

Partition of radiotracers between suspended particles and seawater

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(Received November 18, 1983; accepted in revised form July 9, 1984)

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 γ -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 γ -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:

$$\begin{aligned} \frac{d[M^z]}{dt} &= -k_1[M^z][MeO_A_x] + k_{-1}[A]^x[MeOM^{z-x}] \\ &= -k_1C_p[M^z]\{MeO_A_x\} \\ &\quad + k_{-1}C_p[A]^x\{MeOM^{z-x}\} \quad (1b) \end{aligned}$$

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

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

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) = []/C_p

C_p = 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.

k₁ 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)

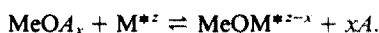
One should keep in mind that K_d is not an equilibrium constant (K_{ap}) and can vary as pH or solution composition ([A]) or physical and chemical properties of suspended particles ({MeO_Ax}) changes.

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,

$$\begin{aligned} K_{\text{sp}}^* &= \frac{[A]^x \{\text{MeOM}^{*z-x}\}}{[\text{M}^{*z}]\{\text{MeOA}_x\}} \\ &= \frac{[A]^x K_d^*}{\{\text{MeOA}_x\}} \end{aligned} \quad (2c)$$

where

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

and

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

K_d^* and K_{sp}^* approach K_d and K_{sp} 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.*,

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

Therefore, in principle, one can determine K_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_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_d 's represent only the values at the end of the experiments (usually 3 weeks of equilibration time). For ease of presentation, K_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 γ -counted by a Ge(Li) detector

with a multichannel analyzer (4096 channels). K_d 's were calculated using the following relationship:

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

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_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_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}Au ($t_{1/2} = 183 \text{ d}$), ^{133}Ba (10.8 y), ^7Be (53.3 d), ^{207}Bi (38 y), ^{141}Ce (32.5 d), ^{139}Ce (138 d), ^{109}Cd (1.24 y), ^{60}Co (5.27 y), ^{134}Cs (2.06 y), ^{56}Fe (45 d), ^{153}Gd (242 d), ^{203}Hg (46.6 d), ^{192}Ir (74 d), ^{54}Mn (313 d), ^{125}Sb (2.7 y), ^{113}Sn (115 d) and ^{65}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 (≈ 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 $\approx 50 \mu\text{M H}_2\text{S}$). 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 δMnO_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_d 's) for various radiotracers as functions of equilibration times and suspended particle concentrations ($\approx 10, 50, 100, 400, 800$ and $1700 \text{ mg per liter of seawater}$) were determined from adsorption and desorption experiments. Figure 1 shows K_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.* ^7Be).

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