

REMOBILIZATION AND ACCUMULATION OF IODINE IN MARINE SEDIMENTS, WESTERN ANTARCTIC OCEAN

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Abstract Remobilization and accumulation mechanisms of iodine in marine sediments, which are divided into several geochemical environment, are studied. The result shows that iodine is characteristically rich in organic fractions of the sediments on the bottom of bay and pelagic sediments. However, it may be associated with oxyhydroxide and adsorptive phase in a higher percentage at the continental shelf and hemipelagic sediments. The environmental characteristics of remobilization of iodine in surficial sediments are similar to that of iron, that is, it is remobilized on anoxic conditions and converted into solid phases when it is in oxic environments, though the iodine does not act as the electron acceptor. The processes of adsorption and oxidation are responsible for the value of I_1/C_{org} in excess of that of planktonic materials other than the organic fraction in surficial sediments. It is a comprehensive effect of organism decomposition, oxyhydroxide reduction, particulate adsorption and pore water diffusion on decrease of ratio of iodine to organic carbon with increasing depth in sedimentary column. The diffusive and depositional fluxes of iodine are of the same magnitude, which could be the cause for the poor iodine contents in sedimentary rocks. Based on the calculation and discussion, a new model for the remobilization and accumulation of iodine in marine sediments is set up.

Key words Southern Ocean, sediment, iodine

Introduction

Unlike sedimentary rocks, recent marine sediments have some highest concentration of iodine over other geological materials (Price *et al.*, 1970). It shows that the enormous existence of iodine in marine sediments is not due to the input of continental inorganic detritus but is largely controlled by some geochemical processes.

The enrichment of iodine in marine sediments is usually considered to be approached in two ways. Most of the authors tend to think it is totally controlled by organic matters, based on the close relation of iodine and sedimentary organic carbon (Vinogradov, 1939; Bojanowski, 1970; Price, 1973; Kennedy, 1987). However, according to difference of iodine concentrations under different redox conditions and lower iodine content in Fe—poor

sediments, Ullman and Aller (1985) proposed that it was mainly due to the adsorption of iodate by Fe oxyhydroxides precipitated on the surface of oxic sediments as a result of diagenetic remobilization.

Harvey (1980) and Francois (1987) have used different methods to separate the geochemical phases of iodine in order to prove the remobilization and accumulation mechanisms of iodine in recent marine sediments. As a result, the former concluded that the iodine is primarily in electropositive state in the form of N-iodoamides, while the latter proposed that it was mainly associated with humic materials. Actually, both of the results told that the geochemical process of iodine should be mainly controlled by organic matters. However, as mentioned above, we envisage a fact that iodine as one of a few biophilic elements which can exist in several oxidation states, its geochemical behavior shows its complexity. For researching the mechanisms, on the basis of previous works, we redesign an experimental procedure and take the Antarctic Ocean sediments as the sample which has no or less been affected by non-natural factors, and compare the results with those in other oceans of the same latitude.

Materials and Experimental Methods

Samples were collected during Antarctic summer (1984—1985). The locations and their geochemical characteristics and the measurement of Fe^{3+}/Fe^{2+} , pH, Eh, organic carbon and ALK can be seen in literature (Cheng Xianhao *et al.*, 1988). Total iodine in sediments and pore waters were analysed using a method described by Wang Wuyi (1989). Iron concentration in pore waters was measured by flame atomic absorption spectrophotometry, the analytical precision was better than 5%. The measurement of iodine association phases leached was made on iodine anion selective electrode, and all the treatment was carried out by duplication method. Relative deviation is better than 10%. The procedure for chemicalspeality leaching of iodine is as following:

Absorptive Phase: This phase is defined to be the iodine that can be replaced by dihydrocarbonate. 1.00g sediment, which was dried to constant weight at 60°C and at vacuum condition, is put into the specially prepared polypropylene centrifuge tube (60ml), and 20ml of 0.05 mol $NaHCO_3$ is added. It is disrupted for one hour with supersonic instrument under room temperature, after the sample is shaken to be homogenous.

Oxyhydroxide phase: This is the iodine associated with noncrystal line iron and manganese oxides, and other compounds which are unstable under reduction conditions. The residue after above treatment is washed two times, with 20 ml of 0.04 M $NH_2OH \cdot HCl-HAc$ was added. Then it was heated to 90°C and maintained at this temperature for four hours with occasional agitation.

After each leaching, separation was made by centrifuging (5000r/min.) for 20

minutes. The supernatant was removed with a pipette and analysed for iodine. Before the second leaching, the residue was washed with superpure water two times, and the supernatants are discarded.

Results

The experimental results are shown in Table 1. Here the authors make a reasonable inference that the content of organic associated iodine is about the difference between total iodine and the absorption + oxyhydroxide iodine (pore water iodine is neglected). The reasons for our inference are based on the following facts: 1) There are almost no crystalline minerals of iodine except for the dissolvable salt minerals in geological materials, and a little iodine bound to mineral lattice is only in the form of isomorphism. 2) The iodine contents in various rocks are commonly lower than 1 $\mu\text{g/g}$ (Wang, 1991). 3) Harve (1980) extracted

Table 1. Analytical results of the surfact sediments in $\mu\text{g/g}$.

| Parameter * | I_t | I_p | I_a | I_o | I_{oc} | Fe-P | G(%) | D(m) | |
|-------------|-----------|-------|-------|-------|----------|-------|-------|-------|--------|
| M_2 | 49.00 | 0.45 | 5.76 | 8.49 | 34.75 | 0.650 | 46.24 | 208 | |
| M_3 | 48.08 | 0.23 | 8.01 | 6.56 | 33.51 | 0.940 | 33.62 | 406 | |
| M_5 | 39.99 | 0.25 | 1.96 | 8.04 | 29.99 | 0.670 | 36.53 | 326 | |
| Bay | R_1 | 50.00 | 0.200 | 10.66 | 9.28 | 30.06 | 32.03 | 522 | |
| | J_1 | 63.50 | 0.17 | 9.91 | 8.84 | 44.75 | 0.205 | 28.21 | 470 |
| | L_1 | 57.80 | 0.22 | 4.82 | 9.38 | 43.60 | 0.013 | 10.68 | 851 |
| | L_3 | 31.03 | 0.23 | 1.35 | 4.65 | 25.03 | 0.060 | 20.77 | 155 |
| | L_5 | 63.50 | 0.36 | 8.10 | 13.91 | 41.49 | 0.980 | 14.21 | 200 |
| | S_{24} | 56.50 | 0.24 | 18.38 | 26.50 | 11.62 | 0.380 | 34.66 | 479 |
| | S_2 | 21.36 | 0.16 | 7.00 | 7.44 | 6.92 | 0.030 | 8.43 | 260 |
| Conti- | S_3 | 43.46 | 0.16 | 8.70 | 7.38 | 27.38 | 0.030 | 7.90 | 450 |
| | S_9 | 24.08 | | 6.74 | 4.92 | 12.42 | 0.072 | 6.28 | 176 |
| mental | S_5 | 26.12 | 0.17 | 2.33 | 7.07 | 16.72 | 0.025 | 8.55 | 478 |
| | S_6 | 32.08 | 0.11 | | | | 0.030 | 38.34 | 451 |
| Shelf | S_8 | 43.07 | 0.18 | 16.23 | 11.79 | 15.05 | 0.120 | 10.32 | 190 |
| | S_{21} | 51.50 | 0.26 | 5.14 | 12.65 | 33.71 | 0.560 | 8.86 | 330 |
| | S_{20} | 33.81 | 0.05 | 4.65 | 8.39 | 20.77 | 0.930 | 10.90 | 300 |
| Hemip- | S_4 | 47.05 | 0.12 | 11.48 | 8.64 | 26.93 | 0.050 | 22.47 | 1834 |
| elagic | S_{23} | 65.20 | 0.22 | 22.18 | 18.75 | 24.27 | 0.030 | 21.18 | 510 |
| | S_{25} | 63.89 | 0.23 | 22.40 | 18.46 | 23.03 | 0.690 | 35.01 | 780 |
| Ocean | S_{10} | 55.00 | 0.15 | 22.80 | 17.56 | 14.64 | 0.042 | 36.67 | 1669 |
| Pelagic | S_{11} | 35.51 | 0.16 | 2.28 | 7.20 | 26.03 | 0.040 | 40.26 | 4150 |
| Ocean | S_{19} | 41.51 | 0.05 | 1.13 | 3.75 | 36.63 | 0.010 | 10.64 | 3026 |
| South | 8355 | 35.61 | | 0.41 | 1.70 | 33.49 | | | |
| China | 8361 | 30.00 | | 0.43 | 5.63 | 23.93 | | | > 3000 |
| Sea | 8366 | 25.74 | | 1.17 | 3.38 | 21.19 | | | |
| Equator | MN_1 | 40.84 | | 0.33 | 3.09 | 38.49 | | | |
| Pacific | MN_{36} | 23.88 | | 1.20 | 0.77 | 21.39 | | | > 4000 |
| Ocean | MN_{42} | 22.16 | | 0.82 | 1.68 | 19.67 | | | |

* I_t - Total iodine, I_p - Pore water iodine, I_a - Oxyhydroxide associated Iodine, I_{oc} - Organic iodine, Fe-P - Pore water iron, G - Clay size Content in sediment

nearly 90% of iodine With 5% of NaOCl and Francois (1987) also extracted 80—90% of iodine with 0.5 mol of NaOH from the residual leached with $\text{NH}_2\text{OH} \cdot \text{HCl}$. All the evidences prove that in comparison with the contents of organic associated iodine, the content in mineral lattice could be ignored but does not affect us to discuss the geochemical tendency of the accumulation and remobilization of iodine.

Discussion

It is known that many researchers have different viewpoints on the geochemical behavior of iodine in marine sediments from different researched areas. In order to get an objective judgement, it is necessary to understand the distribution characteristics of iodine in different representative geographic environments.

1. Regional distribution model of iodine in sediments

Based on the geochemical conditions, we divide the researched area into bay, continental shelf ($D \leq 500\text{m}$), hemipelagic ($D \leq 2000\text{m}$) and pelagic ocean. Fig. 1 shows that the distribution of iodine in various associated phases indicates their specific geochemical characteristics. It is of interest that the relative values of iodine in the associated phases are quite similar in both bay and pelagic sediments, although their concentrations of total iodine are different. The result may be a puzzle but from the parameters measured by the authors,

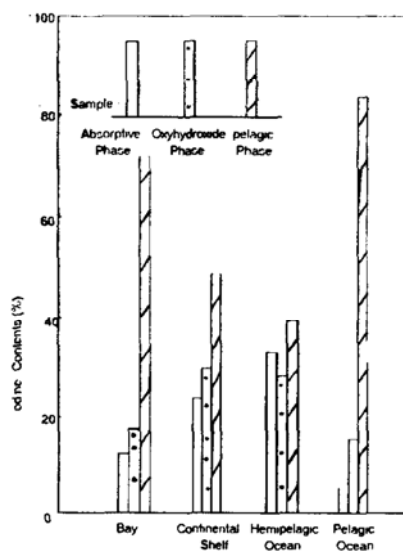


Fig. 1. Regional distribution model of iodine in the sediments.

we can find the reflected geochemical processes.

The decomposition of organic matters from during early diagenetic process in marine sediments is known as a result from drop of potential in the environment and increase of alkalinity (HCO_3^-) in the pore waters (such as Aller, 1983). Therefore, the reaction level of the sedimentary organic matters could be read from the related environmental parameters.

It is shown that the decomposition reaction of organic matters is the strongest in the bay sediments in the researched area, and the next and third are those in continental shelf and hemipelagic area, respectively (Fig. 2). The fact demonstrates what would bring about the organic associated iodine to be the highest ratio is that with higher stability of water mass, plentiful phytoplankton and stable deposition condition, the sediments on the bay bottoms have least ratio of active organic materials being decomposed; however with deep water, complex velocity of flow and almost exhausted active organic materials, the sediments in deep ocean have only undergone weakly diagenetic reaction and most part of iodine still exists in the form associated with refractory organic matters. The deep-sea sediments both in northern and low latitudes also show the same characteristics (Table 1). Besides, the highest and lowest iodine concentrations in pore waters in the sediments of bay and deep

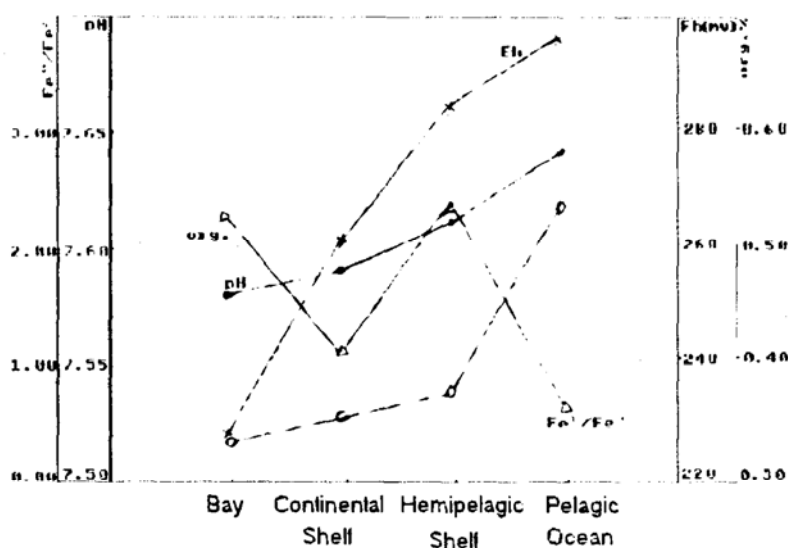


Fig. 2. Environmental characteristics of the sediments.

ocean respectively provide a direct evidence as well (Fig. 4).

In contradiction to organic associated phase, the iodine bound to oxyhydroxides constitutes a prominent ratio either in continental shelf sediments or in hemipelagic ocean sediments. It has an anoxic environment for bay sediments in which oxides are not readily formed. On the contrary, as it was described above, the active organic matters have mostly been exhausted in the deep-sea sediments, so the source of the iodine taking part in the early diagenetic process is limited; in this way, the ratios of iodine associated with oxyhydroxides in both above regions must be less than those in the continental shelf and hemipelagic ocean sediments. Other results also indicate that the ratio of the absorptive iodine which was always neglected by other researchers reaches a noticeable value in continental shelf and hemipelagic sediments. In Fig. 2 we know that these sediments are mainly in weakly oxic states, though the bottom current of Antarctic Ocean is rich in oxygen. Consequently, we can deduce two related mechanisms; Firstly, the accumulation of iodine in surface sediments is not the primary organic matters themselves but

also by the absorption of suspended particles and the following coprecipitation. This is similar to that proposed by Wong (1980), who suggested a cleaning of suspended organic matters for iodine in seawater. Secondly, the iodine released during early diagenesis is redistributed between the oxyhydroxide and absorption phases on redox conditions and the absorptive function of fine materials in the environment. To correlate the analytical result with the granularity of the sediments, we can find a close positive relation between content clay size and absorptive iodine in continental shelf and hemipelagic sediments, which has not

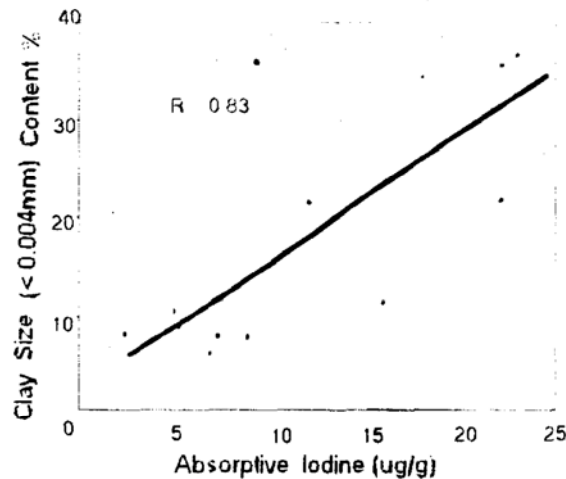


Fig. 3. Relationship between clay content and adsorptive iodine in the sediments.

been found in other regions (Fig. 3).

2. Speciality conversion of iodine

It has been demonstrated by the results that the environmental characteristics of remobilization between iodine and iron is quite similar in the surface sediments, namely, it is remobilized in anoxic environment and converted into solid phases under the oxic conditions (Fig. 4).

Kennedy (1987) reported that sediments have surficial molar I/C_{org} ratios in excess of reported values for planktonic material. On the basis of his study, he set up a cartoon of quasi-closed cycle for iodine at the sediment-water interface, which is almost completely controlled by organic matters. However, our analysis shows that even in the sediments on bay bottom, where exists the strongest early diagenetic reaction of organic matters, significant part of iodine is still controlled by oxyhydroxides or absorbed by fine grained materials; there exists an obvious concentration gradient of iodine in pore water from deep to surface sediments, and in contrary, the higher ratios of absorptive iodine to oxyhydroxide associated iodine are amassed on the surface (Fig. 5). These phenomena suggest that the higher ratio of I/C_{org} is commonly found in surface sediments in joining of the diagenetic reactions other than that of organic matters. On the other hand, the concentration of iodine in pore water does not apparently change with the variation of predominant oxygenants

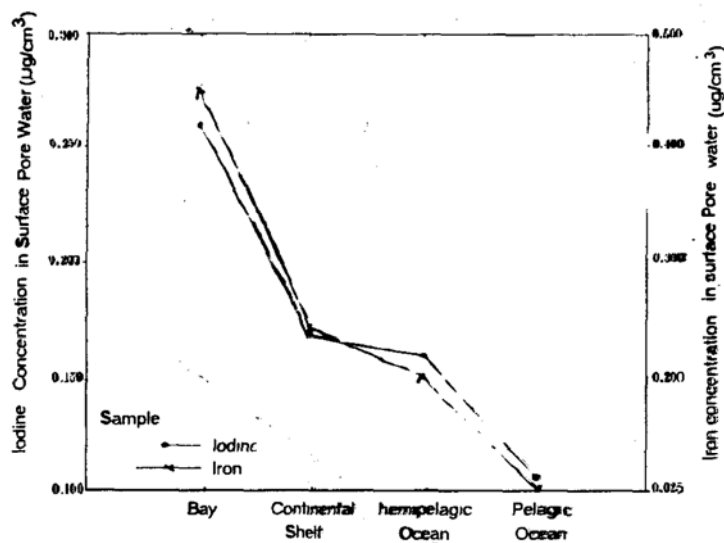


Fig. 4. Environmental similarity between iodine and iron in the process of remobilization.

(Cheng Xianhao *et al.*, 1989) in the decomposition of the organic matters as that of the iron. This indicates that the release of iodine in sediments is not mainly because it acts as an electron acceptor but it entered into pore water with the decomposition of organic matter or the reduction of oxyhydroxides. As it is diffusing, some iodine is absorbed or reassociated by fine materials or oxyhydroxides with the changing environment, which leads to the opposite gradient of iodine in pore water and absorption or oxyhydroxide phases. If this is the case, the fact that I/C_{org} value decreases with increasing depth of sediments can always be observed in marine environment, and should also reflect the release of iodine besides the decomposition of organic matters.

3. A Quasi-quantified Model for Accumulation and Remobilization of Iodine

Supposing the surface sediments are in dynamic balance, which can always be reached, and the total iodine content and the distribution ratios in every associated phase are relatively stable, we discuss the geochemical processes of iodine taking place in the sedimentary columns from the calculated some of specially defined parameters. The columns in the bays were collected and are most active in the early diagenesis. In comparison with other regions of the researched area the processes may be somewhat larger.

4. Diffusing flux

Our previous work (Cheng Xianhao *et al.*, 1992) had estimated the fluxes from surface sediments (0–2 cm) to the overlying waters both in Maxwell (M1) Bay and Admiralty (R2) Bay to be $F_m = -18.3 \mu\text{g}/(\text{cm}^2 \cdot \text{a})$ and $F_r = -26.2 \mu\text{g}/(\text{cm}^2 \cdot \text{a})$.

Our experimental results still indicate that iodine concentration in pore water consistently changes with the depositional rate as reflected by the depth under 2 cm; namely, the concentration gradients in the sedimentary columns appear to be in a linear

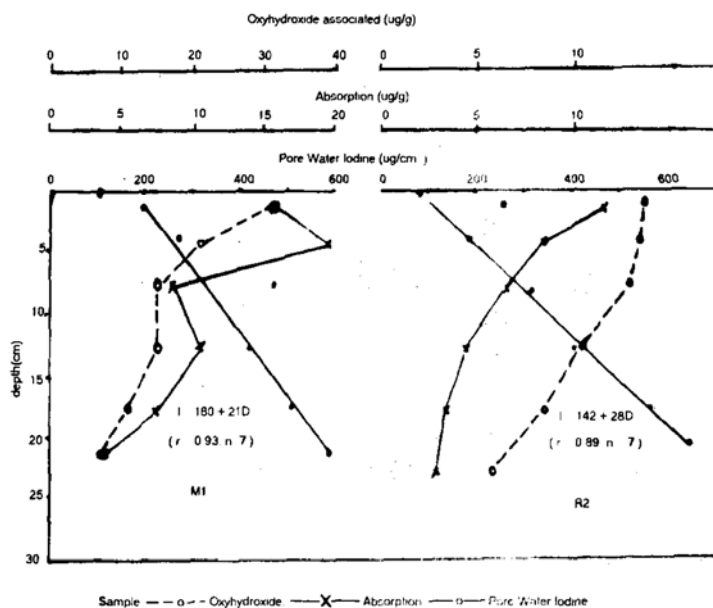


Fig. 5. Conversion of iodine species along the profiles of sediments.

equation. So the Fick's First Law can be nearly expressed to be $F = -\Phi D \frac{dC}{dx} \cdot K$ (D is the diffusing coefficient of iodine in sediments) and the gradients from the depth of 2 cm to overlying water $\Delta C/\Delta X \geq K$ (Fig. 5). Sediment porosity (Φ) is related to the volume ratio of pore water and its solid sediment; on the balance condition, it should decrease with increasing depth. Hence, the diffusing iodine from the depth of sediment at least equals to the escaped flux from the surface sediment to overlying water, though the strong absorption and rapid deposition rate are able to stop some of the diffusing materials.

5. Depositional flux

According to the dynamic balance conditions, we define following equation to calculate the depositional flux of iodine:

$$F_d = C_i(W \cdot Q) - F \quad (\text{positive downward})$$

Where: C_i — Iodine content in shallow surface sediments ($\mu\text{g/g}$); W — Depositional rate (a/cm); Q — Sediment density (g/cm^3).

From the calculation we get

$$F_d(M_1) = 59.8/124 \times 1.39 + 18.3 = 18.6 \mu\text{g}/(\text{cm}^2 \cdot \text{a})$$

$$F_d(R_2) = 45.3/192 \times 1.50 + 26.2 = 26.4 \mu\text{g}/(\text{cm}^2 \cdot \text{a})$$

It has long been puzzled of the extremely low iodine concentration in sedimentary rocks. The calculation results show that depositional and diffusing fluxes in the sediments

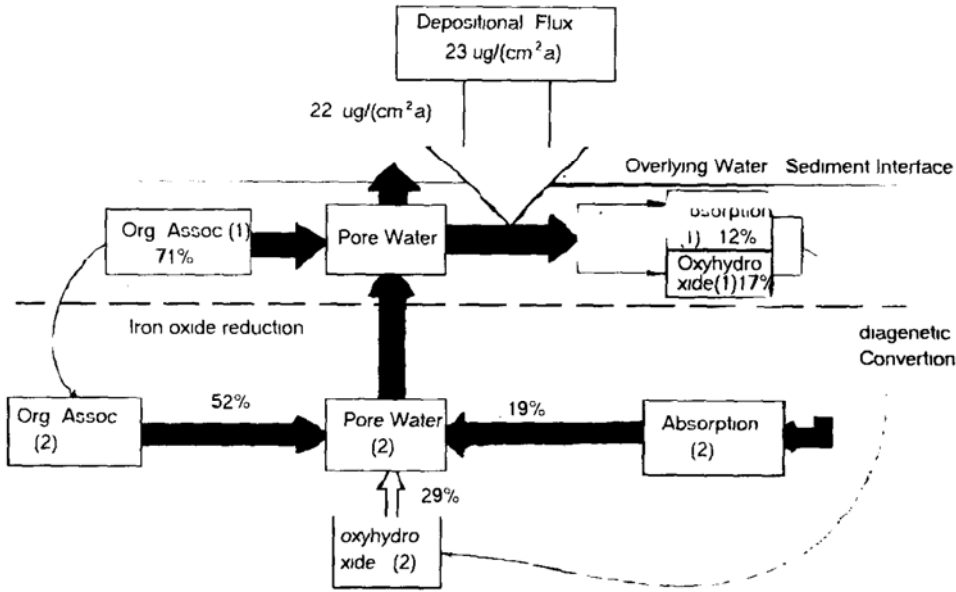


Fig. 6. The quasi-quantitative remobilization and accumulation model of iodine in Western Antarctic Ocean sediments.

are at the same level, and the releasing flux is almost the same as that escaped from sediments. It offers that sedimentary rocks are impossible to accumulate iodine.

6. Diagenetic conversion ratio

The author's researches (Cheng and Wang, 1989; Wang and Cheng, 1990) proved that under the depth of 5 cm in the column, iron oxides act as a dominant oxygenant for the decomposition of organic materials and after that SO_4^{2-} would become the dominant electron acceptor. It means that it could not be formed of the iron and manganese oxides under this level of depth and so did the oxyhydroxide associated iodine. For the same reason, for the formation of anions as HCO^- and HS^- in large quantities under this depth, instead of absorption, the absorbed iodine can not but must be released. The experimental result shown in Fig. 5 directly confirms our deduction. From the above discussed, we define the following equation to calculate the diagenetic conversion amount (DCM) and ratios (DCR) under the depth of 5 cm:

$$DCA = (I_1 - I_2) / (X \cdot W) \text{ and } DCR = DCA_x / DCA_1 \times 100\%$$

Here: I_1 and I_2 are the iodine content associated in certain phase at the top and bottom of the column, respectively; X — the length of the calculated section of the column (cm); W — depositional rate (a/cm); DCA_x and DCA_1 — diagenetic conversion amount of iodine in some phase and the total, respectively.

The calculation results are listed in Table 2.

Table 2. Conversion percentage of sedimentary iodine during early diagenesis

| Station | Layer (cm) | Content ($\mu\text{g/g}$) | | | DCA _i | DCA _a | DCA _o | DCR _a | DCR _o |
|---------|------------|-----------------------------|----------------|----------------|---------------------------------|---------------------------------|---------------------------------|------------------|------------------|
| | | I _i | I _a | I _o | $\mu/(\text{a} \cdot \text{g})$ | $\mu/(\text{a} \cdot \text{g})$ | $\mu/(\text{a} \cdot \text{g})$ | % | % |
| R2 | 5-10 | 48.50 | 6.41 | 12.86 | | | | | |
| | | | | | 4.8×10^{-3} | 9.1×10^{-4} | 1.9×10^{-3} | 19 | 40 |
| | 20-25 | 30.00 | 2.93 | 5.69 | | | | | |
| M1 | 5-10 | 52.97 | 8.70 | 15.44 | | | | | |
| | | | | | 1.1×10^{-2} | 1.9×10^{-3} | 1.9×10^{-3} | 18 | 18 |
| | 20-22 | 29.54 | 4.62 | 11.35 | | | | | |

It is another problem on how to explain the decrease of I/C_{org} value with depth, which has long been disputed. Our calculation results clearly express that in the diagenetic process the release of oxyhydroxide associated iodine are accompanied with adsorptive iodine in the sediments. Accordingly, the decrease of I/C_{org} value with depth should be expected.

To sum up the above described, the authors try to formulate the remobilization and accumulation processes of iodine during early diagenesis in the researched area, (Fig. 6).

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