

GEOCHEMISTRY OF HCO_3^- AT THE SEDIMENT-WATER INTERFACE OF LAKES FROM THE SOUTHWESTERN CHINESE PLATEAU

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Abstract. Sediments were cored, and the sediment-water interface and overlying waters were sampled in 5 lakes from the southwestern Chinese plateau during 1991-95. The geochemistry of HCO_3^- at the sediment-water interface was examined by studying detailed profiles of pH, HCO_3^- concentrations and $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) in overlying lake water and porewater near the sediment-water interface. Dissolution-precipitation equilibrium of carbonates, diffusion flux, and the extent of the influence of diffusion on the whole lake were calculated. The results show that the HCO_3^- near the interface carried isotopic characteristics of decomposition of organic matter during early diagenesis, and that the porewater in surface sediments was unsaturated relative to calcite, and gradually saturated with depth. Furthermore, the interface is a source of HCO_3^- to the overlying water. Alkalinity (Alk) diffusion flux from sediments to the overlying water due to concentration gradients ranged from 0.51 to $24.33 \times 10^{-4} \text{ mol cm}^{-2} \text{ a}^{-1}$. The calculated contribution of the diffusion of Alk to the overlying water ranged from 0.46% to 49.42%. Diffusion is an important source of Alk in lakes with a long residence time and a relatively shallow depth.

Keywords: diffusion, alkalinity, sediment-water interface, southwestern Chinese plateau, carbonates, carbon isotopes

1. Introduction

HCO_3^- is a main component of alkalinity (Acid Neutralizing Capacity) in aquatic environments. With the seriousness of environmental problems, particularly acidification of lakes, many models have been built to predict evolution of acidity-Alk equilibrium (Dillon et al., 1984; Kelly et al., 1987). In most studies, concerns were focused on the influence of Alk from in-lake processes, e.g. the Alk from sediment-water interactions and sulfate reduction during early diagenesis (Carignan, 1985; Schindler et al., 1986; Kelly et al., 1987). Alk diffusion flux from sediments in various lakes also has been calculated (Carignan, 1985; Wu and Wan, 1996a,b). The geochemistry of HCO_3^- near the interface, however, needs to be further investigated, and the impact of the upward diffusion of dissolved substances to the overlying water needs to be quantified.

Carbon cycling is an important topic in the geochemistry of lake systems, particularly with increasing atmospheric CO_2 concentrations, which are believed to be responsible for the changes in global temperature and climate (Kelts and Hus, 1978; Oechel and Hastings, 1993). Therefore it is significant to investigate the response of natural geochemical processes at different interfaces to CO_2 increases, and their contribution to atmospheric CO_2 .

The southwestern Chinese plateau is a large karst area, where the carbonate terrain is suffering severe weathering and erosion. Lake sediments record these processes and possibly influence the chemical composition of overlying water due to in-lake process and early diagenesis. This study aims to evaluate possible impacts of interface diffusion on the acidity-Alk balance of overlying water, to characterize carbon isotopes and dissolution-precipitation equilibrium, and to investigate the geochemistry of HCO_3^- near the sediment-water interface.

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2. Sampling and analysis

The selected lakes are located at the boundary between southeastern monsoon and southwestern monsoon on the eastern slope of the Qinghai-Xizang (or Tibet) Plateau of China. The physical and chemical characteristics of these lakes are presented in Table I. Lake Lugu (LG) (27°41'-25'N, 110°45'-50'E) and Lake Erhai (EH) (25°35'-58'N, 100°05'-17'E) are two deep lakes in Yunnan Province. Lake Aha (AH) and Lake Baihua (BH) are located in the suburb of Guiyang city, and are the main drinking-water reservoirs for Guiyang. Lake Hongfeng (HF) (26°25'-34'N, 106°20'-28'E) is the largest artificial reservoir in Guizhou province.

TABLE I

Physical and chemical features of 5 lakes from the southwestern Chinese plateau

	drainage area km ²	lake area km ²	elevation m	average depth m	water residence time(a)
Lake Lugu	171.4	50.5	2685	40.4	18.50
Lake Erhai	2470.0	249.8	1974	10.2	2.80
Lake Hongfeng	155.1	57.2	1240	9.3	0.26
Lake Aha	190.0	3.4	1108	13.2	0.44
Lake Baihua	183.2	14.5	1100	13.0	0.16

	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺ m mol L ⁻¹	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Lake Lugu	0.81	0.28	0.014	0.39	2.22	0.42	0.005	0.012
Lake Erhai	0.90	0.54	0.049	0.30	2.58	0.36	0.15	0.019
Lake Hongfeng	1.23	0.49	0.041	0.11	2.65	0.49	0.21	0.032
Lake Aha	3.45	0.88	0.073	0.31	2.31	0.41	3.16	0.120
Lake Baihua	*	*	*	*	2.26	*	0.98	0.087

* = not determined

Samples of lake water were collected at about 5 m depth intervals. Sediments were cored at the center of each lake using a sediment-water interface sampler designed by ourselves (Yuang et al., 1993). The cores and porewater were not disturbed during the field coring process. Sediment cores were sliced *in-situ* into 0.5 to 2.0 cm sections, and porewater was extracted through 0.45 µm membrane filters following high-speed centrifugation. pH values were measured *in-situ*, SO₄²⁻ and NO₃⁻ ions were determined by chromatographic analysis, HCO₃⁻ by volumetric analysis, and Ca²⁺, Mg²⁺, Na⁺, K⁺, and dissolved Mn and Fe by AAS after *in-situ* acidification with superpure HNO₃. The δ¹³C values of DIC were measured using mass spectroscopy.

3. Results and Discussion

3.1. DIFFUSION FLUX of ALK FROM POREWATER TO OVERLYING WATER

Profiles of pH and HCO_3^- concentrations in porewater and overlying waters of these lakes, shown in Figure 1, clearly demonstrate that HCO_3^- concentrations and pH rarely change in the overlying water. However, a major increase in HCO_3^- and a decrease in pH occurred at the interface in most profiles except for two. The HCO_3^- concentrations in the porewater were much higher than in the overlying water and increased gradually with depth. Other ions also showed obvious changes at the sediment-water interface. The SO_4^{2-} and NO_3^- concentrations of overlying water were higher than those of porewater, while the concentrations of dissolved Mn and Fe, Ca^{2+} , Mg^{2+} , K^+ , Na^+ in porewater were greater than in overlying water (Wu, 1995). Soluble substances could cross the sediment-water interface by molecular diffusion due to the concentration gradient (Glud et al., 1994; Wu and Wan, 1996a,b). Therefore, SO_4^{2-} and NO_3^- may diffuse downward from overlying water into porewater, while dissolved Mn and Fe, Ca^{2+} , Mg^{2+} , K^+ , Na^+ may diffuse upward, thus influencing the Alk near the interface.

Alk diffusion flux (J in $\text{mol cm}^{-2} \text{a}^{-1}$) can be calculated using the following equation if the coupling effect is ignored:

$$J = -\Phi D_s dc/dx \quad (1)$$

where Φ is the sediment porosity and equals 0.95 (Wu, 1995), dc/dx is the vertical concentration gradient at the interface (mol cm^{-4}), D_s is the sediment diffusion coefficient for sediments (which is a function of tortuosity, θ , and the molecular diffusion coefficient, D), and D ($\text{cm}^2 \text{s}^{-1}$) can be found in Li and Gregory (1974). In the following calculations we assume $\theta=1$. Concentration gradients and the resulting fluxes of HCO_3^- , dissolved Fe, and Mn at the interface of these lakes were then calculated using equation 1 (Table II)

According to the balance of positive-negative ions and the diffusion flux near the interface, the contribution of various ions to Alk can be expressed as (Stumm and Morgan, 1981; Berner, 1980):

$$\begin{aligned} \text{Alk} &= 2m\text{Ca}^{2+} + 2m\text{Mg}^{2+} + m\text{K}^+ + m\text{Na}^+ - (2m\text{SO}_4^{2-} + m\text{NO}_3^- + m\text{Cl}^-) \\ &= m\text{HCO}_3^- + m\text{OH}^- + 2m\text{CO}_3^{2-} - m\text{H}^+ \end{aligned} \quad (2)$$

Therefore, the flux of Alk across the interface can be approximated as:

$$J_{\text{Alk}} = J_{\text{HCO}_3^-} + J_{\text{OH}^-} + 2J_{\text{CO}_3^{2-}} - J_{\text{H}^+} \quad (3)$$

As OH^- and CO_3^{2-} concentrations were very low compared to that of HCO_3^- , they could be omitted from equation 3. In addition, oxidation of upwardly diffused reduced Fe and Mn can produce H^+ and reduce the flux. In this paper, we didn't differentiate between concentrations of different valencies of dissolved Fe and Mn in porewater. However, previous studies from Lake Hongfeng and other lakes from the southwestern Chinese plateau showed that concentrations of oxidized Fe and Mn in porewater were very low compared to those of reduced Fe and Mn (Chen, 1990; Wu, 1995). Thus we used diffusion fluxes of dissolved Fe and Mn to calculate the maximum influence of reduced Fe and Mn on Alk diffusion during early diagenesis. Therefore, from equation 4, further estimates of their influence on Alk in overlying water can be derived:

$$J_{\text{Alk}}^0 = J_{\text{HCO}_3^-} - 2 J_{\text{dissolved Fe}} - 2 J_{\text{dissolved Mn}} \quad (4)$$

The flux of Alk calculated according to equation 4 (see Table II) ranged from 0.51 to $24.33 \times 10^{-4} \text{ mol cm}^{-2} \text{ a}^{-1}$.

3.2. CONTRIBUTION OF UPWARD DIFFUSION OF ALK TO THE OVERLYING WATER

If the amount (E_i) of element (i) accumulated in the overlying water via diffusion is: $E_i = J_e \cdot T_w$ then the concentration (C_{in} in mol L^{-1}) due to diffusion to the whole overlying water would be:

$$C_{in} = E_i / h = J_e \cdot T_w / h \quad (5)$$

The ratio between the concentration due to the diffusion (C_{in}) and total concentration (C in mol L^{-1}) in the overlying water is used here to indicate the contribution via diffusion for this element to the overlying water (Wu, 1995; Wu and Wan, 1996a):

$$C_{in} / C = J_e \cdot T_w / h \cdot C = T_w / T \quad (6)$$

where J_e is the diffusion flux of alkalinity ($\text{mol cm}^{-2} \text{ a}^{-1}$), h is the effective water depth (cm), T_w is water residence time (a) and $h \cdot C / J_e$ can be defined as the residence time of the element (T_e).

Assuming that the waters were homogeneously mixed, the T_w / T_e ratio for HCO_3^- should represent the contribution of Alk diffusion to the overlying water which is associated mainly with diffusion flux, water residence time and effective depth. Based on J_e , T_w , h and C , the contribution of upward diffusion to the overlying water was calculated (see Table II). It can be seen from Table II that the contribution of upward diffusion of Alk varies in different lakes. In Lake Lugu, about one-third of Alk of waters came from diffusion, showing that interface diffusion played an important role in controlling acid-base equilibrium of lake water. In Lake Aha, the contribution of interface Alk diffusion to lake water is very small, only 0.46%. About one-tenth of Alk came from diffusion in the other three lakes.

TABLE II

Vertical Concentration gradients of dissolved Fe, Mn and HCO₃⁻, their resulting diffusion fluxes, and the ratio of *T_w* to *T_c* at sediment-water interface of lakes from southwestern Chinese plateau

	LG9406-5	LG9405-1	LG9101	EH9402-2	EH9102	EH9101	AH9201	BH9402-3	BH9402-1	HF9101	HF9102
water depth (cm)	6000	5000	6500	1200	1600	1600	1900	1500	1500	2000	2000
lake alkalinity (m mol L ⁻¹)	2.52	2.49	2.27	2.39	2.54	2.54	2.05	2.31	2.31	2.74	2.74
residence time (a)	18.5	18.5	18.5	2.8	2.8	2.8	0.28	0.44	0.44	0.26	0.26
HCO ₃ ⁻ gradient (10 ⁻⁶ mol cm ⁻⁴)	1.01	0.56	0.95	0.15	0.54	0.57	0.23	3.15	1.55	6.89	4.23
HCO ₃ ⁻ diffusion flux (10 ⁻⁴ mol cm ⁻² a ⁻¹)	3.54	1.96	3.35	0.53	1.04	2.00	0.81	11.03	5.43	24.33	14.83
dissol. Fe diffusion flux (10 ⁻⁷ mol cm ⁻² a ⁻¹)	1.45	8.31	2.70	5.07	14.02	8.47	21.05	22.77	1.78	0.195	0.195
dissol. Mn diffusion flux (10 ⁻⁷ mol cm ⁻² a ⁻¹)	15.34	103.10	38.68	6.39	13.89	2.81	65.43	296.50	206.5	0.089	0.08
<i>J</i> _{alk} (10 ⁻⁴ mol cm ⁻² a ⁻¹)	3.51	1.74	3.28	0.51	0.98	1.97	0.64	10.39	5.01	24.33	14.83
<i>T_w</i> / <i>T_c</i>	42.9	25.8	41.1	4.9	6.7	13.6	0.46	13.2	6.4	11.5	7.0

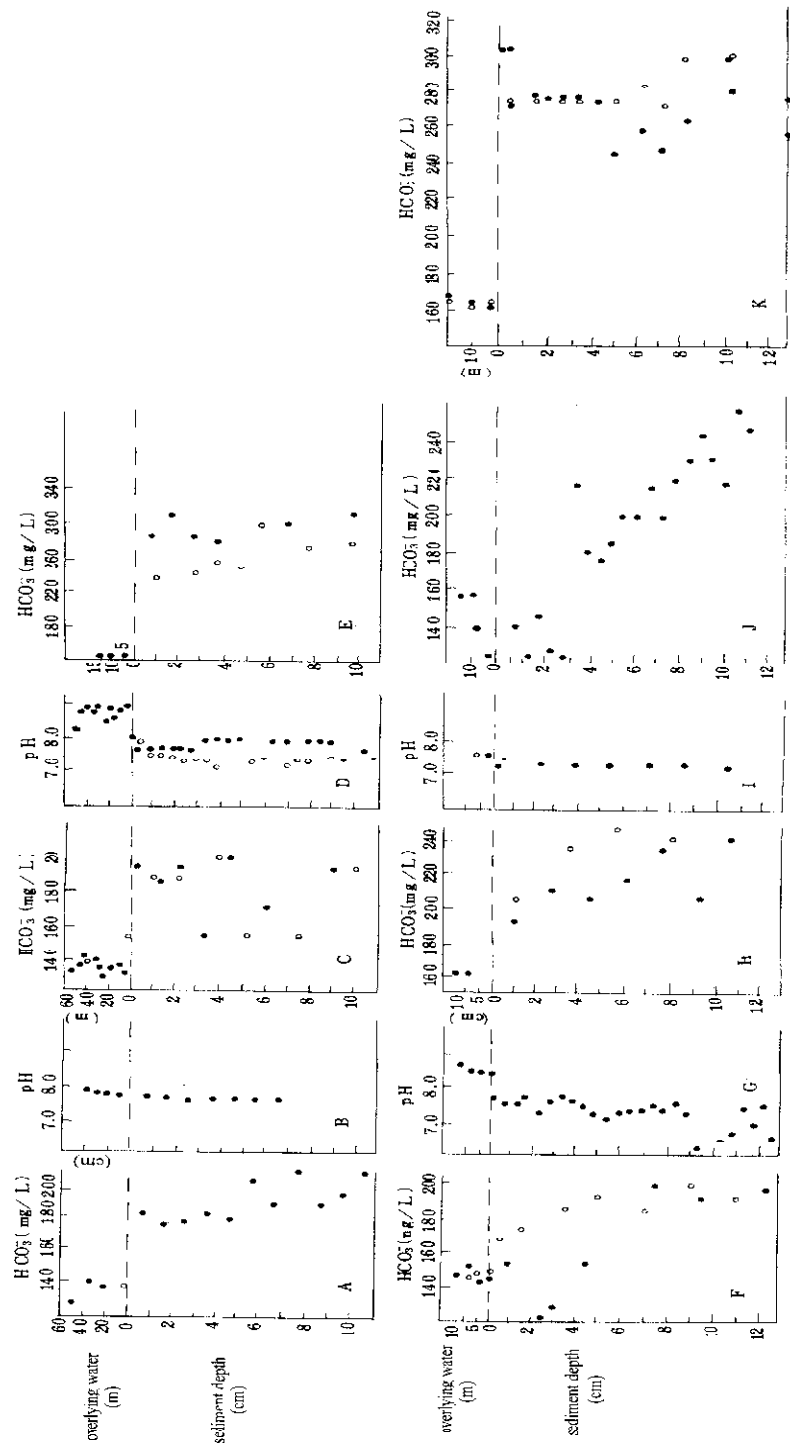


Figure 1 Profiles of pH and HCO_3^- concentrations in porewater and overlying waters of 5 lakes from southwestern Chinese plateau.

[A and B: LG9405-1(●), LG9406-5(○); C and D: LG9402-3 (●), BH9402-1(○), EH9402-1(○), EH9402-2(○), EH9101(○);

J: AH9201; K: HF9101(○), HF9102(●)]

3.3. CARBONATE EQUILIBRIUM AT THE SEDIMENT - WATER INTERFACE

Based on the profiles of Ca^{2+} (Wu, 1995) and HCO_3^- concentrations in porewater and overlying water (Fig.1), we can characterize the solution geochemistry in a carbonate system using the saturated index (SI):

$$SI = IAP / K_{sp} \quad (7)$$

where K_{sp} is the solubility product of calcite and IAP is the ion activity product.

The dissolution and precipitation of calcites in sediments can be expressed by the following equations:



$$\text{Therefore, } IAP = a\text{Ca}^{2+} \cdot a\text{CO}_3^{2-} = r\text{Ca}^{2+} \cdot m\text{Ca}^{2+} \cdot r\text{HCO}_3^- \cdot m\text{HCO}_3^- \cdot K_2 / m_{\text{H}^+} \quad (11)$$

$$\therefore \log SI = \log m\text{Ca}^{2+} + \log m\text{HCO}_3^- + \log r\text{Ca}^{2+} + \log r\text{HCO}_3^- + \text{pH} + P_{ksp} - P_{k2} \quad (12)$$

Where $r\text{Ca}^{2+}$ and $r\text{HCO}_3^-$ are activity coefficients, $P_{ksp} = 8.37$, P_{k2} is the second-order dissolution constant of H_2CO_3 (equation 10) and equals 10.43 for a temperature of 15°C.

Based on $m\text{Ca}^{2+}$, $m\text{HCO}_3^-$ and pH values, the profiles of SI in porewater and overlying waters of 5 lakes were constructed (see Figure 2) according to equation 12. From Figure 2, it can be seen that these lake waters were always saturated with respect to calcite, suggesting endogenic calcite precipitation from the overlying water. Near the sediment-water interface, the porewater was unsaturated relative to calcite, because decomposition of organic matter causes calcite dissolution. With increased burial, the porewater became anaerobic, the CO_2 from decomposition of organic matter in these fine sediments was greatly reduced and calcite precipitation resumed. From Figure 2, it can be seen that the porewater became saturated with increasing burial.

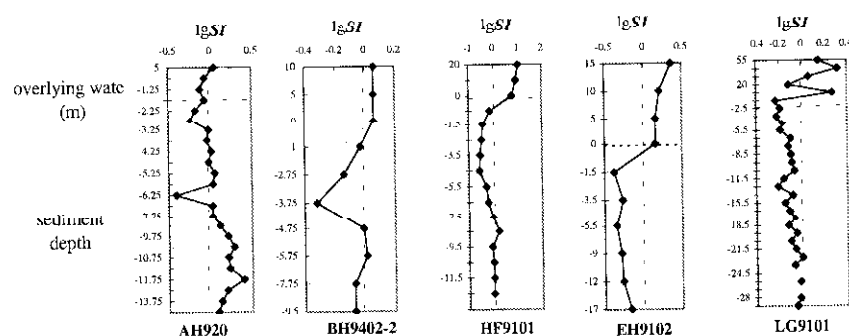


Figure 2 Profiles of saturated index (SI) of calcite in sediment porewater and overlying water.

3.4. CARBON ISOTOPES OF DIC DURING EARLY DIAGENESIS

Table III shows $\delta^{13}\text{C}$ characteristics of DIC in the porewater and overlying water in Lake Hongfeng. The $\delta^{13}\text{C}$ values of DIC in Lake Hongfeng range from -8.1 ‰ to -10.40 ‰. The DIC of surface waters has higher $\delta^{13}\text{C}$ values, whereas the deeper waters have lower $\delta^{13}\text{C}$ values. Because the influence of water atmospheric exchange on the carbon isotopic composition of DIC in lake water was very small (Wan et al., 1996), the lower $\delta^{13}\text{C}$ values at the sediment-water interface were caused probably by decomposition of organic matter, which releases ^{12}C -enriched carbon at the interface (Mckenzie, 1985; Wan et al., 1996).

The $\delta^{13}\text{C}$ values of DIC of sediment porewater are lower than that of overlying water (Table III), indicating the input of ^{12}C -enriched CO_2 from decomposition of organic matter. However, the $\delta^{13}\text{C}$ values of DIC in porewater increased with sediment depth. This indicates that decomposition of organic matter was greatly reduced with increasing burial due to gradual depletion of oxygen.

TABLE III

Carbon Isotopic Composition of DIC in porewater and overlying water of Lake Hongfeng

Water depth(m)	DIC, $\delta^{13}\text{C}$ (‰, PDB)
0	-8.10
10	10.40
20	-10.10
Sediment depth(cm)	DIC of porewater, $\delta^{13}\text{C}$ (‰, PDB)
5	-12.10
8	-9.80
10	-8.70
20	-5.90

4. Conclusions

(1) The lower $\delta^{13}\text{C}$ values of DIC near the sediment-water interface characterize decomposition of organic matter during early diagenesis. The porewater in surface sediments was unsaturated relative to calcite, whereas authigenic carbonate precipitated from the porewater in deeper sediment.

(2) The sediment-water interface was a source of HCO_3^- to overlying water. The flux near the interface was calculated to be 0.51 to $24.33 \times 10^{-4} \text{ mol cm}^{-2} \text{ a}^{-1}$. The influence of diffusion on the whole lake depended chiefly on the flux, water depth and residence time of the lakes. This suggests that models on response of acid precipitation to acid-base equilibrium of lakes should take various Alk sources into account.

(3) Decomposition of organic matter is an important factor controlling geochemistry of HCO_3^- near the sediment-water interface, during which various acceptors (O_2 , NO_3^- , Fe and Mn oxidation, SO_4^{2-}) were reduced, and CO_2 was released into the porewater. This process results in the increase in Alk and DIC, thus changing the saturated index of carbonate, and decreasing the carbon isotopic values.

(4) Carbonates in sediments contain much information about climate and environmental change. C and O isotopes were used to indicate past environmental change in oceans and lakes (Hodell et al., 1991; Talbot and Johannessen, 1992; Kelts and Hus, 1978; Wan et al., 1996). However, these indicators could be influenced by many geochemical processes (Chen, 1994; Talbot et al, 1990; Wu, 1995). Only when we understand these processes (e.g. early diagenesis), can we distinguish and extract environmental information from waters and sediments.

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