Suspended Particulate Elements in Anoxic Hypolimnion of a Eutrophic Lake

Masahito Sugiyama* and Toshitaka Hori**

*Department of Environmental Sciences, Faculty of Integrated Human Studies,
Kyoto University, Kyoto 606-01
**Graduate School of Human and Environmental Studies,
Kyoto University, Kyoto 606-01

ABSTRACT – The distribution of suspended particulate elements was measured at the dredged area in the southern basin of Lake Biwa with a seasonal anoxic hypolimnion. In order to reveal the net effect from authigenic suspended particles, the total particulate concentration measured was corrected by the use of particulate Al content as a tracer for terrigeneous matter. Particulate Fe concentration increased with depth near the bottom in the anoxic hypolimnion. Distributions of Mn, Mg, Ca, Sr, and V also showed profiles similar to Fe. There were positive correlations between these elements and Fe concentrations and, in particular, the plots of Mn, Ca and Sr against Fe showed good linearities. The concentrations of Cu and Zn started to increase from just below the thermocline, at a depth shallower than the above elements did, and were almost constant near the bottom. These geochemical behaviors are discussed in terms of the formation of slightly soluble sulfide precipitate and adsorption of metal ions onto it.

INTRODUCTION

In oxic lacustrine and marine environments, Fe and Mn oxides perform as an effective adsorbate of trace elements (Singh and Subramanian, 1984). These oxides often accumulate at the oxic-anoxic water boundary by repeating reductive dissolution and oxidative re-deposition. It is a typical example to demonstrate these characteristics of Fe and Mn oxides that ferro-manganese nodules which are discovered on the sediment surface of some lakes and the ocean greatly concentrate many kinds of metal in themselves (Cronan, 1976; Takamatsu et al., 1993).

However, where dissolved oxygen is completely depleted and waters become highly reductive, as in the bottom water of eutrophic lakes, fjords or seas, Fe and Mn oxides are not formed and, inversely, reductively dissolve into water phase. In such a water, Fe sulfides are thought to succeed these oxides to play the role of scavenger of trace ele-

ments. This is because Fe^{2+} and S^{2-} ions accumulate by the reduction of Fe oxides and SO_4^{2-} ions, respectively, and Fe sulfides are abundantly precipitated (Davison and Heaney, 1978; Kawashima et al., 1985; Dyrssen and Kremling, 1990). Of course, Mn^{2+} ions also accumulate in the water, but MnS is seldom precipitated because the sulfide is more soluble than FeS (Kawashima et al., 1985; Balistrieri et al., 1992a).

It has been confirmed in many laboratory experiments that various heavy metals and other elements are effectively removed from aqueous phase by the addition of Fe sulfides. Morse and Arakaki (1993) showed that metal ions such as Mn^{2+}, Co^{2+} and Ni^{2+} exhibit good affinities to one of the Fe sulfide minerals, mackinawite (FeS). Pyrrhorite ($Fe_{1-x}S$) and pyrite (FeS_2) were also reported to adsorb many metal ions well (Brown et al., 1979; Jean and Bancroft, 1986; Kornicker and Morse, 1991; Schoonen et al., 1992). However, there are few papers which have discussed the formation of Fe sulfides and their interaction with trace elements in a natural environment. Although Mn, Ca and P were reported to be associated with FeS-rich particles (Davison and Dickson, 1984; Davison et al., 1992), the geochemical behaviors of other elements are poorly understood (Dyrssen and Kremling, 1990; Balistrieri et al., 1992b).

Sulfide formation is observed in most sediments of lakes and oceans, even if the bottom water is strongly oxic. This reaction is known to be one of most important diagenetic processes (Morse et al., 1987). Accordingly, studies of the chemical dynamics of metals in highly reductive waters are closely related to the investigation of the diagenesis which settling particles encounter in the sediment.

In the present paper, based on the distribution profiles of particulate suspended elements measured in the anoxic hypolimnion of a eutrophic freshwater lake, the southern basin of Lake Biwa, we discuss the geochemical behavior of the elements and their association with formation of sulfide precipitates, especially FeS.

SAMPLING AND ANALYTICAL METHODS

Sampling

Water samples were collected at the dredged area of the southern basin of Lake Biwa on 19 July 1989 and 3 August 1990 using a pump system equipped with Tygon tubing (Sugiyama and Hori, 1994). Immediately thereafter, the sample (300-500 ml) was filtered through a 0.4 μm Nuclepore filter (diameter: 47 mm). The substance collected on the filter was defined in the present work as suspended particulate matter (SPM). The filtrate was acidified to pH 1 by adding superpure grade hydrochloric acid (Merck).

Analysis of dissolved iron and manganese

Both Fe and Mn in the filtrate were directly determined with a Japan Jarrel Ash model ICAP 96-953 inductively coupled plasma atomic emission spectrometer (ICPAES).

Analysis of suspended particulate elements

The SPM and Nuclepore filter used were transferred into a 30 ml Teflon screw vial and mixed with 0.5 ml of 25 % aqueous ammonia in order to hydrolyze the filter. After standing for 12 hr, the mixture was dried at 110°C, then digested with 0.5 ml of 70 % perchloric acid at 150 °C for 2 hr with the vial cap fit loosely. Thereafter 0.5 ml of 65 % nitric acid was added. The mixture was digested at 170°C for 4 hr, and then heated to dryness by taking off the cap. To the residue, hydrofluoric acid (40%, 0.5 ml) was added, and the mixture was homogenized ultrasonically for 10 min, then brought to dryness by heating at 150 °C. The residue was dissolved in 3 ml of 0.1 M hydrochloric acid. Concentrations of Fe, Mn, Mg, Ca, Sr, Ba, V, Cu, Zn, Al, and Ti were then determined simultaneously with ICPAES.

All the samples were manipulated in a clean box with a 0.1 μm air-filter. All reagents used were of superpure grade (Merck).

Analysis of terrigeneous manganese fraction in suspended particulate matter

Surface water samples were collected at 7 stations [Ie-1, Kc-3, Lc-4, Lc-2, Mb-3, Nb-5, and Na-3 (Hori et al., 1992)] in the southern and northern basins of Lake Biwa on 6 June 1995. The sample (500-1000 ml) was filtered through a 0.4 μm Nuclepore filter. In order to dissolve the Mn oxide fraction, 1.5 ml of reductive extractant, which contained 1 M hydroxylammonium chloride and 0.175 M sodium citrate and was controlled to pH 5.0, was added to the SPM on the filter kept in a filter folder. After standing for 30 min, the extract was filtered. This treatment was repeated a second time. After washing with pure water, the treated SPM was transferred into a 30 ml Teflon screw vial together with the filter used. The sample was digested and analyzed by the method previously reported (Sugiyama, 1996). This method is essentially the same as the one described in the above section.

RESULTS AND DISCUSSION

Deoxygenation in the hypolimnion

Hypolimnion at the dredged area in the southern basin of Lake Biwa was reported to become anoxic in the summer stratification period because the dissolved oxygen was

completely consumed to decompose organic settling particles from the eutrophic epilimnion (Terashima and Ueda, 1982; Kawashima et al., 1985). In the present work, although dissolved oxygen was not measured, its depletion in the hypolimnion was confirmed by the distribution profiles of dissolved Fe and Mn. These results are shown in Fig. 1, together with that for water temperature (WT). The thermocline was around 8 m depth in 1989, and was around 6 m depth in 1990. Although both dissolved Fe and Mn were at very low level in the epilimnion (Fe: 0.01 - 0.4 μ M; Mn: 0.02 - 0.08 μ M), their concentrations in the hypolimnion sharply increased from just below the thermocline and reached 20-30 mM near the bottom.

Correction for the terrigeneous fraction in suspended particulate matter

Limnetic SPM is divided into terrigeneous, authigenic mineral and biogeneous fractions, according to their origins. In order to reveal the distribution of authigenic particles in the present anoxic hypolimnion more clearly, the terrigeneous fraction was eliminated from the total particulate concentration measured (Sugiyama and Hori, 1994). Figure 2 shows the correlation between particulate Al and another element using all data sets obtained during July 1989 and August 1990. As reported previously, when limited to the results in the hypolimnion, plots of elements against Al were sufficiently linear independently of sampling times for most of the elements analyzed.

Manganese was poorly correlated with Al, because Mn concentration is affected even in the epilimnion by authigenic oxide particles produced from dissolved Mn ions abundantly supplied through rivers (Kawashima et al., 1988). Therefore, we removed the Mn oxide fraction from the SPM by using a reductive extractant. Robbins et al. (1984) reported that pH 5.0 solution containing 1 M hydroxylammonium chloride and 0.175 M sodium citrate is effective to extract an oxide fraction in oxic sediment. After treating with this solution as described above, the Mn and Al concentrations were determined. These plots produced a strong linearity, as shown in Fig. 3.

The slopes and intercepts of the linear regression lines in Figs. 2 and 3 are listed in Table 1. The terrigeneous fraction in the SPM was estimated using these values and the Al concentration in the hypolimnion.

Distribution of suspended particulate element
Aluminum and titanium

Vertical distributions of suspended particulate elements in 1989 and 1990 are shown in Figs. 4 and 5, respectively. Curves A and B in the figures show the profiles before and after the corrections for terrigeneous fraction. Unless specifically stated, the values referred to hereafter have been corrected.
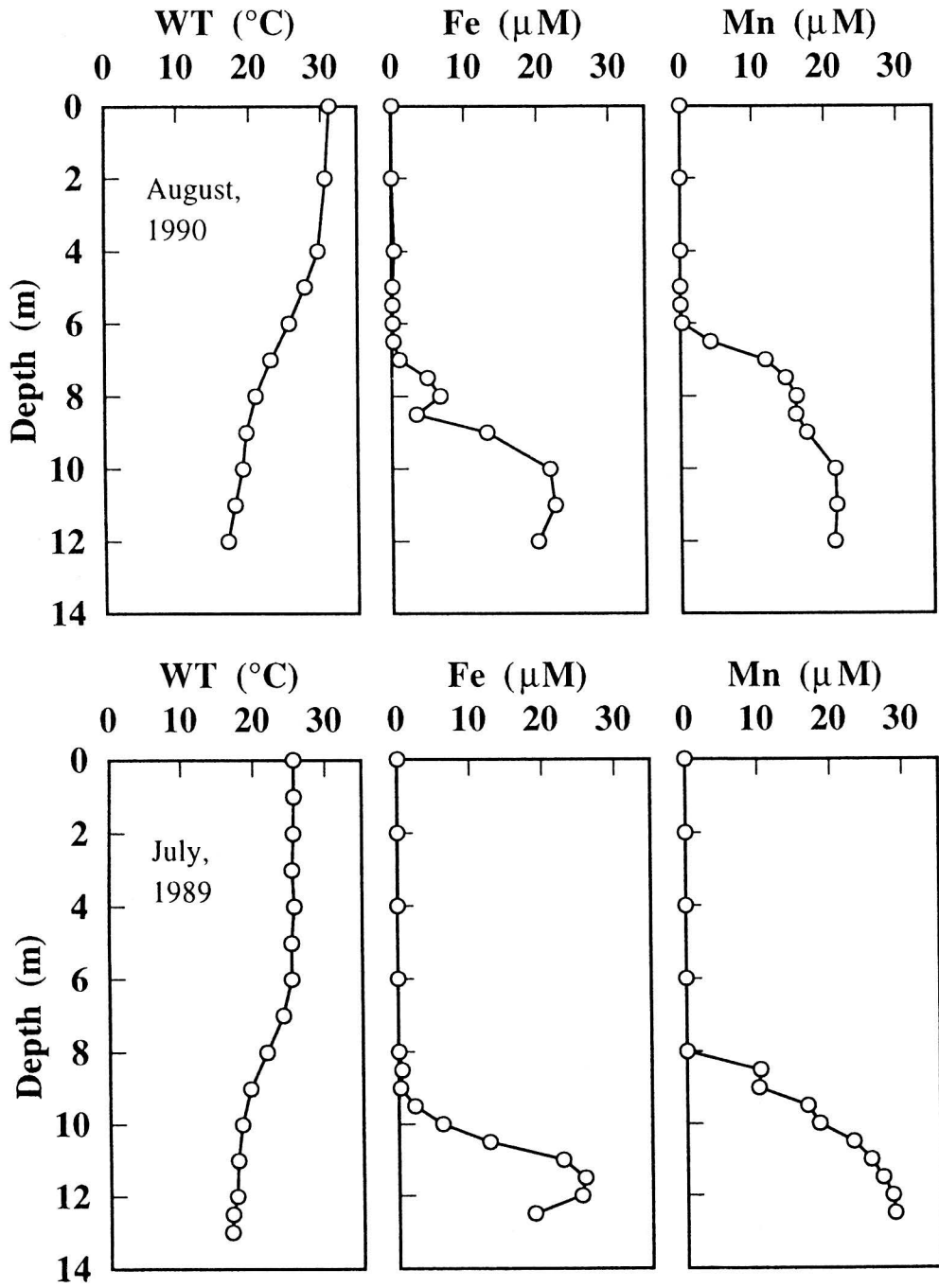
Fig. 1 Vertical distribution of dissolved Fe and Mn on 19 July 1989 and 3 August 1990.
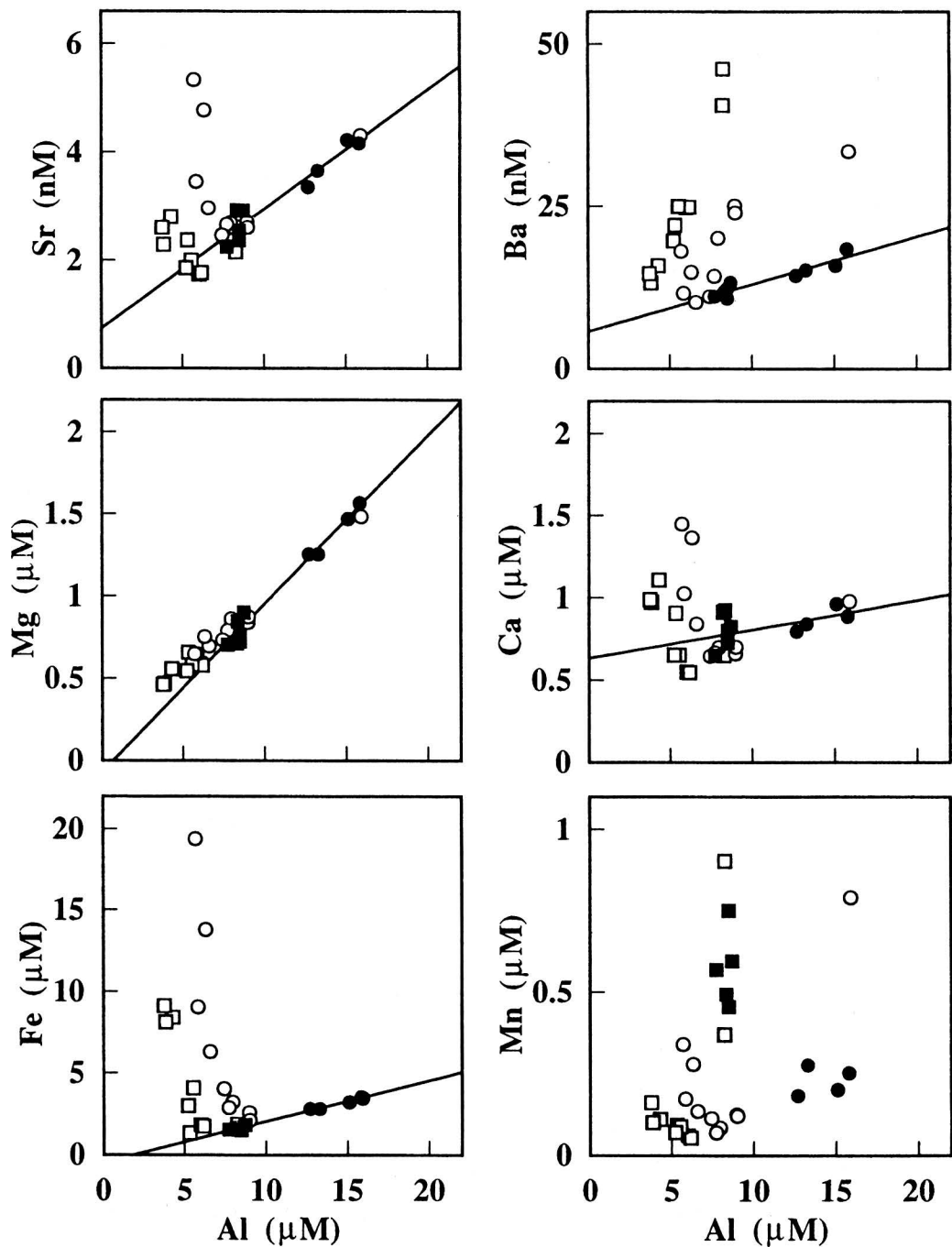
Fig. 2　Correlations between particulate elements and Al concentrations.
● : Epilimnion in July 1989, ○ : Hypolimnion in July 1989, ■ : Epilimnion in August 1990, and
□ : Hypolimnion in August 1990. The lines in the figure were obtained by the linear least squares
method with the data in the epilimnion (data of ▲ were not used in the calculation because of fear
of contamination). The line of Ti was for the data in whole water column.

Fig. 2 (continued)
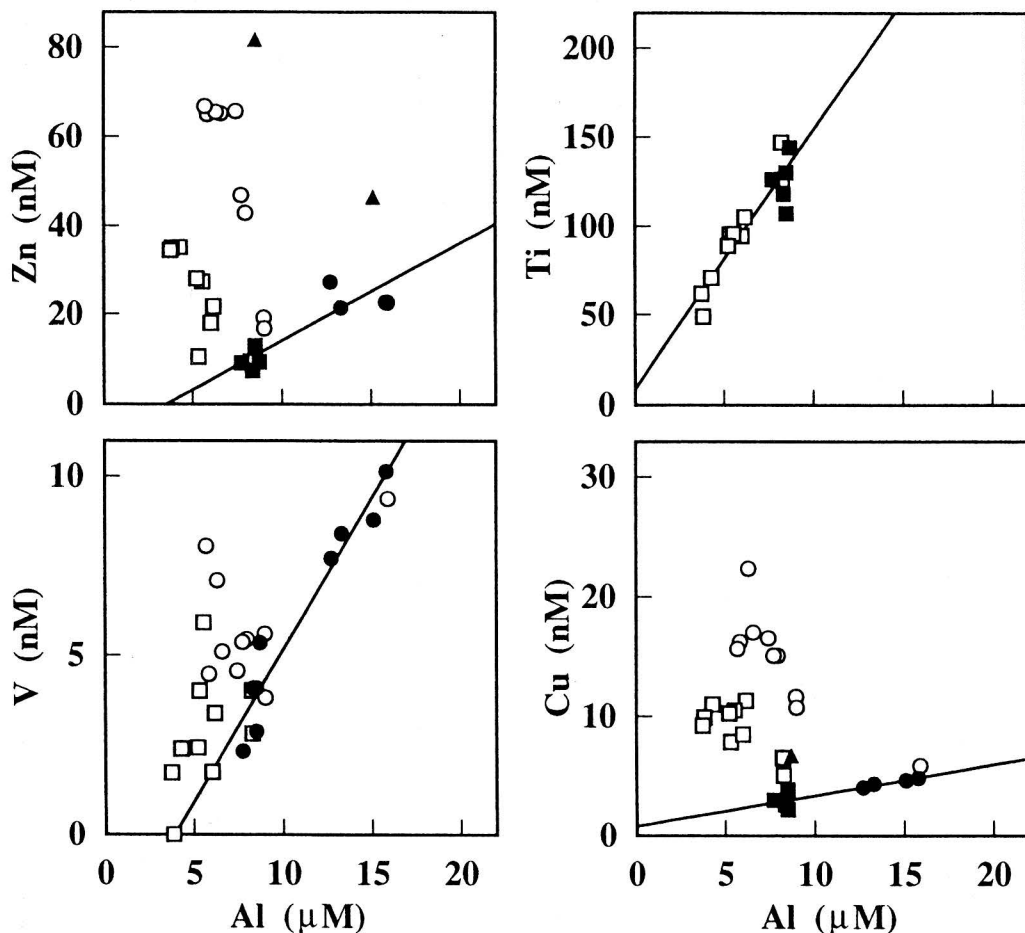
Particulate Al and Ti are often used as a tracer for terrigeneous SPM, because they are not reactive in natural water with a circumneutral pH (Brewer et al., 1980; Stabel, 1985). In the present work, the particulate Al concentration was utilized in the correction for the terrigeneous matter. As shown in Figs. 4 and 5, the distribution profiles of total particulate Al and Ti resembled with each other, being at high concentrations in the epilimnion and low in the hypolimnion. Plots of Ti against Al showed a good linearity for the data sets, not only in the epilimnion but also in whole water column (Fig. 5). These results suggest that Al and Ti are not reactive in anoxic water, and proved that the correction for terrigeneous fraction using these elements is appropriate even in the water.

Iron and manganese

Both the Fe and Mn concentrations peaked below the thermocline and increased with depth near the bottom. Manganese reached a maximum at depths of 8 m in 1989 and 6 m in 1990. Iron peaks were rather diffuse compared with those of Mn, and were at 9.5 m (1989) and 7.5 m (1990) depths. As discussed in detail in our previous report (Sugiyama
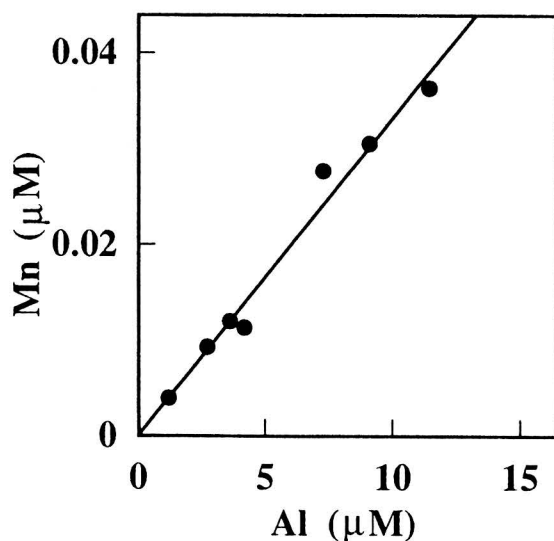
Fig. 3　Correlations between particulate Mn and Al concentrations after extraction treatment of oxide fraction. The line in the figure was obtained by the linear least squares method.

Table 1　Parameters for linear regression line of plots of elements against Al concentrations ([element] = a x [Al] + b) shown in Figs.2 and 3.

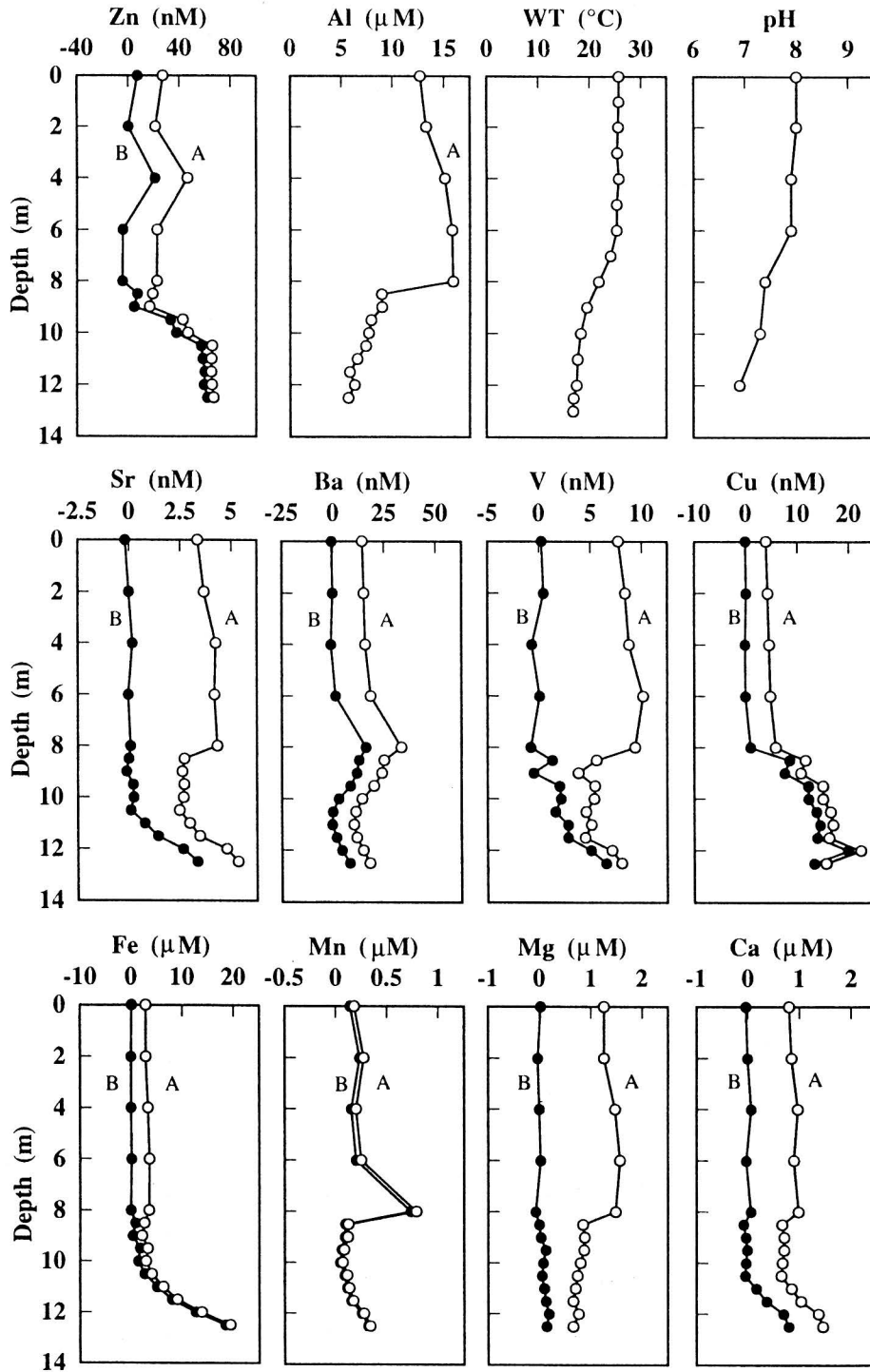| Element	a (mol/mol-Al)	b (mol/l)	r*
Fe	2.51×10^{-1}	-4.67×10^{-7}	0.994
Mn	3.30×10^{-3}	1.22×10^{-4}	0.988
Mg	1.02×10^{-1}	-6.95×10^{-8}	0.989
Ca	2.61×10^{-2}	5.10×10^{-7}	0.843
Sr	2.20×10^{-4}	7.38×10^{-10}	0.959
Ba	7.27×10^{-4}	5.77×10^{-9}	0.943
V	8.46×10^{-4}	-3.30×10^{-3}	0.965
Cu	2.58×10^{-4}	7.97×10^{-4}	0.877
Zn	2.19×10^{-3}	-7.67×10^{-3}	0.878
Ti	1.45×10^{-2}	8.80×10^{-3}	0.926

*r: correlation coefficient.

Fig. 4 Vertical distribution of suspended particulate elements on 19 July 1989.

(A): Total particulate concentration, (B): Particulate concentration corrected using relationship described in Figs. 2 and 3.
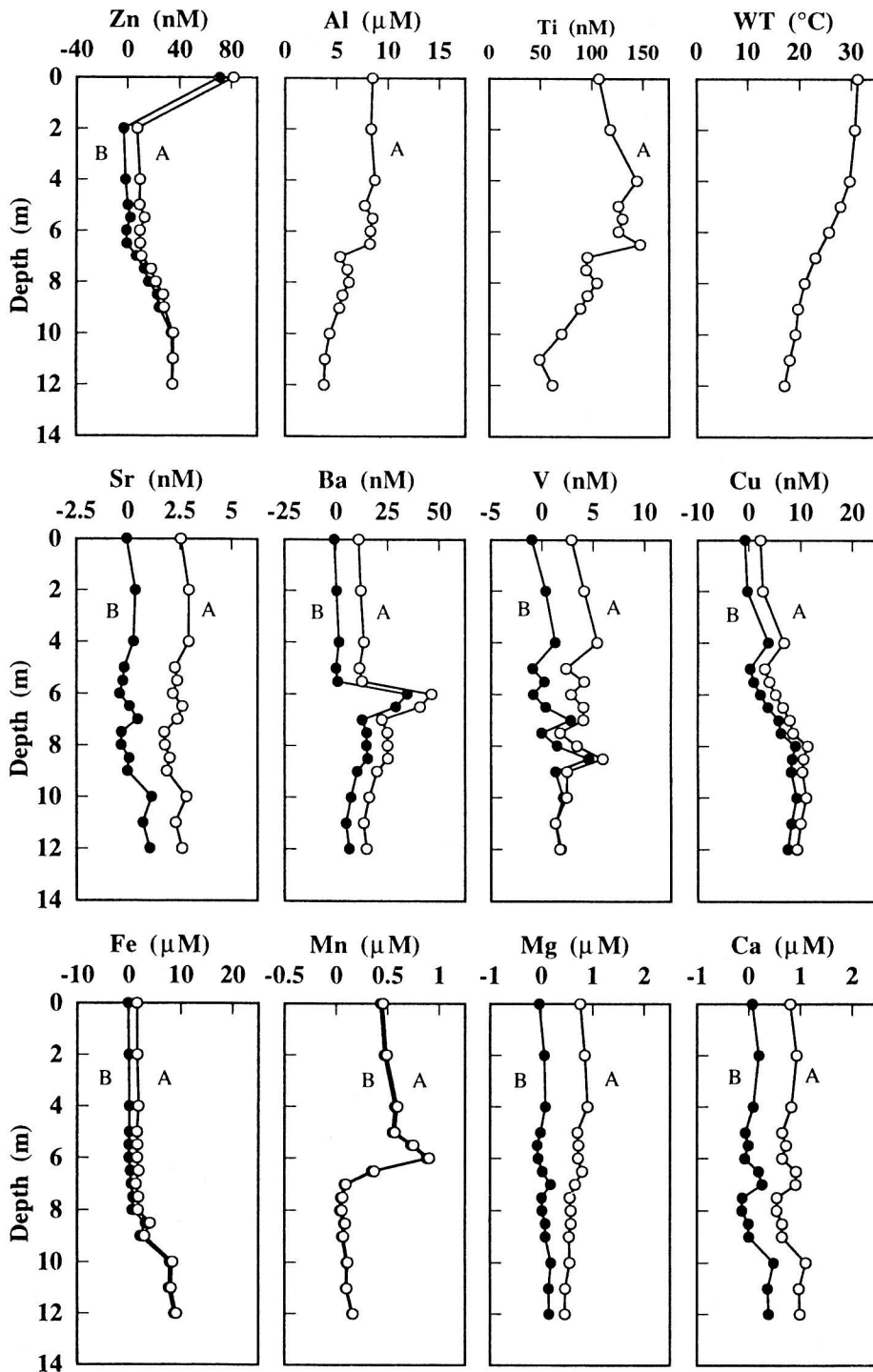
Fig. 5   Vertical distribution of suspended particulate elements on 3 August 1990.

(A): Total particulate concentration, and (B): Particulate concentration corrected using relationship described in Figs. 2 and 3.

and Hori, 1994), these Fe and Mn peaks were due to the hydrous Fe and Mn oxides accumulated at the depths of the respective redox boundaries for these elements. We named these boundaries Fe_2O_3/Fe^{2+} and MnO_2/Mn^{2+} redox fronts, respectively.

The increase in Fe concentration near the bottom suggests the formation of FeS precipitate, as reported by Kawashima et al. (1985). In 1982, they measured dissolved Fe and sulfide concentrations at the same area as studied in our present work, and confirmed that the bottom water was saturated for FeS based on the calculation of ion product of $[Fe^{2+}][S^{2-}]$.

In contrast, MnS was inferred not to be precipitated in the bottom water. If both FeS and MnS were formed, the ratio of $[Mn^{2+}] / [Fe^{2+}]$ should be at the level from 4.4×10^1 to 2.4×10^4 from the solubility products of the sulfides $\{K_{sp} = [M^{2+}][HS^-]/[H^+], K_{sp,MnS} = 0.40 - 1.5$ (Emerson et al., 1983; Dyrssen and Kremling, 1990), and $K_{sp,FeS} = 9.1 \times 10^{-3}$ - 6.3×10^{-5} (Davison, 1991)$\}$. However, [dissolved Mn]/[dissolved Fe] values in the present work ranged from 1.0 to 4.7 in the bottom water and were much lower than the above ratio. Kawashima et al. (1985) also gave the same conclusion from the very low ion product of $[Mn^{2+}][S^{2-}]$ in lake water compared to the solubility of MnS.

The behavior of Mn near the bottom was affected by the precipitation of FeS. In Fig. 6, various elements' concentrations were plotted against those of Fe in the bottom layer (10-12.5 m depth in 1989, and 8-12 m depth in 1990) where FeS precipitate was considered to be formed. The good linearity of the Mn against Fe plots suggests that Mn was associated with FeS particles. Davison and Dickson (1984) also reported that Mn/Fe ratios in FeS particles were similar to each other owing to Mn adsorption onto the sulfide in anoxic hypolimnion. The iron sulfide minerals, pyrite (FeS_2) and mackinawite (FeS), are known to adsorb Mn ions well in laboratory experiments (Kornicker and Morse, 1991; Morse and Arakaki, 1993).

Magnesium, calcium, strontium, vanadium, and barium

The concentrations of Mg, Ca, Sr and V were almost constant in the upper layer of the hypolimnion, but increased with depth near the bottom. Calcium has been reported to be contained abundantly in FeS-rich particles in anoxic water (Davison et al., 1992). Moreover, Mg and Ca are known to be adsorbed onto pyrite and mackinawite (Kornicker and Morse,1991; Morse and Arakaki, 1993). In the present work, the above elements, especially Ca and Sr, were also strongly correlated with Fe concentrations, as shown in Fig. 6. Therefore, these elements are suggested to be removed by FeS particles near the bottom.

The distribution profile of Ba was specific compared to the other alkaline earth elements. The Ba concentration reached a maximum just below the thermocline. This
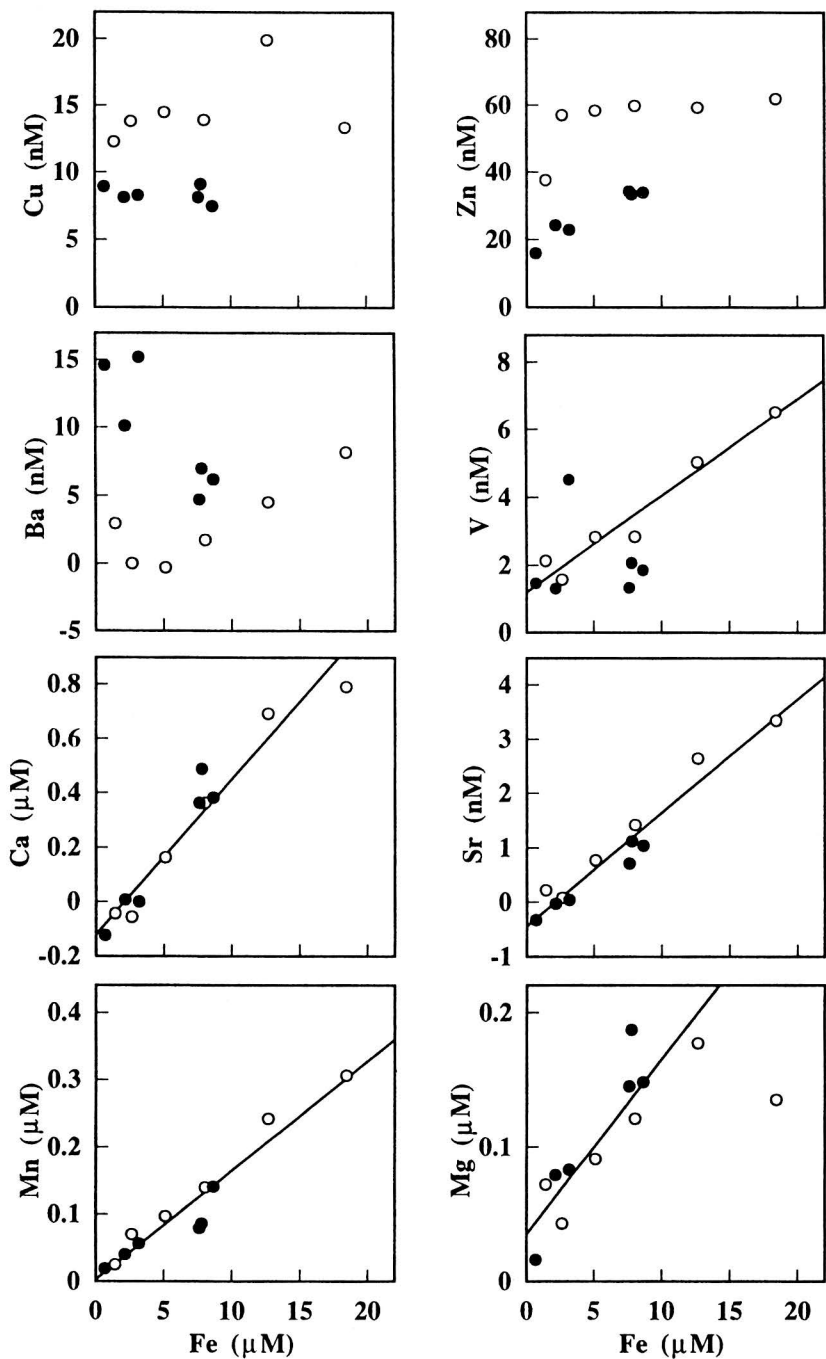
Fig. 6 Correlations between corrected particulate elements and Fe concentrations near the bottom.
○ : 19 July 1989 and ● : 3 August 1990. The line in the figure was obtained by the linear least squares method.

peak was already reported to be due to the adsorption of Ba ions onto hydrous Mn oxide formed at the MnO_2/Mn^{2+} redox front in our previous paper (Sugiyama and Hori, 1994). Barium also increased in the bottom water, but its correlation with Fe was very weak.

Copper and zinc

The distribution profiles of Cu and Zn were different from that of any element aforementioned. These concentrations started to increase with depth from just below the thermocline, and were almost uniform near the bottom. Accordingly, the concentrations were scarcely dependent on those of Fe, as shown in Fig. 6. The mean concentrations of dissolved Cu and Zn in the southern basin of Lake Biwa are 7.8×10^{-9} M and 1.2×10^{-8} M, respectively (Matsui et al., 1987). In the hypolimnion at the dredged area of the lake, HS^- concentration was reported to reach a 2×10^{-6} M level in summer (Kawashima et al., 1985). Solubility products K_{sp} for CuS and ZnS are 6.3×10^{-23} and 1.6×10^{-11}, respectively (Smith and Martell, 1976). Therefore, since the pH value in the present hypolimnion was around 7.0 (Fig.4), it is inferred that both CuS and ZnS particles were formed in the water, as in some other lakes (Davison et al., 1992; Balistrieri et al., 1992b). Even if Cu was dissolved as Cu^+ ion in the anoxic hypolimnion (Balistrieri et al., 1992), the solubility product K_{sp} for Cu_2S, 2.2×10^{-35} (Dyrssen and Kremling, 1990), is much lower than the value of $[mean\ dissolved\ Cu]^2[HS^-]/[H^+]$.

CONCLUSION

Near the top of the anoxic hypolimnion, Fe and Mn oxides are significant for the removal of trace elements. In previous papers (Sugiyama and Hori, 1994 and 1995), we discussed how the dynamics of barium was associated with Mn oxide accumulation at the layer. Behaviors of P and Co were reported to be linked to the formation of Fe oxides (Kawashima et al., 1985; Balistrieri et al., 1992). However, in its highly reductive deep layer, FeS precipitate was confirmed in the present work to play the role of an effective scavenger of metal ions. This was clearly indicated by the results that distributions of Mn, Mg, Ca, Sr and V correlated well with that of Fe near the bottom.

Some elements were scarcely affected by either geochemical process mentioned above. Both Cu and Zn were precipitated as their own sulfides, because of their more slight solubility than that of FeS. Particulate Al and Ti were not geochemically-reactive even in the anoxic water, and these profiles were affected by the terrigeneous fraction alone.

REFERENCES

Balistrieri L. S., Murray J. W. and Paul B. (1992a) The cycling of iron and manganese in the water column of Lake Sammamish, Washington. *Limnol. Oceanogr.* **37**, 510-528.

Balistrieri L. S., Murray J. W. and Paul B. (1992b) The biogeochemical cycling of trace metals in the water column of Lake Sammamish, Washington: response to seasonally anoxic conditions. *Limnol. Oceanogr.* **37**, 529-548.

Brewer P. G., Nozaki Y., Spencer D. W. and Fleer A. P. (1980) Sediment trap experiment in the deep north Atlantic: isotopic and elemental fluxes. *J. Mar. Res.* **38**, 703-728.

Brown J. R., Bancroft G. M., Fyfe W. S. and MacLean R. E. N. (1979) Mercury removal from water by iron sulphide minerals: An electron spectroscopy for chemical analysis (ESCA) study. *Environ. Sci. Tech.* **13**, 1142-1145.

Cronan D. S. (1976) Manganese nodules and other ferro-manganese oxides deposits. *In Chemical Oceanography* Vol. 5, J. P. Riley and R. Chester eds., pp. 217-263, Academic Press.

Davison W. (1991) The solubility of iron sulphides in synthetic and natural waters at ambient temperature. *Aqua. Sci.* **53**, 309-329.

Davison W. and Dickson D. P. E. (1984) Mössbauer spectroscopic and chemical studies of particulate iron material from a seasonally anoxic lake. *Chem. Geol.* **42**, 177-187.

Davison W., Grime G. W. and Woof C. (1992) Characterization of lacustrine iron sulfide particles with proton-induced X-ray emission. *Limnol. Oceanogr.* **37**, 1770-1777.

Davison W. and Heaney S. I. (1978) Ferrous iron-sulfide interactions in anoxic hypolimnetic waters. *Limnol. Oceanogr.* **23**, 1194-1200.

Dyrssen D. and Kremling K. (1990) Increasing hydrogen sulfide concentration and trace metal behavior in the anoxic Baltic waters. *Mar. Chem.* **30**, 193-204.

Emerson S., Jacobs L. J. and Tebo B. (1983) The behavior of trace metals in marine anoxic waters: Solubility at the oxygen-hydrogen sulfide interface. *In Trace Metal in Sea Water*, C. S. Wong et al. eds., pp. 579-608, Plenum Publ.Corp.

Hori T., Sugiyama M. and Fujinaga T. (1992) Environmental chemistry of Lake Biwa. Part 1,characterization of Lake Biwa based on the total-phosphorus and its fractional composition. *Human Environ. Studies, Kyoto Univ.* **1**, 23-41.

Jean G. E. and Bancroft G. M. (1986) Heavy metal adsorption by sulphide mineral surfaces. *Geochim. Cosmochim. Acta,* **50**, 1455-1463.

Kawashima M., Hori T., Koyama M. and Takamatsu T. (1985) Redox cycle of manganese and iron and circulation of phosphorus in a dredged area of the southern lake. *Res. Rep. Nation.Inst. Environ. Studies, Japan* **No. 75**, 47-62.

Kawashima M., Takamatsu T. and Koyama M. (1988) Mechanisms of precipitation of manganese(II) in Lake Biwa, a fresh water lake. *Water Res.* **22**, 613-618.

Kornicker W. M. and Morse J. W. (1991) Interactions of divalent cations with the surface of pyrite. *Geochim. Cosmochim. Acta,* **55**, 2159-2171.

Matsui M., Kihara S. and Sugiyama M. (1987) Dynamic aspect of trace elements in the Lake Biwa water system. *Special Issue Res. Proj. Environ. Sci.* **No. 36**, 85-87.

Morse J. W., Millero F. J. Cornwell J. C. and Rickard D. (1987) The chemistry of hydrogen sulfide and iron sulfide systems in natural waters. *Earth Sci. Rev.* **24**, 1-42.

Morse J. M. and Arakaki T. (1993) Adsorption and coprecipitation of divalent metals with mackinawite (FeS). *Geochim. Cosmochim. Acta,* **57**, 3635-3640.

Robbins J. M., Lyle M. and Heath G. R. (1984) A sequential extraction procedure for partitioning elements among co-existing phases in marine sediments. Corvallis, Oregon State Univ.,*College of Oceanography* Ref. **84-3**, p. 55.

Schoonen M. A. A., Fisher N. S. and Wente M. (1992) Gold sorption onto pyrite and goethite: A radio tracer study. *Geochim. Cosmochim. Acta,* **56**, 1801-1814.

Singh S. K. and Subramanian V. (1984) Hydrous Fe and Mn oxides–scavengers of heavy metals in the aquatic environment. *CRC Critic. Rev. Environ. Contr.,* **14**, 33.

Smith R. M. and Martell A. E. (1976) *Critical stability Constants, Vol 4, Inorganic Complexes.* Plenum Publ. Corp.

Stabel H.-H. (1985) Mechanisms controlling the sedimentation sequence of various elements in prealpine lakes. *In Chemical Processes in Lakes* , W. Stumm ed., pp. 143-167, John Wiley & Sons.

Sugiyama M. (1996) Simultaneous multi-element analysis of aquatic suspended particulate matter. *Bunseki Kagaku,* in press.

Sugiyama M. and Hori T. (1994) Geochemical behavior of barium in the vicinity of MnO_2/Mn^{2+} redox front formed in a eutrophic lake. *Japanese J. Limnol.* **55**, 27-37.

Sugiyama M. and Hori T. (1995) Dynamics of barium associated with the geochemical cycle of manganese. *Proc. 6th Intern. Conf. Conserv. Manag.,* pp. 1160-1163.

Takamatsu T., Kawashima M., Takada J. and Matsushita R.(1993) Characteristics in elemental composition of ferromanganese concretions from Lake Biwa. *Jpn. J. Limnol.* **54**, 281-291.

Terashima A. and Ueda T. (1982) Effects of bottom dredging on some environmental factors and benthic animals in the southern basin of Lake Biwa. *Jpn. J. Limnol.* **43**, 81-87.