

## Early diagenesis of redox-sensitive trace metals in the northern Okinawa Trough

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### Abstract

The early diagenesis processes of several redox-sensitive trace metals (RSMs) (Mo, U and V) were studied with several short sediment cores (~25 cm) collected in the northern Okinawa Trough (OT). Pore water vertical profiles indicated that the sedimentary environments in all cores were between oxic and suboxic, not yet reaching anoxic sulfidic conditions. The recycling process of Mo in sediments was clearly associated with Mn and yielded little authigenic accumulation, while U showed a downcore increase in sediment and its authigenic mass accumulation rate (MAR) was estimated to be ~23% of the Changjiang (Yangtze) and Huanghe (Yellow) riverine flux. Benthic diffusive fluxes and MAR were calculated and the comparison of them showed that U and V fluxes matched relatively well both in direction and in magnitude, implying that diffusion processes at the sediment-water interface is the dominant process controlling the remobilization or burial of V and U in northern OT. This work provided a systematic study (both in pore water and solid phase) on the RSMs geochemical behaviors during early diagenesis process, yielding a quantitative assessment of the remobilization or burial fluxes of the RSMs in northern OT. Such studies are in general lacking in the coastal margin of Northwest Pacific Ocean.

**Key words:** diagenesis, molybdenum, uranium, vanadium, pore water, sediment, Okinawa Trough

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### 1 Introduction

The sediment-water interface (SWI) is an important transitional zone for material transport, exchange, and final burial, at which gradients change dramatically with respect to physical, chemical, and biological processes (Santschi et al., 1990; Shaw et al., 1990). Redox-sensitive trace metals (RSMs), such as molybdenum (Mo), uranium (U), and vanadium (V), due to the differing solubility of oxidized and reduced species, have their own unique responses to changes in redox conditions at the SWI, and thus have attracted attention as potential indicators in paleo-redox environment studies (Calvert and Pedersen, 1993; Brumsack, 2006; Tribovillard et al., 2006; Algeo and Tribovillard, 2009). In the Modern Ocean, the liberation or fixation processes of RSMs in surface sediment are also indicators associated with bottom water oxygen content, biological productivity, and sedimentary environment for carbon burial processes (Crusius et al., 1996; McManus et al., 2005, 2006; Kuzyk et al., 2011, 2017).

The understanding of RSMs is complicated by our present knowledge of their respective ocean mass balances. Morford and Emerson (1999) employed a simple diagenesis model and estimated globally that, in sediments below 1 000 m water depth where oxygen penetrates is less than 1 cm (~4% of the ocean floor), the

released sedimentary fluxes of V and Mo to seawater are at rates of 60%–150% and 5%–10% respectively, highly significant compared to their dissolved riverine fluxes. The burial flux of U in such sediments is also very important, estimated to be 20%–40% of the riverine flux. The estimation was made based on RSMs data from continental margins of Africa, Northwest U.S., and the Arabian Sea. In the past, systematic studies have been carried out looking at pore water and sediment geochemistry of the RSMs during early diagenesis processes in the marginal seas of North-east Pacific, Southeast Pacific, Northwest Atlantic (Shaw et al., 1990; Zheng et al., 2002; Morford et al., 2005, 2009b; Scholz et al., 2011; Olson et al., 2017). However, in the west coast of North Pacific Ocean, where some of the largest marginal seas in the world are located, such studies are in general lacking. We know little about their geochemical behaviors and their quantitative fluxes at the SWI. By far, only Yamada et al. (2006) and Crusius et al. (1996) have reported some authigenic mass accumulation rate (MAR) data on U in Okinawa Trough and on Mo and Re in the Sea of Japan, respectively. However, both studies only focused on solid phase profiles. Up to now, no study has included both pore water and solid phases in its discussion in order to provide a complementary description of RSM's early diagenesis processes,

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which highly limit our understating of the geochemical behavior of RSMs during early diagenesis process and on the quantitative assessment of their fluxes at SWI in this part of the continental shelf.

In this study, bottom water, pore water, and short sediment cores were collected from five stations in northern Okinawa Trough (OT, 29°–30°N, 127°–128°E), which acts as a large sink for metal-containing particles transported laterally from the continental shelf in the East China Sea, one of the largest marginal seas in the world (Qin et al., 1987; Narita et al., 1990). Mo, U, V and related redox species (Mn, Fe and H<sub>2</sub>S), were measured both in dissolved and solid phases, and a systematic look at the early diagenesis processes of these RSMs were provided. Two fluxes, benthic diffusive fluxes and authigenic MAR were calculated and the comparison of the fluxes enabled a qualitative and quantitative evaluation of the important processes that affect the remobilization, accumulation, and retention of these RSMs at the SWI in northern OT, or possibly other hemipelagic continental shelf of the west coast of Pacific Ocean.

## 2 Materials and methods

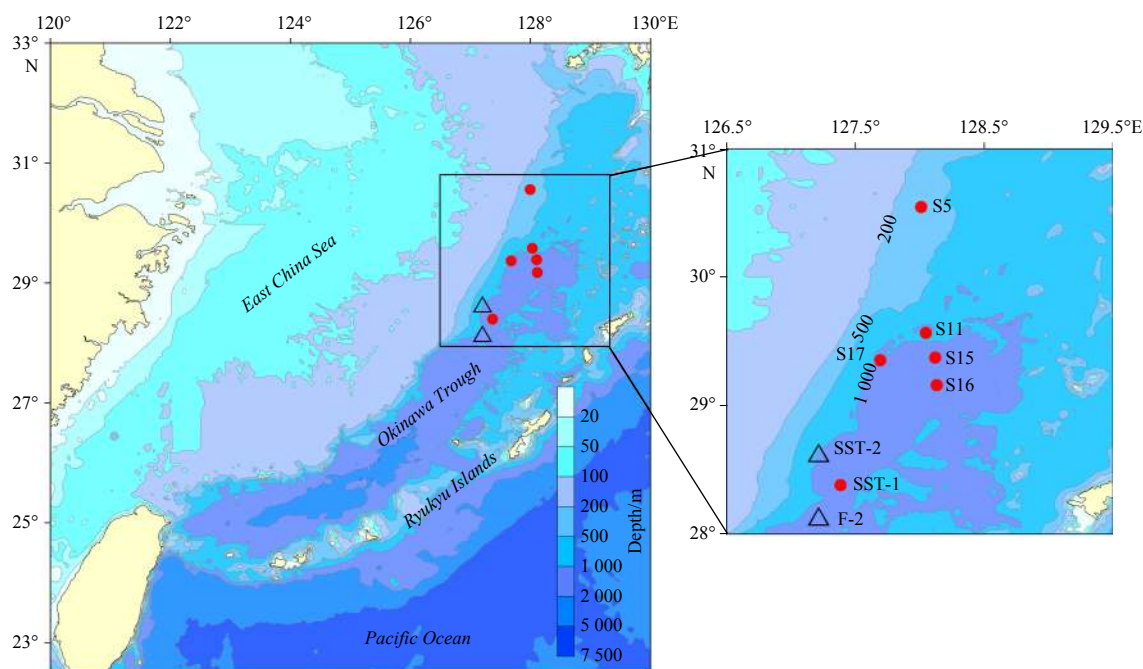
### 2.1 Study region

The Okinawa Trough, an extension of the continental shelf of

the East China Sea, is located in the Northwest Pacific Ocean and is bounded by the Ryukyu Island arc. It is about 1 200 km in length and 80–120 km in width, with a total area of about  $1.5 \times 10^5$  km<sup>2</sup>. A large section is more than 1 000 m in depth; at its deepest, near the Taiwan Island, the depth is about 2 270 m. The sediment composition in OT is mainly terrestrial detritus, biogenic, and volcanic materials, and the biogenic debris in the northern OT is much higher than in the south (Qin et al., 1987; Chang, 2004). As a passage linking the East Asian continent to the West Pacific Ocean, the OT may serve as a sensitive reflection of environmental transition between the ocean and continental settings. The northern section of the trough has a very thick sedimentary cover (up to 8 km) whereas the cover of the southern OT is only 2 km (Sibuet et al., 1987). The main axis of Kuroshio Current enters the OT northeast of Taiwan Island, and flows northeastward along the outer edge of the continental shelf of the East China Sea (Andres et al., 2008). At present, hydrothermal activity are more active mainly in the middle and southern OT (Lee et al., 1980).

### 2.2 Sample collection

The station locations are shown in Fig. 1 and detailed station information are given in Table 1. The research survey was carried out from the R/V *Science No. 1* on the western slope of the



**Fig. 1.** Station locations in northern Okinawa Trough. SST-1 is a station from Yamada et al. (2006), F-2 and SST-2 are stations from Oguri et al. (2003), shown here for discussion purpose in the text.

**Table 1.** Detailed information on the sediment cores collected in the northern Okinawa Trough

Area	Station	East longitude	North latitude	Water depth/m	Core length/cm*	Bottom water	
						T/°C	S
Slope	S5	128°00.58'	30°32.76'	415	26	9.0	34.2
Slope	S11	128°02.78'	29°33.99'	972	28	4.5	34.3
Trough	S15	128°07.16'	29°22.44'	1 063	26	4.5	34.3
Trough	S16	128°07.84'	29°09.57'	1 134	24	4.0	34.4
Slope	S17	127°41.53'	29°21.20'	994	26	n.a	n.a

Note: \* The core lengths reported here are cores used for sediment analysis. A parallel core (often with shorter length) at each station was used for pore water analysis.

northern OT in August 2013. Five short sediment cores (~25 cm), at water depths of 415–1 134 m, were collected either with a multiple-coring system (at Sta. S5) or by subcores of boxcores (at the other stations), which boxcore surfaces were relatively intact based on visual observation. S5 was located on the upper slope, with the shallowest water depth. S11 and S17 were both located at the lower slope with water depths of ~1 000 m. S15 and S16, the stations with deepest water depths (>1 000 m), were located in the trough of the northern OT. Upon collection, sediment cores were immediately transported to a N<sub>2</sub>-filled glove bag. Rhizon sampler (Rhizonsphere Inc., The Netherlands) was used to collect pore water samples. We coupled the Rhizon sampler with thin Teflon tubes and a peristaltic pump (LongerPump® Inc., China), which formed a trace-metal clean sampling pathway for pore water samples. The sampling intervals were 1 cm within the top 10-cm depth, and 2 cm for the rest of the core. Collected pore water samples were acidified to pH ~2 with HNO<sub>3</sub> (Optima grade, Thermo Fisher Scientific Inc.), and stored at 4°C in a refrigerator before analysis.

At each site, a parallel sediment core was sliced at intervals (1 cm within the top 10 cm, 2 cm for the rest of the core) on the ship, and the sediment samples were sealed in plastic bags and kept at 4°C until further processing. The bottom seawater samples (~30 m above the seafloor) were collected using Niskin bottles mounted on the CTD rosette. Upon collection, seawater samples were filtered immediately through 0.2 µm AcroPak® filters (Pall Inc.), collected into LDPE bottles (Nalgene™, Thermo Fisher Scientific Inc.), and acidified to pH ~2 with HNO<sub>3</sub>.

The filters, tubes, sampling bottles, and other labware that had been in contact with samples were thoroughly cleaned, following cleaning procedures used for trace metals (details in Li et al., 2015). A 15 mL PE vials (BD Falcon) were used for storing pore water, and they were cleaned with 10% HNO<sub>3</sub> (trace metal grade, National Chemical Production Inc., China), then thoroughly rinsed with Milli-Q (18.2 MΩ resistivity) water before use.

### 2.3 Pore water and seawater analysis

Seawater and pore water samples were processed under HEPA-filtered working benches (Class-100) in trace-metal clean laboratories (Class-1000) at the First Institute of Oceanography, Ministry of Natural Resources, China. Pore water samples were diluted 20-fold with 2% HNO<sub>3</sub> and analyzed using the ICP-MS (X series II, Thermo Fisher Scientific Inc.) under collision cell technology (CCT) mode for Fe, Mn, Mo, U and V. Sc, Rh and In were added to all samples as internal standards. The precision and accuracy of analytical procedures of Mo, U and V were controlled by the reference materials NASS-6 (National Research Council, Canada). The results of measured values were in good agreement with the certified values (Table 2). Because Mn and Fe concentrations were much higher in pore water than in the original reference material, the precision and accuracy of their data were tracked with the standard addition method and their recoveries were satisfactory (95%–105%). A random selection of 10% of samples was spiked with metal standards (High-Purity Standards, US) to two incremental concentrations to track the recovery, and to correct the matrix effect that may exist for all elements. The analytical results showed that recovery was, in general, within 85%–115%.

Total dissolved sulfide (here termed as S<sup>2-</sup>) in pore water samples of the OT was measured on board ship inside a N<sub>2</sub>-filled glove bag. The S<sup>2-</sup> concentration was determined using the methylene-blue colorimetric method (Cline, 1969) with a UV spectrophotometer (7200 series, Shanghai Unico Inc., China).

**Table 2.** Analytical results of the reference seawater (NASS-6)

NASS-6	Mo/nmol·L <sup>-1</sup>	U/nmol·L <sup>-1</sup>	V/nmol·L <sup>-1</sup>
Measured value ( <i>n</i> =11)	102.8±4.6	12.6±0.3	28.8±2.1
Certified value	103.1±7.5	12.6 <sup>1)</sup>	28.7±3.3

Note: <sup>1)</sup> Not certified, only for information (National Research Council, Canada).

Sulfide standard solution and its dilution stabilization solution (Beijing Aoke Biotechnology Inc., China) were used to generate the calibration curves. The detection limit of the analytical method for sulfide was 2.0 µmol/L.

### 2.4 Sediment analysis

Sediment samples were freeze-dried and homogenized before total metal concentration analysis. Briefly, 50 mg sample was digested with 1.5 mL HNO<sub>3</sub> and 1.5 mL HF at 190°C for 48 h in closed Teflon bombs. In the final step, the digested solution was diluted to 50 mL with Milli-Q water before analysis with ICP-OES and ICP-MS. The concentrated HNO<sub>3</sub> and HF used were distilled in the laboratory from trace-metal grade acid (National Chemical Production Inc., China) using acid purification systems (Savillex DST-1000). Finally, Al, Fe, and Mn were measured using ICP-OES (iCAP 6300, Thermo Fisher Scientific Inc.), and Mo, U and V were measured by ICP-MS. The accuracy and precision of the digestion procedure were monitored by the reference material GBW07309 (China Reference Material), and the recovery of all elements of interest was within 95%–102%. Replicate measurements were conducted on 10% randomly selected samples, and the relative standard deviations (RSD) were <1% for Fe, Mn and Al, and <5% for Mo, U and V.

TOC samples were treated with 4 mol/L HCl to remove carbonate and subsequently rinsed with deionized water to remove salts before drying overnight at 60°C. The carbonate-free samples were analyzed for TOC in duplicates by the Elemental Analyzer (Model EL-III, Vario). The recovery of TOC was 95%–102% (*n*=4) assessed by GBW07309 (China Reference Material), and the relative error of the samples analyzed in triplicate was less than 5%. Grain sizes were determined using a laser particle size analyzer (Master Sizer 2000, Malvern Instrument) and categorized as clay (<4 µm), silt (4–63 µm), and sand (>63 µm).

Sedimentation rate was calculated based on the excess <sup>210</sup>Pb data. <sup>210</sup>Pb activities were determined by α-spectrometry (7200-8 series, Canberra Inc.) at the Third Institute of Oceanography, Ministry of Natural Resources, China. A <sup>209</sup>Po spike was added as the yield determinant. <sup>210</sup>Pb activity was determined by counting the α decay of its granddaughter, <sup>210</sup>Po. Excess <sup>210</sup>Pb activities were determined by subtracting the supported levels of <sup>210</sup>Pb activity from the total <sup>210</sup>Pb measured. More detailed description of the radiochemical methodology can be found in He et al. (2015), which is a method modified based on Nozaki (1986) and Masqué et al. (2002).

### 2.5 Calculation of fluxes

#### 2.5.1 Diffusive benthic flux

On the basis of Fick's first law, the diffusive flux at the SWI can be calculated using Eq. (1) (Bernier, 1980):

$$\text{flux} = -\Phi D_{\text{sed}} \frac{dC}{dx}, \quad (1)$$

where  $D_{\text{sed}}$  denotes the diffusion coefficients for metal ions in sediment;  $\Phi$  represents porosity, which is assumed to be 0.8 here

(Barnes and Cochran, 1990); and  $dC$  is the concentration gradient between the bottom seawater (collected from the CTD bottles) and uppermost centimeters of the pore water (collected at 1 cm intervals in this study). The diffusive boundary layer thickness is  $dx$ , which can range from 0.1 mm to a few millimeters. Here we chose an average thickness, 0.5 mm (Jørgensen and Revsbech, 1985; Santschi et al., 1991). The final flux value can be positive or negative: positive flux is directed into the sediment by definition and negative flux is leaving the sediment:

$$D_{\text{sed}} = \frac{D_{\text{sw}}(T^{\circ}\text{C})}{\theta^2} \quad (2)$$

$$\theta^2 = 1 - \ln(\Phi^2), \quad (3)$$

$$D_{\text{sw}}(T^{\circ}\text{C}) = \frac{D_{\text{sw}}(25^{\circ}\text{C})}{2.19} + \frac{T}{25} \times \left( D_{\text{sw}}(25^{\circ}\text{C}) - \frac{D_{\text{sw}}(25^{\circ}\text{C})}{2.19} \right), \quad (4)$$

where  $D_{\text{sed}}$  was calculated based on the diffusion coefficient for metal ions in seawater ( $D_{\text{sw}}$ ) and sediment tortuosity ( $\theta^2$ ).  $D_{\text{sw}}(T^{\circ}\text{C})$  was calculated using Eq. (4) based on the  $D_{\text{sw}}(25^{\circ}\text{C})$  provided in Li and Gregory (1974), adjusted for the *in situ* bottom water temperature of 4–9°C. As there was no published  $D_{\text{sw}}(25^{\circ}\text{C})$  value for  $\text{VO}_4^{3-}$ , we used the value for  $\text{MoO}_4^{2-}$  instead, because they exist in seawater as similar oxyanions (similar as Scholz et al., 2011). Based on Eq. (2), the calculated  $D_{\text{sed}}(4^{\circ}\text{C})$  values for Mo, U and V are  $3.72 \times 10^{-6} \text{ cm}^2/\text{s}$ ,  $1.60 \times 10^{-6} \text{ cm}^2/\text{s}$ , and  $3.72 \times 10^{-6} \text{ cm}^2/\text{s}$ , respectively.

### 2.5.2 Calculation of authigenic mass accumulation rate

Mass accumulation rate (MAR) of authigenic metals were calculated using Eq. (5):

$$\text{MAR} = s\rho_{\text{dry}}[\text{Me}]_{\text{auth}}, \quad (5)$$

where  $s$  is sedimentation rate;  $\rho_{\text{dry}}$  is dry sediment density ( $0.54 \text{ g/cm}^3$ ); and  $[\text{Me}]_{\text{auth}}$  refers to the average authigenic metal concentration, the difference between the total metal concentration ( $[\text{Me}]_{\text{tot}}$ ) and the detrital background concentration ( $[\text{Me}]_{\text{detr}}$ ), which is calculated using Eq. (6):

$$[\text{Me}]_{\text{auth}} = [\text{Me}]_{\text{tot}} - \frac{[\text{Me}]_{\text{detr}}}{[\text{Al}]_{\text{detr}}} [\text{Al}]_{\text{tot}}, \quad (6)$$

where the  $[\text{Me}]_{\text{detr}}/[\text{Al}]_{\text{detr}}$  represents the ratio between detrital metal and detrital Al contents, calculated based on the metal and Al values of the upper continental crust (UCC) reported in Gao et al. (1998), which data are suitable for this study because Gao et al. (1998) is a recent and comprehensive study of UCC values based on 905 samples in eastern China. The crustal ratios of Mo/Al, U/Al, and V/Al used in this study are  $1.08 \times 10^{-5}$ ,  $2.14 \times 10^{-5}$ ,  $1.36 \times 10^{-3}$ .  $[\text{Me}]_{\text{tot}}$  is calculated as the average metal content in downcore ( $\geq 15 \text{ cm}$ ) sediment.

## 3 Results and discussion

### 3.1 The sedimentary environment

To properly interpret the vertical distributions of RSMs in pore water and solid phase, it is necessary to characterize the redox and sedimentary environment in the study region. The extent of redox conditions in surface sediments during early dia-

genesis are mainly determined by bottom water oxygen concentration and organic carbon settling rate (McManus et al., 2005; Morford et al., 2009b). Based on the oxygen concentrations at the SWI, oxic ( $>63 \mu\text{mol/L O}_2$ ), hypoxic ( $<63 \mu\text{mol/L O}_2$ ), anoxic ( $0 \mu\text{mol/L O}_2$ ) or anoxic sulfidic ( $0 \mu\text{mol/L O}_2$ ,  $>0 \mu\text{mol/L H}_2\text{S}$ ) environments are classified (Middelburg and Levin, 2009). In northern OT, bottom water oxygen data obtained from multiple sampling trips in summer 2004 varied from 69–98  $\mu\text{mol/L O}_2$  (Yanguang Dou, Qingdao Institute of Marine Geology, China, personal communication), which is in accordance with the bottom water oxygen concentration reported by Sohrin et al. (1999) in this region (77–79  $\mu\text{mol/L O}_2$ ). These data indicate that bottom water overlying northern OT trough sediment often exhibits an oxic or near hypoxic condition.

A triangular plot of Shepard classification revealed that the grain size distribution varied from silty sand to clayey silt (Fig. 2). Most core sediments fell into the sandy silt domain, while S15 was characterized as clayey silt. In general, the cores located in the trough basin (S15 and S16) had finer-grained textures compared to the cores located on the slope. The TOC content in cores, though showing no trends vertically (Fig. 3), is correlated significantly with the mean grain size ( $p < 0.01$ , Table 3). The TOC content in sediment cores increased from the continental shelf to the trough ( $p < 0.05$ ). S5 had the lowest average TOC content (0.85%), while S15 and S16 had highest average TOC contents (1.4%–1.7%), similar to TOC values previously found in this area by Chen et al. (2000). Studies of sediment organic carbon content and isotopic signatures in southern OT suggested a coastal belt of elevated organic carbon content extending from the mouth of the Changjiang River toward southern OT, implying that there might be a pathway for channeling fine-grained sediments from the inner shelf to the depocenter, and that a major fraction of the sedimentary organic matter may be originated from the inner shelf (Kao et al., 2003; Gao and Song, 2006), which is also supported by several sediment trap studies in the OT (Honda et al., 2000; Iseki et al., 2003; Oguri et al., 2003).

The  $^{210}\text{Pb}$  data are shown for Cores S5, S11 and S17 in Fig. 4. Based on the data, slight vertical mixing in surface sediment ( $\leq 3 \text{ cm}$ ) may exist in Core S11 and S17, whilst the calculations with these data points included can still yield a reasonable sedi-

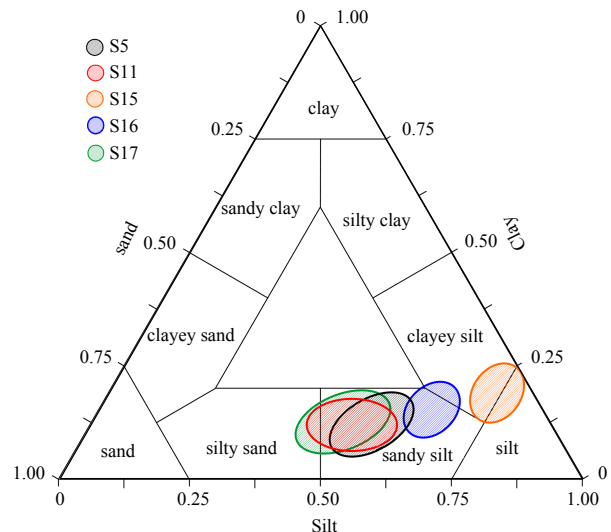


Fig. 2. Shepard classification of sediment types of sediment cores.

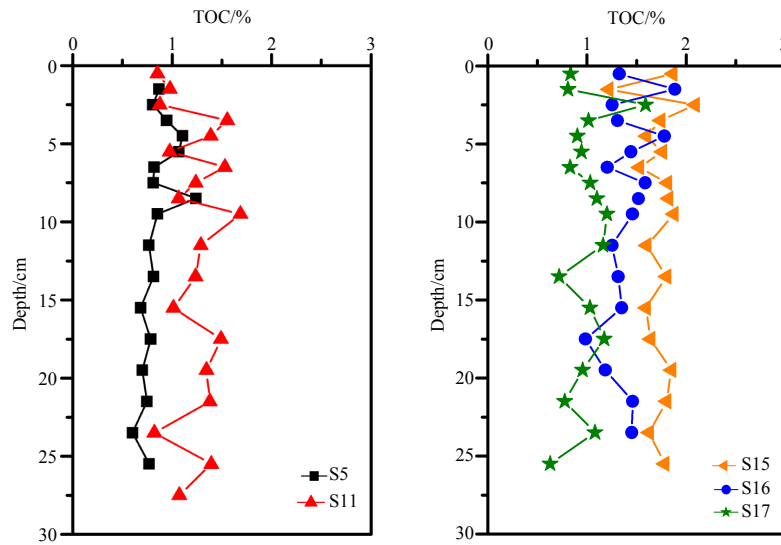


Fig. 3. Vertical distributions of TOC contents in sediment cores.

Table 3. Spearman correlation analysis result among metal/Al ratios and TOC in sediment cores

	TOC	Fe/Al	Mn/Al	Mo/Al	U/Al	V/Al	Mean particle size
TOC	1						
Fe/Al	0.25*	1					
Mn/Al	0.57**	0.21*	1				
Mo/Al	0.12	-0.54**	0.53**	1			
U/Al	-0.30**	-0.11	-0.57**	-0.32**	1		
V/Al	0.66**	0.64**	0.55**	-0.16	-0.16	1	
Mean particle size	0.64**	0.68**	0.43**	-0.29**	-0.06	0.84**	1

Note: \*\* Correlation is significant at the 0.01 level (2-tailed); \* correlation is significant at the 0.05 level (2-tailed).

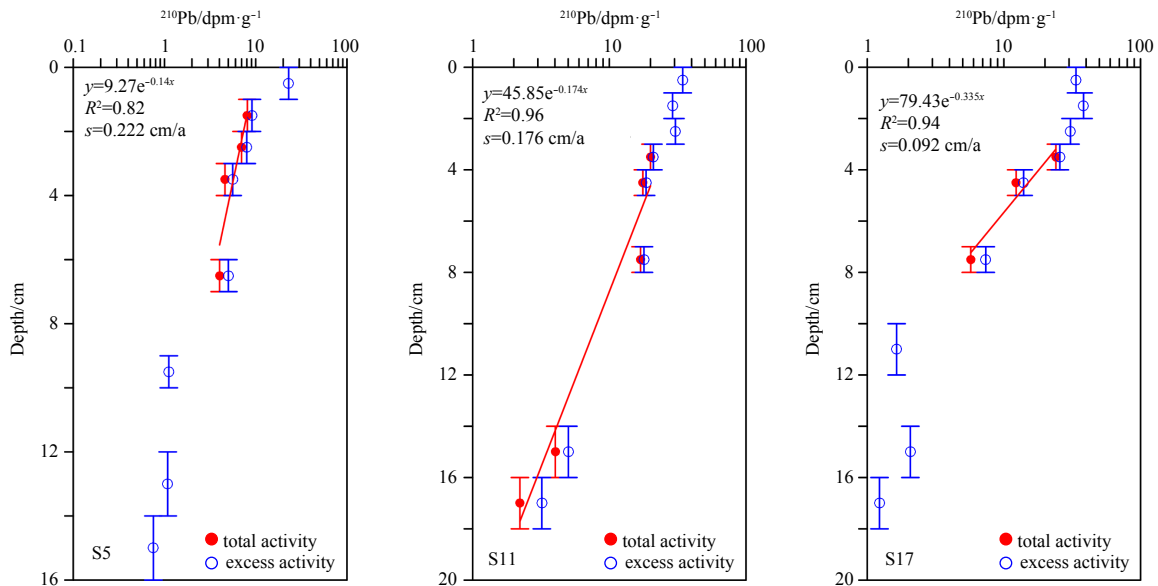


Fig. 4.  $^{210}\text{Pb}$  data for Cores S5, S11 and S17 in the northern Okinawa Trough. Open blue circles are total  $^{210}\text{Pb}$  data. Red filled circles are excess  $^{210}\text{Pb}$  data that were used for the sedimentation rate calculations.

ment chronology in this environment. The result showed that, S5, the station with the shallowest water depth and located on the continental slope, had the highest sediment accumulation rate (SAR) ( $\sim 120 \text{ g}/(\text{cm}^2 \cdot \text{ka})$ ), based on the relationship:  $\text{SAR} = \rho_{\text{dry}} S$ . While S11 and S17 had relatively slower sediment accumulation

rates, being  $95.0 \text{ g}/(\text{cm}^2 \cdot \text{ka})$  and  $49.7 \text{ g}/(\text{cm}^2 \cdot \text{ka})$ , respectively. Because of unexpected loss of samples during mail delivery, the sediment accumulation rate of Cores S15 and S16 were not measured and the data of S17 were used for them instead. S17 had deeper water depth (994 m) than S11, similar to the water depths

of two trough stations (1 063–1 134 m), and the sediment accumulation rate found at S17 (49.7 g/(cm<sup>2</sup>·ka)) was in excellent agreement with the data reported for nearby trough basin stations by Huh and Su (1999) (43.2–70.2 g/(cm<sup>2</sup>·ka)) and by Oguri et al. (2003) (49 g/(cm<sup>2</sup>·ka)) (F-2 and SST-2, located close to station SST-1 in Fig. 1). On average, three depth intervals were used to calculate the supported levels. The supported values are (0.99±0.20) dpm/g for S5 and (1.65±0.42) dpm/g for S17. The <sup>210</sup>Pb data of S11 did not reach supported level till the end of the core, therefore it used the supported value of S17 for calculation because those two cores are highly similar in terms of water depth, organic carbon content and grain size. In general, our finding is in agreement with previous studies, which showed that the sedimentation rate is relatively higher in the slope area compared to the trough (DeMaster et al., 1985; Narita et al., 1990; Chung and Chang, 1995). In addition, Oguri et al. (2003) also suggested that higher excess <sup>210</sup>Pb found in trough sediment may be due to higher <sup>210</sup>Pb activities in depositing particles, which is caused by boundary scavenging process (Nozaki et al., 1991).

### 3.2 Vertical distribution of the RSMs in pore water

#### 3.2.1 Fe and Mn, S<sup>2-</sup> in pore water

The vertical profiles of Fe and Mn in pore water are shown in Fig. 5. In most cores, dissolved Mn and Fe concentrations were depleted in pore water within the top ~1 cm. As previously discussed, the SWI in the northern OT was observed to be an oxic environment, where Fe and Mn should mainly be present in sediments as their oxides, and precipitated from the dissolved phase (Shaw et al., 1990; Thomson et al., 1993). When depth increases, oxygen depleted and Fe/Mn oxides start to be used as electron donors and reduced to dissolved Fe and Mn in pore water (Froelich et al., 1979; Middelburg et al., 1987; Rajendran et al., 1992). Profiles of Cores S5, S11 and S17 showed pronounced concentration maxima for Mn at 5–8 cm (16–50 μmol/L) and Fe at ~10 cm depth (25–80 μmol/L). The vertical profiles also showed that Mn was reduced to dissolve phase before Fe, as often found in sediment pore water profiles, because Mn oxides has priority thermodynamically over Fe oxides when being utilized in organic matter degradation (Froelich et al., 1979).

When Fe/Mn oxides are consumed, the pore water Fe and Mn

concentrations fall and sulfate is then used for biological metabolism and reduced to sulfide (Froelich et al., 1979). In this study, the Fe and Mn concentrations decreased gradually with depth to nonzero concentrations (>10 μmol/L) in the bottom of the cores, while the S<sup>2-</sup> concentrations in pore water of all cores were below the detection limit (<2 μmol/L) in all cores. Although the absence of pore water sulfide does not imply that sulfate reduction is not occurring because Mn/Fe oxides may be used to oxidize sulfide when present at a small amount (Myers and Nealson, 1988), it clearly showed that no strong anoxic sulfidic environment has reached until the bottom of all sediment cores.

A major difference between Core S15, S16 and the remaining cores is that dissolved Fe was barely detectable within the top 10 cm. Such vertical Fe profiles are often seen in hemipelagic sediments, where a relatively oxic sedimentary environment are found (Shaw et al., 1990; Zheng et al., 2002; McManus et al., 2005; Morford et al., 2005). This suggested that S15 and S16, the stations located in the trough basin, exhibited a relatively more oxic sedimentary environment at the SWI compared to the rest of the sites. In addition, Core S16 further differed from S15 in that pore water Mn concentration did not increase much till 10 cm, implying an even more oxic environment at Sta. S16 within the top 10 cm.

#### 3.2.2 Mo, U and V in pore water

Vertical profiles of dissolved Mo, U and V in pore water are shown in Fig. 6. In contrast to the Fe and Mn, RSMs were found enriched in surface pore water. The enrichment of Mo and V is possibly a result of particle degradation or dissolution, whilst downward diffusion from bottom water may result in higher U concentration in surface pore water (Heggie et al., 1986; Shaw et al., 1990; Klinkhammer and Palmer, 1991). With depth increasing, Mo, U and V concentrations dropped, reducing stepwise to lower valence species that are less soluble (Wehrli and Stumm, 1989; Klinkhammer and Palmer, 1991; Wanty and Goldhaber, 1992; Helz et al., 1996; Erickson and Helz, 2000). Eventually, they would form insoluble complexes with humic materials, oxides, or sulfide, precipitated from the dissolved phase and eventually fixed in the sediment (Anderson et al., 1989; Breit and Wanty, 1991; Emerson and Huested, 1991; Wanty and Goldhaber, 1992; Vorlicek et al., 2004).

Pore water Mo, U and V concentrations at S11 and S17 had a

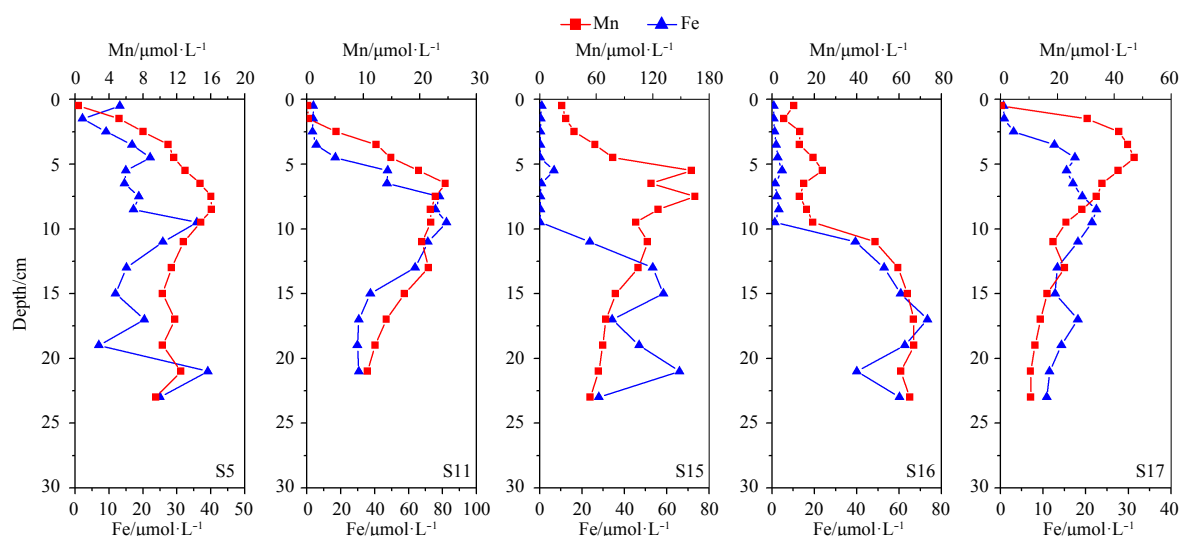
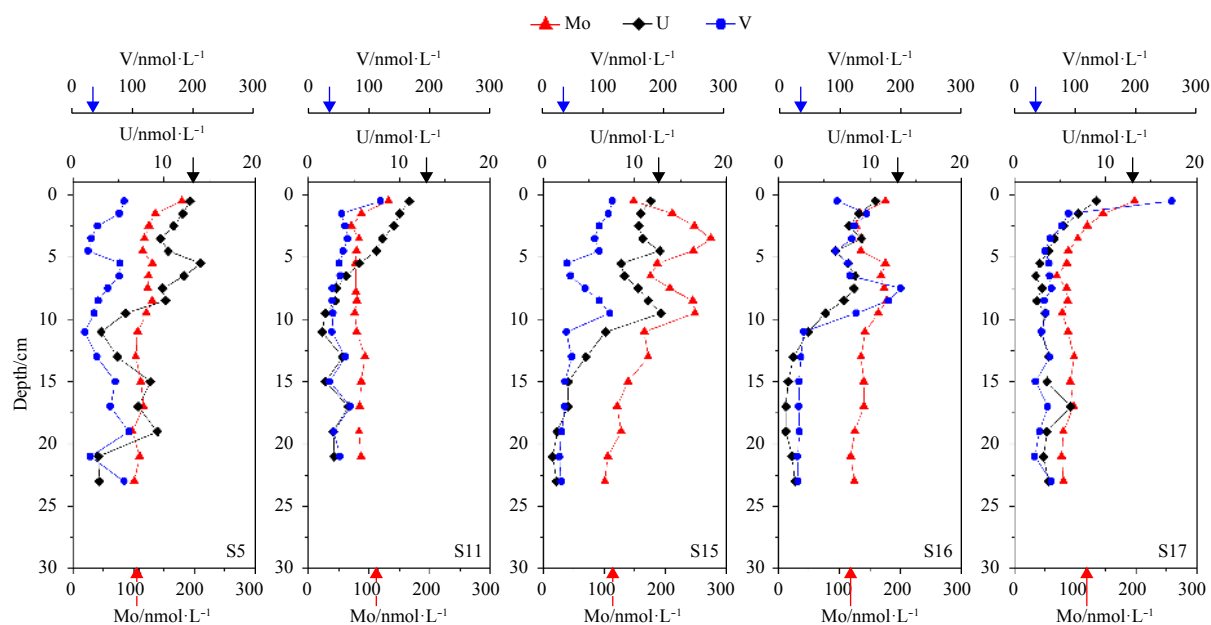


Fig. 5. Vertical distributions of dissolved Fe, Mn concentrations in pore water.



**Fig. 6.** Vertical distributions of dissolved Mo, U and V concentrations in pore water. Arrows indicate bottom water concentrations of Mo, U and V at each station.

typical decreasing trend, while at S5, S15 and S16, one or two subsurface peaks were found in the manganous zone (5–10 cm), and then decreased with depth. Subsurface peaks can be an indication of coupling between Mo, U and V with the Mn oxides recycling processes in surface sediment, as often reported for Mo and V (Morford and Emerson, 1999; Elbaz-Poulichet et al., 2005; Morford et al., 2005; Beck et al., 2008). Such release and retention of RSMs associated with Mn oxides may not be apparent when the manganous zone is compressed, such as in Cores S11 and S17 (Shaw et al., 1990). U and V concentrations in pore water again increased between 16–20 cm in Core S5 (Fig. 6), which may be a result of bioturbation-induced oxidation at that depth (Brumsack and Gieskes, 1983; Morford et al., 2009a). In this study, pore water profiles have indicated very similar reduction depths for dissolved Mo, U and V in pore water, which is different compared to the previous study showing that Mo being reduced in a deeper depth than U (Morford et al., 2005). In addition, U is often found to be associated with Fe oxides rather than Mn oxides (Sani et al., 2004; Senko et al., 2005).

### 3.3 Vertical distribution of the RSMs in sediment

Vertical distributions of RSMs in sediment are shown in Fig. 7. Metal contents in solid phases are present in terms of their content ratio with respect to Al, an element often represents the terrigenous detrital fraction of sediments. Statistical analysis was conducted among all metal/Al ratios and TOC, and the result is shown in Table 3.

Mn showed significant enrichment in surface sediments, and it decreased quickly with depth to detrital background in all cores. The Mn enrichment in surface sediments is often observed in marine sediments and it is a result of re-oxidization of upwardly diffusing  $Mn^{2+}$  that previously was produced by reduction of Mn oxides and oxyhydroxides in deeper sediments (Froelich et al., 1979; Chester, 1990; Calvert and Pedersen, 1993; Canfield et al., 1993). The recycling of Mo is often found closely associated with Mn (Morford and Emerson, 1999; Adelson et al., 2001; Sundby et al., 2004), so it is in this study. The vertical profiles of

Mo in sediment are highly similar to the one of Mn, as shown in Fig. 7. Mo had enriched surface layers with similar thickness as the ones of Mn, and drop rapidly to the detrital background with depth increasing. Statistically, Mo is also significantly correlated with Mn ( $p < 0.01$ , Table 3).

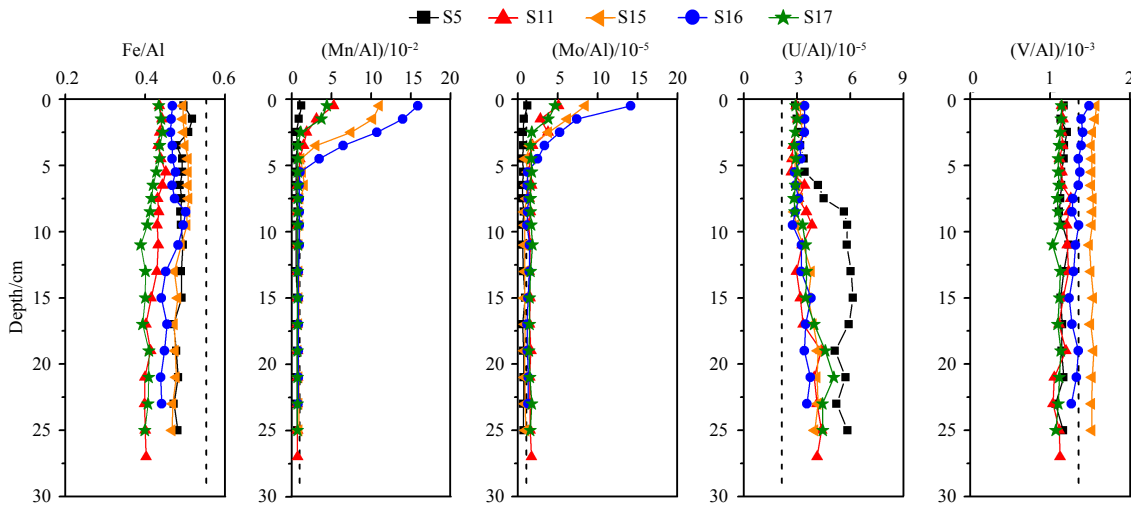
U content remained at a constant level in surface sediments, and started to increase at the base of Mn enriched layer till the remainder of the sediment cores, and S5 elevated to a relatively higher level than other sites. The relatively low U content in the Mn enriched surface layer imply that downward diffusion of soluble U(VI) from the water column is the main source of authigenic enrichment of U (Cochran et al., 1986; McManus et al., 2005; Kuzyk et al., 2011). The increasing vertical profile of U is similar to what have been found at Sta. SST-1 in Yamada et al. (2006) near the study region, or other hemipelagic suboxic and anoxic sediment environment (Zheng et al., 2002; McManus et al., 2005; Morford et al., 2005, 2009a). In contrast to U, a more reducing sediment environment is often required for Mo and V authigenic accumulation, to which extent sulfide is often present in sediment cores (Wanty and Goldhaber, 1992; Zheng et al., 2000; Morford et al., 2007; Scholz et al., 2011).

In this study, no clear vertical trend can be discerned for V in sediments, whilst it seemed that V/Al in all cores correlated with the TOC and mean grain size ( $p < 0.01$ ; Fig. 8 and Table 3). Vanadyl ( $VO^{2+}$ ) tends to form strong bonds with organic ligands in sediments (Cheshire et al., 1977; Wehrli and Stumm, 1989). Previous study has attributed elevation of V to relatively high TOC content (5%–10%) in marine sediments (Scholz et al., 2011). Böning et al. (2004) also found correlation between TOC and V in a number of coastal areas. Therefore, TOC or sediment grain size, which two are co-vary, may play a role in retaining V in sediments.

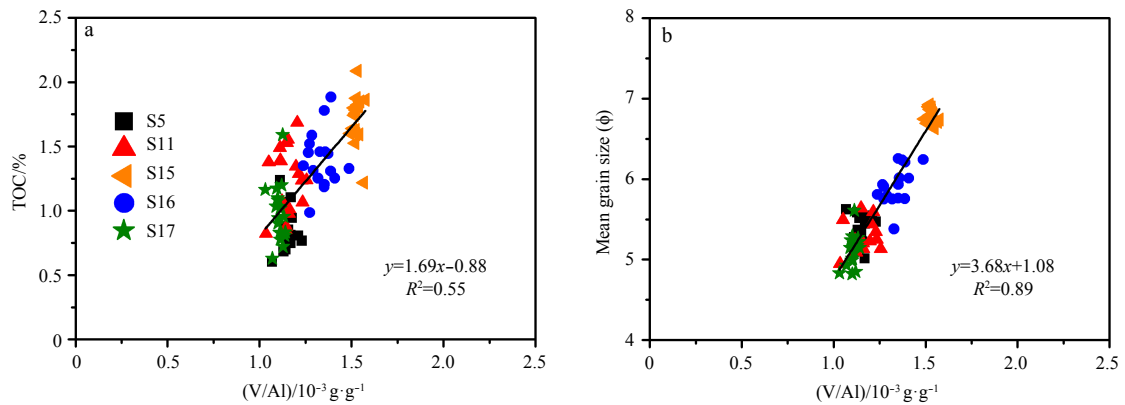
### 3.4 Flux calculation and comparison

#### 3.4.1 Diffusive benthic fluxes at sediment-water interface

Bottom seawater concentrations of Mo, U and V found in all five stations were relatively similar, with average Mo being



**Fig. 7.** Vertical distributions of metal/Al in sediment cores. The dashed lines indicate the metal/Al ratios of upper continental crust (Gao et al., 1998).



**Fig. 8.** Cross plots of V/Al weight ratios versus TOC (a) and mean particle size ( $\Phi$ ) (b). The solid black line is a linear regression through samples in sediment cores.

(118.5±1.9) nmol/L, average U being (13.4±0.3) nmol/L, and average V being (38.4±3.3) nmol/L, as indicated in Fig. 6. Compared with the dissolved Mo concentrations reported by Sohrin et al. (1999) in the study region (99–107 nmol/L), our Mo data are a little higher, while U and V are in similar concentration ranges as the ones reported in Sohrin et al. (1999).

For the flux calculation, the dissolved metal concentrations in surface pore water concentrations (extracted from the top 1 cm of the cores) and in bottom seawater were used for flux calculation based on Eq. (1), and the results are shown in Table 4. For the bottom seawater concentration, we prefer to use the metal concentrations in water samples collected from the CTD (30 m above the seafloor), which we assume to be equal to bottom water concentrations close to the surface sediment. In reality, this concentration may be higher due to sediment resuspension processes in the bottom water nepheloid or benthic boundary layer (Thorpe and White, 1988; Warnken et al., 2003; Kalnejais et al., 2007). However, seawater sampling very close to the sea floor is impractical by conventional bottle sampling and metal concentrations in overlying water from multi-corer devices are likely higher too due to disturbance of sediment surface. Therefore, metal concentrations from bottom water samples provide the best available data for estimating dC, and the gradient derived for (dC/dx) likely

represents an upper limit (Homoky et al., 2011)

The diffusive flux result found considerable fluxes of Mo and V leaving the sediments, being –2.7 to –14.9 nmol/(cm<sup>2</sup>·a) for Mo and –10.5 to –43.1 nmol/(cm<sup>2</sup>·a) for V. The upward fluxes are in accordance with the fact that surface Mo and V concentrations in surface pore water never dropped below the bottom water concentrations. In contrast, pore water U showed a general depletion (9.0–12.9 nmol/L) when compared with the bottom water values (13.1–13.9 nmol/L), indicating the potential of significant diffusive U into the sediment. The downward diffusive flux of U was estimated to be 0.09–0.35 nmol/(cm<sup>2</sup>·a) in the northern OT in this study, relatively higher than those diffusive fluxes reported in the Changjiang River Estuary and Northwest Atlantic Ocean (0.04–0.08 nmol/(cm<sup>2</sup>·a) (Barnes and Cochran, 1990; Zou et al., 2010), but comparable to the diffusive flux found in the continental shelf and slope off central California (0.08–0.36 nmol/(cm<sup>2</sup>·a) (McManus et al., 2005).

#### 3.4.2 Authigenic mass accumulation rate for RSMs

The calculated authigenic MAR for RSMs, based on Eq. (6), is shown in Table 4. Mo showed little authigenic accumulation ((0.04±0.20) nmol/(cm<sup>2</sup>·a)), while V exhibited a negative flux leaving the sediment into overlying water column, averaged to be

**Table 4.** The calculated results for benthic diffusive flux and authigenic mass accumulation rate

Station ID	Diffusive flux/nmol·cm <sup>-2</sup> ·a <sup>-1</sup>			Authigenic mass accumulation rate/nmol·cm <sup>-2</sup> ·a <sup>-1</sup>		
	Mo	U	V	Mo	U	V
S5	-14.5	0.09	-11.1	-0.21	0.83	-24.2
S11	-2.7	0.18	-14.8	0.30	0.47	-29.9
S15	-5.6	0.12	-14.0	-0.08	0.27	11.6
S16	-10.3	0.23	-10.5	0.05	0.20	-4.2
S17	-14.9	0.35	-43.1	0.15	0.30	-16.0
Average	-9.6	0.19	-18.7	0.04	0.41	-12.5
Std.ev.	5.4	0.10	13.8	0.20	0.25	16.6

~8% depletion of the detrital background content ( $[V]=0.08 \times [V]_{\text{crustal}}$ ). Other studies have reported V exhibited 10%–30% depletion rate of the detrital background in more reducing sediment (CA margin, Mexican margin, NW Africa) (Shaw et al., 1990; Morford and Emerson, 1999; Nameroff et al., 2002). The U MAR in the northern OT are averaged to be  $(0.41 \pm 0.25)$  nmol/(cm<sup>2</sup>·a), which is consistent with the flux estimated by Yamada et al. (2006)  $(0.20 \text{ nmol}/(\text{cm}^2 \cdot \text{a}))$ , whose samples were collected during 1993–1995. The good agreement between our result and that of Yamada et al. (2006) suggested that the sedimentary environment in northern OT has not changed much over the past ~20 years.

With riverine input of dissolved U from both the Changjiang River and the Huanghe River being  $6.45 \times 10^8$  g/a (Palmer and Edmond, 1993; Dunk et al., 2002; Jiang et al., 2011), the amount of authigenic U accumulated in the OT sediments (given the area being  $\sim 1.5 \times 10^5$  km<sup>2</sup>) averaged to be  $1.46 \times 10^8$  g/a, which accounted for approximately 23% of the riverine U supply from these two rivers. Based on our result and previous studies, it is shown that the suboxic sediments appear to be an important sink for U, and play an important role in balancing the global U fluxes in the world's oceans (Barnes and Cochran, 1990; Legeleux et al., 1994; Yamada et al., 2006). Unfortunately, no riverine Mo and V fluxes can be found for the Changjiang River and Huanghe River, therefore no comparison between the sedimentary fluxes and riverine fluxes for Mo and V can be made here.

The calculated diffusive flux and authigenic MAR were compared too. First of all, the two fluxes agreed relatively well for U and V, not only in flux direction (downward into sediments), but also in the order of magnitude. The well-matched flux results seem to support the premise that the dominant processes controlling the burial or remobilization of U and V in the study region is the diffusive process at the SWI. In the case of U, this accumulative mechanism has been suggested by quite a few studies (Cochran et al., 1986; McManus et al., 2005; Kuzyk et al., 2011), while in the case V, it is less so. We notice that, though average V fluxes are quite similar between those two flux calculations, the agreement vary from station to station. Especially the trough Sta. S15, with the highest TOC content, yielded opposite flux direction. As we discussed previously, the accumulation of V seem to be affected by organic content or grain size of the sediment, it is therefore suggested that, besides diffusive fluxes, it seems that there are other processes controlling the remobilization of V in sediments in suboxic sediment environment. V may be redistributed among different organic matter groups and incorporated into porphyrins (Lewan and Maynard, 1982) and later into secondary clay minerals, where it is present as V (IV) and V(III) (Breit and Wandy, 1991).

Secondly, both diffusive flux and MAR indicated little to none authigenic accumulation for Mo. The magnitude comparison,

however, is a bit off. Due to the enriched Mo concentration in surface pore water, the diffusive flux calculation indicated a much higher Mo flux out of sediment. It is important to remember MAR is calculated based on metal contents in downcore sediment. The MAR indicates a long-term accumulation rate, not reflecting the flux at SWI. The latter can be part of the internal cycling process, i.e., Mo is scavenged with Fe/Mn oxides from water column, regenerated at surface sediment and diffuses back to the overlying water. Therefore, the diffusive flux itself does not represent a sole source/sink term that can be used in the global budget calculation. So for Mo, we would conclude that there is little accumulation of Mo in the study, which is in agreement with what Crusius et al. (1996) have found in the Sea of Japan.

#### 4 Conclusions

This work studied the vertical distribution of several RSMs (Mo, U and V) in bottom seawater, pore water, and sediment phases in five short sediment cores collected from the northern OT. The depositional environments in the northern OT were found to be oxic to suboxic, and no anoxic sulfidic environment was reached till the end of the short cores (at ~25 cm depth). The vertical distribution of RSMs in pore water and sediment was presented and discussed. During the early diagenesis phase, Mo, U and V recycling processes in upper sediment layers were closely related with redox conditions, organic matter degradation and the recycling processes of Fe/Mn oxides. The benthic diffusive fluxes and authigenic MAR of the RSMs were calculated and compared, and the following conclusions are reached: (1) authigenic U accumulation was found in all cores. The calculated MAR for U agreed well with previous work in this region, and accounted for approximately ~23% of the riverine U from the Changjiang River and Huanghe River. This confirms that suboxic hemipelagic sediments act as an important sink for U in the world's oceans. Comparison of U diffusive flux and MAR showed that they agreed in direction and magnitude, indicating that diffusive process is a dominant mechanism that drives U downcore accumulation in sediment; (2) the recycling process of Mo is closely associated with Mn, reflecting both in pore water and sediment vertical profiles. Mo showed little authigenic accumulation in the study area; (3) showing no distinct vertical trend in solid phase, V is correlated with TOC and mean particle size in sediments. The average diffusive and MAR flux values for V are quite similar, however, besides the diffusive process, higher TOC content, or finer particle size, seem to play a role in retaining V in sediment and inhibit its remobilization at the SWI.

Over all, based on both pore water and solid phase profiles, this study provides a first systematic look on the geochemical behavior of Mo, U and V, along with Fe and Mn, during early diagenesis processes in northern OT, part of the largest continental margins along the west coast of North Pacific. Such study is in

general lacking in this part of the continental margins, and it provided important information on these important paleo-environment tracers for future global mass balance studies.

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