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Inorganic carbon of sediments in the Yangtze River Estuary and Jiaozhou Bay

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Abstract. JGOFS results showed that the ocean is a major sink for the increasing atmospheric carbon dioxide resulting from human activity. However, the role of the coastal seas in the global carbon cycling is poorly understood. In the present work, the inorganic carbon (IC) in the Yangtze River Estuary and Jiaozhou Bay are studied as examples of offshore sediments. Sequential extraction was used to divide inorganic carbon in the sediments into five forms, NaCl form, $NH_3 \cdot H_2O$ form, NaOH form, $NH_2OH \cdot HCl$ form and HCl form. Studied of their content and influencing factors were also showed that NaCl form < $NH_3 \cdot H_2O$ form < NaOH form < $NH_2OH \cdot HCl$ form < HCl form, and that their influencing factors of pH, Eh, Es, water content, organic carbon, organic nitrogen, inorganic nitrogen, organic phosphorus and inorganic phosphorus on inorganic carbon can be divided into two groups, and that every factor has different influence on different form or on the same form in different environment. Different IC form may transform into each other in the early diagenetic process of sediment, but NaCl form, $NH_3 \cdot H_2O$ form, NaOH form and $NH_2OH \cdot HCl$ form may convert to HCl form ultimately. So every IC form has different contribution to carbon cycling. This study showed that the contribution of various form of IC to the carbon cycle is in the order of NaOH form > $NH_2OH \cdot HCl$ form > $NH_3 \cdot H_2O$ form > NaCl form > HCl form, and that the contribution of HCl form contributes little to carbon cycling, HCl form may be one of end-result of atmospheric CO_2. So Yangtze River estuary sediment may absorb at least about 40.96×10^{11} g atmospheric CO_2 every year, which indicated that offshore sediment play an important role in absorbing atmospheric CO_2.

Introduction

The ocean is evidently a major sink of carbon dioxide and plays an important role in the global carbon cycle. However, the carbon flux between seawater and sediment in the coastal seas is still poorly understood (Fasham et al. 2001; Borgne et al. 2002; Song 2003; Li et al. 2004a). Knowledge on the Carbonate mineral dissolution in sediment during the processes of diagenesis, lithification and evolution is of central importance to develop an insight into the carbon flux (Frye et al. 1993; Sternbeck et al. 1997; Morse et al. 2002). The pattern of calcium carbonate accumulation rates can be used to decipher the Pliocene-Pleistocene history of biogenic production and its relationship with global and local changes in oceanic circulation and climate (Tajika 2002; Giraudeau 2002; Beek 2004). Calcium carbonate dissolution or precipitation is controlled mainly by bottom water (or pore water) saturation state, sediment pH and metabolic release of carbon dioxide. Moreover, salinity also affects the chemical reactions that occur in sediment, like precipitation/dissolution of $CaCO_3$.

Inorganic carbon (IC) in sediment varies little, or increases with depth due to the dissolution near the water-sediment interface. The direct tracer of $CaCO_3$ dissolution is the increase in the calcium concentration of the pore water below the sediment-water interface (Mucci et al. 2000; Adler et al., 2001; Bhushan et al. 2001; Lopez 2003; Vreca 2003). Most studies focused on the total inorganic carbon in sediment, few on IC forms. In fact, there are many kinds of carbonate mineral in sediment such as aragonite, siderite, calamine, cerusite, phosgenite, magensite, and dialogite (Preda et al. 2004) with different dissolvability under different pH solution, for example; calamine can be dissolved in $NH_3{\cdot}H_2O$; cerusite and phosgenite can be dissolved in NaOH; calcite and aragonite can be dissolved in acid. To understand the burial and diagenesis of inorganic carbon in marine sediments, it is necessary to identify, separate and quantity the various solid-phase reservoirs of deposited carbon, but it is very difficult because of the fine-grained nature of most marine sediments. So it is necessary to find an indirect means to determine the identity and size of sedimentary IC reservoirs. One approach is physical separation of different sedimentary fractions by grain size, and measurement of total inorganic carbon (TIC) in the different fraction after each has been separately dissolved (Yang et al. 2002). However, this method can easily lead to ambiguous or incorrect identification of C-bearing phase. Complete physical separation of different phases from fine-grained sediment rarely can be achieved and surface coating of various sorts, potentially important in IC removal to sediments, can remain undetected and unidentified in such treatment. The most promising methods for separating and quantifying the various IC reservoirs in marine sediment are sequential extracted. So according to IC characters, IC in sediment are divided into five forms: NaCl form, NH_3H_2O form, NaOH form, NH_3HCl form and HCl form (Li et al. 2004b).

Inorganic carbon in Yangtze River Estuary and Jiaozhou Bay were studied as examples of offshore sediments.

Materials and methods

Geographical setting

The Yangtze River extends about 6300 km from the Qinghai-Tibet Pleateau eastwards to the East China Sea, whose basin is characterized by many industrial and urban centers, especially along its lower reaches and the estuary (e.g. Shanghai, Nanjing etc.). The river annually transports an average of 9.24×10^{10} m^3 of water and 4.80×10^8 tons of sediment to its estuary. Mixing of fresh and saline water occurs from the head of the mouth bar to the mouth of the estuary. Due to the large water discharge and sediment loads from the

Yangtze River drainage basin, the mouth bar is wide, ranging from Nanhui to Qidong. Its length is 60–70 km in the south channel (water depth less than 10 m) and about 40 km in the northern channel. Off the mouth bar, the sub-aqueous delta fore-set extends eastward, connecting with a submarine channel, whose southern edge may extend to as far as the middle part of Hangzhou Bay. The total area of the sub-aqueous delta is about 10,000 km^2 (Shen and pan 2001).

Jiaozhou Bay is a partially enclosed bay on the western part of the Shandong Peninsula, China (Figure 1). The Bay is surrounded by Qingdao with area of ca. 390 km^2 and mean water depth of ca. 7 m. The Bay mouth is narrow, only ca. 2.5 km wide and connects the Bay with the South Yellow Sea. More than 10 small rivers enter the Bay with the largest one being the Dagu River with annual

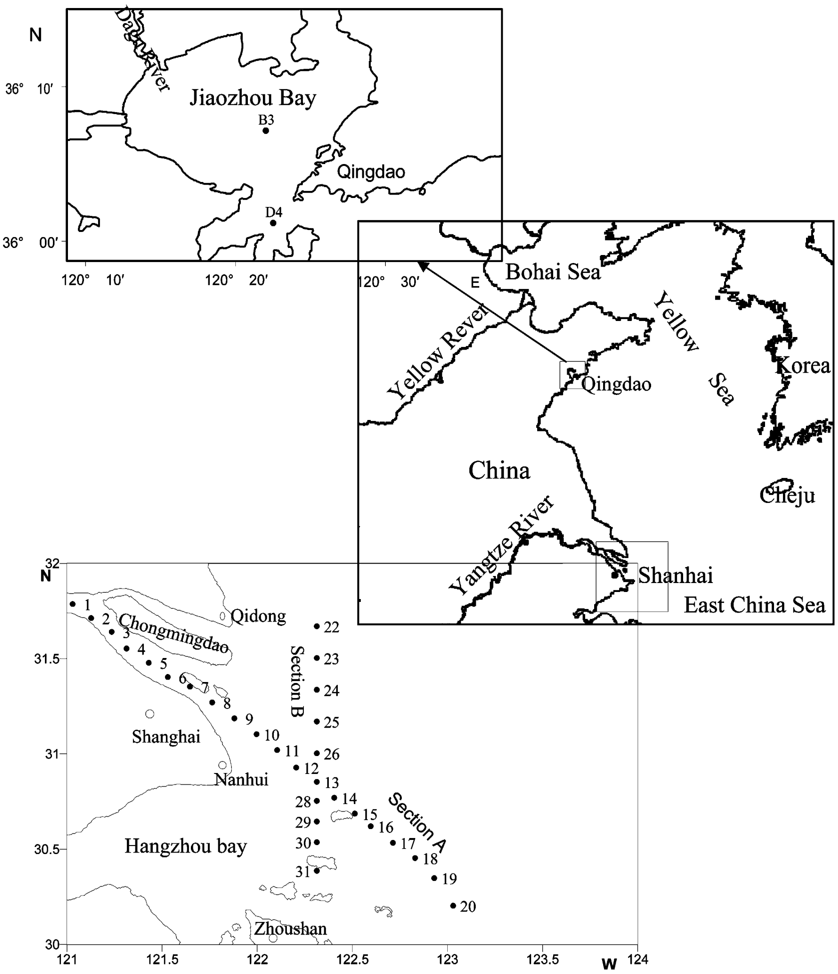

Figure 1. location of the sampling station.

average runoff of 6.61×10^8 m^3. Most of these rivers are the discharge trenches for industrial and domestic wastes from Qingdao City (Shen 2001b).

Sampling

Sediment samples were collected in May and September 2003 (Figure 1). Thirty-one surface sediment samples were collected with Grab bucket in the Yangtze River estuary onboard "*Zhe Hai Huan Jian*". Two sediment cores were collected with a gravity corer in Jiaozhou Bay onboard "*Jinxing II*". The cores were successively cut into 2.0 cm thick slices from surface to bottom. Eh was measured at 2 cm depth intervals using a Pt electrode coupled with an Ag/AgCl reference electrode. Simultaneously, Es was determined with a multi-electrode, and pH was measured using a multi-electrode and a HANA pH meter. Eh and Es were corrected to the standard hydrogen electrode. Eh, Es, pH were measured in situ within 30 min after samples were acquired from the sea bottoms. All samples were sealed in polyethylene bags and brought to the laboratory for further analyses.

Laboratory analyses

Sequential extraction method is based on the difference of IC chemical combined strength to give five forms: NaCl form (step I), $NH_3{\cdot}H_2O$ form (step II), NaOH form (step III), NH_2OHHCl form (step IV) and HCl form (step V). The procedure is shown in Figure 2 (cf. Li, 2004b). All IC forms were determined by a LECO CR-12 elemental analyzer with an analytical precision of 0.5%.

N and P content in sediments were simultaneous determined by colorimetric method with an analytical precision of 0.5%. Inorganic N and P were extracted by 0.1 mol l^{-1} HCl with vibration for 2 h, and then determined after centrifugation. Total N and total P were extracted by the potassium persulfate-sodium hydroxide mixture solution in stainless steel autoclave and maintained at 124 °C for 1 h. The content was determined after the solution cooled naturally. Organic N and P were calculated from the difference between the total N, P and inorganic N, P.

Organic carbon was determined by the revised Walkley–Black titration method (Leong and Tanner 1999). Water content was measured by drying wet sample in a ventilated oven at 60 °C until weight become constant.

Results

Inorganic carbon

Inorganic carbon in Yangtze River Estuary sediments

The content of different inorganic carbon forms in surface sediment of the Yangtze River estuary is shown in Table 1. The frequency of the content in

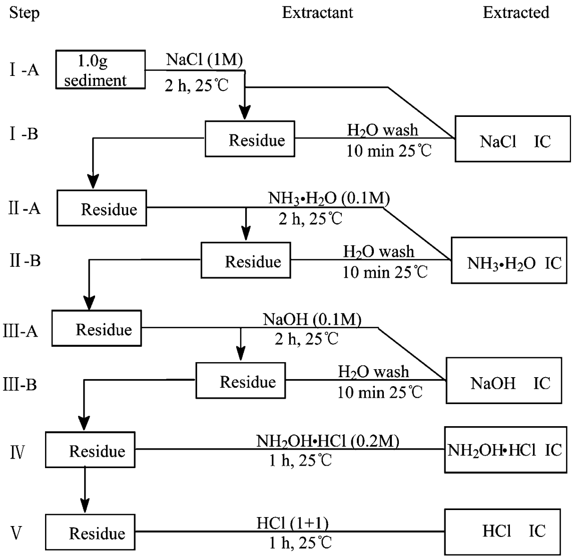

Figure 2. Scheme of sequential extraction method for different forms of IC in marine sediment.

different forms is shown in Figure 3. The content of different IC forms increased obviously from NaCl form to HCl form. Particularly, the content of NaCl form ranged mostly from 0.20 mg g^{-1} to 0.40 mg g^{-1} with average of 0.29 mg g^{-1}, and accounted for 2.84% in total IC. The content of NH_3H_2O form ranged mostly from 0.49 mg g^{-1} to 0.78 mg g^{-1}, with average of 0.54 mg g^{-1}, and accounted for 5.75% in total IC. The content of NaOH form ranged mostly from 0.60 mg g^{-1} to 1.00 mg g^{-1} with average of 0.80 mg g^{-1}, and accounted for 7.88% in total IC. The content of $NH_2OH{\cdot}HCl$ form ranged mostly from 2.00 mg g^{-1} to 4.00 mg g^{-1} with average of 3.11 mg g^{-1}, and accounted for 30.33% in total IC. The content of HCl form ranged mostly from 4.00 mg g^{-1} to 6.50 mg g^{-1} with mean of 5.38 mg g^{-1}, and accounted for 53.61% in total IC. $NH_2OH{\cdot}HCl$ and HCl form accounted for the most in total IC in the Yangtze River Estuary sediments.

Inorganic carbon(IC) in Jiaozhou Bay sediments

The content of different IC forms in Jiaozhou Bay sediments was overall similar to that in the Yangtze River Estuary sediments. The content of different IC form was in the order: NaCl form < $NH_3{\cdot}H_2O$ form < NaOH form < $NH_2OH{\cdot}HCl$ form < HCl form. The content of NaCl form, $NH_3{\cdot}H_2O$ form and NaOH form was similar, while the content of $NH_2OH{\cdot}HCl$ form and HCl form was similar. $NH_2OH{\cdot}HCl$ form and HCl form occupied the majority of total IC. The character of vertical distribution is obvious in Jiaozhou bay as shown in Figure 4. The content of every form except $NH_3{\cdot}H_2O$ form increased from surface to bottom. This trend accorded with the decrease of mud flux in Jiaozhou Bay in recent years.

Table 1. The content of different inorganic carbon forms in surface sediment of the Yangtze River estuary.

Station	NaCl phase mg g^{-1}	$NH_3 \cdot H_2O$ phase mg g^{-1}	NaOH phase mg g^{-1}	$NH_2OH \cdot HCl$ phase mg g^{-1}	HCl phase mg g^{-1}	Total IC mg g^{-1}
1	0.064	0.173	0.198	1.798	5.177	7.410
2	0.129	0.271	0.363	1.301	2.929	4.994
3	0.229	0.319	0.930	2.933	6.392	10.802
4	0.280	0.259	0.645	2.241	7.427	10.852
5	0.319	0.495	0.597	2.713	5.356	9.481
6	0.224	0.463	0.736	1.962	4.639	8.023
7	0.109	0.267	0.234	2.313	6.768	9.691
8	0.216	0.487	0.624	2.735	5.460	9.522
9	0.381	0.577	0.970	3.620	6.012	11.561
10	0.289	0.573	0.995	2.030	4.800	8.686
11	0.284	0.658	0.769	3.481	5.246	10.439
12	0.251	0.512	0.913	2.754	5.766	10.197
13	0.248	0.491	0.605	2.922	5.921	10.187
14	0.253	0.543	0.886	2.527	5.242	9.451
15	0.286	0.566	0.875	5.863	4.233	11.824
16	0.287	0.538	1.113	4.187	4.257	10.382
17	0.313	0.686	1.306	3.841	7.575	13.721
18	0.353	0.679	1.386	3.405	4.188	10.011
19	0.338	0.732	1.273	3.994	4.772	11.108
20	0.311	0.646	0.723	4.516	4.486	10.682
22	0.381	0.563	0.702	4.818	5.326	11.789
23	0.301	0.616	1.184	2.229	4.015	8.345
25	0.353	0.791	0.939	2.718	5.948	10.748
26	0.349	0.692	0.798	2.903	6.048	10.789
28	0.357	0.749	0.815	3.876	5.875	11.671
29	0.518	0.677	0.730	2.837	5.903	10.665
30	0.357	0.590	0.434	2.661	5.986	10.028
31	0.311	0.542	0.611	3.965	4.825	10.255

Water content

Water content is the percentage of pore water which wet sediments contained. As a medium of matter exchange between solid-solid and solid-liquid, the role of pore water in sediment can not be replaced in matter exchange within sediment and in interchange of matter between sediment and overlying water (Papadimitriou et al. 2002; Pfeifer et al. 2002; Vreca 2003). Water content was closely related with the speed and intention of matter exchange. Water content in the Yangtze River estuary sediment was $44.9 \sim 78.2\%$, and its spatial distribution decreased from west to east (section A); but varied little from north to south (section B) (Figure 5).

Negative correlation between water content and every IC form in the Yangtze River estuary sediment (Table 2) showed that the higher the water content was, the easier IC could dissolve, so that the lower was the IC content in sediment. The large coefficient of correlation between water content and every IC form except HCl form indicated pore water plays an important role in the transformation of one IC form to another IC form.

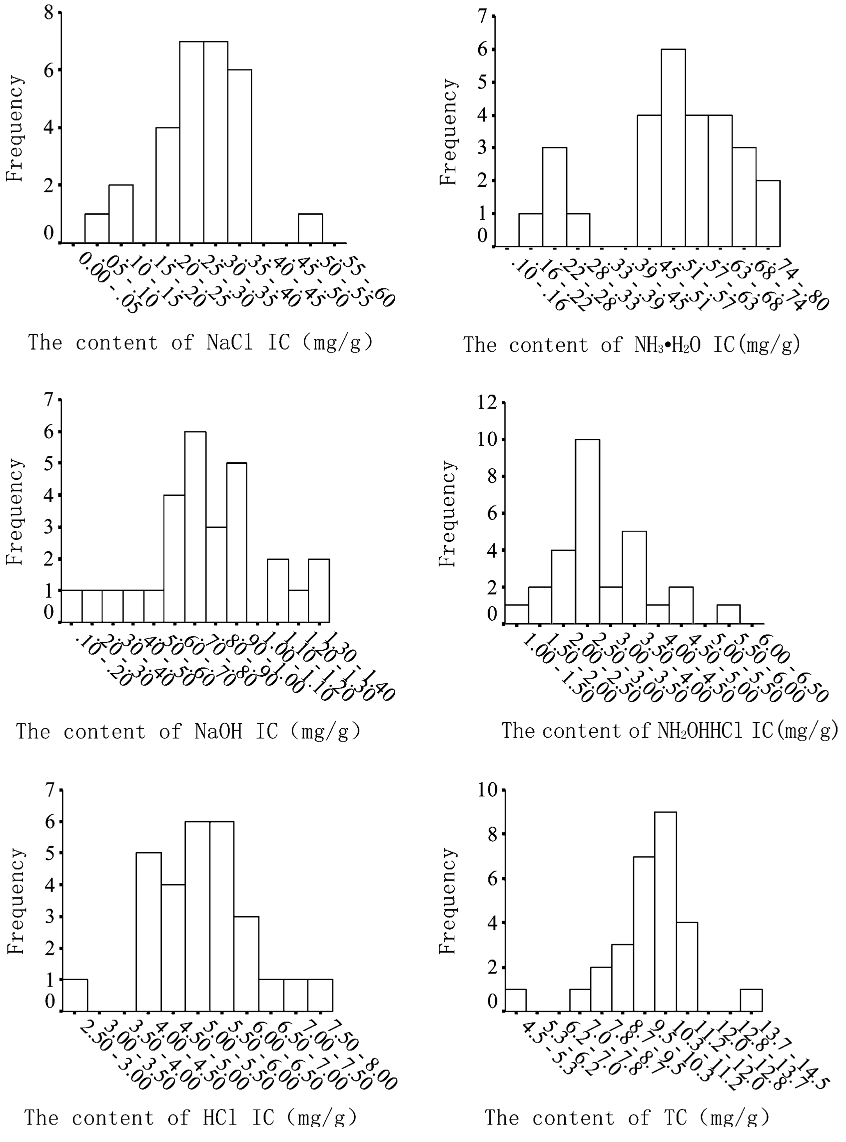

Figure 3. The frequency of the content for different IC forms.

Separate investigation of inorganic nitrogen (IN), organic nitrogen (ON) and total nitrogen (TN) in Yangtze River estuary sediment showed that ON occupied the majority of TN (about 64%) and that IN occupied 36% in Yangtze River estuary. The content of IN, ON and TN were about 0.02 ~ 0.33, 0.04 ~ 0.57, and 0.06 ~ 0.67 mg g^{-1}, with mean values of 0.15, 0.26, and 0.41 mg g^{-1}, respectively.

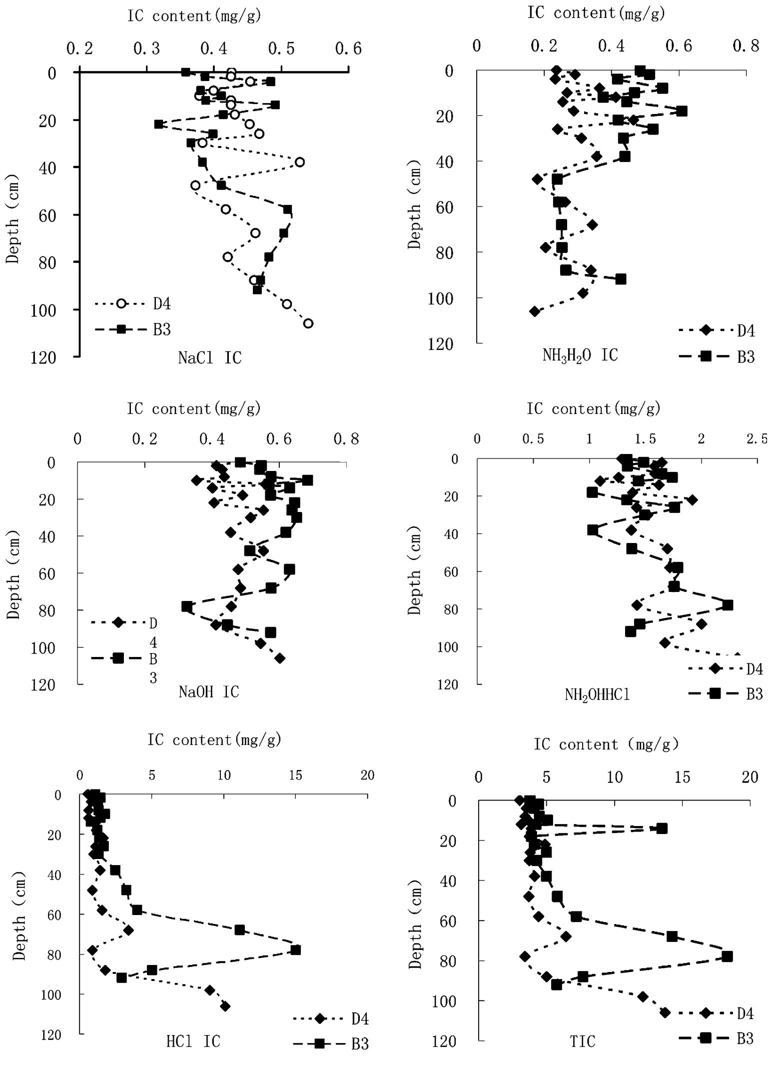

Figure 4. Vertical distribution of different IC form in Jiaozhou bay.

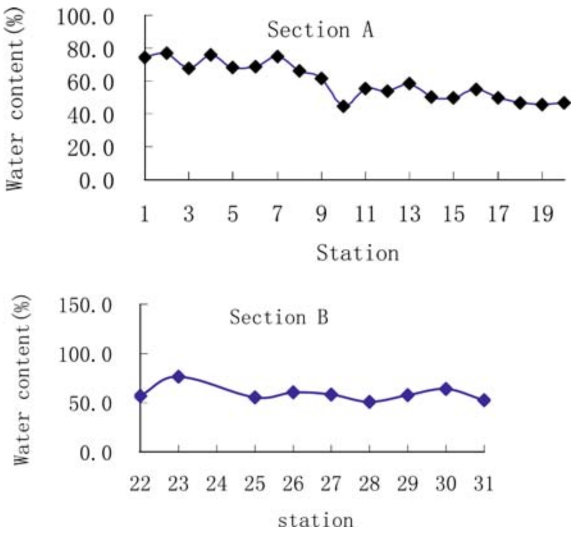

Figure 5. Distribution of water content in surface sediment of the Yangtze River estuary.

Table 2. Correlation between different IC form and OC, N, P and water content in the Yangtze River estuary sediments.

IC form	OC	TN	IN	ON	TP	IP	OP	Water content
NaCl form	0.61	0.05	0.22	− 0.06	0.43	0.28	0.27	− 0.50
$NH_3{\cdot}H_2O$ form	0.65	0.19	0.17	0.16	0.23	− 0.04	0.32	− 0.72
NaOH form	0.73	0.04	0.20	− 0.06	0.23	0.08	0.21	− 0.58
$NH_2OH{\cdot}HCl$ form	0.65	0.32	0.44	0.19	0.53	− 0.04	0.68	− 0.64
HCl form	0.04	0.00	− 0.05	0.03	0.11	0.15	0.01	− 0.03
TIC	0.56	0.10	0.23	0.01	0.55	0.24	0.45	− 0.54

The spatial distribution of IN, ON, and TN was similar. But the change of IN was smaller than that of ON and TN. Figure 6 shows the distribution of IN, ON and TN in section A and B. Their distribution can be divided into three regions (station 1–4, station 4–11 and station 11–20) in section A according to their regular variation, while in section B the change of IN, ON and TN were more stable.

As shown in Table 2, the positive coefficient of relation between N and IC was smaller than that between organic carbon (OC) and IC, which indicated that the influence of N on IC is less than the influence of OC, and that the influence of IN on IC was higher than that of ON. The influence on $NH_2OH{\cdot}HCl$ IC is the greatest, but the influence on HCl IC was very small, and the influence on other IC forms was also weak. These indicated that N in the process of nitrification and de-nitrification mainly influenced the formation and evolution of $NH_2OH{\cdot}HCl$ IC.

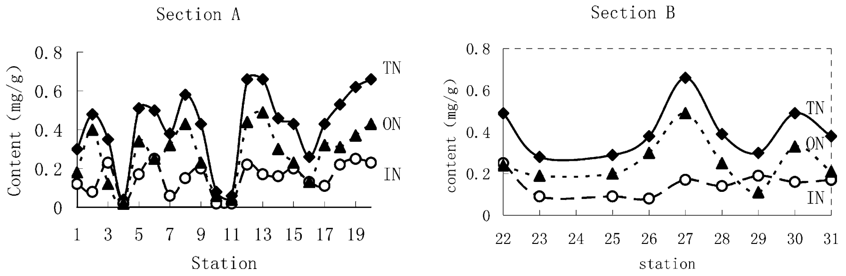

Figure 6. N distribution in the Yangtze River estuary sediment.

P

Inorganic phosphorus (IP), organic phosphorus (OP) and total phosphorus (TP) in Yangtze River estuary sediment were also studied separately. Compared to N, IP occupied the majority of TP (about 77%) while OP occupies 23% in the Yangtze River estuary. The content of IP, OP and TP was about 0.25 ~ 0.5 mg g^{-1}, 0.02 ~ 0.25 mg g^{-1} and 0.29 ~ 0.61 mg g^{-1} respectively, with mean value of 0.36, 0.11 and 0.49 mg g^{-1}.

The spatial distribution of P was different obviously compared to N. Figure 7 shows the distribution of P in section A and B, and that the change of P was smaller in all regions except the area of station 1 to 5 in section A.

From the positive correlation between P and every IC form (Table 2), we could see the effect on IC was stronger than that of N but weaker than that of OC, and that the effect of OP was stronger than that of IP. The effect of OP on $NH_2OH{\cdot}HCl$ form is prominent, but its effect on HCl form was small while IP had certain effect on HCl form, and little effect on $NH_2OH{\cdot}HCl$ form. OP was oxidized to phosphate with the organic matter's oxidation, so that the change of OP was more prominent than that IP. At the same time, steady calcite may be transformed to apatite, so that IP had certain effect on HCl form, but little effect on $NH_2OH{\cdot}HCl$ form.

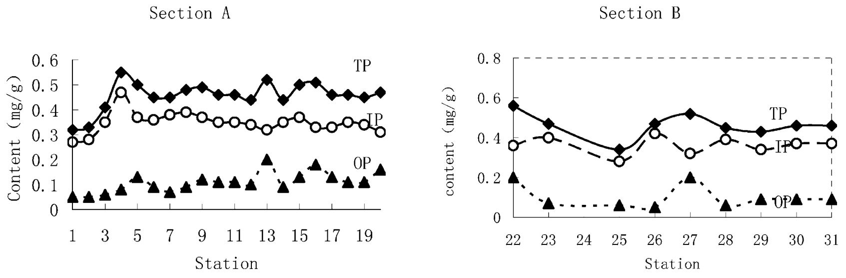

Figure 7. P distribution in the Yangtze River estuary sediment.

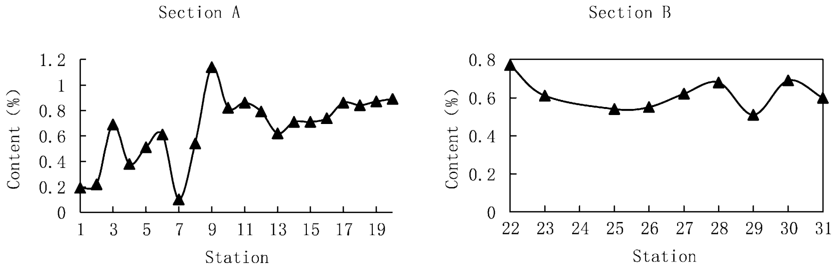

Figure 8. OC distribution in the Yangtze River estuary sediment.

Organic carbon

The area of lowest content of organic carbon (OC) in sediment of Yangtze River estuary was located at stations 1, 2 and 7, where the sediments were dominated by gray sand. OC content was usually less than 0.2%, lowest was 0.07%. But in other regions of the Yangtze River estuary the OC content was higher, mainly from 0.48 to 0.69%. Figure 8 showed the OC distribution in surface sediment of the Yangtze River estuary. It indicated that OC content in the east of station 9 is lower obviously than in the west of station 9 in section A. The change of OC content was not obvious in section B, but accorded with the change of salinity.

The coefficient of correlation between OC and IC showed that they had significant positive correlation except the correlation between OC and HCl IC (Table 2). So the IC content in the Yangtze River estuary increased with the increasing of OC. There may be two reasons for the positive correlation between IC and OC. One is the source of matter: the higher the OC content is, the higher the phytoplankton produced, leads to higher abundance of zooplankton which eat phytoplankton, so IC of biogenesis is higher. The other is the transformation of OC to IC after the decomposition of OC. The more OC is, the more IC resulting from the transformation of OC.

Discussion

Influencing factors

The change of different IC form in sediment was influenced by many factors, such as pH, Eh, Es, organic carbon (OC), total phosphorus (TP), total nitrogen (TN), organic phosphorus (OP), organic nitrogen (ON), inorganic phosphorus (IP), inorganic nitrogen (IN), water content, and so on. But the influence of various factors was not isolated, and was mutually restricting. So cluster analysis and factor analysis were used to estimate synthetically the influence of all factors in this paper.

Cluster analysis

Cluster analysis encompasses a number of different algorithms and methods for grouping objects of similar kind into respective categories. In other words cluster analysis is an exploratory data analysis tool aimed at sorting different objects into groups in a way that the degree of association between two objects is maximal if they belong to the same group and minimal otherwise. So, cluster analysis can be used to discover structures in data without providing an explanation/interpretation, and may reveal deeper associations in data which, though not previously evident, but nevertheless are sensible and useful once found. In this paper, the aim for using cluster analysis is to sort all influencing factors into groups, and reveal the association among influencing factors and different IC form.

Figure 9 showed the result of cluster analysis for the factors which influence IC in sediment. The cluster analysis classified the factors into two homogenous clusters: physical factors and chemical factors, which can be subdivided into N-cluster, P-cluster and OC. Physical factors can be subdivided into Eh, Es and pH-cluster. The influence of all factors belonging to one cluster (or sub-cluster) on IC is similar.

Figure 10 showed the results of cluster analysis for all forms of IC and their influencing factors, which can indicate which factor has close relationship with which IC form. On the whole, all the IC forms are influenced by physical factors indirectly through acting with chemical factors. But chemical factors influence IC directly, and moreover, OC has a close relationship with NaOH form, $NH_3 \cdot H_2O$ form and NaCl form, has closest relationship with NaOH form and weak relationship with HCl form. Its relationship with $NH_2OH \cdot HCl$ form and TIC (total inorganic carbon) is weaker than its relation with NaCl form, but closer than its relation with HCl form. OP and TP have close relationship with $NH_2OH \cdot HCl$ form and TIC, but weakest relation with HCl form and weaker relation with other forms of IC. TN, IN, and ON have only weak relation with all IC forms. All these revealed that the association between HCl form and most influencing factors was weak; and that HCl form may play a special role in carbon cycling.

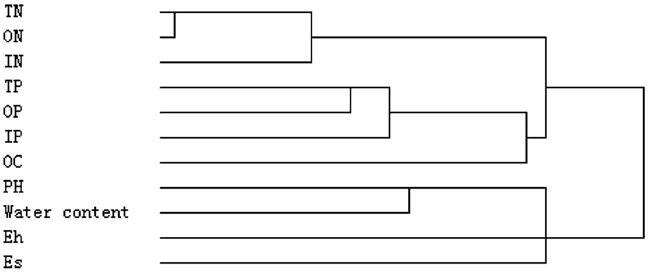

Figure 9. Results of cluster analysis for IC influencing factors in the Yangtze Estuary sediment.

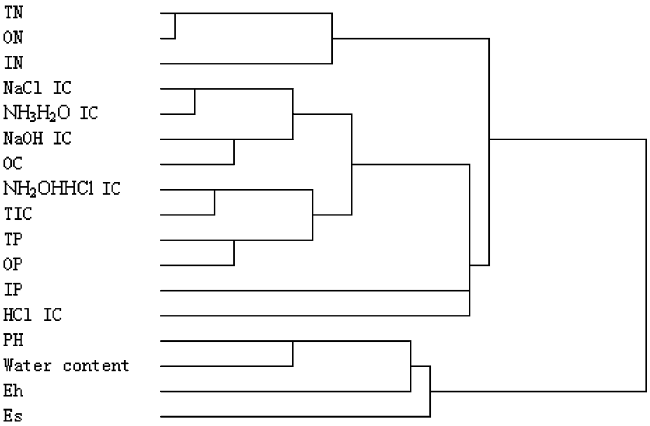

Figure 10. Results of cluster analysis for all forms of IC and their influence factors in Yangtze Estuary sediment.

Factor analysis

The main applications of factor analysis are to reduce the number of variables and detect structure in the relationships between variables. Therefore, we used factor analysis to reveal which factor plays the main role in carbon cycling. Table 3 shows the result of factor analysis for influencing factors of IC in the Yangtze River estuary sediment. Four factors can be used to represent all influencing parameters. They contribute 80% of all information, and every factor's contribution gradually decreases from factor 1 to factor 4. Table 4 is factor loading matrix of factor analysis. Factor 1 mainly includes TN, IN, and ON, factor 2 mainly includes pH, Es, water content and OC, factor 3 mainly includes TP and OP, and factor 4 mainly includes Eh and IP. These results indicated that TN, IN and ON provided the biggest contribution to all IC forms in the Yangtze River estuary; followed by the contribution of pH, Es, water content and OC; then the contribution of TP and OP, Eh and IP's contribution was the least. So we can conclude that nitrogen, pH, Es, water content and OC may play an important role in the change of IC.

Transformation of different IC form

All matter in sediment might be changed at different rate during early diagenesis when organic matter was degraded by benthic macro- and microorganisms and accompanied by consumption of oxygen and other electron acceptors, by the production of CO_2 and other metabolites (Hammond et al. 1996; Jahnke, 1997; Silverberg et al. 2000; Freudenthal et al. 2001; Madron et al. 2003; Aller 2004; Gogoul and Stephanou 2004; Stahl et al. 2004). For example, with OC continues oxidation, N may transform to some other N form

Table 3. Result of factor analysis for influence factors of IC in Yangtze River estuary sediment.

Factor	Eigenvalue	Percentage of Variance	Percentage of accumulated variance
1	3.629081	32.99164	32.99164
2	2.439065	22.17332	55.16496
3	1.559507	14.17734	69.3423
4	1.189572	10.81429	80.15659
5	0.704013	6.400117	86.55671
6	0.651339	5.921263	92.47797
7	0.437943	3.981304	96.45928
8	0.264626	2.405695	98.86497
9	0.124853	1.135028	100
10	3.56E-16	3.24E-15	100
11	−2.8E-17	−2.5E-16	100

Table 4. Factor loading matrix of factor analysis (after rotation).

	1	2	3	4
pH	−0.15	0.83	−0.04	0.02
Eh	−0.25	0.49	0.11	−0.68
Es	0.29	0.63	0.11	−0.22
Water content	−0.17	0.67	−0.48	0.32
OC	0.12	−0.78	0.41	0.10
TN	0.98	−0.03	0.12	−0.07
IN	0.75	−0.22	0.16	0.04
ON	0.89	0.08	0.07	−0.11
TP	0.02	−0.05	0.80	0.58
IP	−0.27	0.10	0.12	0.88

by nitrification or de-nitrification. And P may transform to PO_4^{3-} or form apatite (Song 1997; Song 2002). Due to the continued dissolution or participation of carbonate, any IC form in sediment may also be changeable.

The vertical distribution of the ratio of every IC form to total IC should be stable when the matter source is stable. Change of the ratio of one IC form should indicate that the content of this form of IC was increased or decreased. The increase of content indicates that other forms of IC transformed to it, otherwise this form is transformed to other form. Figure 11 showed the ratio of every IC form to total IC in Jiaozhou Bay sediment. The ratio of NaCl form, $NH_3{\cdot}H_2O$ form, NaOH form and $NH_2OH{\cdot}HCl$ form have similar vertical distribution in Jiaozhou Bay core samples, but the HCl form's vertical distribution is reverse to them, which indicates that all IC forms have a trend of transforming from NaCl form, $NH_3{\cdot}H_2O$ form, NaOH form and $NH_2OH{\cdot}HCl$ form to HCl form. That is to say, NaCl form, $NH_3{\cdot}H_2O$ form, NaOH form and $NH_2OH{\cdot}HCl$ form are instable, and easy to change in matter exchange in sediment, and will be changed to HCl form ultimately.

The contribution of every IC form to carbon cycling

Part of IC in sediment would return to water to participate in carbon recycle. (Song 2004) Precipitation or dissolution of IC in sediment is affected by physical and chemical factors in overlying water except in sediment, such as dissolved inorganic carbon (DIC), temperature, salinity, dissolved oxygen

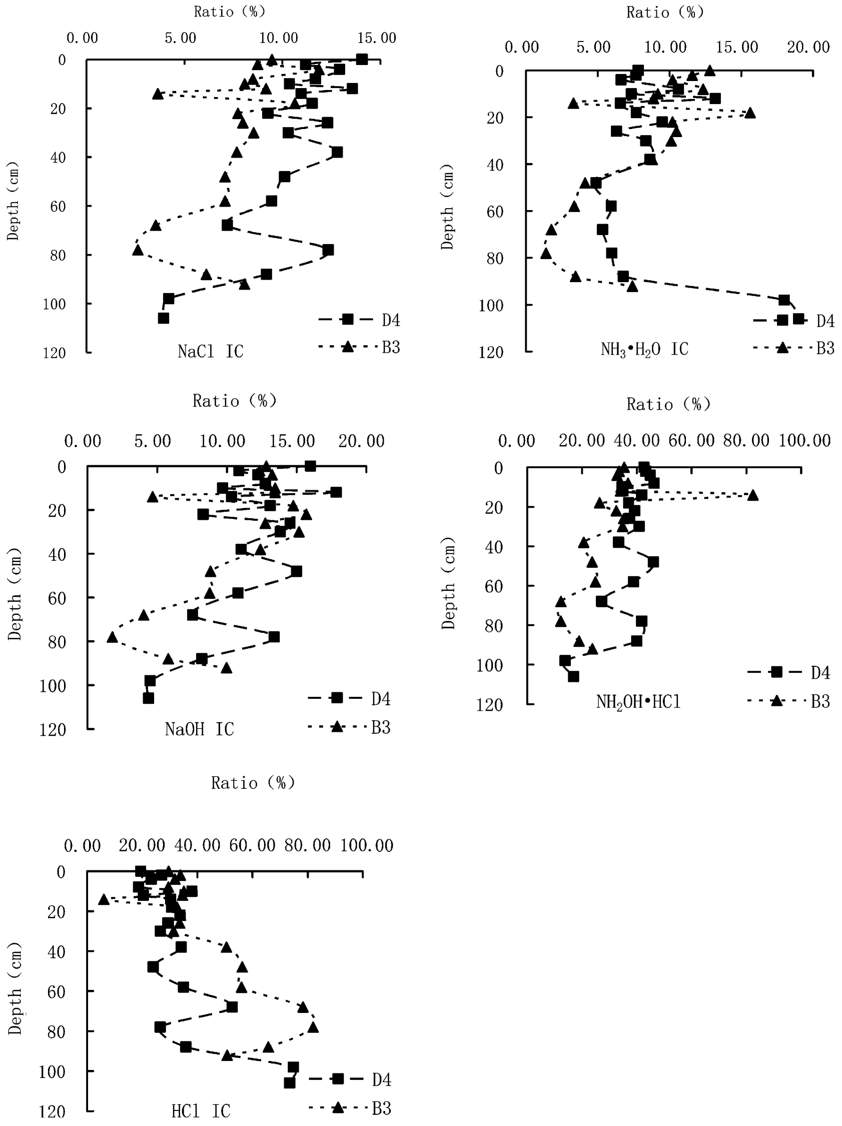

Figure 11. Vertical change for ratio of every IC form to total IC in Jiaozhou Bay sediment.

(DO), NO_3^-–N, PO_4-P, active silicon, chl-*a*, phytoplankton, zooplankton, and so on. Although these factors in overlying water play an important role, the function of every factor is different. Some factors such as nitrogen and phosphorus may improve the dissolution of IC, whose consumption will promote the absorption of carbon by phytoplankton, then promote the dissolution of IC in sediment; while other factors such as zooplankton may improve IC precipitation, whose growth will increase the deposition of IC. The correlation between one factor and IC can reflect this relationship. The correlation between different IC form and every affecting factor of IC in overlying water indicates every IC form has different ability to return to water from sediment. In other words, the contribution of different IC form to carbon cycling is different. So the correlation can be used to deduce one IC form's contribution to carbon cycling. The correlation between different IC form in the Yangtze River estuary sediment and physical, chemical and biological factors in overlying water are listed in Table 5.

In order to assess the contribution, a new parameter – contribution score was designed. The correlation between every IC form and DIC, temperature, salinity, DO, NO_3^-–N, PO_4–P, active silicon, chl-*a*, phytoplankton, zooplankton was used to determine the contribution synthetically. The calculation of contribution score is explained below.

The coefficient of correlations between the same factor and 5 different IC forms were calculated and sorted by their absolute value, and given score of 5, 4, 3, 2, 1 respectively, in the order of maximum(score 5) to minimum(score 1). Negative correlation indicates that this factor can improve IC dissolution, and more IC may take part in carbon cycling, and its score will be positive. Positive correlation indicates that this factor improves IC precipitation, so less IC participates in carbon cycling, its score will be negative. The sum of all scores of one IC form to every influencing factor is the contribution score of this IC form. The results are shown in Table 6. According to the value of the contribution score, the contribution of NaOH form to carbon cycling is the biggest, $NH_2OH{\cdot}HCl$ form is the second, and the contribution of $NH_3{\cdot}H_2O$ form is smaller than that of the $NH_2OH{\cdot}HCl$ form. The contribution of NaCl form is smaller than that of the $NH_3{\cdot}H_2O$ form. The contribution of HCl form is the smallest. The contribution of NaOH form to carbon cycling being the biggest may be due to its weaker combined strength, and its higher content than NaCl form and $NH_3{\cdot}H_2O$ form. The contribution of $NH_2OH{\cdot}HCl$ form being bigger than that of NaCl form may be due to its much higher content than NaCl form, and its advantage of higher content compensates for the inadequacy of its bigger combined strength. The combined strength of HCl form is the biggest, so it cannot easily participate in carbon recycling.

From the positive and negative contribution score, NaCl form, $NH_3{\cdot}H_2O$ form, NaOH form, and $NH_2OH{\cdot}HCl$ form may take part in carbon cycling during early diagesis, and may be a potential carbon source. HCl form may not participate in carbon recycling within the short-term, and will be buried in the long time.

Table 5. Correlation between different IC form in the Yangtze River estuary sediment and physical, chemical and biologic parameter in overlying water.

IC form	Temperature	Salt	DO	N-NO_3^-	Active P	Active Si	Chl-*a*	Zooplankton dry weight	Cell counts of phytoplankton	DIC
NaCl IC	−0.57	0.47	−0.27	−0.45	−0.27	−0.40	−0.09	0.13	0.03	0.64
$NH_3{\cdot}H_2O$ IC	−0.69	0.65	−0.46	−0.61	−0.39	−0.46	−0.13	0.30	0.18	0.75
NaOH IC	−0.60	0.60	−0.64	−0.51	−0.41	−0.60	−0.14	0.49	0.29	0.61
$NH_2OH{\cdot}HCl$ IC	−0.53	0.61	−0.32	−0.58	−0.57	−0.61	0.01	0.63	0.23	0.47
HCl IC	0.23	−0.17	0.08	0.12	0.23	0.13	0.15	−0.09	−0.03	−0.19

Table 6. Contribution score of different IC form in Yangtze River estuary sediment.

	Temperature	Salt	DO	N-NO_3^-	Active P	Active Si	Chl-*a*	Zooplankton dry weight	Cell counts of phytoplankton	DIC	contribution score
NaCl IC	3	−2	2	2	2	2	2	2	2	−4	8
$NH_3{\cdot}H_2O$ IC	5	−5	4	5	3	3	3	3	3	−5	14
NaOH IC	4	−3	5	3	4	4	4	4	5	−3	23
$NH_2OH{\cdot}HCl$ IC	2	−4	3	4	5	5	−1	5	4	−2	19
HCl IC	−1	1	−1	−1	−1	−1	−5	−1	−1	1	−9

It is well worth attending that HCl IC may be one of the final resting places of atmospheric CO_2. Regarding the source of HCl IC, if it came from organism, equivalent CO_2 would surely be depleted in its genetic process; if it came from terrestrial, carbonate would deplete CO_2 in the weathering process because CO_3^{2-} might be transformed into HCO_3^- by absorbing CO_2.(Wong 1995). So wherever it came from, HCl IC will deplete atmosphere CO_2. If the amount of all HCl IC in global marine sediment is known, the amount of absorbed atmospheric CO_2 can be calculated from the sediment rate.

Sedimentation flux of different IC form in the Yangtze River estuary

According to the above results, offshore sediment is the sink of atmospheric CO_2. But its capacity of sinking is controlled mainly by the input of inorganic carbon from rivers, high level of primary productivity, sedimentation rate and hydrodynamic conditions, and other factors.

In the Yangtze River estuary, the enormous primary production increased from west to east (Liu 2001), abundant matter from the Yangtze River was deposited here (Shen 2001a), where sedimentation rate is faster, about 2.0 cm^{-1} year (Demadter 1985; Xu 1997). In addition, the not too strong wave, tide and coastal current are favorable for sedimentation. So there is a strong ability to fix carbon in the Yangtze River estuary. Sedimentation flux can be used to assess the strength of sinking.

Sedimentation flux of every IC form can be calculated by the follow equation.

$$BF = C_i \times D_\mathrm{R} \times S \times \rho_\mathrm{d}$$

$$\rho_\mathrm{d} = \frac{1 - W_\mathrm{c}}{(1 - W_\mathrm{c})/\rho_\mathrm{s} + W_\mathrm{c}/\rho_\mathrm{w}}$$

Where BF is the sedimentation flux of carbon in sediment, C_i is the content of every IC form, D_R is the sedimentation rate, S is the area of sub-aqueous delta, ρ_d is the dry density of sediment, W_c is the water content, and ρ_w is the density of seawater.

The results showed that the sedimentation flux of total inorganic carbon (TIC) is 11.17×10^{11} g C^{-1} year, which is more than organic carbon fluxes. About half (HCl IC) will be buried for a long time, the other half may be the potential source of carbon cycling. So the Yangtze River estuary sediment may absorb at least about 40.96×10^{11} g atmospheric CO_2 every year, which indicates that offshore sediment play an important role in absorbing atmospheric CO_2.

Table 7. Sedimentation flux of different IC form in the Yangtze River estuary($\times 10^{11}$ g C/yr).

OC	NaCl IC	$NH_3{\cdot}H_2O$ IC	NaOH IC	$NH_2OH{\cdot}HCl$ IC	HCl IC	TIC
7.11	0.32	0.60	0.88	3.43	5.93	11.17

Conclusions

A new concept in the study of IC in marine sediment was brought forward, in which inorganic carbon can be divided into different forms by their combined strength in sediment. IC in sediment was divided into 5 forms by sequential extraction method in this paper, and their close relationship becomes small continually from NaCl form to $NH_3{\cdot}H_2O$ form, NaOH form, $NH_2OH{\cdot}HCl$ form and HCl form. The content of $NH_2OH{\cdot}HCl$ form and HCl form are much higher than other forms, and they occupy the majority of total IC. Their content and distribution are influenced by pH, Eh, Es, water content, OC, ON, IN, OP and IP, which have different influence on different forms in different region, but the influence of OC on all forms of IC is the greatest.

Every IC form is changeable in early diagenesis, NaCl form, $NH_3{\cdot}H_2O$ form, NaOH form and $NH_2OH{\cdot}HCl$ form convert to HCl form ultimately. Their contribution to carbon cycling has close relationship with the property of overlying water, and this contribution can be assessed by their contribution score. The contribution score decrease from NaOH form to $NH_2OH{\cdot}HCl$ form, $NH_3{\cdot}H_2O$ form, NaCl form and HCl form. NaCl form, $NH_3{\cdot}H_2O$ form, NaOH form, and $NH_2OH{\cdot}HCl$ form may be the potential source of carbon cycling, but HCl form may be buried for a long time, It may be one of the final places of atmospheric CO_2.

The sediment in Yangtze River estuary may absorb at least about 40.96×10^{11} g atmospheric CO_2 every year, which indicates that offshore sediments play an important role in absorbing atmospheric CO_2.

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