

## Partition of radiotracers between suspended particles and seawater

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**Abstract**—Distinctive uptake mechanisms of different radiotracers by red clays in seawater are elucidated from the magnitude and change of distribution coefficients ( $K_d$ ) for up to 17  $\gamma$ -emitting radiotracers as functions of equilibration time, suspended particle concentration and compositions of solids and seawaters. The adsorption of ionic metals onto colloids and subsequent coagulation of colloids onto larger particles are the dominant removal processes of metals in the aquatic environments of low suspended particle concentration.

### INTRODUCTION

THE PURPOSE of the present study is to use multiple radiotracers (up to 17, having widely different chemical properties) to simultaneously determine the relative affinity of trace elements for different solid phases in seawater. With improvements in gamma-ray detection techniques, one can analyze 10 to 20  $\gamma$ -ray emitting radionuclides in one sample with ease. From the magnitude and change of distribution coefficients ( $K_d$  = activity of radiotracer per unit weight of solid phase/activity of radiotracer per unit volume of solution) for various radiotracers as functions of equilibration time, suspended particle concentrations, composition of solid phase, and the concentrations of dissolved organic carbon and  $H_2S$ , one can gain some useful insights as to the sorption mechanisms and the general geochemical behavior of different trace elements in the ocean. Duursma and his co-workers (DUURSMA and BOSCH, 1970; ASTON and DUURSMA, 1973; DAWSON and DUURSMA, 1974; DUURSMA and EISMA, 1974), as well as Schell and his co-workers (see the summary report by SCHELL and SIBLEY, 1982) have done extensive work on the  $K_d$  determinations for many radiotracers in various natural solution-sediment systems. Their findings will be discussed along with our results whenever relevant. The most comprehensive review of adsorption/desorption studies of radiotracers is given by ONISHI *et al.* (1980).

The often asked question is how well can results from the radiotracer experiments be extrapolated to the natural environments. The following is an attempt to answer the question by showing what parameters may affect the  $K_d$  determinations.

The adsorption of a cation,  $M^z$ , on the surface hydroxyl groups of heterogeneous solid oxides in an electrolyte solution such as seawater can be described by the following generalized reaction:



The rate of change of the concentration of  $M^z$  is:

$$\begin{aligned} \frac{d[M^z]}{dt} &= -k_1[M^z][MeO_{A_x}] + k_{-1}[A]^x[MeOM^{z-x}] \\ &= -k_1Cp[M^z]\{MeO_{A_x}\} \\ &\quad + k_{-1}Cp[A]^x\{MeOM^{z-x}\} \end{aligned} \quad (1b)$$

assuming a first order reaction kinetics and at a steady state or equilibrium:

$$\begin{aligned} K_{ap} &= \frac{k_1}{k_{-1}} = \frac{[A]^x\{MeOM^{z-x}\}}{[M^z]\{MeO_{A_x}\}} \\ &= [A]^xK_d/\{MeO_{A_x}\} \end{aligned} \quad (1c)$$

where

Me = metals (*e.g.* Mn, Fe, Si, Al, C) of solid oxides

[ ] = concentration of species dissolved or suspended in aqueous solution (moles/ml)

{ } = concentration of surface species on solid oxides (moles/g) = [ ]/Cp

Cp = concentration of solid oxides in aqueous solution (g/ml)

A =  $H^+$  or major cations in seawater.

x = the average number of A released per cation adsorbed.

$k_1$  and  $k_{-1}$  = forward and backward reaction rate constants respectively.

$K_{ap}$  = apparent equilibrium constant

$K_d$  = distribution coefficient at steady state =  $\{MeOM^{z-x}\}/[M^z]$  (ml/g)

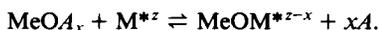
One should keep in mind that  $K_d$  is not an equilibrium constant ( $K_{ap}$ ) and can vary as pH or solution composition ([A]) or physical and chemical properties of suspended particles ( $\{MeO_{A_x}\}$ ) changes.

If a minute amount of radioisotope  $M^{*z}$  of cation  $M^z$  is added to a solution where the concentration of cation  $M^z$  is already in equilibrium with the containing solid oxides,  $M^{*z}$  would exchange with  $M^z$  according to the following reaction:



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By adding equations (1a) and (2a), one obtains:



Therefore,

$$\begin{aligned} K_{\text{ad}}^* &= \frac{[A]^x \{\text{MeOM}^{*z-x}\}}{[M^{*z}] \{\text{MeO}A_x\}} \\ &= \frac{[A]^x K_{\text{d}}^*}{\{\text{MeO}A_x\}} \end{aligned} \quad (2c)$$

where

$$K_{\text{d}}^* = \{\text{MeOM}^{*z-x}\} / [M^{*z}]$$

and

$$[M^{*z}] \ll [M^z].$$

$K_{\text{d}}^*$  and  $K_{\text{ad}}^*$  approach  $K_{\text{d}}$  and  $K_{\text{ad}}$  respectively because  $M^{*z}$  and  $M^z$  in the solution and on the surface sorption sites are assumed to be homogenized relatively fast, *i.e.*,

$$\frac{[M^{*z}]}{[M^z]} = \frac{\{\text{MeOM}^{*z-x}\}}{\{\text{MeOM}^{z-x}\}}.$$

Therefore, in principle, one can determine  $K_{\text{d}}$ 's for various elements in natural systems by using a set of carrier-free (or near carrier-free) radioisotopes. In reality things are not always so simple. For example, the radioisotopes and their natural stable counterparts may not be exchanged rapidly especially with those not in the surface sorption sites. Sorption of certain cations may not follow the reaction in equation (1a), but may involve oxidation and precipitation, ion exchange inside crystal lattices through diffusion, and adsorption of radiotracers on colloids, then coagulation of colloids on larger particles etc. (NYFFELER *et al.*, 1984). Since  $K_{\text{d}}$ 's are such complicated functions of many variables, we are not interested in their absolute values per se, but rather in their relative magnitude and changes under similar experimental conditions. As will be shown in the result and discussion section, the experimental systems for some radiotracers never reach a steady state condition. In this case, the  $K_{\text{d}}$ 's represent only the values at the end of the experiments (usually 3 weeks of equilibration time). For ease of presentation,  $K_{\text{d}}$  will hereafter represent the distribution coefficient for both stable and radioactive tracers.

## EXPERIMENTAL METHODS

An adaptation of the constant suspension method of DUURSMA and BOSCH (1970) was used to determine the partition or distribution coefficients for various radiotracers. In adsorption experiments, known amounts of fine solid particles and seawater were put into one liter Nalgene plastic bottles for more than one week. They were then mixed constantly but gently by a wrist action shaker (SCHELL and SIBLEY, 1981) to keep fine solid particles in suspension in a dark cold room ( $\approx 2 \pm 1^\circ\text{C}$ ) one day before spiking. Known amounts of radiotracers were then added to the solution and shaken for the duration of the experiments. At predetermined time intervals (usually 1 hour, 1 day and once a week for about 3 weeks), 100 ml of solution were removed and filtered through two 0.4  $\mu\text{m}$  nucleopore filters. The activities of the various radiotracers in filter, filter blank (the second filter in-line behind the top filter) and filtrate were  $\gamma$ -counted by a Ge(Li) detector

with a multichannel analyzer (4096 channels).  $K_{\text{d}}$ 's were calculated using the following relationship:

$$K_{\text{d}} = \frac{A_{\text{filter}} - A_{\text{filterblank}}}{A_{\text{water}}} \cdot \frac{10^5}{m \cdot f} \quad (\text{ml/g})$$

where:

$A$  = activity of a radiotracer (cpm/100 ml water or cpm/filter)

$m$  = dry weight of solid particles on the filter (mg)

$f$  = factor to convert filter geometry to 100 ml plastic bottle geometry.

For our experiments, the filter blank corrections turned out to be negligible. In desorption experiments, the fine solid particles which had adsorbed radiotracers in separate adsorption experiments were put into spike-free seawater and allowed to equilibrate. Experimental procedures which followed were the same as in the adsorption experiments. The pH of the seawater media was kept constant ( $\approx 7.8 \pm 0.1$ ) throughout the experiments.

It is common practice to express the adsorption results of metals in terms of the "% adsorbed" by particles. However, at high (or low) suspended particle concentration, the "% adsorbed" approaches 100% (or zero %) and the resolution is lost. On the other hand, the  $K_{\text{d}}$  is a much more sensitive parameter. For example, when the "% adsorbed" shifts from 99% to 99.9% (only a factor of 1.01), the  $K_{\text{d}}$  increases by a factor of 10. Furthermore, the radiotracer technique here allows us to detect easily minute activities both in suspended particles and solution.

The radiotracers used in our experiments include:  $^{195}\text{Au}$  ( $t_{1/2} = 183$  d),  $^{133}\text{Ba}$  (10.8 y),  $^7\text{Be}$  (53.3 d)  $^{207}\text{Bi}$  (38 y),  $^{141}\text{Ce}$  (32.5 d),  $^{139}\text{Ce}$  (138 d),  $^{109}\text{Cd}$  (1.24 y),  $^{60}\text{Co}$  (5.27 y),  $^{134}\text{Cs}$  (2.06 y),  $^{56}\text{Fe}$  (45 d),  $^{153}\text{Gd}$  (242 d),  $^{203}\text{Hg}$  (46.6 d),  $^{192}\text{Ir}$  (74 d),  $^{54}\text{Mn}$  (313 d),  $^{125}\text{Sb}$  (2.7 y),  $^{113}\text{Sn}$  (115 d) and  $^{65}\text{Zn}$  (244 d). These were in HCl solution, and hence cationic, except Au which was in a KCN solution. Our spikes did not greatly change the natural concentration of various trace elements in seawater as most radiotracers were carrier free, and the spikes added for each experiment were very small ( $\approx 100$  to 500 cpm/100 ml for each radiotracer).

The seawaters used were the New York coastal water, Pacific bottom water (MANOP site M) and Cariaco Trench bottom water (containing  $\approx 50 \mu\text{M}$   $\text{H}_2\text{S}$ ). The sediments were red clays from MANOP site R, fine black sediments from the Cariaco Trench and dry Montmorillonite #27 supplied by Ward's Natural Science Establishment, Inc. Goethite and  $\delta\text{MnO}_2$  were prepared in our laboratory according to ATKINSON *et al.* (1967) and MURRAY (1974) respectively. Ocean sediments were always kept cold and wet. Seawaters were also kept in the same cold darkroom.

## RESULTS AND DISCUSSIONS

### Red clay—New York coastal water

The distribution coefficients ( $K_{\text{d}}$ 's) for various radiotracers as functions of equilibration times and suspended particle concentrations ( $\approx 10, 50, 100, 400, 800$  and 1700 mg per liter of seawater) were determined from adsorption and desorption experiments. Figure 1 shows  $K_{\text{d}}$ 's as a function of equilibration time at two different suspended particle concentrations. Missing data for some radiotracers in Fig. 1 as well as other figures are either caused by the activities below the detection limit in solution (*e.g.* Sn, Fe, Bi) and filter (*e.g.* Ba, Ir) or simply the radiotracers were not available at the time of the experiments (mostly short half life radiotracer, *e.g.*  $^7\text{Be}$ ).

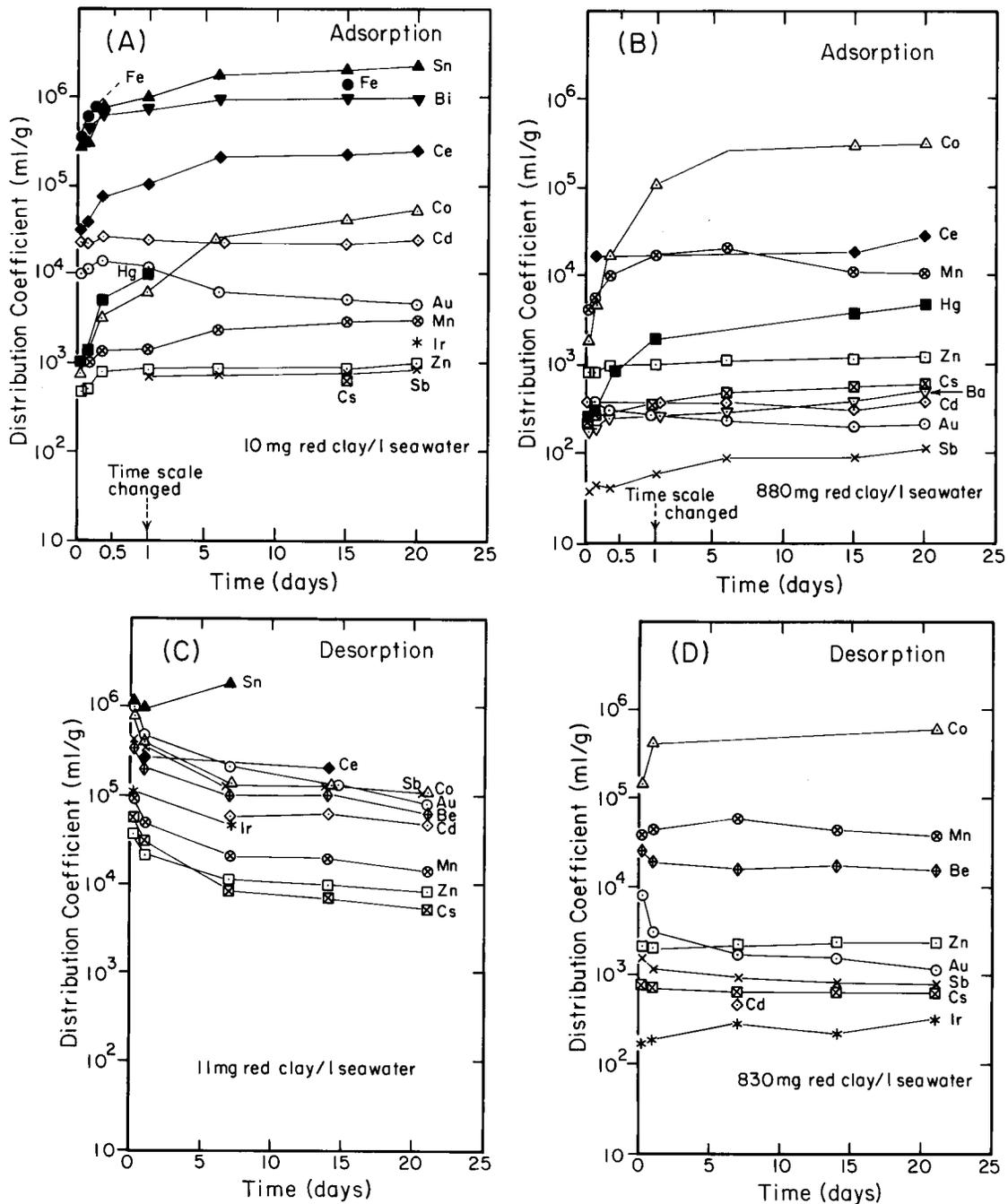


FIG. 1. Adsorption and desorption  $K_d$ 's for various radiotracers in the New York coastal water—red clay systems as a function of equilibration time at two different suspended particle concentrations.

In the adsorption experiments,  $K_d$ 's for most radiotracers increase with time and reach constant values within one week (Fig. 1A and 1B). Differences between  $K_d$ 's at one hour and one week for Cd, Zn, Cs, Sb, Ba and Au were small, indicating fast equilibration. However, the differences for Fe, Bi, Sn, Ce, Mn, Co and Hg were large and the  $K_d$ 's continued to increase slightly with time even after one week. NYFFELER *et al.* (1984) also observed the similar phenomena for these isotopes.

The slow increase of  $K_d$ 's with time may indicate

the processes of oxidation (Mn and Co), aggregation of "radiocolloids" onto red clay particles (Fe, Bi, Sn, Ce, Hg) and exchange of adsorbed radiotracers with metals inside crystal lattice through diffusion (NYFFELER *et al.*, 1984). These hypotheses will be discussed later.

The  $K_d$  for Au always reached a maximum (Fig. 1A and 1B), then decreased gradually with time to a constant value, probably indicating dissolution of fine Au-containing particles in the spike solution of Au. A

blank experiment using filtered coastal seawater, indeed, showed that a significant fraction of the Au spike was in particulate form ( $\approx 30\%$  at the beginning) and the particulate Au fraction decreased with time implying dissolution (down to 9% after 3 weeks). Other tracers did not show this behavior. Therefore, one should be cautious in interpreting Au results.

In desorption experiments with low suspended particle concentration (Fig. 1C), the  $K_d$ 's were all very high after one hour of equilibration time, then decrease drastically in the first week (except Sn and Ce) and continue to decrease slightly with time. When the suspended particle concentrations were high,  $K_d$ 's reached a steady state relatively fast (Fig. 1D). As predicted from Eqn. (1b), the higher the suspended particle concentration ( $C_p$ ), the faster the overall reaction rates for both adsorption and desorption processes are.

The  $K_d$ 's for various radiotracers as a function of suspended particle concentrations ( $C_p$ ), after 3 weeks of equilibration time, are summarized in Fig. 2A (adsorption) and Fig. 2B (desorption). The adsorption and desorption  $K_d$ 's for Sb, Ir, Au, Cd, Hg, Ce, Sn and probably Fe and Bi decrease initially and reached constant values when  $C_p$  continued to increase. The adsorption  $K_d$ 's for these tracers are, in general, always lower than desorption  $K_d$ 's at the same  $C_p$  value, indicating irreversibility of adsorption-desorption processes (exceptions are  $K_d$ 's for Sn and Ce which show no difference) as already shown by many workers (DUURSMA and BOSCH, 1970; SCHELL and SIBLEY, 1982; and references therein).

Higher adsorption  $K_d$ 's at lower suspended particle concentrations were also observed for  $^{85}\text{Sr}$ ,  $^{106}\text{Ru}$ ,  $^{237}\text{Pu}$ ,  $^{241}\text{Am}$  and  $^{244}\text{Cm}$  in Hudson River estuary sediment-

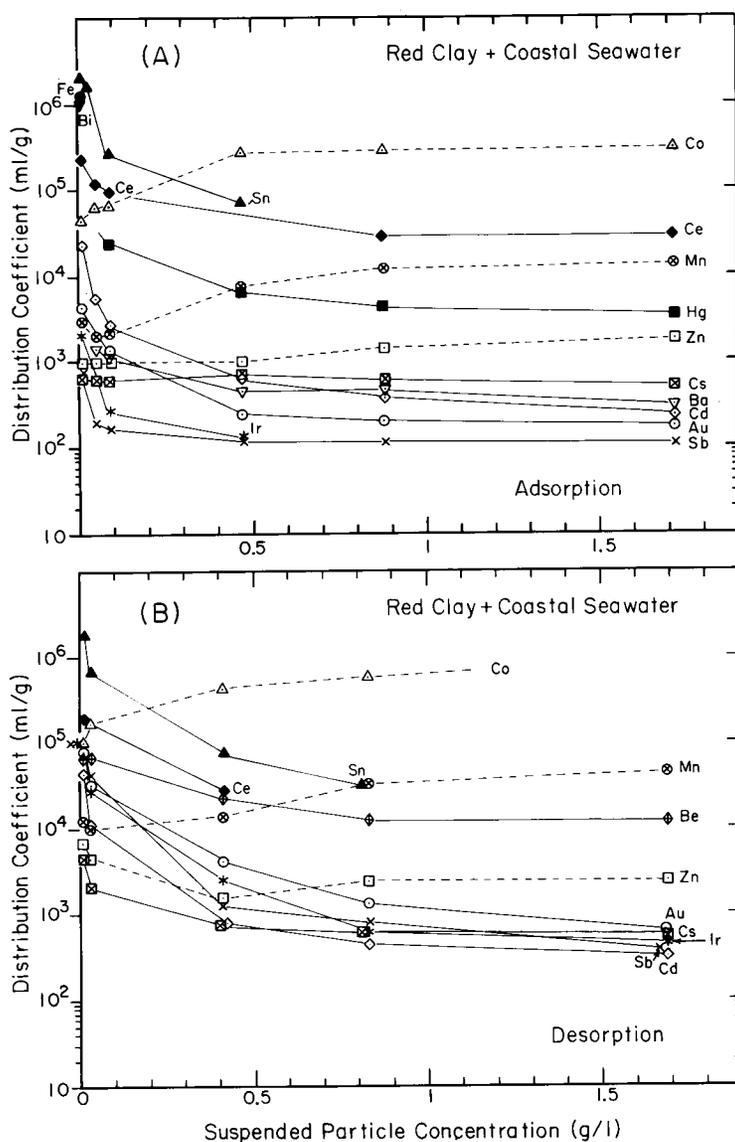


FIG. 2. a) Adsorption and b) desorption  $K_d$ 's after 3 weeks of equilibration as a function of suspended concentrations in the New York coastal water—red clay system.

seawater systems (SANCHEZ *et al.*, 1982) and for  $^{137}\text{Cs}$ ,  $^{106}\text{Ru}$ ,  $^{65}\text{Zn}$  and  $^{60}\text{Co}$  in various marine sediment-seawater systems, with some exceptions for  $^{65}\text{Zn}$  and  $^{60}\text{Co}$  (ASTON and DUURSMA, 1973). ASTON and DUURSMA (1973) explained the enhancement of adsorption  $K_d$ 's at lower suspended particle concentration ( $C_p$ ) by the nucleation or particle formation of spiked radiotracers in addition to their regular surface adsorption onto larger filterable particles (through the formation of chemical bonds between partially hydrolyzed cations and the oxygen of hydrous oxide surface of suspended particles, equation 1a). At higher  $C_p$ , the finite nucleation processes of radiotracers may be masked by the dominant surface adsorption processes.

Though ASTON and DUURSMA (1973) did not explain how the minute quantities of carrier free radiotracers nucleate into particles, there are two possible hypotheses (see the summary by KEPACK, 1977): 1) the radiotracers with high hydrolysis constants (*e.g.* Fe, Sn, Bi, Hg and Ce, BAES and MESMER, 1981) can form "true colloids" through hydrolysis and coagulate into larger filterable hydroxide particles if the radionuclide concentrations are high enough to surpass the solubility products of their respective hydroxides, and 2) ionic radiotracers first adsorb onto pre-existing colloids according to Eqn. (1a) to form so-called "adsorption colloids", then the "adsorption colloids" coagulate onto larger particles. In our experimental setup, the second explanation is a plausible one. In any case, we will use a general term "colloid sorption" to represent both. The "colloid sorption" hypothesis may also explain why the desorption  $K_d$ 's are always higher than the adsorption  $K_d$ 's. For example, the coagulation of colloids (including both true and adsorption colloids) may cause the adsorbed radiotracers to be buried inside the coagulated particles and, hence, difficult to desorb.

Another possible partial explanation for the high  $K_d$  at low  $C_p$  is that the higher the suspended particle concentration, the higher the degree of particle aggregation, therefore, effective surface area per gram for sorption is reduced (*i.e.* the average particle size is larger at high  $C_p$ ) and  $K_d$  lowered. Certainly further study is needed.

In the open oceans, the concentrations of suspended particles are much lower than that used in our experiments, therefore the formation of colloids of metal ions and their subsequent coagulation onto larger particles should be the dominant removal processes of metals from the water column. TSUNOGAI and MINAGAWA (1978) invoked a similar mechanism in their settling model for the removal of elements in the ocean. The  $K_d$ 's for many metals should be very high. On the other hand, the water-sediment interface or pore water systems can be considered as high  $C_p$  environments, where the direct adsorption of ionic radiotracers or trace metals onto sediment surfaces should be the dominant process, and the adsorption and desorption  $K_d$ 's should be relatively constant.

Both the adsorption and desorption  $K_d$ 's for Co and Mn increased with  $C_p$  and reached constant values.

ASTON and DUURSMA (1973) also observed a similar behavior for Co in some of their adsorption experiments. The uptake of Co and Mn by red clay particles is probably in part controlled by the oxidation of  $\text{Mn}^{+2}$  and  $\text{Co}^{+2}$  and the formation of Co and Mn oxide coatings over the particles. Oxidation of  $\text{Co}^{+2}$  and  $\text{Mn}^{+2}$  is enhanced by autocatalytic effects of pre-existing Co and Mn oxide coatings on the red clay particles (STUMM and MORGAN, 1981). Therefore, the higher the  $C_p$ , the higher the autocatalysis sites per unit volume of the system, hence the higher  $K_d$ 's for Mn and Co. The adsorption  $K_d$  for Zn increased slightly with  $C_p$  but its desorption  $K_d$  decreased with  $C_p$  initially then again increased. There is no ready explanation for this peculiar behavior of Zn.

The adsorption  $K_d$  for Cs was nearly constant with  $C_p$ , while the desorption  $K_d$  for Cs decreased with  $C_p$  and approached a constant value identical to the adsorption  $K_d$ . As suggested by LI (1981), the uptake of Cs by particles is not due to the formation of chemical bonds between  $\text{Cs}^+$  and the oxygen of hydrous oxide surfaces but is due to the electrostatic attraction between  $\text{Cs}^+$  and negatively charged particle surfaces and/or cation exchange of  $\text{Cs}^+$  with  $\text{K}^+$  in channel or interlayer positions of clay mineral particles (EVANS *et al.*, 1983; NYFFELER *et al.*, 1984). This may explain why the  $K_d$  for Cs is almost independent of pH in the range between 4 to 10 (SIBLEY *et al.*, 1982). SANTSCHI *et al.*, (1983) found that large fractions of adsorbed Cs and Sb radiotracers in the deep Pacific sediments ( $70 \pm 10\%$  and  $30 \pm 20\%$  respectively) could not be leached out with 25% acetic acid with or without 1 M  $\text{NH}_2\text{OH}$  solution. At low  $C_p$ , particles need to desorb a lot of tightly held Cs and Sb to reach sorption equilibrium between particles and solution but in reality they cannot. This may explain why the desorption  $K_d$ 's are much higher than the adsorption  $K_d$ 's for Cs and Sb at low  $C_p$  (Fig. 2B). However, how Sb was locked into less accessible positions is not clear yet.

#### *Red clay—deep Pacific water*

Adsorption  $K_d$  results for the red clay—deep Pacific water experiments are summarized in Fig. 3. Because the dissolved organic carbon concentration is about 2.3 mg/l in the New York coastal water and only about 0.4 mg/l in our deep Pacific water (analyzed by S. Warren at Lamont), this experiment allowed us to study the effect of dissolved organic matter concentration on  $K_d$ 's in addition to the effect of slight salinity change ( $\text{NY} \approx 29\text{‰}$ ,  $\text{DP} \approx 35\text{‰}$ ).

There are no significant differences between Fig. 3 and Fig. 2A except for Hg and Au. An additional rare earth tracer Gd behaved almost like Ce. The adsorption  $K_d$  for Be was almost constant with  $C_p$  and slightly lower than its desorption  $K_d$  at a higher  $C_p$  (Fig. 2B).

The  $K_d$  for Hg in the deep Pacific water system was about two orders of magnitude lower than that in the coastal water system (compare Figs. 2A and 3). The same large  $K_d$  difference for Hg between the Narra-

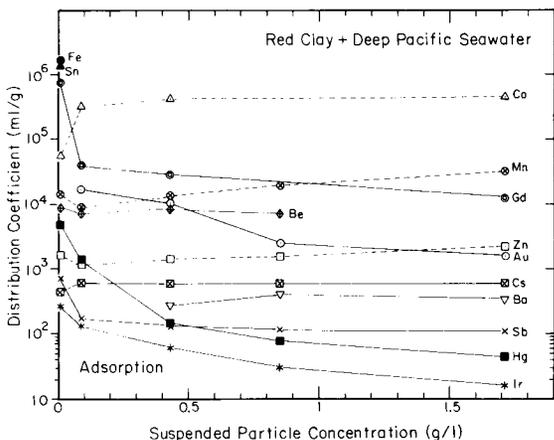


FIG. 3. Adsorption  $K_d$ 's after 3 weeks of equilibration as a function of suspended particle concentrations in the deep Pacific water—red clay system.

gansett Bay system (NYFFELER *et al.*, 1984) and the MANOP benthic chamber system deployed at the Eastern Pacific (SANTSCHI *et al.*, 1983) was observed. In contrast, the  $K_d$  for Au in the deep Pacific water system was one order of magnitude higher than that in the coastal water system.

In order to verify whether dissolved organic matter (not salinity) really affects the adsorption of Hg and Au by red clays in different ways, the dissolved organic carbon concentration of New York coastal water was reduced to 0.3 mg/l by UV irradiation over 24 hours. The adsorption  $K_d$  for Hg decreased two orders of magnitude and that for Au increased about one order of magnitude in a montmorillonite-U.V. irradiated coastal water system as compared to that in the same system without UV treatment (Fig. 5C). For other radiotracers, there was again no discernible organic matter effect on  $K_d$ 's. DAVIS and LECKIE (1978) showed that the uptake of metals by hydrous oxides were enhanced by the presence of certain adsorbed organic ligands at the surface. In other cases, organic ligands form nonadsorbing complexes in solution and compete with hydrous oxide surface for coordination of metal ions. Hg is probably an example of the first case and Au of the second case. Apparently the dissolved organic matter concentration in the Pacific bottom water and the New York coastal water is too low to greatly effect the degree of adsorption of other radiotracers by red clays.

Figure 4 shows a logarithmic plot of  $K_d$  values for various radiotracers in red clay-seawater systems against the natural partition coefficients in the ocean (*i.e.* elemental concentration ratios of oceanic pelagic clays,  $C_{op}$  and average seawater,  $C_{sw}$ , as summarized by LI, 1982, however,  $C_{op}/C_{sw}$  value for Sn should be replaced by 6.5 due to new  $C_{sw}$  datum for Sn by BYRD and ANDREA, 1982). The  $K_d$  values for most of the radiotracers are obtained from Fig. 2A and Fig. 3 for  $C_p$  between 0.4 g/l and 1.7 g/l (arrows in Fig. 4 indicate the range).  $K_d$  values for Hg and Au are from Fig. 3

only.  $K_d$  values for Na and Ca are from LI and GREGORY (1974). Though Sn and Sb were cationic in the spike solutions, they were hydrolyzed to become oxyanions in the  $O_2$ -containing sea water (STUMM and MORGAN, 1981).

Even though  $C_{op}/C_{sw}$  values are about two orders of magnitude larger than  $K_d$  values, the two quantities are, in general, linearly correlated except for Au (Fig. 4). The linearity suggests that the uptake mechanisms of these elements by red clays in the short term laboratory experiments may be essentially similar to the processes occurring in the ocean. In the ocean, however, there is ample time for red clays to be continuously coated by layers of Fe and Mn oxides which provide additional adsorption sites for other trace elements. Also in the ocean, the "colloid sorption" may be the dominant process.

The higher  $C_{op}/C_{sw}$  than  $K_d$  for Be, Na and Cs (probably also K, Rb, Al, Si, Ti, Cr, Ta, Sc, Ga, Zr,  $^{232}\text{Th}$ ) may be partially explained by their high detrital components in red clays (LI, 1982b). The offset of the Au point from the linear correlation line in Fig. 4, again strongly suggests an artifact caused by the existence of Au containing particles in the laboratory experiments.

#### Pure solid phases—New York coastal water

The purpose of this adsorption experiment was to study the relative affinity of radiotracers to three important natural solid phases in the ocean.  $K_d$ 's obtained with  $\alpha\text{FeOOH}$ ,  $\delta\text{MnO}_2$  and montmorillonite are summarized in Fig. 5A to 5C.

The  $K_d$ 's for Fe, Sn, Bi, Ce and Hg are all very high

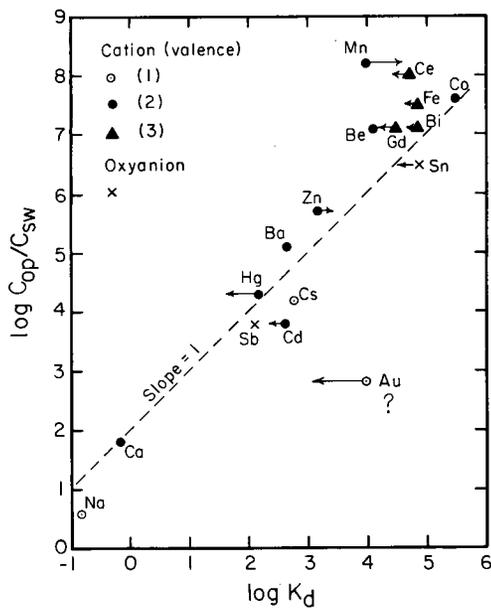


FIG. 4. Adsorption  $K_d$ 's for various radiotracers at suspended red clay concentrations between 0.4 to 1.7 g/l plotted against their natural partition coefficient in the ocean ( $C_{op}/C_{sw}$ ).

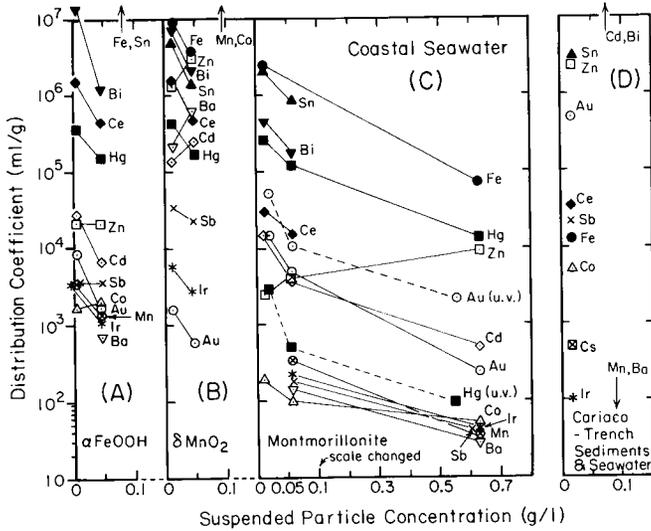


FIG. 5. Adsorption  $K_d$ 's after 3 weeks of equilibration as a function of suspended particle concentrations in a) the New York coastal water— $\alpha\text{FeOOH}$ , b) N.Y. coastal water— $\delta\text{MnO}_2$ , c) N.Y. coastal water—montmorillonite, and d) Cariaco Trench water—sediments systems.

in both the  $\alpha\text{FeOOH}$  and  $\delta\text{MnO}_2$  systems and only slightly lower in the montmorillonite system, even though the surface properties (*e.g.* total exchange capacity, specific surface area and the pH of zero point of change etc.) of these three phases are widely different (LI, 1981). This fact again strongly suggests the formation of “adsorption colloids” and/or “true colloids” of these radiotracers before adherence to larger particles, since the “colloid sorption” processes do not depend so much on the surface properties of the solid phases. The extremely high  $K_d$ 's ( $>10^7$ ) for Mn and Co in the  $\delta\text{MnO}_2$  system again indicate the importance of oxidation and precipitation processes of these radiotracers.

The  $K_d$ 's for Mn, Co, Zn, Ba, Cd, Sb and Ir in the  $\delta\text{MnO}_2$  system are the highest among the three systems (Fig. 5A to 5C). TAKEMATSU (1979) also showed this to be the case for Cu and Ni in addition to Mn (II), Co and Zn. This is consistent with the fact that these elements are enriched in Mn oxide phases of Mn nodules and oceanic pelagic clays (LI, 1982b). The increase of  $K_d$ 's for Zn, Ba and Cd with  $C_p$  along with their high values (Fig. 5B) indicates that the uptake of these radiotracers may be enhanced by cation exchange with structural Mn of  $\delta\text{MnO}_2$  in addition to the regular surface adsorption. LOGANATHAN and BURAU (1973) also suggested the same exchange mechanisms to explain the release of Mn during Co and Zn adsorption on  $\delta\text{MnO}_2$ .

The  $K_d$ 's for Mn, Co, Zn, Ba, Cd, Sb and Ir in the montmorillonite system (Fig. 5C) are the lowest among the three systems. An interesting observation is that the  $K_d$ 's for Mn and Co decreased with  $C_p$ , instead of increasing as was the case for the red clay systems (Figs. 2A, 2B and 3). Since montmorillonite has no Mn and Co oxide coatings, it cannot oxidize  $\text{Mn}^{+2}$  and  $\text{Co}^{+2}$  through autocatalysis mechanisms as was

hypothesized for red clays. One mystery is that the  $K_d$  for Zn still increased with  $C_p$  as it did in the red clay systems (Figs. 2A and 3).

The  $K_d$  for Au may not be very reliable, but its highest value is in the montmorillonite system, again consistent with the observation that Au mainly associates with aluminosilicate phases of pelagic clays and Mn nodules (LI, 1982b).

#### Cariaco Trench sediments and seawater

In an adsorption experiment using  $\text{H}_2\text{S}$  containing ( $\approx 50 \mu\text{M}$ ) Cariaco Trench water and sediments, the  $K_d$ 's for Bi, Cd, Zn, Sn, Au and Sb (all B-type metal cations, STUMM and MORGAN, 1981) were much higher than those in  $\text{O}_2$ -containing systems while  $K_d$ 's for Mn, Co, Ba and Fe were lower (compare Fig. 5D against Fig. 2A and Fig. 3). Apparently, Bi, Cd, Zn, Sn, Au and Sb form sulfide particles in the Cariaco Trench system, while Fe, Mn and Co stay as +2 cations in this relatively low sulfide water. Sn and Sb were cationic in the spike solutions and became mostly insoluble sulfides in  $\text{H}_2\text{S}$  containing sea water before being hydrolyzed to become oxyanions. The low  $K_d$  for Ba is caused by the lack of Mn oxide coatings on the Cariaco Trench sediments to adsorb extra Ba. As shown in the last section, Ba has a high affinity for  $\delta\text{MnO}_2$ . Our results are consistent with the field observation in Saanich Inlet (JACOBS and EMERSON, 1982) and anoxic Baltic water (KREMLING, 1983), and with thermodynamic predictions (EMERSON *et al.*, 1983). Cs and Ir are the only two tracers which did not change their  $K_d$  values between oxidizing and reducing environments.

The abnormally high Ir content at the Cretaceous-Tertiary boundary has been explained by either episodic extraterrestrial inputs (ALVAREZ *et al.*, 1980) or

by some unknown geochemical enrichment processes under reducing conditions. Our observed insensitivity of  $K_d$  for Ir with regard to redox potential change does not favor the latter explanation. However, further testing is necessary to determine whether the  $K_d$  for Ir would increase drastically relative to  $K_d$ 's for Fe and Mn under a much higher  $H_2S$  concentration in seawater. From the  $^{187}Os/^{186}Os$  ratio data in the sediments from the Cretaceous-Tertiary boundary, LUCK and TUREKIAN (1983) strongly support the extraterrestrial origin.

### CONCLUSIONS

- 1) The change of  $K_d$ 's for various radiotracers ( $^{195}Au$ ,  $^{133}Ba$ ,  $^7Be$ ,  $^{207}Bi$ ,  $^{141}Ce$ ,  $^{139}Ce$ ,  $^{109}Cd$ ,  $^{60}Co$ ,  $^{134}Cs$ ,  $^{56}Fe$ ,  $^{153}Gd$ ,  $^{203}Hg$ ,  $^{192}Ir$ ,  $^{54}Mn$ ,  $^{125}Sb$ ,  $^{113}Sn$ , and  $^{65}Zn$ ) as functions of equilibration time, suspended particle concentration, compositions of solid and liquid phases has provided important insight into the uptake mechanisms of radiotracers by marine sediments.
- 2) The  $K_d$ 's for most radiotracers (except Mn, Co, Zn and Cs) decrease with increasing  $C_p$  and reach constant values at high  $C_p$ . At low  $C_p$ , the formation of colloids of radiotracers ("true and adsorption colloids") and their subsequent coagulation onto larger filterable particles are the dominant removal processes of metals from seawater. At high  $C_p$ , a large fraction of ionic radiotracers is directly adsorbed by larger particles through the formation of chemical bonds between hydrolyzed radiotracers and the oxygen of hydrous oxide surfaces.
- 3) The uptake of Mn and Co by red clays is in part controlled by oxidation of  $Mn^{+2}$  and  $Co^{+2}$  through autocatalysis effect of the pre-existing Mn and Co oxide coatings on red clays.
- 4) The dissolved organic matter concentration in Pacific bottom water and New York coastal water is too low to greatly affect the degree of adsorption of many trace elements by red clays. One outstanding exception is Hg. The dissolved organic matter greatly enhance the adsorption of Hg by red clays. The effect of dissolved organic matter on Au adsorption needs further confirmation.
- 5)  $K_d$ 's for radiotracers determined in short term laboratory experiments using radiotracers are about two orders of magnitude smaller than their respective natural partition coefficients in the ocean ( $C_{op}/C_{sw}$ ). However, the values of  $K_d$  and  $C_{op}/C_{sw}$  for most elements studied are linearly correlated, indicating similar partitioning processes.
- 6) A high affinity to any solid particles (e.g.,  $\alpha$ - $FeOOH$ ,  $\delta MnO_2$ , montmorillonite and red clays) by radiotracers with large hydrolysis constants (e.g., Fe, Sn, Bi, Hg and Ce) again indicates the formation of colloids of these tracers (as "adsorption colloids" and/or "true colloids") before they adhere to any larger particles.
- 7) The adsorption of Zn, Cd and Ba by red clays can be greatly enhanced by cation exchange with structural Mn of  $MnO_2$  coatings on red clays.

8) Significant fractions of adsorbed Cs and Sb in red clays are positioned in less accessible interlayers of clay minerals.

9) In the  $H_2S$  containing Cariaco Trench system, B-type metal cations (e.g., Bi, Cd, Zn, Sn, Au and Sb) form sulfide particles, while transition metal cations like  $Fe^{+2}$ ,  $Mn^{+2}$  and  $Co^{+2}$  stay very soluble.

10) There is no change in  $K_d$  for Ir from the oxidizing environment of the open ocean to the reducing environment of Cariaco Trench. This fact favors the extraterrestrial origin of the high Ir content at the Cretaceous-Tertiary boundary.

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