STUDY OF REMOVAL MECHANISMS OF METAL ELEMENTS FROM SEAWATER USING RADIOACTIVE MULTITRACERS

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Abstract The adsorption of metal elements on hydrated ferric oxide, clay minerals, and marine sediments from artificial seawater is studied using radioactive multitracers produced by RIKEN Ring Cyclotron. The distribution coefficients (K_d) of Co, Ga, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Eu, Gd, Tb, Tm, Yb, Lu, Hf, Re and Hg were determined. The order of K_d for each element is summarized as follows: hydrated ferric oxide > deep-sea sediment > montmorillonite $\geq$ nearshore sediment $\geq$ kaolinite. It is inferred from the observation that hydrated ferric oxide plays an important role in removing metal elements from seawater.

Key words multitracer, adsorption, seawater, removal mechanism, metal elements

Removal mechanisms of elements from the ocean have been discussed by many researchers[1-9]. It was suggested that the partition of elements between particulate solid phases (pelagic clays, manganese and iron oxides, organisms, etc.) and seawater is, for the first approximation, controlled by the affinity of cations and oxyanions for the hydrolyzed particulate surfaces[2,9]. Adsorption of metal elements on hydrated ferric oxide, clay minerals (montmorillonite and kaolinite), and marine sediments (deep-sea and nearshore sediments) from artificial seawater is studied by a radioactive multitracer method. On the basis of the distribution coefficients of metal elements for the particulates, the ultimate removal mechanism of metal elements from seawater is discussed.

MATERIALS AND METHODS

Adsorbents Hydrated ferric oxide was prepared by hydrolyzing ferric ions at pH 7.5. Deep-sea and nearshore sediments were obtained from the Penrhyn Basin (12°26.44'S, 157°57.20'W, depth 5351 meters) and Suruga Bay (34°44.52'N, 169°27.05'E, depth ca. 600 meters), respectively. The adsorbents were stored in artificial seawater as a suspension (2 mg cm⁻³).

Multitracer The multitracers were separated from gold and copper foils irradiated with a ¹⁴N beam of 135 MeV/nucleon accelerated by the RIKEN Ring Cyclotron in a carrier- and salt-free state[10]. The multitracers were stored as 6 mol dm⁻³ HCl solutions.

Adsorption procedure Artificial seawater and a small amount of a multitracer solution were put in a polyethylene bottle. After the pH value was adjusted to 7.5 with a 1 mol dm⁻³ Na₂CO₃ solution, the adsorbent suspension was added to the solution. Its pH value was readjusted to 7.5 when necessary. The suspension was shaken in an 8-shape mode with a shaker at 25°C. After centrifugation, a portion of the supernatant solution was pipetted. The γ -ray spectrum of radioactive nuclides in the solutions were measured with a Ge detector. The distribution coefficients (K_d) for each nuclide were calculated as follows:

$$K_d = (A_{ads}/m) / (A_{soln}/V) = ((A_i - A_f)/A_f)(V/m).$$

A_{ads} and A_{soln} are the radioactivity in the adsorbent and the solution after adsorption equilibrium, respectively. V is volume of the solution (cm³). m is the amount of the adsorbent (g). A_i and A_f are the radioactivity in the solution

before and after adsorption equilibrium, respectively.

RESULTS AND DISCUSSION

The distribution coefficients (K_d) of Co, Ga, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, In, Sn, Eu, Gd, Tb, Tm, Yb, Lu, Hf, Re and Hg at pH 7.5 and at 25°C are given in TABLE 1. The order of K_d for each element is summarized as follows: hydrated ferric oxide > deep-sea sediment > montmorillonite $\geq$ nearshore sediment $\geq$ kaolinite. The deep-sea sediment used in this study is red clay containing about 1.5 % iron oxide and 0.5 % manganese oxide. The nearshore sediment is green clay and contains a much smaller amount of iron and manganese oxides than does the deep-sea sediment. It is evident that the adsorbent rich in the oxides has high distribution coefficients. Consequently, it is inferred that hydrated ferric oxide plays a more important role than does clay minerals (kaolinite and montmorillonite) in removing metal elements from seawater and interstitial water in marine environments.

The logarithmic plots of distribution coefficients (K_d) versus electron binding energy (I_z , the energy necessary to remove one electron from the metal ion in question) for the hydrated ferric oxide and deep-sea sediment are shown in Fig. 1. The distribution coefficients of elements between the particulates and seawater tend to increase with

TABLE 1. Distribution coefficients of metal elements for hydrated ferric oxide, deep-sea sediment, montmorillonite, nearshore sediment and kaolinite ($\text{cm}^3 \text{mg}^{-1}$)*

	H.F.O.**	D. sediment	Montmorillonite	N. sediment	Kaolinite
Co	1.3×10^5	1.5×10^5	8.5×10^3	1.0×10^4	1.3×10^3
Ga	1.4×10^6	2.8×10^5	4.3×10^4	6.4×10^4	3.0×10^4
Rb	2.9×10^2	1.2×10^3	3.3×10^2	1.7×10^2	7.4×10^2
Sr	2.6×10^3	1.9×10^3	1.0×10^3	2.6×10^2	4.8×10^2
Y	2.6×10^5	1.5×10^5	6.4×10^4	1.0×10^4	5.0×10^4
Zr	9.1×10^4	1.1×10^4	8.5×10^3	5.3×10^3	3.5×10^3
Nb	5.3×10^4	5.8×10^3	6.3×10^3	7.0×10^3	2.8×10^3
Mo	6.4×10^3	5.5×10^2	—	—	7.1×10^2
Ru	1.5×10^4	1.3×10^4	5.2×10^3	3.8×10^3	4.0×10^3
Rh	8.3×10^3	2.6×10^3	4.1×10^3	1.3×10^3	1.9×10^3
Pd	1.3×10^4	7.7×10^3	2.9×10^3	9.1×10^3	9.3×10^3
Ag	—	2.5×10^3	4.4×10^3	3.5×10^3	9.1×10^3
In	1.5×10^4	7.2×10^3	2.0×10^4	1.9×10^4	1.9×10^4
Sn	2.2×10^4	7.2×10^3	8.4×10^3	2.7×10^3	6.5×10^3
Eu	2.5×10^5	3.0×10^5	2.4×10^5	3.6×10^5	1.7×10^5
Gd	5.7×10^5	4.9×10^5	1.4×10^5	1.7×10^5	1.4×10^5
Tb	1.0×10^5	1.5×10^4	5.8×10^4	7.2×10^3	2.8×10^4
Tm	3.7×10^5	5.7×10^5	6.6×10^4	1.0×10^5	4.7×10^4
Yb	5.2×10^4	4.3×10^4	3.3×10^4	4.0×10^4	4.4×10^4
Lu	2.6×10^5	2.6×10^5	5.6×10^4	1.0×10^5	5.8×10^4
Hf	1.0×10^5	1.1×10^4	2.1×10^4	4.4×10^3	1.1×10^4
Re	1.3×10^4	—	9.7×10^3	—	1.2×10^3
Hg	1.2×10^5	5.6×10^4	1.1×10^5	3.7×10^4	2.6×10^4

* The concentration of an adsorbent is 0.1 mg cm^{-3} . **Hydrated ferric oxide

Fig. 1. Logarithmic plot of distribution coefficients (K_d) of metal elements for hydrated ferric oxide and deep-sea sediment versus the electron binding energies (I_z).

increasing I_z from free cationic elements to strongly hydrolyzed cations and then decrease to oxyanionic elements. The results obtained agree well with the observed partition of elements between pelagic clays and seawater [2,4]. According to Martin and Whitfield [5], the logarithms of distribution coefficients (K_d) of metal elements for hydrated ferric oxide and kaolinite are plotted against the mean oceanic residence time (τ) of metal elements (Fig. 2). The distribution coefficients are well correlated with the mean oceanic residence time. From the surface complexation model, Balistrieri et al. [11] derived the relationship between the residence time of the sinking particulate matter (τ_p) and the mean oceanic residence time of metal elements (τ) as follows:

$$\tau / \tau_p = ([Me] + \sum_{n,j} [MeL_nj] + [Me]_{ads}) / [Me]_{ads} \quad (1)$$

Eq. (1) is changed to Eqs. (2), (3) and (4).

$$\tau / \tau_p = ([Me] + \sum_{n,j} [MeL_nj]) / [Me]_{ads} + 1 = C / K_d + 1 \quad (2)$$

$$(\tau - \tau_p) / \tau_p = C / K_d \quad (3)$$

$$\log (\tau - \tau_p) = -\log K_d + \log \tau_p + \log C \quad (4)$$

Fig. 2. Logarithmic plot of distribution coefficients (K_d) of metal elements for hydrated ferric oxide and kaolinite versus the mean oceanic residence times (τ) of metal elements.

τ_p (0.365 year)[11] is overwhelmingly smaller than τ , and then Eq. (4) can be simplified to Eq. (5):

$$\log \tau = -\log K_d + \log C' \quad (5)$$

By the method of least squares, the following relationships from plots as in Fig. 2 are obtained:

$$\log \tau = -0.61 \log K_d + 7.4 \quad \text{for hydrated ferric oxide} \quad (6)$$

$$\log \tau = -0.60 \log K_d + 6.6 \quad \text{for kaolinite} \quad (7)$$

$$\log \tau = -0.51 \log K_d + 6.4 \quad \text{for montmorillonite} \quad (8)$$

$$\log \tau = -0.54 \log K_d + 6.7 \quad \text{for deep-sea sediment} \quad (9)$$

$$\log \tau = -0.51 \log K_d + 8.0 \quad \text{for nearshore sediment.} \quad (10)$$

It is concluded that the adsorption of metal elements on hydrated ferric oxide and clay minerals is a very important removal mechanism of metal elements from the ocean.

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