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# Geochemistry of the Anoxic Great Ghost Lake

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## ABSTRACT

The Great Ghost (Ta-Kuei) Lake is the only natural, pollution free, but anoxic lake in Taiwan ever reported in the literature (Chen and Wang, this issue). It was found that the distribution of pH was dichotomous in summer. The depth of minimum pH coincided with the layer immediately above the anaerobic layer. This was caused by the change in respiration patterns.

Much of the alkalinity produced in the hypolimnion was from the anoxic respiration reactions called "in-lake alkalinity generation". The generation of ferric iron, accompanied by consumption of  $H^+$ , contributed the most to the in-lake generated alkalinity, with minor contribution from nitrate and manganese reduction. When the lake overturned in winter, the alkalinity was reduced again.

*Keywords:* Great Ghost Lake, Ta-Kuei Lake, pH, manganese, iron, anoxic, alkalinity, stratification, overturn, nitrate, acid rain, eutrophication

## I. Introduction

The Great Ghost (Ta-Kuei) Lake is a rather unique lake with strong temperature stratification in summer but little or no stratification in winter (Chen and Wang, the preceding paper). It has low biological productivity and low nutrients, yet is anoxic in deep waters in summer because of high organic matter loading from land and poor ventilation.

The hydrogen sulfide produced in anoxic waters is toxic to fish larvae at concentrations as low as 1 ppb. Hydrogen sulfide is also toxic to adult fish at 2ppb (Boyd, 1979). The overturning of the Great Ghost Lake in winter, distributing hydrogen sulfide throughout the lake, may explain why there are no fish. Studies of such anoxic lake in a pollution-free natural environment may help in understanding the eutrophication of lakes with human pollution.

The vertical distributions of temperature, oxygen and nutrients were given in the preceding paper (Chen and Wang, this issue) and are not repeated here.

## II. Material and Methods

**Study area** — The Great Ghost Lake ( $22^{\circ} 58'N$ ,  $120^{\circ} 58'E$ ) is a 650 X 300 m oligo-mesotrophic lake surrounded by 100 m high hills, and has an area of 11.25 ha. We found a maximum depth of 34 m, a mean depth of 14.8 m, and a volume of  $1.67 \times 10^6 m^3$  with the help of a fish finder. The draining basin consists mainly of argillite, phyllite and slate with rich vegetation. There is

no river inflow and the outflow is at the northeast corner.

**Sampling and analysis** — Water samples were collected with a 21 Hydro-Bios TPN sampler at stations A and B (Fig. 1) between 5 ~ 10 July, 1988 (summer)

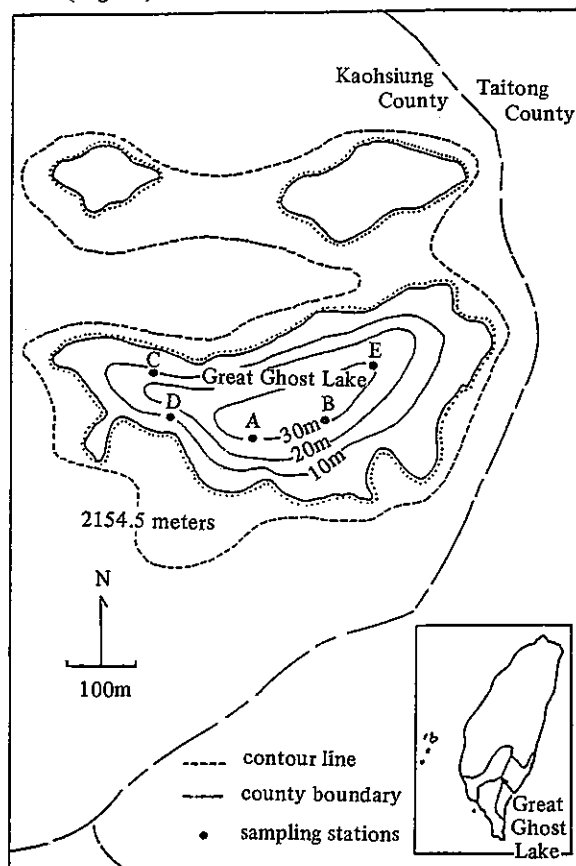


Fig. 1. Location of the lake and sampling stations.

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and between 3 ~ 7 February, 1989 (winter). Temperature and dissolved oxygen were measured in situ at stations A ~ E with a YSI model 58 DO meter. pH was measured with a Basic portable pH meter calibrated with NBS 4.004 and 7.415 buffers. Subsamples were then filtered with a pre-washed 0.45  $\mu\text{m}$  nylon 66 filter. Portions of the subsamples were acidified with distilled clean acid. Water samples were shipped back in PE bottles packed in ice for further analysis.

Alkalinity was measured at 25°C with a titration system consisting of a Radiometer PHM85 pH meter and a Radiometer ABU80 automatic burette (Zimmerman and Harvey, 1978; Chen *et al.*, 1988). Iron and manganese were measured with a Perkin Elmer Model 2380 Atomic Absorption Spectrophotometer (Chen and Wang, this issue).

### III. Results and Discussion

#### pH:

The vertical distribution of pH in summer is shown in Fig. 2. pH decreased with depth and was gradually reduced to a minimum value of 4.27 ~ 4.54 at a depth of 16m. Below this depth, the pH gradually increased to a value of 5.14 ~ 6.26 at the bottom (Fig. 2). Aerobic respiration (Eq.1 in Table 1) is the major process between 0 ~ 16m in the Great Ghost Lake. This process produces  $\text{CO}_2$  but decreases pH (Chen *et al.*, 1982). On the other hand, in the anoxic environment below 16m, anaerobic respiration occurs. Equations 2 ~ 6 in Table 1 are the reactions responsible for the decomposition of organic matter using different oxidants in the anoxic environment (Stumm and Morgan, 1981; Kelly *et al.*, 1982). Reactions 2 ~ 5 all increase pH.

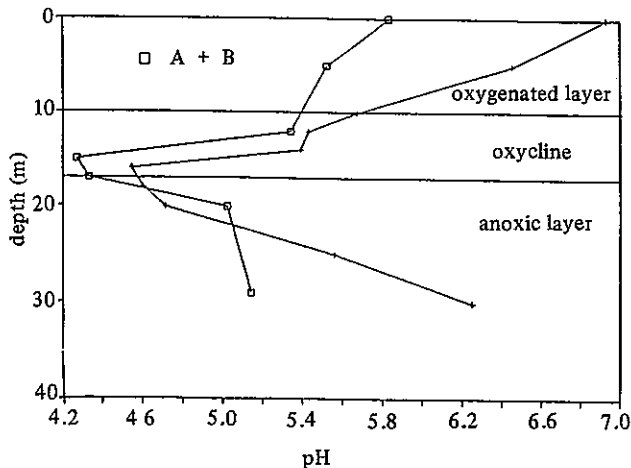


Fig. 2. Profiles of pH in summer.

Table 1. Reactions Involved in the Decomposition of Organic Material

(1) Aerobic respiration:	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138 \text{O}_2$ — $106\text{CO}_2 + 122 \text{H}_2\text{O} + 16\text{HNO}_3 + \text{H}_3\text{PO}_4$
(2) Nitrate reduction:	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 84.8\text{HNO}_3$ — $106\text{CO}_2 + 148.8\text{H}_2\text{O} + 42.4\text{N}_2 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
(3) Manganese reduction:	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 236\text{MnO}_2 + 472\text{H}^+$ — $106\text{CO}_2 + 236\text{Mn}^{+2} + 8\text{N}_2 + \text{H}_3\text{PO}_4 + 366\text{H}_2\text{O}$
(4) Iron reduction:	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 424\text{Fe}(\text{OH})_3 + 848\text{H}^+$ — $106\text{CO}_2 + 742\text{H}_2\text{O} + 424\text{Fe}^{+2} + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
(5) Sulfate reduction:	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 53\text{SO}_4^{-2} + 106\text{H}^+$ — $106\text{CO}_2 + 106\text{H}_2\text{O} + 53\text{S}^{-2} + 16\text{NH}_3 + \text{H}_3\text{PO}_4$
(6) Methane production:	$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$ — $53\text{CO}_2 + 53\text{CH}_4 + 16\text{NH}_3 + \text{H}_3\text{PO}_4$

(From Stumm and Morgan, 1981; Kelly *et al.*, 1982)

#### $\text{Fe}^{+2}$ and $\text{Mn}^{+2}$ :

Iron and manganese are the metals most likely to be involved in the anaerobic respiration. The vertical profiles of these metals in summer are shown in Fig. 3. The concentrations in the aerobic zone were, as expected, quite low.  $\text{Mn}^{+2}$  started to increase in the oxycline but  $\text{Fe}^{+2}$  increased in concentration only in the anoxic zone.

Since the concentrations of nitrate, sulfide, and  $\text{Mn}^{+2}$  were all very low in the lake (Chen *et al.*, 1988),  $\text{Fe}^{+2}$  production (Eq.4 in Table 1) was probably responsible for the pH increase in the anoxic layer. This anaerobic process, combined with the aerobic respiration, resulted in the dichotomous pH distribution in summer, with the minimum falling at the boundary of the oxygenated-anoxic layers. Similar phenomenon has been reported elsewhere (Yoshimura, 1932).

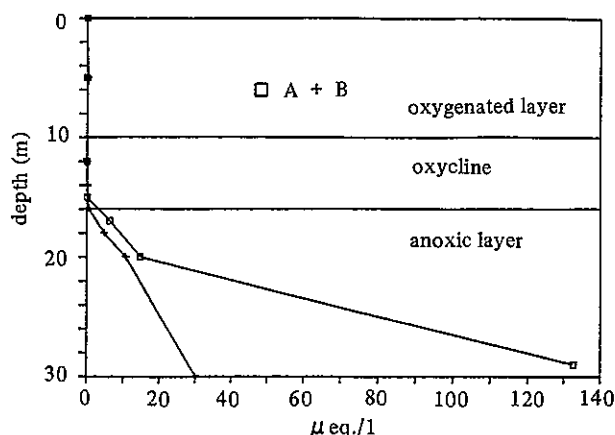


Fig. 3a. Profiles of  $Fe^{+2}$  content in summer.

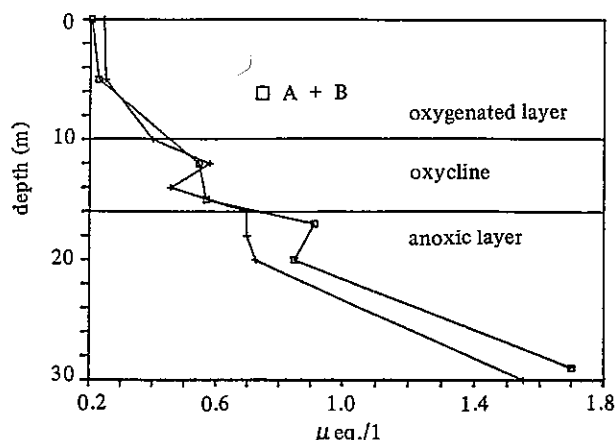


Fig. 3b. Profiles of  $Mn^{+2}$  content in summer.

**Alkalinity:**

The alkalinity of the Great Ghost Lake is rather low compared with most other lakes in Taiwan (Chen and Hung, 1987; Chen *et al.*, 1988). The vertical distribution was relatively homogeneous in winter but the anaerobic respiration consumed  $H^+$  and increased the alkalinity in

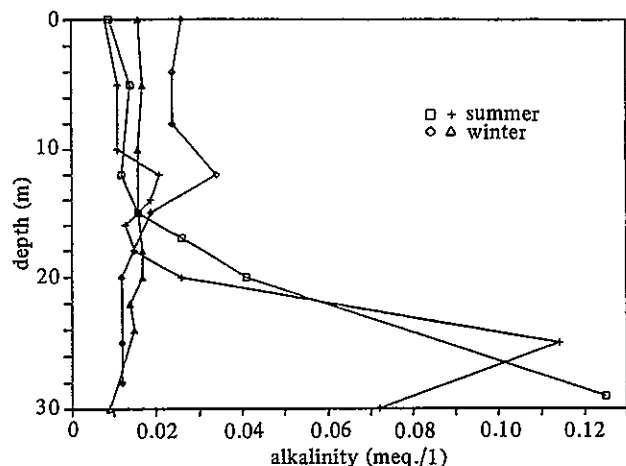


Fig. 4. Profiles of alkalinity in summer (□+) and winter (◇Δ).

summer (Fig. 4).

The iron reduction discussed above not only increased pH but also alkalinity by removing  $H^+$  (Eq.4 in Table 1). The alkalinity produced by this reaction, called in-lake alkalinity generation, differs from alkalinity generation by soil and rock weathering. This function makes the alkalinity increase starting from the top of the anoxia (Fig. 4).

The alkalinity produced by removing  $H^+$  during summer stratification was not permanent. During winter overturning, when the water was re-circulated and oxygenated,  $Fe^{+2}$  and  $Mn^{+2}$  were rapidly oxidized. This reaction would reduce the alkalinity. However,  $NH_4^+$  was oxidized more slowly than  $Fe^{+2}$  and  $Mn^{+2}$ .  $SO_4^{-2}$  was reduced to  $S^{-2}$  and deposited as  $FeS$ , which could preserve the alkalinity and could not be reoxidized by aerobic water.  $NO_3^-$  was reduced to  $N_2$ , which would escape to the atmosphere. Finally, when the water was recharged with oxygen, the alkalinity which was produced by the reduction of  $NO_3^-$  would be preserved (Kelly *et al.*, 1982). The latter process, however, was relatively unimportant because of the low nitrate concentration (Chen *et al.*, 1988). We did not measure methane and, thus, do not know what the contribution of methane reduction to alkalinity was (Eq.6 in Table 1).

The end result of the above reactions was that the biogenic alkalinity produced in summer was spent mostly in winter. That explains why the alkalinity in summer was higher than in winter (Fig. 4).

Quantitatively, alkalinity is roughly defined as the chemical species which can neutralize hydrogen ions ( $H^+$ ) at the bicarbonate end point. The most common chemical species contributing to alkalinity in fresh water are:

$$Alk = 2[CO_3^{-2}] + [HCO_3^-] - [H^+] + 2[S^{-2}] + [HS^-] + [NH_3]$$

where all units are in mole/l. Silicates, phosphates and organic bases may also contribute to alkalinity but usually only to a very small degree (Stumm and Morgan, 1981). Also, at neutral or acidic pH ranges,  $CO_3^{-2}$ ,  $S^{-2}$  and  $NH_3$  are insignificant; thus, for all practical purposes, the above equation can be reduced to:

$$Alk = [HCO_3^-] - [H^+] + [HS^-]$$

Further, the net change of charges must be zero:

$$0 = 2\Delta Fe^{+2} + 2\Delta Mn^{+2} + \Delta NH_4^+ + \Delta H^+ - \Delta HCO_3^- - \Delta NO_3^- - 2\Delta SO_4^{-2} - \Delta HS^-$$

Combining the above equations gives:

$$alk = \Delta HCO_3^- - \Delta H^+ + \Delta HS^- = 2\Delta Fe^{+2} + 2\Delta Mn^{+2} + \Delta NH_4^+ - \Delta NO_3^- - 2\Delta SO_4^{-2}$$

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As a result, the change of alkalinity can be predicted by the changes in ions like  $\text{Fe}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{-2}$ . We assumed that the water was homogeneous after complete overturning in late winter, and used the mean value of each species in the upper layer in summer as the base line. We then calculated alkalinity from the changes in  $\text{Fe}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{-2}$  concentrations in the anoxic layer and compared them with the measured alkalinity (Fig. 5). The results agree qualitatively, albeit

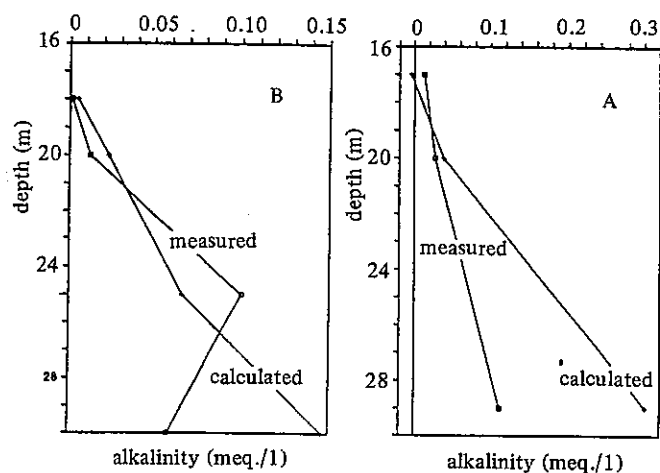


Fig. 5. Comparison between measured alkalinity and alkalinity calculated from  $\Delta\text{Fe}^{+2}$ ,  $\Delta\text{Mn}^{+2}$ ,  $\Delta\text{NH}_4^+$ , and  $\Delta\text{SO}_4^{-2}$ .

the quantitative agreement is poor for most bottom samples. This difference could be caused by the error in measurements or by exchange of material across the water-sediment interface. Better sample preservation and/or field measurements should provide better data in the future.

The alkalinity produced by those reactions is very important because the generated alkalinity reduces the impact of acid rain, especially for slightly acidic lakes which do not receive much buffer capacity from run off (Kelly *et al.*, 1982; Baker and Brezonik, 1986).

### IV. Conclusion

The pH of the Great Ghost Lake showed dichotomous distribution in summer. The dichotomous point was at a depth of 16m, the top of the anoxic layer. The pH value decreased with depth in the oxygenated layer but increased with depth in the anoxic layer. This phenomenon was caused by the change in respiration processes. Aerobic respiration decreased pH but anaerobic respiration increased pH.

The concentrations of  $\text{Fe}^{+2}$ ,  $\text{Mn}^{+2}$  and alkalinity increased with depth in summer. The gradients became steeper below the aerobic layer because the above mentioned anaerobic processes generated  $\text{Fe}^{+2}$  and  $\text{Mn}^{2+}$  but used up  $\text{H}^+$  in the anoxic layer. The alkalinity of the

lake water was homogeneously low in winter. This was caused by the overturning of the water, which destroyed the stratification and carried oxygen into the anoxic layer. As a result, the alkalinity which was produced in the anoxic layer in summer, the "in-lake alkalinity generation", was removed. The in-lake generated alkalinity could be very important in the Great Ghost Lake, which is slightly acidic, has low alkalinity, and is without influx of river run off. The  $\text{SO}_4^{-2}$  and  $\text{NO}_3^-$  provided by acid rain could be consumed in the anoxic respiration processes and could limit the impact of acid rain.

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## 大鬼湖之缺氧地球化學

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### 摘 要

大鬼湖是台灣唯一曾經報導過，少有人為污染但卻有無氧層存在的天然高山湖泊。夏天湖水 pH 值呈分叉型分佈，分叉點在溶氧陡降、進入無氧層處，此現象是呼吸作用型態改變所引起。

夏天湖水鹼度在無氧層處明顯遞增，此乃由無氧呼吸作用之“水體產生鹼度”的機制所運作。無氧呼吸作用籍著產生亞鐵及少量硝酸鹽、錳的還原，耗掉  $H^+$ ，因而提供了鹼度。此量在冬天水體翻滾後減少，使得冬天的鹼度較夏天來得低。