Remobilization of transition elements in pore water of continental slope sediments

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Abstract—Profiles of dissolved Mn, Mo and V in pore waters and reducible Fe, Mn, Mo, V and Cu in solid phase have been determined in sediment cores collected along continental slopes beneath the eutrophic Oyashio and the oligotrophic Kuroshio regions. The profiles along the two different transects extending seaward from the coast display a transitional change of diagenesis of elements expelled by degradation of organic matter.

The decreasing trend of Fe oxides, the reducible part of total sedimentary Fe extracted by a reducing reagent, with depth in cores changes vertically and horizontally with the redox condition of sediments. The lateral transitional change of Mn profiles in both pore waters and solid reducible phases is characterized by enhanced enrichment in Mn oxides in the subsurface layer and concentrations of Mn^{2+} below the layer increasing essentially with distance from the coast. Mo diagenesis is affected by both affinities of dissolved species with Mn oxide and with organic matter in sediments and pore waters, and the enrichment of Mo in Mn oxide phase is further intensified by Mn recycling. The adsorptivity of V on both Mn and Fe oxides is an important factor of the remobilization of the element in sediments.

The plots between concentrations of elements in the reducible phase in the surficial sediments and water depth at coring sites suggest that seaward lateral migration of Mo is accompanied with that of Mn oxides as a carrier, and those of V and Cu are mainly promoted with that of Fe oxides.

INTRODUCTION

The primary production in oceanic surface waters is high in marginal area, and diminishes offshore (BERGER, 1989). Although the rain rate of the biogenic organic matter to sea floor decreases with increasing water depth (SUSS, 1980; TSUNOGAI and NORIKI, 1987, 1991) and with distance from the continent (MARTIN et al., 1987), this spacial change of biological production influences the organic carbon content in surface sediments (HEATH et al., 1977). Nevertheless, a sufficient amount of organic matter reaches the seafloor to expel diagenetic processes of O₂ consumption and nutrients regeneration (REIMERS and SUSS, 1983; REIMERS et al., 1984; JAHNKE and JACKSON, 1987; JAHNKE et al., 1990; MURRAY and KUVILA, 1990). Thus, this

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rain of organic matter is a major driving force for the early diagenesis of marine sediments.

Pore water chemical composition is a very sensitive tracer in determining the diagenetic processes of benthic respiration, redox couple remobilization, dissolved element transport, calcium carbonate preservation and the like. Previous studies have established that, as expected thermodynamically, a sequential utilization of O₂, NO₃⁻, MnO₂, FeOOH and SO₄²⁻ by oxidation of metabolizable organic matter proceeds in seafloors under suboxic to oxic conditions (BERNER, 1971, 1980; FROELICH et al., 1979; JAHNKE et al., 1982, 1989; SAWLAN and MURRAY, 1983; MASUZAWA and KITANO, 1983; MASUZAWA, 1987; BERELSON et al., 1990; THOMSON et al., 1993; SCHULZ et al., 1994). The topography of a marginal area with high production of organic matter is characterized by continental shelf, continental slope, trench (trough) or rise, and abyssal basin. The gradual increase in water depth toward offshore influences sedimentation of organic matter, and induces sediments from near shore to be more reducing and those from pelagic basin to be more oxidizing. Therefore, the diagenetic remobilization of elements in sediment column can be substituted by their lateral migration via the benthic boundary layer, where rapid remineralization of organic matter in sinking particle takes place (SUÉSS, 1980; TSUNOGAI and NORIKI, 1987; JAHNKE and JACKSON, 1987).

In this study, we obtained sediment cores from each of the seafloors beneath the eutrophic Oyashio water and the oligotrophic Kuroshio water. The primary productivity in these regions reported by SAITO and ICHIMURA (1960) is 2–10 times higher in the Oyashio region than in the Kuroshio region. So, through a comparative investigation from region to region, we can realize the difference of intensifying degree of diagenesis. Especially, Mn and Fe oxides are common constituents in pelagic sediments, and transition elements, Mo, V and Cu, are readily adsorbed on these oxide phases due to their nature of large distribution coefficients of dissolved species for the oxides (TAKEMATSU et al., 1985, 1993; SATO, 1989). This suggests that as well as early diagenesis of Mn and Fe oxides proceeds, the remobilization of such adsorbed transition elements is occurring in the upper oxidizing layer. We will discuss in this paper the remobilization and lateral migration of Mo, V and Cu along with the fates of Mn and Fe oxides.

**SAMPLING AND METHODS**

Sediment samples were collected along each transect in two regions (Fig. 1), using a stainless-steel box corer with 1600 cm² opening (KINOSHITA et al., 1981) during cruises of the R.V. *Tokaidaiakaguki Maru II*, as given in Table 1. Four box cores of the Oyashio transect were collected from the continental slope, Hidaka Trough, under the Oyashio water (HB-1 to 4; Fig. 1). In the region from HB-1 to HB-3, the gradient of the seafloor is very gentle relative to that of the outer slope from which HB-4 was obtained (Fig. 2). Another set of sediment cores was also obtained from the continental slope off Shikoku to the northern region of the Shikoku Basin along the Kuroshio transect under the Kuroshio water (Fig. 1). The topographic gradient of this slope is somewhat steeper than that of the Oyashio transect, and TT-4 exists at the very bottom of the slope, the Nankai Trough (Fig. 2).
Fig. 1. Locations of sediment cores from the Oyashio (O) and Kuroshio (K) regions. HB stations range along the Oyashio transect extending seaward (above right) in Hidaka Trough. T and TT stations also range along the Kuroshio transect (below).

Table 1. Locations of box cores collected during R.V. Tokaidaigaku Maru II cruises

<table>
<thead>
<tr>
<th>Core</th>
<th>Cruise</th>
<th>Date</th>
<th>Lat. N</th>
<th>Long. E</th>
<th>Water Depth m</th>
</tr>
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<tr>
<td>HB-1</td>
<td>TO-87-16</td>
<td>1987/10/15</td>
<td>42°14.9'</td>
<td>141°32.8'</td>
<td>540</td>
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<tr>
<td>HB-2</td>
<td>TO-87-16</td>
<td>1987/10/15</td>
<td>41°50.5'</td>
<td>142°11.9'</td>
<td>1080</td>
</tr>
<tr>
<td>HB-3</td>
<td>TO-87-16</td>
<td>1987/10/16</td>
<td>41°09.4'</td>
<td>143°10.1'</td>
<td>2050</td>
</tr>
<tr>
<td>HB-4</td>
<td>TO-87-16</td>
<td>1987/10/16</td>
<td>40°42.0'</td>
<td>144°02.8'</td>
<td>4620</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T-4</td>
<td>TO-87-03</td>
<td>1987/05/10</td>
<td>33°09.4'</td>
<td>133°40.5'</td>
<td>620</td>
</tr>
<tr>
<td>T-3</td>
<td>TO-87-03</td>
<td>1987/05/09</td>
<td>32°53.5'</td>
<td>133°54.2'</td>
<td>1060</td>
</tr>
<tr>
<td>T-1</td>
<td>TO-87-03</td>
<td>1987/05/08</td>
<td>32°26.3'</td>
<td>134°14.1'</td>
<td>2860</td>
</tr>
<tr>
<td>TT-5</td>
<td>TO-88-17</td>
<td>1988/10/26</td>
<td>32°33.3'</td>
<td>134°03.1'</td>
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<td>TO-88-17</td>
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<td>31°47.1'</td>
<td>134°43.2'</td>
<td>4400</td>
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<td>TO-88-17</td>
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<td>31°36.2'</td>
<td>134°56.0'</td>
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<td>TO-88-17</td>
<td>1988/10/24</td>
<td>30°58.8'</td>
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<td>4360</td>
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<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>TT-4</td>
<td>TO-88-17</td>
<td>1988/10/27</td>
<td>31°56.6'</td>
<td>134°11.3'</td>
<td>4830</td>
</tr>
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Hidaka Trough
Continental slope off Shikoku
Shikoku Basin
Nankai Trough
Box core sediments recovered on board were immediately divided into subcores, using 8-cm diameter acrylic pipes, which were extruded at 0.5 to 1.0 cm intervals. Pore waters were squeezed from the extruded sediments to be collected into plastic syringes through a 0.45 μm pore size membrane filter in a thermostated refrigerator at 4 ± 2°C, using modified devices of that of MANHEIM (1968). After collection, they were acidified to be less than pH 1 with 5 M HCl.

Pore water Mn and Mo were determined using a Hitachi 180-80 flame and flameless atomic absorption spectrophotometer with a Zeeman-Effect device, respectively, Dissolved V was measured by direct injection into a Seiko SPS7000 ICP-AES. Calibrations for Mn and V were carried out using an open ocean surface seawater (22°35.8' N, 153°36.2' E; June '87) in order to cancel the matrix effect. Concentrations of both elements in uncontaminated open ocean water are, as well known, too low to interfere with pore water analyses. This surface seawater was
utilized as a solvent for the working standard solution of Mo, too. The calibration was corrected for the value of 0.10 μmol l⁻¹ of Mo in the seawater which was determined by the standard addition method.

Fe, Mn, Mo, V and Cu in reducible phases of sediments were determined using a selective leaching technique basically described by Chester and Hughes (1967, 1969) and call them reducible Fe, Mn, Mo, V and Cu, respectively. We used two leaching solutions; one is composed of 6%(v/v) acetic acid and another is a mixture of 6%(v/v) acetic acid and 1 M hydroxylamine hydrochloride, recommended by Tsunogai et al. (1982). Wet sediments were dried by freeze drying. To polypropylene screw top centrifuge tubes we added 0.5 g aliquot of powdered sediment with 50 ml of each leaching solution pre-warmed up to 70°C. The suspended solutions in the tubes were kept at 70°C in a water bath for 5 hrs. After leaching, each of the solutions was filtered through a Millipore 0.45 μm pore size filter and analyzed for Fe, Mn, V and Cu using an ICP-AES, and for Mo by flameless atomic absorption spectrometry. The difference between concentrations in the two leaching solutions represents the sedimentary abundance of each transition metal in the reducible phase, as follows;

\[ \text{Reducible Metal} = C_{\text{HOAc}+\text{NH}_2\text{OHCl}} - C_{\text{HOAc}} \]

where, \( C_{\text{HOAc}+\text{NH}_2\text{OHCl}} \) is the concentration of metals in the mixed solution included the reducing regent, and \( C_{\text{HOAc}} \) is that in the acetic acid solution. In this work, the reducible fraction of sediments is very much important to understand the early diagenesis of transition elements. Iron and manganese oxides occur in the marine sediments are directly dissolved by the mixed reducing solution. However, Mo, V and Cu in the reducible fraction originate from those adsorbed on and incorporated in Fe and Mn oxide phase.

SEDIMENT DESCRIPTIONS

According to Saijo and Ichimura (1960), the primary productivity in the Oyashio water off northern Japan is as high as 0.2–0.4 gC m⁻² day⁻¹, against 0.05–0.1 gC m⁻² day⁻¹ in the Kuroshio water. The surface productivity significantly influences diagenesis in bottom sediments. Lithologies of cores from the two transects are summarized in Fig. 3 based on The Rock-Color Chart (The Rock-Color Chart Committee, 1984). In the Oyashio transect, the surface sediments of HB-1 to 3 are moderate olive brown (5Y4/4) except that the deeper layer of HB-2, where hydrogen sulfide generates, is in highly reducing. There is no typical brown oxic sediment in the surface of these cores. Only in HB-4, mildly oxidizing sediments (5YR4/4) cover the top. Pumice layers were found in the cores HB-1 to 3 and their depth becomes shallower pelagic ward. Sedimentation rates estimated by the Pb-210 method are as high as 300 cm kyr⁻¹ at HB-2 and 170 cm kyr⁻¹ at HB-3, and even exceed 4000 cm kyr⁻¹ at HB-4 (Narita et al., 1989).

In the Kuroshio transect, the sediments are in oxidizing seaward. The grayish olive sediments of T-4 are mildly reducing, but the thickness of upper oxidizing layer (5YR to 10YR) increases down along the slope and toward the abyssal plane. At
Fig. 3. Description of sediment cores.

TT-4 in the Nankai Trough, the upper-most layer is light olive brown (5Y5/6) and is in suboxic. The sedimentation rate at T-1 was measured by C-14 dating to be 9.4 cm kyr⁻¹ (Dr. Masuzawa, personal communication).

RESULTS AND DISCUSSION

Pore water distributions

(1) Oyashio transect

Manganese: Pore water Mn profiles obtained from the stations along the
Oyashio transect are given in Fig. 4. In HB-1, Mn is not detected in the entire depth. In HB-2, the concentrations range from 0.6 to 1.6 μmol l⁻¹ in the layer of 0.5 to 13 cm, but are below the detection limit in the other layers. Also in HB-3, the detectable amount of Mn decreases from 1.4 μmol l⁻¹ in the layer of 2.0 cm to 0.6 μmol l⁻¹ at the bottom of the core. Mn concentrations in these pore waters, however, are extremely low. This implies that most Mn oxides serving as oxidants for organic matter do not exist in the surface sediments. Then Mn oxide reduction must take place predominantly near the sediment-seawater interface before burial in such sediments.

In HB-4, the profile somewhat differs from those resulting from steady state diagenesis, i.e., recycling due to reduction, oxidation and diffusion. The profile shows a gap between the depths of predominant Mn(IV) reduction (at the depth of ca. 15 cm) and the Mn redox boundary (at 2 cm depth) expected from the sediment color change from brown (5YR4/4) to olive brown (5Y5/6), and also shows double peaks. The diffusion coefficient generally represents a degree of dispersal of a given molecule per unit time. Assuming that there is a point source of pore water Mn at a depth in the core, a time required, as established by steady state distribution, is expressed by a quotient of the square of distance z by the diffusion coefficient D, time = z²/D. Substituting the diffusion path for 30 cm in this core, and using 50 cm² yr⁻¹ for the diffusion coefficient of Mn in pore water (roughly estimated from the data of L1 and GREGORY, 1974), we obtain the time to be 18 yrs. This means that the steady state Mn distribution is accomplished within a period of at least 20 yrs or so. Nevertheless, in HB-4 core, the pore water Mn profile fluctuates, and the sedimentation rate is too high to be determined by the Pb-210 method, as stated above. The non-steady state deposition of fresh massive sediments which contain Mn oxides as a source material is responsible for perturbing the pore water Mn profile of such an outer slope sediment.

*Molybdenum:* Pore water Mo profiles are shown in Fig. 5. The concentrations change from the minimum of 0.07 μmol l⁻¹ at the layer of 4–5 cm to the maximum
of 3.16 \mu\text{mol} \text{ l}^{-1} at the layer of 25–26 cm in HB-2. Most of the values are higher than the average 0.11 \mu\text{mol} \text{ l}^{-1} in open seawaters (Sugawara and Okabe, 1960; Bruland, 1983). Although the profile patterns are somewhat different from core to core, the distributions tend to increase in concentration with depth in the core as a whole. In the lower part of HB-2, especially, dissolved Mo rapidly increases in highly reducing sediment below 20 cm depth, where \text{H}_2\text{S} generates. Another feature is the distinct peak in the subsurface layer of HB-3 core.

(2) Kuroshio transect

Manganese: Pore water Mn profiles in cores obtained from the continental slope and the outer basin floor under the Kuroshio, along the Kuroshio transect, are shown in Fig. 6. The sequence of profiles presents a typical example of the lateral transition spectrum of early diagenesis of Mn. The respective Mn redox boundaries (MnRB), which correspond to the layer at which dissolved Mn first appears in pore water, are indicated by arrows in the figure. The concentration gradients just below MnRBs increase down along the slope, while the oxidizing layers above the boundaries grow from 0 cm at T-4 to 6.5 cm at T-1, as shown in Fig. 3. Mn recycling across MnRB results in enrichment of Mn oxides in the upper oxic layer (Froelich et al., 1979). In TT-4 at the bottom of the slope, the Nankai Trough, the concentration level is rather low. Most Mn oxides rapidly dissolve before burial in sediment, because decomposable organic matter is easily to gather in the sea floor such as the bottom of a slope and/or trough. Moreover, in the outer-most site of the Kuroshio transect, dissolved Mn concentrations are nearly equal to the detectable level and less than that at TT-3 and TT-1, respectively. Nevertheless, the concentrations in TT-2 increase in the deeper layer. These sediments are still in the suboxic condition as Mn oxide formation and reduction proceed, though the core was sampled from the deep-sea hemi-pelagic region. Thus, Mn oxide reduction would presumably be actively taking place in the deeper part of the core in this area.

Molybdenum: Vertical distributions of dissolved Mo in pore waters are summarized in Fig. 7. The characteristics are as follows: in the slope sediments, (1) there are subsurface peaks of dissolved Mo above MnRBs at T-4 to TT-5, and the
concentrations trend to decrease gradually as down along the slope; (2) dissolved Mo displays a concentration minimum just above MnRB, especially in TT-5 and T-1, the depth of the layer corresponding to that with the reducible Mn concentration maximum, as mentioned later in connection with Fig. 9; (3) Mo concentrations gradually increase with depth below MnRBs; (4) while at TT-2 and TT-1 in the outer basin, overall concentration levels are almost coincident with the average seawater value.

Vanadium: Pore water V profiles were obtained from 3 cores as shown in Fig. 8. An average concentration of 1.2 µg kg⁻¹ in seawaters is reported by Morris (1975). Sato (1990) also gives 1.5 µg l⁻¹ (0.029 µmol l⁻¹) for open seawaters. Most of the values determined in the pore waters are significantly high in comparison with those in seawaters. In TT-5 and TT-4, the V profiles display top peaks, minima just above MnRB, and are slightly increasing or nearly constant with depth, looking somewhat like those of Mo. The most striking features were observed at T-1, where V has a downward increasing concentration gradient across MnRB, and the concentration decreases with depth below the layer with the maximum value.
Reducible metal distributions and early diagenesis

**Manganese and Iron**: Reducible Mn and Fe, respectively, can be referred to as hydrogenous metal oxides or oxyhydroxides existing in sediments. The laboratory experiments show that not all Fe oxides are extracted from sediments by this leaching method, but that most Mn oxides dissolve into the mixed reducing regent. Nevertheless, the relative change of reducible Fe content is still meaningful in discussing the profiles. Figure 9 shows reducible Mn and Fe distributions along the Kuroshio transect.

There is little reducible Mn in the surficial sediment at T-4 core near the coast. As the sampling sites of cores are further off the coast, the surface brown-yellow oxidizing layers grow thicker, and the concentrations of reducible Mn in the upper layers increase. In TT-3 to TT-1 from the outer basin floor, the oxidizing layers are thicker, and appreciable reducible Mn can be measured in the whole depths in cores. However, a decreasing trend below the maximum is observed in the deeper layers in light olive brown (5Y5/6) to light olive gray (5Y5/2). But at TT-4 in the Nankai Trough the concentrations are rather low.
Fig. 8. Pore water V profiles at 3 stations along the Kuroshio transect.

Fig. 9. Reducible Fe and Mn profiles in sediment cores from the Kuroshio transect.
The sequence of reducible Mn profiles well documents suboxic early diagenesis, matching with those of pore water Mn. The processes of Mn reduction and remobilization proceed via degradation of biogenic organic matter as the primary reducing species. As seen in the pore water profiles of Fig. 6, the drastic change of the state of Mn in sediments is observed above and below MnRB. We herewith explain Mn diagenesis using T-1 as a representative profile. The overlying dissolved O₂ is suspected to penetrate into the depth of MnRB by diffusion. The O₂ is exhausted by organic matter degradation until arriving at this boundary. In the layer above MnRB, Mn is stable as oxides due to the higher redox potential of O₂/H₂O relative to MnO₂/Mn²⁺. On the other hand, Mn²⁺ diffuses upward from the deeper reducing layer into such an oxidizing layer along the great concentration gradient at the boundary. Consequently, a Mn oxide concentration peak develops at the depth where bothfluxes of O₂ diffusing downward and Mn²⁺ diffusing upward are just balanced. Generally, the rate of diffusive transport of dissolved species in pore waters, i.e., a diffusivity of ca. 50 cm² yr⁻¹ in the case of Mn²⁺, is very high relative to that of sediment particle burial, 9.4 cm kyr⁻¹ at T-1. Froelich et al. (1979) have concluded that the diffusional transport of Mn²⁺ is enough to balance the Mn oxide burial flux through the simple mass balance calculation. Indeed, we can calculate the characteristic time required for a diffusive flux sufficient to transport a 1-cm thick solid phase layer, much in the manner of Froelich et al. (1979). The characteristic time \( T \) is given by:

\[
T = \frac{[\text{Mn}]_s/F_{\text{Mn}}}{\rho_{\text{dry}}[\text{Mn(IV)}]/(D*CG)}
\]

where \([\text{Mn}]_s/F_{\text{Mn}} \) is the concentration of reducible Mn in 1 cm slice of sediment, \( F_{\text{Mn}} \) is the upward diffusive flux of Mn²⁺, \( \rho_{\text{dry}} \) is the content of dry sediment in 1 cm slice (as g cm⁻²), \([\text{Mn(IV)}] \) is the reducible Mn concentration per unit dry weigh sediment, \( D \) is the diffusion coefficient of Mn²⁺, and \( CG \) is the concentration gradient just below MnRB. In order to check for the case of T-1, we choose the following values, \( \rho_{\text{dry}} = 0.75 \text{ g cm}^{-2}, [\text{Mn(IV)}] = 6.75 \text{ g kg}^{-1} (123 \mu\text{mol g}^{-1}) \) as an average value in the upper oxidizing layer, \( D = 50 \text{ cm}^{2}\text{yr}^{-1} \) as mentioned above, and \( CG = 2.45 \times 10^{-2} \mu\text{mol cm}^{-4} \). Considering to transport 1 cm thickness sediment layer contained reducible Mn, we obtain:

\[
T = 75 \text{ yr.}
\]

Therefore, this value indicates that a one-time diagenetic recycling of MnO₂-Mn²⁺ takes less than 100 yrs. Next, the estimation of fluxes across MnRB at T-1 using the sedimentation rate proves that both the MnO₂ burial flux and the Mn²⁺ upward diffusive flux are roughly equal to 1 μmol cm⁻²yr⁻¹. So, the calculations demonstrate that the Mn oxide peak concentration is maintained by the process in which the sedimentary input of reducible Mn oxides is balanced by effective reduction and upward migration via pore water column.

The formation of the peaks in TT-3 to TT-1 can be explained by the similar process of the case of T-1 (Fig. 9). Gentle convex profiles from TT-3 and TT-1 cores,
rather than in TT-5 and T-1, imply that the overlying O2 extends into the deeper part of the cores due to less utilization by low organic matter content, and the input of Mn2+ from the deeper layer is also low. This inadequate recycling of Mn results from low content of metabolizable organic matter. It may be noted the average content of total organic carbon measured in these three cores is 0.52 ± 0.08% (n = 67), which is one third lower than the average 1.55 ± 0.23% (n = 113) in all the slope sediments (unpublished data). In TT-2, however, there appears to be two peaks on the pore water Mn profile, with a somewhat disturbed distribution (Fig. 6). These double peaks may have resulted from a change in the organic matter rain rate, because the layer with the pore water peak and reducible Mn loss at around 20 cm depth corresponds to the section in light olive brown between the dark yellowish brown layers above and below (see Fig. 3).

At TT-4, the top reducible Mn concentration is rather low. This is reflected in the low concentration of pore water Mn (Fig. 6). No enrichment of Mn oxides in the upper layer is consequent on the effectiveness of gathering decomposable organic matter as a reductant on such a trough floor. In other words, reducible Mn oxides as the source of Mn2+ in pore water do not readily form in the surface sediments.

One of the characteristics of reducible Fe profiles is their decreasing trend in most cores (Fig. 9). In the cores without Mn oxides enrichment found in T-4, T-3 and TT-4, reducible Fe concentrations decrease under the tops of cores. In TT-5 and T-1, greater decreasing concentration gradients are observed below MnRBs. The redox potential of Fe2O3/Fe2+ is lower than that of MnO2/Mn2+. Thermodynamically, Fe oxides reduction starts from the end of Mn oxides reduction, but not all oxides disappear even below MnRB. This is different from the case of Mn oxides. Hence, a convex up distribution of pore water Fe would be observed as a mirror image against the reducible Fe concave profile.

**Molybdenum:** Reducible Mo profiles are shown in Fig. 10. The profiles of reducible Mo are very much similar to those of reducible Mn. The peak concentrations are greater than 2.6 ppm in the low organic carbon content normal shale (BRUMSACK, 1980). It has been well known that Mo is incorporated into and adsorbed on Mn nodules and oxides in ocean floor sediments (TAKEMATSU et al., 1985, 1990; SHIMMIELD and PRICE, 1986). SATO (1989) also indicated that the distribution coefficient between dissolved Mo in seawater and Mn oxides is one magnitude larger than that in the case of Fe oxides. So, reducible Mo represents mostly the adsorbed Mo on Mn oxides. In our cores, Mo enrichment predominates only in Mn oxide occurring layers, and no relation to Fe oxides is found.

There have been several studies on early diagenesis of Mo in suboxic and anoxic marine sediments. Some of the possible remobilization processes postulated for Mo are as follows; adsorption on and desorption from manganese oxides (BERRANG and GRILL, 1974; SHIMMIELD and PRICE, 1986), releasing into pore water and association with dissolved organic matter originated from sedimentary organic matter decomposition (CONTRERAS et al., 1978; BRUMSACK and GIESKES, 1983; MALCOLM, 1985), and coprecipitation with iron sulfides due to sulfate reduction (SUGAWARA et al., 1961; BERTINE, 1972). Moreover, BERTINE (1972) pointed out that under mildly reducing condition (Eh > −0.2 volts; slightly higher than redox potential of
Fe(III) oxides), a part of Mo(VI) existing as MoO$_4^{2-}$ in natural waters is reduced to Mo(V), probably MoO$_2^{2+}$, by some but not all sedimentary organic acids, like humic acids. And he showed this reducing Mo(V) is capable to adsorb to various solid phases in sediments, including humic acids.

In the Oyashio transect, the process related to Mn oxide reduction is not essential at HB-1 to 3. Furthermore, the content of organic carbon measured was relatively high, av. 2.09 ± 0.26% ($n = 72$) in all HB cores (unpublished data). This suggests the importance of diagenesis associated with degradation of organic matter. The elevation of pore water Mo concentration with depth, particularly in HB-2, may result from the formation of complex with dissolved organic matter in pore waters. In HB-3, there is a subsurface peak in the pore water Mo profile shown in Fig. 5. However, there is also another effect, namely that source materials for Mo remobilization in sediments are diluted by sand-size pumice concentration at a depth of 3–9 cm (Fig. 3). Just as the section of 9–20 cm in HB-2 core, the pore water Mo concentrations are rather lower because of the sedimentation of particles of different origins.

On the other hand, in the Kuroshio transect, Mo remobilization significantly correlates with the fate of Mn oxides. With the typical profile of T-1 (Figs. 7, 9 and
10), dissolved Mo in seawaters diffuses into the sediment across the sediment-water interface like dissolved O\textsubscript{2}. Because of the adsorption of dissolved Mo on Mn oxides in the subsurface layer, the decreasing concentration gradient is caused by the removal from pore waters. Below MnRB, Mo is once released into the pore water accompanied with Mn oxide reduction, but a part is removed to be incorporated into solid phases other than Fe oxides. This is supported by the fact that the pore water increasing concentration gradient of Mo is not so much greater relative to that of Mn\textsuperscript{2+}. The gradual convex profile of pore water Mo below MnRB may result from the complex formation with dissolved organic matter released during sedimentary organic matter degradation.

The top peaks of pore water Mo observed at T-4 to TT-5 also relate to the Mn diagenetic recycling in the microenvironment. To check this, we measured the oxidation state of Mn in sediments using a potentiometric titration (KALHORN and EMERSON, 1984; MURRAY et al., 1984; SHIMMIELD and PRICE, 1986). According to the theory of the measurement, when the oxidation state \( x \) as MnO\textsubscript{x} is equal to 1, Mn is in a divalent state Mn(II), and \( x = 2 \) represents Mn(IV)O\textsubscript{2} (details will be discussed elsewhere). The respective average values of \( x \) measured in the top 1 cm were:

\[
1.0(T-4) = 1.0(T-3) < 1.5(TT-5) < 1.7(T-1) > 0.53(TT-4)
\]
\[
< 1.5(TT-3) < 1.6(TT-2) < 1.8(TT-1).
\]

The values show a gradual increase down along the slope, but are less than 2 even at the most seaward site TT-1. This trend implies that although Mn oxide formation is promoted with distance from the coast, part of them can be reduced even in surficial sediments exposed continuously to O\textsubscript{2} in overlying seawaters. Because the adsorption of released Mn\textsuperscript{2+} to residual Mn(IV) oxides is enhanced by an autocatalytic reaction (STUMM and MORGAN, 1970), \( x \) is apparently lowered by this excess Mn\textsuperscript{2+} in the oxides. Further, from adsorption experiments using some Mn oxide minerals which are abundant in the sea-floor Mn nodule, TAKEMATSU (1979) obtained \( 3 \times 10^6 \) ml g\textsuperscript{-1} to the distribution coefficient of Mn\textsuperscript{2+} for birnessite. SATO et al. (1984) found the coefficient 2–3 \( \times 10^4 \) ml g\textsuperscript{-1} between dissolved Mo and mixed Mn oxides composed of birnessite and todorokite. The adsorptivity of Mn\textsuperscript{2+} to Mn oxides is two order of magnitude higher than that of dissolved Mo. Therefore, we postulate a possible mechanism of these types of Mo top peaks in pore waters as follows; Mo adsorbed on Mn oxide phase in settling particles deposits on the sea floor, where Mn oxides are partially reduced by degradation of organic matter, and the Mo is released from Mn oxides to be left in pore waters, in spite of active removal of Mn\textsuperscript{2+} due to large affinity for Mn oxides. The effect of such a rapid Mo remobilization is significantly reflected in the core from the upper slope. In the nearest coast core of T-4, the apparent value of \( x \) is \( \sim 1.0 \) in the top 1 cm. The fact that the pore water Mn peak below the depth indicated by the arrow in Fig. 6 was observed in this core should indicate the existence of Mn oxides. So, the formation of the pore water Mo peak may be attributed to the steady and quick processes of sedimentation and Mo remobilization in the surface sediments.

**Vanadium:** Figure 11 shows the reducible V profile of T-1 core. This profile
Fig. 11. Reducible V profile in the sediment core of T-1 from the Kuroshio transect.

shows the subsurface peak and downward decrease. The depth of the peak corresponds to those in reducible Mn and Mo profiles. Below MnRB, appreciable reducible V still remains. From this point of view, the profile is different from that of reducible Mo (Fig. 10). The effective removal of dissolved V in seawater is enhanced by Fe and Mn oxyhydroxides (Takematsu et al., 1985; Shieh and Duedall, 1988; Sato, 1989; Wehrl and Stumm, 1989). Therefore, this V represents adsorbed V on particles like Mo, and V remobilization is concerned with early diagenesis of Fe and Mn oxides.

In T-1, the subsurface peak at the depth ~9 cm is formed by input of dissolved V originating from overlying seawaters and pore waters under MnRB (Fig. 11). Dissolved V is removed from pore waters to be adsorbed on Mn oxides. As seen in Fig. 8, the striking pore water V concentration gradient observed in just MnRB at T-1 compared with that of pore water Mn results from rapid desorption during Mn oxide reduction. Below MnRB, the fraction of reducible V represents the adsorption on Fe oxides, where a loss of dissolved V is occurring.

**Correlation between Manganese and Molybdenum:** As mentioned above, the diagenetic remobilization of Mo is strongly affected by the fate of Mn oxides, at least in the oxidizing layers. The correlative plots between reducible Mn and Mo in core to core are shown in Fig. 12. The plots are clearly distinguished above and below depths of reducible Mn maxima. From the top to the maximum depth in the sediment column, they have linear correlations with concentration ratios of Mo to Mn ranging from 0.0010 to 0.0021. These compares with the ratio of 0.001 obtained from the relation between suspended Mo and Mn in Saanich Inlet water samples (Berrang and Grill, 1974), and a constant value of 0.002 in a wide variety of Mn-rich sediments and ferromanganese deposits (Shimmield and Price, 1986). The source of Mo in this upper layer mainly originates from overlying seawaters.
Fig. 12. Relationship between reducible Mn and Mo in 3 cores from the Kuroshio transect.

The concave trends below the maximum, however, imply a deficiency of Mo in Mn oxide. In this layer, following three processes are suggested: (1) upward diffusive fluxes of pore water Mn and Mo across MnRB are different each other, (2) Mo released from Mn oxides is rapidly adsorbed to other solid phases, notwithstanding Mn$^{2+}$ adsorption to Mn oxides, and (3) Mo released associates with dissolved organic matter to be not readily adsorbed on the oxides. The upward diffusive flux of Mo is much smaller than that of Mn as expected from the pore water concentration gradients of the two at T-1 (Figs. 6 and 7). In the cases of TT-1 and TT-3, in spite of lack of data, the difference between the diffusive fluxes can not explain the concave trends. So, the latter two processes are still available.

Figure 13 shows a good correlation between reducible Mn and Mo, plotted by means of data in peak to peak. On the other hand, there is no distinct relationship between reducible Mo and Fe (Fig. 14). These figures show that diagenesis of Mn plays an important role on Mo recycling in suboxic sediments.
Fig. 13. Correlation between reducible Mn and Mo obtained using peak to peak concentrations of the two in subsurface sediments from the Kuroshio transect.

Fig. 14. Reducible Mo against reducible Fe in top 2 cm sediments from the Kuroshio transect.
Fig. 15. Change of each concentration of reducible Fe, V, Cu, Mn, and Mo with water depth at sampling site along the Kuroshio transect.
Offshore migration of transition elements

An offshore decrease in the intensity of organic matter degradation in sediments is also suggested from our pore water data for Mn.

Along the Kuroshio transect, the plot of reducible Fe concentration in the top 2 cm against water column depth at each sampling site shows almost a linear relation, as in Fig. 15. In this area, the water depth shown in the horizontal axis is able to be replaced with distance from the coast. Thus, even Fe, recycling sedimentation and resuspension in benthic boundary layer, migrates offshore to deposit in more oxidizing deep sea sediments. Similar offshore increasing trends of reducible V and Cu stress the adsorptivities of V and Cu on Fe oxide phase in particles. Fe oxides serve as good carriers for migration of V and Cu in the benthic environments. Assuming two endmembers, one the value in T-4 as a coastal component and the other in the most seaward of TT-1 as a pelagic component, the plots for V and Cu in the slope sediments, respectively, tend to go up and go down from each increasing line (Fig. 15(b)). The convex trend of V can be explained by the affinity for Mn oxides, as well as Fe oxides (TAKEMATSU et al., 1985). The slightly concave trend of Cu may show the difficulty of adsorption on Fe oxides caused by association with sedimentary organic matter and/or dissolved organic matter (NISSENBAUM and SWAIN, 1976).

On the other hand, as seen in the relations with respect to Mo and Mn in Fig. 15, the depth at which the enrichment of reducible Mn and Mo appears corresponds to the middle of the continental slope. This effective trapping, never seen in the case of Fe, may result from a topographic feature, such as the bowl displayed in Fig. 2. The estimation by JAHNKE et al. (1990) that benthic O₂ respiration exceeds sediment trap sinking flux of organic carbon in the marginal area also suggests a lateral mass transport out of the continental margin toward the ocean floor through the near benthic boundary layer. Particles including metabolizable organic matter and remobilizable constituents are laterally transported near the bottom by sinking and resuspension, and deposit on such a basin floor. Consequently, intensified Mn recycling contributes to enrichment of Mn oxides and Mo in surficial sediments.

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