

BIOGEOCHEMICAL MECHANISM OF POSTDEPOSITIONAL MIGRATION OF Fe AND Mn IN LAKE AHA, CHINA^①

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ABSTRACT: Lake Aha in Guizhou Province, China is a medium-sized artificial reservoir with seasonally anoxic hypolimnion. Long-term sedimentary accumulation of iron and manganese resulted in their enrichment in the upper sediments. In anoxic season, Fe^{2+} and Mn^{2+} formed from biological oxidation, would diffuse upto upper water from sediments. However, the concentration of Fe^{2+} increased later and decreased earlier than that of Mn^{2+} . Generally, sulfate reduction occurred at 6 cm below the sediment-water interface. Whereas, in anoxic season, the reduction reached sediment top, inhibiting the release of Fe^{2+} . As the oxidation of Mn^{2+} required molecular oxygen as catalyst, serious anoxia caused the violent diffusion of Mn^{2+} . Based on the bio-effects on the accumulation of Mn in natural fresh water, it's necessary to seek a way to control manganese rerelease through accumulated manganese bacteria action.

KEY WORDS: postdepositional migration of Fe and Mn, biogeochemical effect, Lake Aha

I. INTRODUCTION

Lake Aha is a medium-sized artificial reservoir with seasonally anoxic hypolimnion, and a water resource of Guizhou Province, China, built in 1958, worked in 1960 and expanded in 1982. It has a drainage basin of 190 km² with average annual temperature of 15.3°C and precipitation of 1109 mm. Open plant cover, containing shrub and grass, surrounds the lake, and siallitic and sifeic yellow soil is developed on Permian limestone and coal layer, meanwhile,

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black and brown lime soil on Trias carbonate and mud stone in the watershed. Lake Aha has a volume of $0.445 \times 10^8 \text{ m}^3$, surface area of 3.4 km^2 , mean depth of 13 m, maximum depth of 24 m. Its water flux is $1.04 \times 10^8 \text{ m}^3/\text{a}$ with water residence time of 0.44 a.

As acid mine water and leaching solution of coal mine spoil containing iron and manganese from hundreds of coal mines inputs to the lake waters, it has been worsened with the increasing concentration of Fe^{2+} and Mn^{2+} and decreasing pH two months per year recently. The biogeochemical processes of lake sedimentation participated by microorganism are important to the material cycles in the sediment-water interface where most organism are oxidized and CH_4 , NH_4^+ , H_2S , Fe^{2+} and Mn^{2+} are formed. It is the redox change that causes the seasonal postdepositional migration of iron and manganese in the sediment-water interface (Davison, 1993; Furrer, 1991; Johnson, 1991; Stumm, 1992).

In order to find out mechanism of lake water variation, we took sediment cores and overlying water samples with sediment-water interface equipment (Wu *et al.*, 1988) in different sites and months from November 1992 to September 1993. Pore-water of sediments was centrifugalized and extracted in nitrogen. Ion selective electrode, ion chromatography, element analyzer, AAS, colorimetric and volume method were applied for hydrochemical analysis. More detail about geochemical behaviour of Fe and Mn in sediment-water interface of Lake Aha has been discussed. ① In this work, we would like to seek a biogeochemical way to control postdepositional migration of Fe and Mn.

II. INHIBITED Fe^{2+} AND MIGRATION OF Mn^{2+} IN DIFFUSION BOUNDARY LAYER OF SEDIMENTS

1. Seasonal Variation of Fe and Mn in Lake Water

From Fig. 1, it was observed that the concentration of Mn^{2+} , which was mostly low ($< 0.01 \text{ mg/l}$) in deep waters, was increased from July to September. Although similar to variation of Mn^{2+} concentration, the increase of Fe^{2+} started later, ended earlier and the increase range was less than that of Mn^{2+} . This implied that the diffusion of Fe was strongly inhibited.

2. Seasonal Variation of Physio-chemical Conditions in Lake Water

Seasonal variation of Fe and Mn was closely related to physio-chemical conditions in lake water. During July to September, water temperature went up obviously and the difference between temperatures in upper and lower layer was 10°C (Fig. 2a), pH value was clearly lower (Fig. 2 b), saturated percentage of dissolved oxygen (DO) declined to minimum ($< 10\%$) (Fig. 2c), and the concentration of SO_4^{2-} degraded more violently, owing to dilution of

① Wan Guojiang *et al.*: The impact of water quality of Lake Aha. Report of the State Key Lab. of Environmental Geochemistry. 1994.

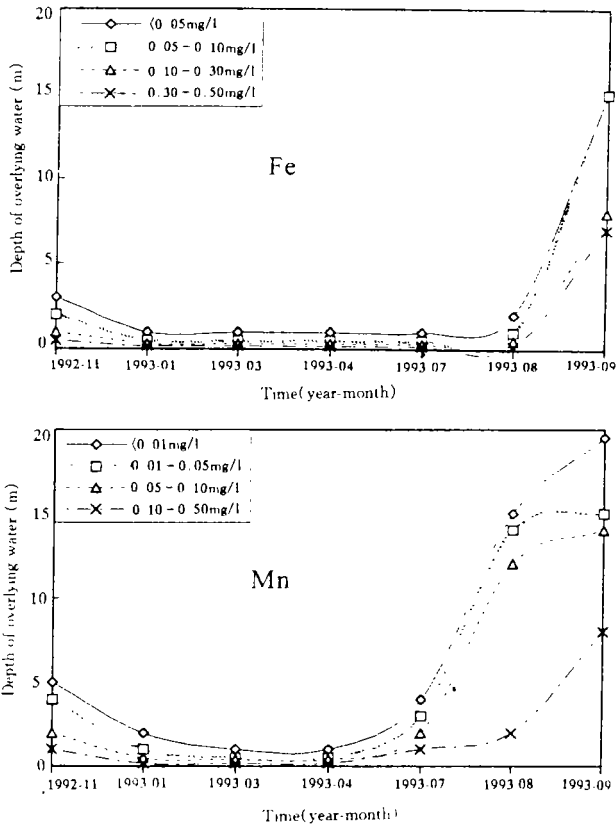


Fig. 1 Seasonal variation of Fe and Mn in Lake Aha

rainwater or SO_4^{2-} reduction (Fig. 2d).

3: Migration Difference of Fe and Mn in Sediment-water Interface

No matter in sediments of sediment-water interface, particle-water distribution coefficient of Fe (K_d) in autumn was evidently lower than that in winter, indicating that Fe^{2+} diffused upto overlying water from sediment in anoxic season. Meanwhile, the increasing K_d exhibited that cycling of Fe^{2+} was restrained by diffusion boundary layer. However, K_d of Mn in autumn not only degraded more actively than that in winter, also K_d of interface water was lower than that in sediment, demonstrating that release of Mn^{2+} was very violent in the sediment-water interface (Fig. 3).

The above features are closely involved with the reduction of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$, $\text{Mn}^{4+} \rightarrow \text{Mn}^{2+}$ and $\text{SO}_4^{2-} \rightarrow \text{S}^{2-}$ under anoxic conditions. Redox equilibrium model shows that the concentrations of Fe^{2+} and Mn^{2+} in aqueous solutions tend to increase with decreasing of P_e value. In CaSO_4 saturated solution, when pH is less than 7, SO_4^{2-} will be reduced to S^{2-} . In case of pH

=7, only when $P\epsilon$ is less than -3, SO_4^{2-} will be remarkably reduced into S^{2-} (Stumm, 1981).

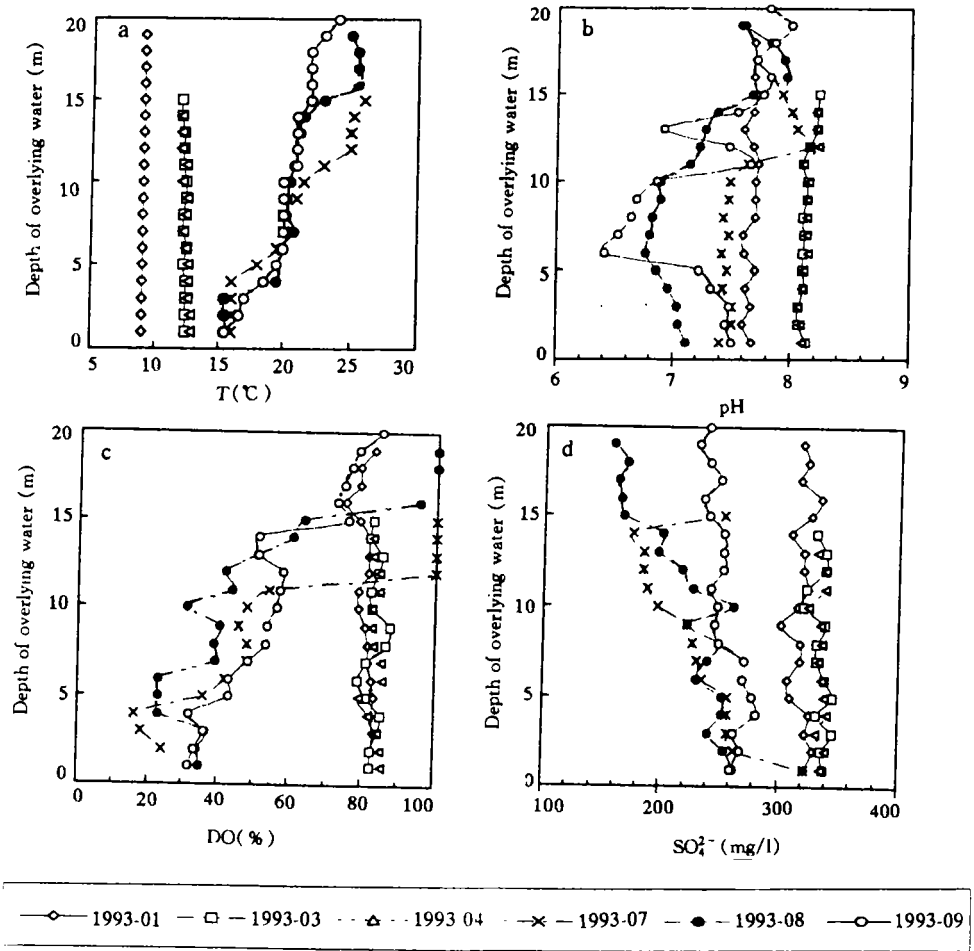
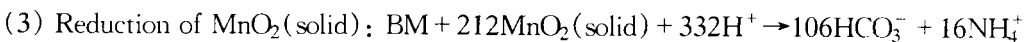
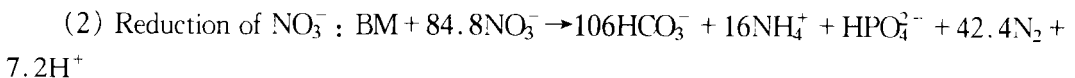
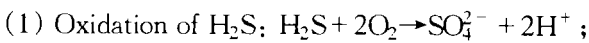


Fig. 2 Vertical variation of T , pH , DO and SO_4^{2-} in Lake Aha

III. REDUCTION OF SULFATE AND MANGANESE IN SEDIMENTS

1. Depth Variation of SO_4^{2-} Reduction

The thermodynamic redox equations for the bio-oxidation of sediments include (Furrer, 1991):



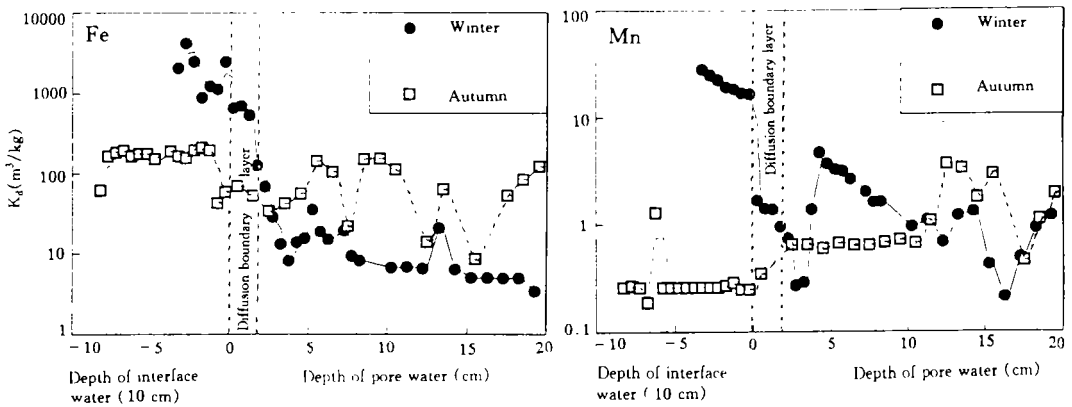
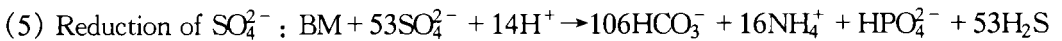
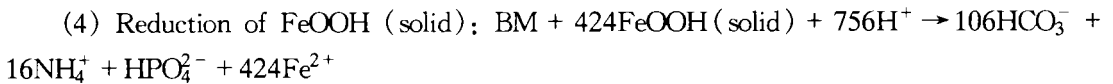
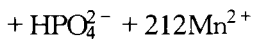


Fig. 3 Vertical variation of particle-water distribution coefficient of Fe and Mn in the sediment-water interface of Lake Aha



In each of above redox equation, H_2O can be neglected, BM stands for biomass in accordance with the Redfield method, i. e. $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4$. The characters of surface sediments in deep water vary with changing season: in winter and spring, suspected particle at the top of sediments (about 2 cm in thickness of suspected layer) is light brown in color, i. e., Fe and Mn are in the oxidizing state, with contents of 12% and 2%, respectively. Under it, the sediments are grayish-black in color, belonging to the Fe sulfide-bearing layer. In early autumn, the suspected layer of sediments turned to black in color, forming the layer containing sulfides of iron, i. e., the sulfide layer is transferred to the top of sediments, and the percentage contents of Fe and Mn decreased to 5% and 0.2%, respectively (Wan *et al.*, 1997).

2. Reduction Process of Sulfate

SO_4^{2-} is one of the major cations in waters of Lake Aha and it is estimated at 2.5–3.0 mmol/l both in winter and in spring, approximately 10 times the saturated dissolved oxygen in lake water. So the depth where SO_4^{2-} can penetrate is also ten times deeper than that for oxygen (Fig. 4). Analyses of samples collected in early winter (November 1992) showed that the concentration of SO_4^{2-} , which is 1.6 mmol/l in pore water at the top of sediments in deep water, is decreased to 0.1 mmol/l at the depth of 6 cm in sediment and then rapidly depleted with increasing depth. As a result, the reduction of sulfate was inhibited. In anoxic season, content of SO_4^{2-} in water declined slightly. However, percentage content of saturated dissolved oxygen degraded from 80% in upper water to 20% in hypolimnion. Obviously, reduction of SO_4^{2-}

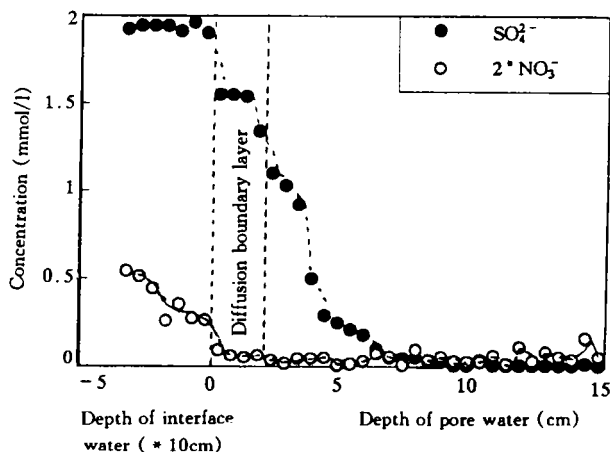
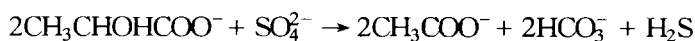


Fig. 4 Vertical profile of SO_4^{2-} and NO_3^- in the sediment-water interface in deep water of Lake Aha

involved with sulfate-reducing bacteria seemed to shift to sediment-water interface.

Moreover, as can be seen from Fig. 4, the reduction of NO_3^- is restricted only to the boundary of sediments, and the concentration of NO_3^- in pore water below the sediment-water interface drastically decreased. At the same time, the reduction of MnO_2 and FeOOH shifts toward the sediment-water interface, resulting in the decrease of the contents of Fe and Mn in diffusive boundary layer. It is generally considered that *Desulfovibrio* sp. can play an important role in the sulfate reduction of sediments. The basic condition of reducing environment, the presence of SO_4^{2-} and proper energy supply determines, to a large extent, the growth and metabolism of the sulfate-reducing bacteria. Therefore, when SO_4^{2-} concentration in pore-water of sediments decreased with increasing depth and enriched sulfide, it would be strongly evidenced that there exist sulfate-reducing bacteria in sediments (Krumbein, 1983).

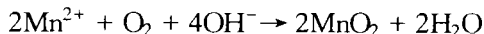
Desulfovibrio sp. is a kind of strictly anaerobic bacillus, utilizing organism as carbon and energy sources in lake sediment, such as lactate, C-4 decarboxylate and pyruvate, etc. This kind of bacteria possesses an incomplete enzyme system for tricarboxylic acid cycle, so organisms are oxidized to CH_3COO^- in stead of CO_2 , while SO_4^{2-} acts as the final electron acceptor:



At the sediment-water interface, iron bacteria have a fundamental role in the accumulation and precipitation of iron. After Fe^{2+} in sediment finds its way into pore-water, Fe^{2+} would be most likely to form FeS or even FeS_2 by *Desulfovibrio*, or to be oxidized to Fe^{3+} which will be precipitated or incorporated into organic chelates by iron bacteria under moderate pH conditions. It can be seen that in anoxic seasons, the diffusion of dissolved Fe^{2+} upward to upper waters is inhibited by reduction of sulfates.

3. Redox Process of Mn

Oxidation of Mn^{2+} requires the involvement of molecular oxygen. The reaction is presented below:



When concentration of Mn^{2+} , O_2 and OH^- increase in lake water, the above reaction will proceed toward the right side. In the presence of slightly aerobic bacteria, Mn^{2+} can also be oxidized into Mn^{4+} even under low oxygen conditions. Oxidation caused by microorganisms usually takes place in case pH is 6.5–7.5. As a result of the oxidation of organic carbon influenced by bacteria, the more organic carbon in sediments, the more intense the reduction of Mn^{4+} . This mechanism may be a reasonable explanation of the serious postdepositional migration of Mn in seasonally anoxic waters.

Although with decreasing pH value, Mn^{4+} in the sediments is easily transformed into soluble Mn^{2+} and can diffuse upward to overlying water through pore-water, many kinds of bacteria are capable of accumulating Mn even if the content of Mn is extremely low. $10^5 - 10^6$ Mn-accumulating bacteria can be recognized in 1-ml pore-water in sediments of natural fresh lakes (Krumbein, 1983). The association of Mn bacteria with lake sediments may be the result of sedimentation rather than cause of precipitation. The presence of active bacteria in large amounts in lake sediments implicates that there exists a kind of biogeochemical process which can accelerate the accumulation of Mn by bacteria. Therefore, the accumulation of Mn bacteria can be used to control the postdepositional migration of Mn.

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