 17, 1987 and compared to model predictions. From 08.10–13.40 the upper 6 m of the water column gained  $1650 \times 10^{10}$  J of heat, which translates to a heating rate of  $0.077^\circ\text{C h}^{-1}$ . Using  $k=0.4 \text{ m}^{-1}$ ,  $Q_s=880 \text{ W m}^{-2}$  and  $B=225 \text{ W m}^{-2}$ , the theoretical mean heating rate predicted for the same upper 6 m of water is  $0.082^\circ\text{C h}^{-1}$ . This compares very well to the measured rate. Kusakabe et al. (1989, this issue) present an analysis of potential temperature increases resulting from iron oxidation in surface waters, although measured iron concentrations in Lake Nyos seem too low for this mechanism to be as important as solar heating.

### Water chemistry

Observed changes over time in profiles of ion concentrations in Lake Nyos are presented in Figures 3 and 4. There has been a slight freshening of the surface water as the upper mixed layer deepened since September. Below this, major ion concentrations have remained fairly constant except in the depth layer from 185 m

TABLE 2

Chemical changes in Lake Nyos bottom waters over time (in  $\text{mg L}^{-1}$ )

Date	Sep. 86	Jan. 87	Mar. 87	May 87
Depth (m)	200	198	198	198
$\text{HCO}_3^-$	725	836, 846	903, 1020	964
$\text{Ca}^{2+}$	46	47, 50	57, 66	66
$\text{Mg}^{2+}$	57	62, 77	75, 85	78
$\text{Na}^+$	19	17, 22	20, 23	27
$\text{K}^+$	7	6, 6	7, 7	8
$\text{Fe}^{2+}$	71*	88, 87	97, 115	95
$\text{Mn}^{2+}$	1.6	1.85, 1.86	2.18, 2.21	1.75
Si	26	31, 33	36, 39	39
$\text{NH}_4^+$	-	-	-	3.4

\*An underestimate because iron hydroxide precipitated before filtering.

to the bottom (Figs. 3 and 4; Table 2). In this bottom layer, concentrations of all ions have increased. The largest change has been  $\text{HCO}_3^-$  concentrations; alkalinity increased by about  $3.92 \text{ meq L}^{-1}$  from September 1986 to May 1987.

This large increase in  $\text{HCO}_3^-$  is most likely due to input of concentrated groundwater rather than to dissolution of carbonates or other in situ processes that generate alkalinity such as reduction of  $\text{SO}_4^{2-}$ ,  $\text{Fe}(\text{OH})_3$  and  $\text{MnO}_4^-$  or denitrification. For example, concentrations of  $\text{N}_2$  and  $\text{Mn}^{2+}$  would be expected to increase if  $\text{MnO}_4^-$  reduction or denitrification were important sources of alkalinity. However, their concentrations in Lake Nyos are very low and have not changed significantly from September to May (Tables 2 and 3). Second, almost  $2 \text{ mmol L}^{-1}$  of sulfate would need to have been reduced over this time period to account for the observed increase in alkalinity. But  $\text{SO}_4^{2-}$  concentrations have remained at less than  $5 \mu\text{mol L}^{-1}$  and reduced sulfur burial in the sediments is very small (total sediment  $S=0.11\%$ ; Kling et al., 1987). Finally, reduction of  $\text{Fe}(\text{OH})_3$  formed in oxygenated surface waters and transported to anoxic bottom waters also would produce alkalinity. As a result,  $\text{Fe}^{2+}$  would accumulate at lower depths. Table 2 shows, however, that increases in  $\text{Fe}^{2+}$  concentrations in bottom waters are insufficient to account for the observed alkalinity change. Our equilibria calculations indicate that siderite ( $\text{FeCO}_3$ ) was oversaturated at 200 m in May 1987. These calculations used a pH of 5.18 and resulted in a saturation index (SI- $\text{FeCO}_3$ ) of 0.51, i.e., the product of  $\text{Fe}^{2+}$  and  $\text{CO}_3^{2-}$  concentrations was 3.2 times ( $10^{0.51}$ ) that required (theoretically) for precipitation of  $\text{FeCO}_3$ . However, a loss of iron in bottom waters from precipitation of  $\text{FeCO}_3$  cannot be invoked, because precipitation of  $\text{FeCO}_3$  and its burial in the sediments would consume the alkalinity produced by reduction of  $\text{Fe}(\text{OH})_3$ .

Another possible explanation for the observed alkalinity increase is the dissolution at depth of carbonates formed in surface waters.

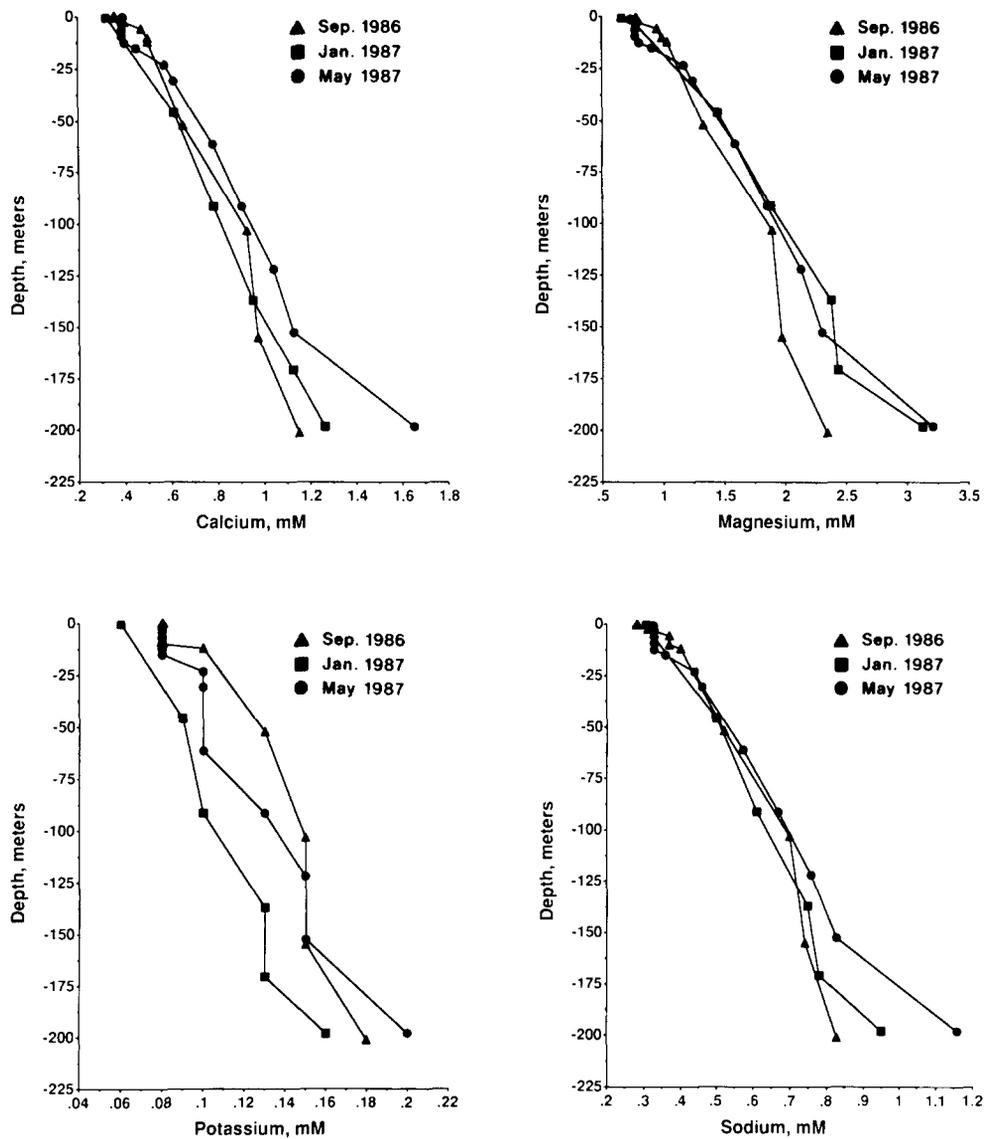


Fig. 3. Depth profiles of major ions (mM) in Lake Nyos.

Chemical equilibria calculations show that  $\text{CaCO}_3$  and  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  are undersaturated by at least 1.7 orders of magnitude at all depths and dates in Lake Nyos ( $\text{SI-CaCO}_3 < -1.7$ ;  $\text{SI-MgCO}_3 \cdot 3\text{H}_2\text{O} < -4.7$ ). Thus precipitation of these minerals in surface waters followed by downward transport is unimportant to bottom water chemistry. Given the concurrent increases in all major ions at depth in Lake Nyos, the input of groundwater is the most viable ex-

planation for observed changes in bottom water chemistry.

A ternary diagram plotting the proportional cationic composition of Lake Nyos waters compared to the composition of various spring waters supports this assertion (Fig. 5). Hypolimnetic chemistries from all dates plot very close to values for water issuing from ultramafic rocks (Hem, 1970; Siever and Woodford, 1979), which are similar in composition to pyro-

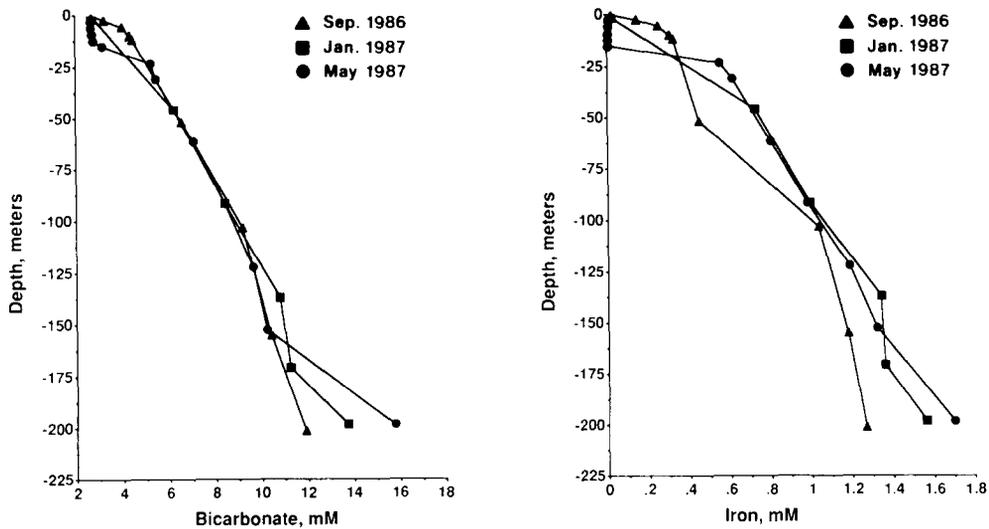


Fig. 4. Depth profiles of major ions (mM) in Lake Nyos.

TABLE 3

Concentrations of dissolved gases ( $\mu\text{mol kg}^{-1}$ ) in Lake Nyos

Depth (m)	N <sub>2</sub>	O <sub>2</sub>	Ar	CO	CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub> S
<i>23 Jan. 1987</i>							
17	628	<0.5	10.9	<0.5	0.3	22500	<0.05
35	205	<0.5	4.64	<0.5	78.7	48600	<0.05
76	198	<1.0	3.6	<1.0	111	70000	<0.1
107	225	33.1	4.1	<1.0	186	110000	<0.1
131	196	81.6	3.1	<3	118	108000	<0.3
198	146	2.6	4.5	<2	308	159000	<0.2
<i>23 Mar. 1987</i>							
99	86.7	1.1	2.1	<0.1	81.1	74900	<0.1
198	159	1.1	2.2	<0.4	205	177000	<0.4
198	58	0.72	1.4	<0.3	170	146000	<0.3
<i>18 May 1987</i>							
61	226	1.8	4.7	-	121	62800	-
99	75.7	2.0	0.71	-	79.1	78750	-
99	3110	330	37.2	-	162	92260	-
143	172	6.0	3.2	-	255	129500	-
171	166	<0.8	2.9	-	272	131800	-
198	55.4	2.3	<1.2	-	154	124400	-
198	95.5	3.9	<2.3	-	255	184200	-
198	1560	21.8	16.8	-	413	193200	-

clastic flow deposits around Lake Nyos (Tuttle et al., 1987; Kusakabe et al., 1989, this issue). Surface waters in Lake Nyos lie on the trajectory from ultramafic derived waters to lake inflow, nearby springs issuing from granite, and pre-event surface waters. This indicates simple but incomplete mixing of upper and lower water

masses, consistent with a hypothesis of partial lake turnover caused by the August 1986 gas release. There may also be some in situ weathering of exposed subsurface rocks contributing to the changes in Lake Nyos bottom water chemistry, although it is unknown what surface area of rock is exposed to weathering, how much increased  $p\text{CO}_2$  affects weathering rates, and to what extent this mechanism of ion input has altered the trajectory shown in Figure 5.

Changes in Lake Nyos bottom water chemistry since the gas release can be measured, but chemical evolution of the lake prior to the event must be inferred. The chemical character of bottom water in the two lakes that have released  $\text{CO}_2$ , Nyos and Monoun, is unique among all crater lakes in Cameroon. The most distinguishing features are the high concentrations of reduced iron and dissolved  $\text{CO}_2$  (Sigurdsson et al., 1987; this paper). If the  $\text{CO}_2$  released during the 1986 disaster was moved through the lake from below by volcanic injection, as suggested by several authors (Tazieff et al., 1987; papers in this issue), then it becomes difficult to explain the high concentrations of reduced iron and alkalinity now present. For example, how did the iron accumulate and what prevented its loss by iron carbonate precipitation? Subsurface weathering in the high  $p\text{CO}_2$  environment

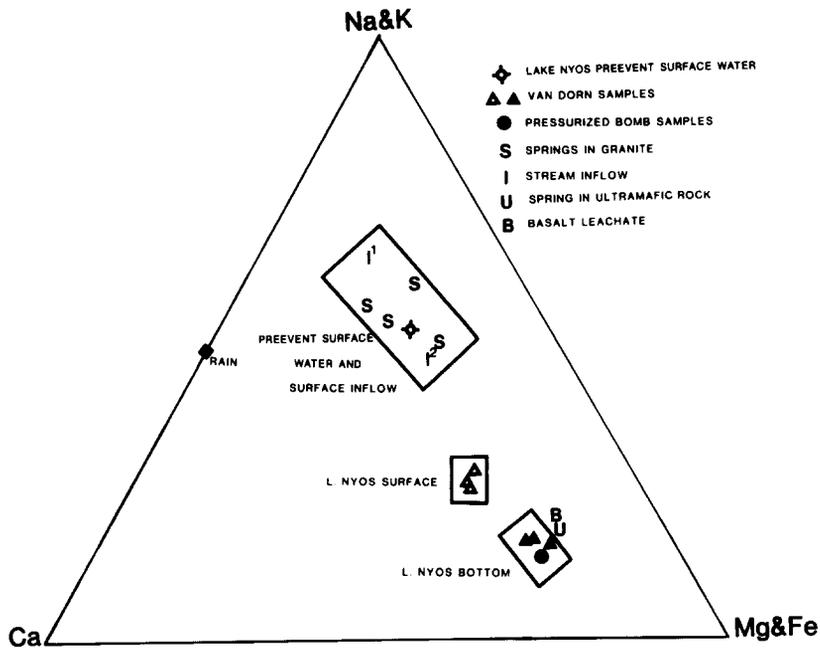


Fig. 5. Ternary diagram showing the proportion of major cations (molar basis) in surface (van Dorn) and bottom (pressurized bomb) water samples from Lake Nyos; stream inflow (Kusakabe et al., 1989, this issue); springs issuing from granitic rocks above Lake Nyos; rain in Cameroon and surface water before the event (Kling, 1987b); spring water associated with ultramafic rocks (Hem, 1970); and leachates from experimental weathering of basalts (Siever and Woodford, 1979).

below Lakes Nyos and Monoun may supply more iron to these lakes relative to supply rates in other Cameroonian lakes. However, substantial accumulation of these ions only begins when dissolved  $\text{CO}_2$  added to bottom waters increases stratification strength and water column stability. In addition, high  $p\text{CO}_2$  stabilizes the reduced iron by lowering pH and  $\text{CO}_3^{2-}$  concentrations. Thus the current chemistry of Lakes Nyos and Monoun supports the idea that  $p\text{CO}_2$  was high in the hypolimnion prior to these gas releases.

Observations of reddish patches and streaks on the surface of Lake Nyos have been used to argue for renewed volcanic activity beneath the lake (Tazieff, 1987). These patches are caused by the formation of iron hydroxide as dissolved  $\text{Fe}^{2+}$  is brought from depth into oxygenated surface waters. However, entrainment of deep water from above as well as injection from be-

low can account for this phenomenon. For example, a common mechanism of deep water entrainment in lakes and oceans is Langmuir circulation. This circulation forms a set of convective helices resulting in upwelling and windrows of particulate material such as plankton on the surface (Faller, 1978). The windrows are oriented roughly parallel to the wind but often remain unseen for lack of surface marker. The iron hydroxide streaks observed in Lake Nyos are, as far as we know, a novel form of surface marker and indicate entrainment of iron-rich anoxic water to the surface. In addition, these streaks were not accompanied by noticeable gas bubbles (S.G. Tebor, pers. commun., 1989). This is consistent with the hypothesis that shallow, anoxic waters were entrained to the surface by Langmuir circulation, rather than deep,  $\text{CO}_2$ -laden waters being driven upward by volcanic events.

### Gas chemistry

Chemical composition of dissolved gases in Lake Nyos is presented in Table 3. Comparison of these values with values in Kling et al. (1987) show that the general character of dissolved gases has changed little since September 1986. Carbon dioxide is still the dominant dissolved gas and makes up greater than 97% of all gases even in samples taken as shallow as 17 m. The nonvolcanic nature of the dissolved gases has not changed from samples taken directly after the event, and is most apparent in the low concentrations of CO, H<sub>2</sub>, and H<sub>2</sub>S.

Concentrations of dissolved CO<sub>2</sub> in Lake Nyos ranged from 18 to 28% of saturation (Fig. 6). We calculate that if water at all depths was saturated the lake could hold  $\approx 1.45 \text{ km}^3 \text{ CO}_2$  (at 20°C; or  $\approx 5.3 \times 10^{10} \text{ mol CO}_2$ ). In May 1987 there remained  $\approx 0.38 \text{ km}^3 \text{ CO}_2$  in the lake ( $1.41 \times 10^{10} \text{ mol CO}_2$ ). Thus a maximum of about 1 km<sup>3</sup> of CO<sub>2</sub> could have been released during the August 1986 event. This volume is sufficient to account for the distribution of fatalities around the lake (Kling et al., 1987).

There has been little change in average CO<sub>2</sub> concentrations over time; values in January,

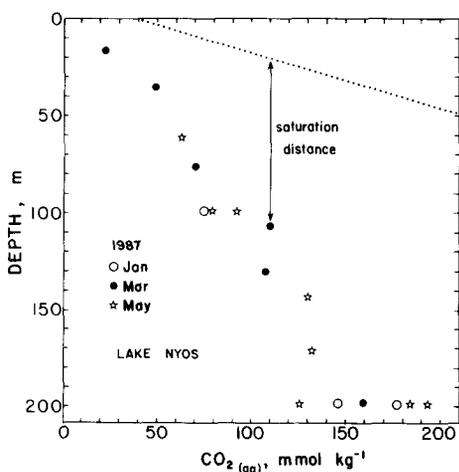
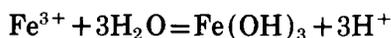
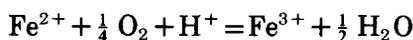


Fig. 6. Depth profile of CO<sub>2</sub> concentrations in Lake Nyos. Dotted line gives depth of saturation for values of CO<sub>2</sub> shown on x-axis; for example, water with 200 mmol kg<sup>-1</sup> of CO<sub>2</sub> would be saturated at a depth of 45 m.

March, and May of 1987 (Table 3) are similar for each depth to values reported by Tietze (1987) for November 1986 and by Kusakabe et al. (1989, this issue) for October 1986. There is, however, distinct horizontal variation in  $p_{\text{CO}_2}$  at any depth. For example, two samples from May 1987 at 198 m have  $p_{\text{CO}_2}$  values of 3.57 and 5.55 atm (at 24°C), which are the lowest and highest  $p_{\text{CO}_2}$  values measured on any date at this depth. The cause of this heterogeneity is unclear; it could be due to localized inputs of CO<sub>2</sub> to bottom waters, internal waves, or chemical reactions in the sample cylinders after collection.

The relative contribution of chemical reactions in sample cylinders to  $p_{\text{CO}_2}$  variability can be estimated from measured concentrations of N<sub>2</sub>, O<sub>2</sub>, and Ar, because excesses of these gases result from leakage of evacuated cylinders to the atmosphere prior to filling. For example, the worst case of contamination is in the 99 m sample taken in May 1987. Assuming that all 3110  $\mu\text{mol kg}^{-1}$  of N<sub>2</sub> is from atmospheric contamination, a corresponding concentration of O<sub>2</sub> equal to about 830  $\mu\text{mol kg}^{-1}$  would have entered the sampler, which contained only 330  $\mu\text{mol kg}^{-1}$  when analysed. According to the reactions:



each mole of O<sub>2</sub> consumed can produce 8H<sup>+</sup>, converting 8HCO<sub>3</sub><sup>-</sup> to 8CO<sub>2(aq)</sub> + 8H<sub>2</sub>O. Thus a maximum of 4000  $\mu\text{mol CO}_2 \text{ kg}^{-1}$  could have been added to this sample, resulting in an overestimate of in situ CO<sub>2</sub> concentration by 4%. In all other samples the potential for oxygen contamination is much less.

Progressive temperature changes characteristic of internal waves were not seen in the metalimnion or hypolimnion in May. A primary mode seiche in the metalimnion of Lake Nyos in May would have a period of 2–3 hr. Because lengths of temperature observation were on the order of 30 min, any strong seiche probably

would have been detected. In addition, the vertical density structure of Lake Nyos constrains the amplitude of an internal seiche. As a rough estimate, and using equations in Hutchinson (1957), wind speeds of  $20 \text{ m s}^{-1}$  would produce seiche amplitudes of no more than 5 m in the metalimnion, and no more than 15 m in the hypolimnion. Thus the observed  $\text{CO}_2$  distribution in Lake Nyos may be affected to some degree by internal waves, as well as by localized inputs of  $\text{CO}_2$ . Such localized inputs have yet to be identified.

Given the horizontal variability of  $p_{\text{CO}_2}$ , a nine month period of observation is marginal to estimate a true recharge rate of  $\text{CO}_2$  into the lake. This is especially true if recharge events are episodic or seasonal. However, our data indicate that no major recharge has occurred to date.

Concentrations of  $\text{CH}_4$  and  $\text{N}_2$  are important in that they contribute to the total gas pressure and thus to the potential for degassing. For example, in the May 1987 samples the relative contribution of  $\text{CH}_4 + \text{N}_2$  amounts to 6% of the total gas pressure at 198 m. Their contribution increases to 24% of the total pressure at 61 m. In May,  $p_{\text{CH}_4}$  ranged from 0.03 to 0.29 atm (at  $24^\circ\text{C}$ ) at 24 m and 198 m, respectively. However,  $\text{CH}_4$  pressures before the event could have been much higher. For example, hypolimnetic methane pressures in other Cameroonian crater lakes sampled in May 1987 are up to 7 times that found in Nyos: Lake Manengouba, 91 m,  $p_{\text{CH}_4} = 0.95 \text{ atm}$ ; Lake Benakuma, 130 m,  $p_{\text{CH}_4} = 2.08 \text{ atm}$ ; Barombi Mbo, 98 m,  $p_{\text{CH}_4} = 0.85 \text{ atm}$ . If pre-event pressures in Lake Nyos were higher than present, they would have facilitated initial exsolution because  $\text{CH}_4$  is about 25 times less soluble than  $\text{CO}_2$ . In any case, concentrations of  $\text{CH}_4$  and  $\text{N}_2$  should be monitored in Lake Nyos in order to accurately predict total gas pressure and thus the stability of the system.

### Isotopes

The isotopic composition of carbon species in the lake is relatively unchanged since the

event. For samples below 20 m,  $\delta^{13}\text{C}-\text{CO}_2$  values for  $\Sigma\text{CO}_2$  are  $-3.0$  to  $-3.5$  ‰ PDB. Methane from samples below 90 m yielded  $\delta^{13}\text{C}$  values of  $-45$  to  $-52$  ‰ PDB and  $\delta\text{D}$  values of  $-240$  to  $-270$  ‰ SMOW. None of the three isotopes show regular changes with depth over the time interval from September 1986 to May 1987. It appears from this isotopic evidence that the major sources of these dissolved gases are unchanged; the  $\text{CO}_2$  is magmatic in origin and the methane is probably from biological decomposition (see Kling et al., 1987).

### Lake stability and degassing

Overall water column stability ( $S$ ) is a fundamental measure of the strength of thermal plus chemical stratification in a lake. The strength of stratification constrains the initiation of degassing and can be used in predicting the likelihood of future gas releases. More formally,  $S$  is the amount of energy required to mix a lake to uniform density without the addition or subtraction of heat. In Lake Nyos the concept of stability is complicated by the high pressure of dissolved gas. As a parcel of water is lifted to the surface, at some point the total ambient pressure decreases sufficiently to cause oversaturation and bubble formation. The effervescence of gas that occurs produces an increase in bulk buoyancy of the fluid and also an increase in turbulence. In such an event  $S$  will be reduced independent of external energy inputs. It is important to note that in a gas-charged lake, when gas concentrations approach saturation the conventional models of water column stability break down. In the prediction or assessment of potential gas releases then, stability values should be interpreted in conjunction with an estimate of the minimum vertical distance a water mass must move in order to create oversaturated conditions.

Water column stability increased from  $48,800 \text{ J m}^{-2}$  in September of 1986 (assuming a  $\text{CO}_2$  profile identical to the averaged profile measured in January 1987), to  $50,700 \text{ J m}^{-2}$  in Jan-

uary, and to  $64,700 \text{ J m}^{-2}$  in May. Water density increases due to the input of solutes to bottom waters over this time period are mainly responsible for the higher  $S$  values in January and May. In addition, surface waters cooled slightly from September to January and warmed slightly from January to May. This explains the smaller increase in  $S$  during this first time period compared to the increase in  $S$  from January to May. These stability values are ten times greater than those for Barombi Mbo, the most stable low- $\text{CO}_2$  lake in Cameroon (Kling, 1988). In addition, the Lake Nyos values are more than twice that for Lake Atitlan, which is the most stable low- $\text{CO}_2$  lake known (Kling, 1988). By comparison, using data for gas-charged Lake Kivu in East Africa taken from Tietze (1978) and Degens et al. (1973), we calculate Kivu's stability to be  $\approx 340,000 \text{ J m}^{-2}$ . Lake Kivu is extremely stable because of its great depth (485 m) and because solutes in its bottom water are five times more concentrated than those found in Lake Nyos. These comparisons among gas-charged lakes are for perspective only, because localized gas saturation can quickly reduce stability.

The vertical movement of water required to achieve localized gas saturation is equal to sample depth minus saturation depth. In May this 'saturation distance' ranged from 170 m for the 198 m samples, to 49 m for the 61 m sample (Fig. 6). In other words, if water at 61 m was raised to 12 m, exsolution of gas would occur given suitable nucleation sites. In this specific case, degassing of a small volume of water brought from 61 to 12 m would not trigger a massive gas release, because  $\text{CO}_2$  concentrations in epilimnetic water are small. The common limnological processes that transport water vertically, such as an internal seiche or currents driven by wind or convection, are insufficient in magnitude to move water 50 m or more through the strong density gradients in this lake. If saturation levels remain unchanged, only large scale external inputs of energy (rockslides, subsurface injection of gas, seismic

events) could destabilize Lake Nyos and precipitate large-scale degassing of  $\text{CO}_2$ .

Two possible models of large-scale degassing are isenthalpic (see Henley et al., 1984) or isentropic (see Kieffer, 1982). In either process there is a rapid transition from low velocity buoyant gas flow to a high velocity flow regime driven by the expansion force produced during exsolution. For example, water at 200 m in Lake Nyos contains about  $0.7 \text{ mol L}^{-1}$  of  $\text{CO}_2$  at saturation. Isenthalpic decompression of this  $\text{CO}_2$  exsolved at the bottom of Lake Nyos (21 atm) and brought to the surface (1 atm) would produce 928 J of energy through expansion. This is sufficient to drive 1 kg of water to a height of 95 m above the lake. Isentropic decompression would produce even more energy. Regardless of which model is chosen to best represent the thermodynamics of degassing at Lake Nyos, the energy gained from this expansion force is sufficient to generate the tremendous water surges caused by the August event (described by Kling et al., 1987).

### *Regional survey*

We completed our survey of all Cameroon crater lakes in May 1987. Morphometric descriptions, thermal profiles, and some chemical characteristics of these lakes are presented in Kling (1988). Bottom water temperatures in all lakes were no higher than those in other tropical lakes at similar elevation and latitude; we found no abnormal input of heat attributable to volcanic activity. Only Lakes Nyos and Monoun had elevated concentrations of dissolved gas or ions in the hypolimnion. Given that the buildup of  $\text{CO}_2$  and solutes must have preceded the gas bursts in Lakes Nyos and Monoun (as discussed above), in the absence of premonitory chemical changes in bottom waters there is a low probability of any other Cameroonian lake releasing a substantial volume of  $\text{CO}_2$ .

## Summary

There is now good evidence suggesting that the Lake Nyos disaster was non-volcanic in nature and that the released CO<sub>2</sub> was stored in the hypolimnion rather than in or below the lake sediments. For example, several observations require high CO<sub>2</sub> concentrations in the lake prior to the August 1986 event. Increasing solute concentrations with depth argue for gas buildup before the event in order to create strong density stratification. This density stratification is needed also to allow for the accumulation of heat and to maintain the inverse temperature profile of Lake Nyos. Without high pCO<sub>2</sub> values before the event, Fe<sup>2+</sup> would precipitate as FeCO<sub>3</sub> and thus dissolved iron concentrations would remain low.

Most likely the effervescence of gas due to locally oversaturated conditions was the mechanism of release during the event. The trigger creating these conditions is unknown. If the release of gas was initiated in near surface waters, as described by the model of Tietze (1987), several of the more common water movements such as internal seiches or strong penetrative convection may have triggered the release. A model of near surface release does not, however, eliminate potential triggers originating in deep water, such as a thermal plume or subsurface landslide. For example, the only possible location of an injection of CO<sub>2</sub>, accumulated in diatreme voids, is from cliffs below the water surface that are clear of sediment. Such an injection also could act as a trigger for the initial gas release as suggested by Kling et al. (1987). It must be emphasized that at present there are no data which demand a unique interpretation of the processes involved.

There is distinct horizontal variation in the concentration of CO<sub>2</sub> in Lake Nyos and overall its distribution is still poorly characterized. It is apparent that no major recharge of CO<sub>2</sub> has occurred since the 1986 event, although it would be premature to assign a recharge rate with statistical bounds. Water column stability has in-

creased recently due to solar warming of surface waters and input of solutes to the hypolimnion from groundwater. At present the level of stability and the level of CO<sub>2</sub> saturation combine to create conditions that could be disrupted only by strong external inputs of energy such as rockslides or seismic events. Of more immediate concern appears to be the potential for catastrophic flooding resulting from loss of the weak natural dam holding back the upper 40 m of Lake Nyos (Lockwood et al., 1988). Such an event could trigger the release of much of the gas remaining in the lake. This danger seems to warrant continued evacuation of low-lying areas downstream of Lake Nyos.

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## Appendix 1

(1) Lake stability (*S*) was calculated following Idso (1973) and expressed in J m<sup>-2</sup>:

$$S = g/A_0 \int (z - z_*) (p_z - \langle p \rangle) A_z dz$$

where *g* is acceleration due to gravity, *A*<sub>0</sub> and *A*<sub>*z*</sub> are surface area and area at depth *z*, *z*<sub>\*</sub> is the depth of mean density, *p*<sub>*z*</sub> is the density at depth *z*, and  $\langle p \rangle$  is the mean density calculated as:

$$\langle p \rangle = (1/V_0) \int A_z p_z dz$$

(2) Fluid density at each depth was calculated as:

$$\rho = [1000 + (mM)] / [(m\Phi_v) + (1000/\rho_0)]$$

where  $m$  is the mean molality of the lake water,  $M$  is the mean molecular weight of solutes in the water,  $\rho_0$  is the density of pure water at temperature  $T$  ( $^{\circ}\text{C}$ ) and pressure  $P$  (bar), and  $\Phi_v$  is the mean apparent molal volume of the lake water (Millero, 1972). Values for the density of pure water were calculated using the relations in Chen and Millero (1977). In mixed electrolyte solutions the apparent molal volume ( $\phi_v$ ) of an ion is a function of the molar concentration ( $c$ ) of the medium as shown by the Redlich-Meyer equation (Redlich and Meyer, 1964) where:

$$\phi_v = \phi_v^0 + S_v(p_0 m)^{\frac{1}{2}} + B_v(p_0 m)$$

$\phi_v^0$  is the ionic partial molal volume. Conventional partial molal volumes reported in Millero (1972) were corrected to ionic partial molal volumes using  $V_0(\text{H}^+) = -5.0 \text{ cm}^3 \text{ mol}^{-1}$ . The  $\phi_v^0$  of  $\text{CO}_2$  was taken from Weiss (1974) and that of  $\text{CH}_4$  was taken from Tiepel and Gubbins (1972).  $S_v$  is a theoretical limiting slope given in mixed solutions by  $kz^2I^{\frac{1}{2}}$  where  $k$  is determined by temperature,  $z$  is ionic charge, and  $I$  is  $\frac{1}{2} \sum c_i z_i^2$ .  $B_v$  is an empirical deviation constant determined for each ion. These deviation constants were calculated assuming additivity and using  $B_v$  for NaCl, KCl,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , KF, NaF, and  $\text{K}_2\text{SO}_4$  from Millero (1971), and  $B_v$  for  $\text{NaHCO}_3$  from Perron et al. (1975). Mean apparent molal volume was then calculated using the mixture rule of Young and Smith (1954) where:

$$\Phi_v = \sum m_i \phi_{vi} / \sum m_i$$

(3) Fugacity of  $\text{CO}_2$  was determined by the use of the fugacity-pressure relationship  $\ln(f/P) = B_t P/RT$ , where  $f$  is the fugacity at pressure  $P$  and absolute temperature  $T$ ,  $R$  is the universal gas constant, and  $B_t = -0.1233 \text{ L}$

$\text{mol}^{-1}$  at  $295^{\circ}\text{K}$  (Weiss, 1974).  $\text{CO}_2$  concentrations were then calculated as:

$$[\text{CO}_2] = K_0 f \exp[(1-P)v^*/RT]$$

where  $K_0$  is the virial equation of state derived from the van't Hoff equation and  $v^*$  is the partial molal volume of  $\text{CO}_2$  (Weiss, 1974).

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