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Contents and benthic fluxes of nutrients in sediment pore water of the Southern Ocean

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Abstract The concentration and profile characters of nutrients in sediment pore water of the South Ocean, sampled during the cruise of CHINARE-18 of the austral summer 2001/02 were determined. The results show that the content of SiO_3-Si and NH_4-N were much higher than other nutrients. The profile of SiO_3-Si was characterized with sharp gradients near the sediment-water interface, profile distribution of silicate show that during the diagenetic reaction of silicate, dissolution was the main part. The organic matter decomposition was occurred under the anaerobic condition. Benthic fluxes of SiO_3-Si, NH_4-N were from pore water to overlying water, and regeneration of silicate and ammonium were the main part of the nutrient regeneration from the pore water of the study area.

Key words nutrient, interstitial water, sediment, the South Ocean.

1 Introduction

Sediments and their pore water play an important role in the cycling of many chemical substances, such as nutrients and organic contaminants. Both chemical and microbiological transformation processes are responsible for cycling elements between water and sediments. Bellow the sediment and water interface, mineralization of organic matter is the main part of early diagenic processes[1], during which nutrients that preserved in sediments could release to pore water, and exchanged with overlying water by gradient of concentration, and by physical and biological stirring. Therefore, study on pore water compositions of nutrients in the sediment is very important to understanding nutrients biochemical cycling[2].

The data set presented in this study is mainly focused on the pore water concentrations of nutrients and their fluxes across the sediment-water interface at the stations in the Prydz Bay, east Antarctica, and adjacent area of the Great Wall Station, west Antarctica, during the cruise of CHINARE-18, the austral summer of 2001/02.

2 Material and methods

Four sediment cores (G-1, IV-8、IV-10, D-1) were collected by no-perturbation- sediment-collector with four tubes, during the cruise of CHINARE-18 of the austral summer 2001/2002. Fig 1 and table1 shows the investigation area and the sampling stations. The diameter and length of the collector tube is 10 cm and 60 cm, respectively. And the lengths of our cores are from 10cm to 30 cm. The sediment in the upper 10 cm of each core was sliced into 1 cm intervals, and below 10 cm then into 2 cm intervals. Samples for analysis of nutrients concentrations in the bottom water were also collected from the cores by drawing water from 5 cm above the undisturbed sediment-water interface. The separation of the pore water from the sediment slices was operated by centrifugation ((at 4000 g for 30 minutes). All the water samples filtered through 0.45 μm pore size cellulose acetate filters and $HgCl_2$ were added in all filtered samples and stored for further analysis. Nutrients concentrations in pore water were analyzed in the laboratory using an autoanalyzer (Brown Lubbi), and the methods recommended by the "Standards of Marine Survey" (The STSA, 1991) were used. The standard solutions for analysis of the content of nutrients were provided by the Second Institute of Oceanography, SOA. Sediment-water flux incubations were held by using one tube of sediment in G-1 and IV-10, and fluxes of nutrients across the sediment-water interface were calculated from the time-varying concentration of them in the overlying water of the incubated tube. All sediment processing was carried out at in situ temperature (2 ℃) to avoid temperature artifacts.

Table 1. Sampling stations

Station	Longitude	Latitude	Depth (m)	Date
Great wall station G-1	58°55.0′W	62°13.0′S	6	2001.12.17
Prydz Bay IV-8	72°59.1′E	66°51.2′S	510	2002.02.23
Prydz Bay IV-10	72°56.5′E	67°30.0′S	596	2002.02.23
Davis station D-1	77°53.0′E	68°33.0′S	30	2002.02.25

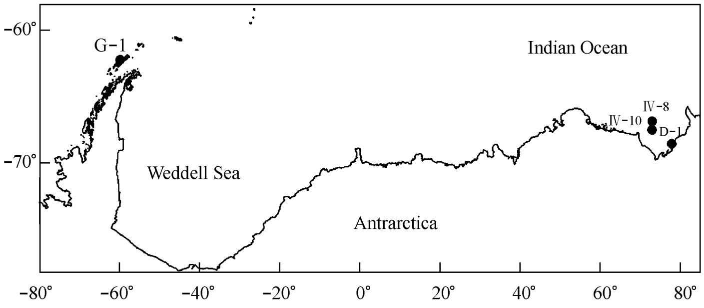

Fig 1 Sampling stations in the Southern Ocean.

3 Result and discussion

3.1 *Dissolved silicate (DSi) down core profiles*

Fig 2 shows the concentrations of silicate in the overlying water and pore water. The pore water concentrations of DSi display a larger range of variation, from 229.00-759.57 μmol/dm^3. The average concentration of IV-8, IV-10, G-1, D-1 was 566.79, 617.01, 547.88 and 454.98 μmol/dm^3, respectively. We can see that the average at Ⅳ-8 and G-1 were similar and that at D-1 was the lowest. Sharp gradients appeared near the sediment-water interface in all the profiles and are more pronounced at the station Ⅳ-8 and Ⅳ-10 in the Prydz Bay. The DSi concentration increased from 74.35 μM, which represents the mean DSi concentration in the bottom water, to the value of 349.08 μmol/dm^3 at 0 cm, and with depth increased the concentration of DSi in each pore water except in the G-1, exponentially approached to a stable asymptotic concentration of C_d in upper 10 cm of the core, which closed to the typical distribution of sediment-water interface undergoing low physical and biological stirring[3,4]. In G-1 further increase in DSi below ~10 cm are obviously, and under ~15 cm the increase is small ranging between 599.47-719.57 μmol/dm^3.

Archer *et al.* (1993) assumed that the pore water concentration of DSi regulate biogenic silica dissolution rates as it increases down-core until reaching saturation for the biogenic opal present, and C_d is assumed to be the solid phase solubility[5]. However other researchers did not think the C_d was the solubility[6], because the early diagenic processes include not only the dissolution process but also other chemistry processes. Moreover the adsorption by clay made the pore water concentration of DSi lower than the solubility[7], so the C_d is a concentration of equilibrium. Fig 3 is the "dissolution-diffusion-reaction" mode of DSi in pore water raised by Song (1991). According to the mode, dissolution is the main part of the early diagenic processes in Ⅳ-8, Ⅳ-10 and D-1. However, in G-1, except the dissolution process there also adsorption and precipitation processes in the early diagenic process. The C_d value of Ⅳ-8, Ⅳ-10 and D-1 is 624, 651 and 488 μmol/dm^3, respectively, which are less than the solubility of biogenic silica measured in the laboratory (1100 μM at 2 ℃[8]), but higher than that in Northeast Atlantic, which varied between 180 and 230 μmol/dm^3[3].

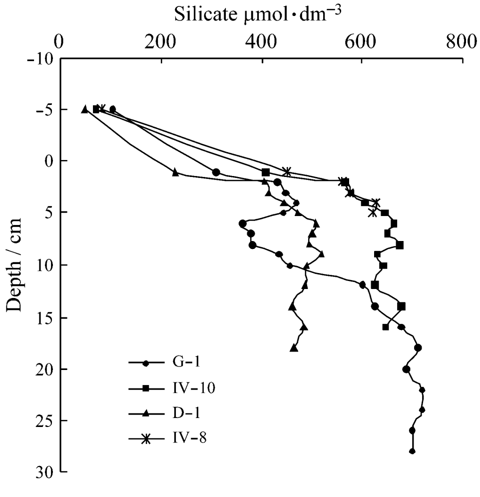

Fig 2 Profile distribution of silicate in sediment pore water (μmol/dm^3).

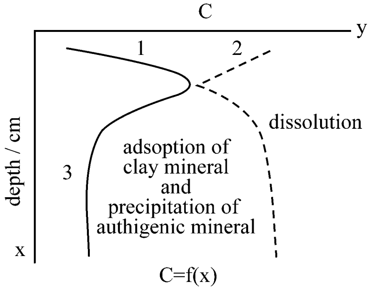

Fig 3 Mode of "diffusion-advection-reaction" of dissolved silicate in sediment interstitial water[9].

3. 2 *Dissolved inorganic nitrogen down core profiles*

The pore water concentration range of nitrate, nitrite and ammonium for all samples of the present study were 2. 86-56. 20, 0. 14-2. 43 and 10. 70-623. 60 μmol/dm^3, respectively. Concentrations of ammonium were much higher than the former two. And of the three forms of inorganic nitrogen nutrients, ammonium nitrogen took up about 98% of the total in G-1 (average concentration: 305. 97 μmol/dm^3) and D-1 (average concentration: 263. 72 μmol/dm^3). Whereas the nitrate concentrations in pore water at G-1 and D-1 were only 5. 77 and 6. 73 μmol/dm^3, respectively. On the contrary, nitrate was the main part of the three forms of inorganic nitrogen nutrients in Ⅳ-8 and Ⅳ-10, 35. 26 and 29. 16 μmol/dm^3, and they contained the lowest average concentration of ammonium, 29. 73 μmol/dm^3 at Ⅳ-10 and 42. 90 μmol/dm^3 at Ⅳ-8.

The forms and concentrations of inorganic nitrogen nutrients in the pore water are mainly controlled by the early diagenic process. In G-1 and D-1, ammonium was the main form of inorganic nitrogen nutrients, which indicate that degradation occured under anoxic conditions induced by reducing bacteria. Fig 4 is the profile distribution of Eh in sediments of G-1 and Ⅳ-10. The value of Eh decreased with depth, which ranged from -45 to 194 mv in G-1 and 268-497 mv in Ⅳ-10, means that sediment in G-1 was under weak anoxic conditions and increased with depths sediment became much more reductive, and the top sediment in Ⅳ-10 was under oxidative in some extent than the sediment under 9 cm, based on the correlation between reductive-oxidative characteristic and Eh of sediment[10, 11].

Ammonium concentrations in the pore water increased with depth, especially it was much higher than that of the surface layer bellow 10 cm (Fig 5-a). However, the nitrate profiles were contrary to the ammonium profiles, which were decreased with depth (Fig 5-b), which we infer that is because of nitrate acting as oxidation agent[12-16]. In surface sediments, where under oxidation condition, ammonium could be oxidized into nitrate, but with depth increasing, sediment became much more reductive and under anoxic condition, nitrate acted as oxidation agent. Thus, the nitrate concentration in the top surface sediment was relatively high, but rapidly decreased with depth.

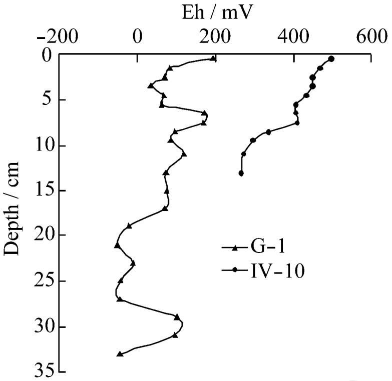

Fig 4 Profile distribution of Eh in sediments(mv).

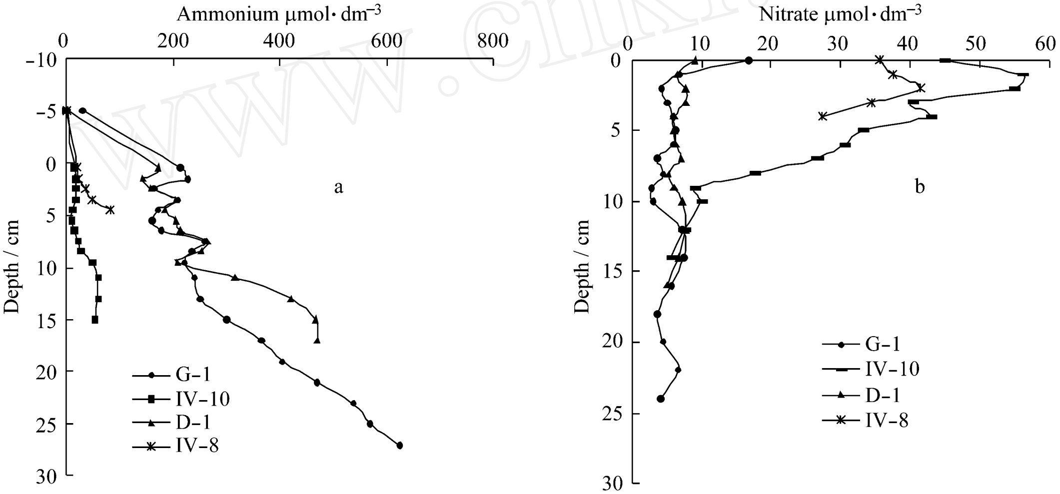

Fig 5 Profile distribution of ammonium and nitrate in sediment pore water (μmol/dm^3).

3.3 *Nutrients fluxes at the sediment-water interface*

3.3.1 *Fluxes estimated from pore water gradients*

Considering only the state of molecular diffusion, the bottom flux of nutrients in sediment pore water can be calculated from Fick's First Law as:

$$Fs = Ds\Phi \frac{\partial C}{\partial Z} \qquad (1)$$

Where Fs is the flux from sediment to overlying water (mmol/(m^2 · d)); Φ denotes the porosity of the sediment(0.78[3]); Ds is the coefficient of molecular diffusion in sediment (cm^2/s), from Li (1974)[17]; $(\partial C/\partial Z)$ is the concentration gradation of nutrients in interstitial water of the sediment; Considering $Ds = \Phi^2 Do$ (Do molecule diffusion coefficient in seawater, NH_4^+: 9.8×10^{-6} cm^2 s^{-1}, Si: 5.5×10^{-6} cm^2/s, NO_3^-: 9.78×10^{-6} cm^2/s[17]) thus the equation is:

$$Fs = Ds\Phi \frac{\partial C}{\partial Z} = Do\Phi^3 \frac{\Delta C}{\Delta Z} \qquad (2)$$

The DSi profiles were fitted by Eq. (3)[4]:

$$C_x = C_d - (C_d - C_0)\exp(\beta x) \qquad (3)$$

C_x is the DSi concentration at the depth x, C_d is the asymptotic DSi concentration, β is the second fitting parameter, the curvature of the profile[4]. The flux is then determined using Eq. (4), which is the first derivative of Eq. (3) at the interface, substituted into Eq. (2):

$$Fs = \Phi^3 D_O \beta (C_d - C_0) \qquad (4)$$

Nutrients in sediment interstitial water except nitrate have the upward fluxes from sediment to overlying water, and nitrate has the downward fluxes from overlying water to sediment in G-1 and D-1 sediment cores. Fluxes of DSi fluctuated between 0.70 and 1.22 mmol/(m^2·d), and NH_4 between 0.13 and 2.03 mmol/(m^2·d) (Tab. 2, 3). Although nitrate has the downward fluxes, compared with silicate and ammonium it was much lower (Tab. 4). So we can conclude that in study areas, regeneration of silicate and ammonium are the main part of nutrients regeneration in the sediments.

3.3.2 *Fluxes measured in situ incubation*

The changes in the gradients of the DSi concentration in the tube incubation were used to calculate the flux of silicic acid coming from the dissolution of biogenic silica, either at the sediment-water interface or within the sediment column. Fluxes were estimated using linear regressions applied to the data presented in Fig 6. The measured fluxes of G-1 and Ⅳ-10 were 1.74 and 1.22 mmol/(m^2·d) (Table 2), respectively. The measured flux of Ⅳ-10 was very similar to the fluxes calculated using pore water gradients, which was based

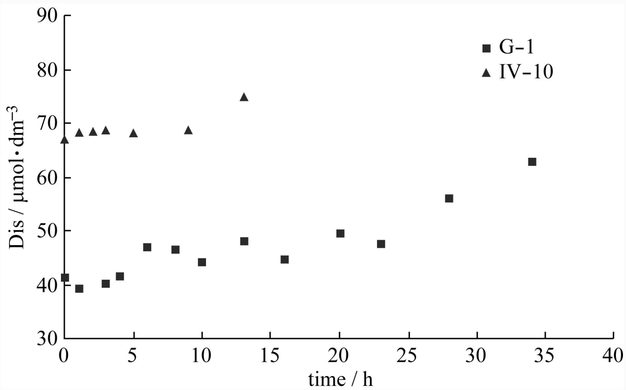

Fig 6 DSi concentration in the tube incubation as a function of time.

Table 2 The benthic diffusion fluxes of nutrients in sediment pore water in the study stations

Station	C_0 SiO_3-Si μmol/dm^3	C_d SiO_3-Si μmol/dm^3	β cm^{-1}	Calculated fluxes mmol/(m^2·d)	Measured fluxes mmol/(m^2·d)
G-1	102.75	309.71*		0.93**	1.74
Ⅳ-10	68.74	651.30	0.82	1.19	1.22
Ⅳ-8	79.53	624.30	0.90	1.22	
D-1	46.36	487.80	0.64	0.70	

*: the content of DSi in the surface pore water, not the C_d; **: the flux of G-1 was calculated based on the Eq. (1)

on the Eq. (4). It can be presumed that most of the diffusive fluxes are result from dissolution of BSi in the upper 5 cm of the sediment column in Ⅳ-10.

4 Conclusion

From the resulted data, it is possible to draw the following conclusions

(1) High silicate and ammonium concentration was the main characteristics of Nutrients composition in sediment pore water of study areas, which concentration rang from 229.00-759.57 μmol/dm^3 and 10.70-623.60 μmol/dm^3, respectively.

(2) Ammonia nitrogen comprised up to 98% of the three forms of total inorganic nitrogen. Profile distribution of ammonium increased with depth. However the profile distribution pattern of nitrate was contrary to ammonium. For ammonium and nitrate, the profile distributions basically agree with the anoxic process. Profile distributions of silicate indicate that the main diagenetic reactions of silicate were dissolution of silicate.

(3) Nutrients in sediment pore water except nitrate have the upward fluxes from sediment to overlying water. Regeneration of nutrients was mainly achieved by silicate and ammonium. Most of the diffusive fluxes are result from dissolution of BSi in the upper 5 cm of the sediment column.

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