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FACTORS CONTROLLING RARE-METAL CONCENTRATIONS IN THE SEA

By

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FACTORS CONTROLLING RARE-METAL CONCENTRATIONS IN THE SEA

By Konrad B. Krauskopf

ABSTRACT

The factors controlling the concentrations of 13 metals (Zn, Cu, Pb, Bi, Cd, Ni, Co, Hg, Ag, Cr, Mo, W, V) in sea water have been studied. The possible controls investigated are (1) precipitation of insoluble compounds with ions normally present in aerated sea water, (2) precipitation of sulfides locally in reducing environments, (3) adsorption by ferrous sulfide, hydrated ferric oxide, hydrated manganese dioxide, apatite, clay, and organic matter. The precipitation reactions were studied both by calculations based on solubility data and by experiments in which equilibrium concentrations of the metal ions were determined in sea water in contact with their precipitates. Adsorption was measured by adding or precipitating the various adsorbents in sea water samples containing an excess of one of the metal ions.

The principal conclusions are: (1) Sea water is greatly undersaturated with respect to all 13 metals; in other words, precipitation of compounds with the ions normally present in aerated sea water, even under extreme conditions of temperature and pH, cannot be responsible for the observed concentrations. (2) Local precipitation of sulfides is a possible control mechanism for seven of the elements (Cu, Zn, Hg, Ag, Cd, Bi, Pb), but is probably not the chief control because the concentrations are unrelated to sulfide solubilities. (3) Adsorption is a possible mechanism for all elements except V, W, Ni, Co, and Cr; if Cr is assumed to be removed by local reduction and precipitation of the hydroxide, and the other four metals by organic reactions, the existing concentrations can be fairly adequately accounted for. Adsorption processes supplemented by organic reactions also furnish a qualitative explanation for the distribution of rare metals in sedimentary rocks of marine origin.

These conclusions can probably be extended to other metals in the middle of the periodic system, but not to those on either side.

INTRODUCTION

Rare metals are notably concentrated in certain marine sedimentary rocks, especially black shales and phosphorites. The source of the metals is commonly thought to be the sea water in which the sediments were deposited. This postulate leads to several questions regarding the rare metal content of sea water. In what form do the various metals exist in the sea? By what process or processes may the metals be removed from sea water during sedimentation? What factors control the amount of a given metal in sea water? Why, for instance, should the concentration of copper lie between 1 and 10 parts per million-rather than between 0.1 and 1, or between 10 and 100? Such questions are the subject-matter of this paper.

The investigation has been limited to simple experiments and calculations of a strictly exploratory nature. Since the problem concerns a complex natural system in which many variables are necessarily uncontrolled, the effort required to obtain more precise results is hardly justified. The discussion is furthermore restricted to present-day sea water and does not touch the question as to how the rare metal content of the sea may have changed in the geologic past.

The fact that sea water is apparently undersaturated with respect to several of the rare metals has been noted repeatedly. Goldschmidt (1937) suggested that rare metal concentrations are kept low by adsorption, particularly on iron oxide precipitates. Harvey (1945, p. 33) reports experiments showing that copper salts are readily soluble in sea water, but that excess copper can be markedly reduced by adsorption on clay or organic matter. The importance of adsorption is also emphasized by Goldberg (1954), who points out that nickel chloride dissolves in sea water but that Ni^{++} is readily adsorbed by manganese dioxide. Goldberg further suggests that the distribution of rare metals in iron and manganese oxide precipitated from sea water should indicate which metals are present in the sea as cations and which as anions, since colloidal particles of the two oxides carry opposite electric charges.

A conceivable explanation for the observed concentrations of rare metals in the sea is that the present amounts represent simply the accumulation to date of material weathered from the land and carried to the sea during geologic time. This possibility was disposed of many years ago by Goldschmidt (1932), and his method of calculation has been verified by Correns (1948). Goldschmidt estimated for each element the total quantity weathered and eroded from the land; a comparison of these figures with concentrations of metal ions in sea water shows that for all metals except possibly sodium the amount added to the sea far exceeds the present quantity.

A part of Goldschmidt's table, showing the effectiveness of removal of rare metals from the sea, is reproduced as table 1. (The table is a revision of the original, taken for the most part from Rankama and Sahama, 1950, p. 295). Most of the figures in the table are somewhat uncertain.

The extent of the uncertainty for the analytical values in the third column is well illustrated by the surprisingly high concentrations of Mo, Ni, V, and Cr (numbers in parentheses) recently reported by Black and Mitchell (1952). Goldschmidt's estimates of amounts supplied to the sea (second column) are of course even less reliable, since they depend not only on limited analytical data but also on at least two somewhat questionable assumptions: that the sodium of sea water has been increasing through geologic time to the present, and that rare metals go into solution during weathering in proportion to their concentrations in igneous rocks. Nevertheless, even large revisions in some of the values could hardly change the general conclusion that the metal content of the present ocean is but a tiny fraction of the amount of metal ions poured into it. It is reasonable to suppose further that each metal long ago reached a concentration determined by a balance between the processes adding it to sea water and processes removing it from sea water.

Another inference from table 1 is that the processes of removal are more effective for some metals than for others. A few metals, for example Ag, and Bi, are present in a relatively large fraction (greater than 0.2%) of the amount supplied; a second group, including Cu, Zn, and Pb, have their concentrations reduced to 0.005--0.2% of the amount supplied; and a third group, including V and Ni, show still more effective removal. The possible significance of these differences will be considered later.

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INFERENCES FROM PHYSICO-CHEMICAL DATA

Introduction

The concentrations of some metals in sea water are controlled by the slight solubilities of their compounds with the ions ordinarily present in the sea. The amount of Ca^{++}, for example, probably depends chiefly on the solubility of $CaCO_3$. The possibility that rare metal concentrations are similarly controlled will be examined first by calculations based on solubility data, and later by experiments designed to check and supplement the calculations.

The abundant anions of ordinary oxygenated sea water are Cl^-, SO_4^{--}, and CO_3^{--}. These are known to form relatively insoluble compounds with many of the rare metals, and solubility products permit calculation of the amounts of the metals that can exist in equilibrium with them in the sea. Rare metals that exist as anions in sea water might be precipitated by one or more of the abundant cations (Na^+, K^+, Mg^{++}, Ca^{++}), but solubility data are insufficient to explore this possibility in detail. The less abundant anions and cations of the sea might also play a role if solubilities of their compounds with the rare metals are extremely low; this possibility will be examined later, but for the present only the abundant ions will be considered.

In order to carry out the calculations, one must know first the form in which the rare metals exist in sea water, and secondly the effect of other ions in the sea on solubility products. These questions will be examined in the following sections.

Mode of occurrence of rare metals in aerated sea water

Metals can exist in the sea in at least four different forms: (1) as a part of living organisms, (2) as colloidal particles, (3) adsorbed on other colloidal particles, and (4) in true solution. The first three may be difficult to distinguish experimentally one from the other, but all represent metals in the form of suspended particles as opposed to true solution. That gold may exist largely in particulate form is indicated by Haber's (1928) work; more recent studies by Patterson and others (1953) suggest that lead occurs at least partly as suspended particles. It is probable that particles account for a part of the concentration of other metals also, so that calculation from physico-chemical data can give at best only a minimum figure for the amount of a metal which should be present at equilibrium with the ions of sea water.

The nature of the ions (or neutral molecules) which exist in true solution can be specified with confidence for some of the metals but only guessed at for others. Copper, for example, in chloride solution forms the ions Cu^{++}, $CuCl^{+}$, $CuCl_2$, $CuCl_3^{-}$, and $CuCl_4^{--}$; according to the data of Bjerrum (1950), a solution with 0.55M Cl^{-} (like sea water) should have mostly Cu^{++}, about one-third as much $CuCl^{+}$, one-thirtieth as much $CuCl_2$, and negligible quantities of the negative ions. The numerical values of the equilibrium constants may not be quite the same in sea water as in Bjerrum's solutions, and there may be some complication from the formation of $Cu(OH)^{+}$, but it seems certain that dissolved copper will be largely in the form of positive ions and it seems at least probable that the most abundant ions will be Cu^{++} and $CuCl^{+}$. Similarly zinc is present in sea water chiefly as $Zn^{++}$and $ZnCl^{+}$ (from the data of Sillen and Liljeqvist, 1944), cadmium as $CdCl^{+}$ and $CdCl_2$ (from the data of Vanderzee and Dawson, 1953), and lead chiefly as $PbCl^{+}$(Gucker and Garrels, 1949). Mercury and silver, on the other hand, exist chiefly as negative ions, $HgCL_4^{--}$and $AgCl_2^{-}$(Lindgren, Johnson, and Sillen, 1947; Jonte and Martin, 1952). For cobalt, more indirect reasoning from adsorption studies leads Kurbatov, Wood, and Kurbatov (1951) to the conclusion that the "effective valence" of cobalt in chloride solutions is 1.2, which means that the principal ions present are probably Co^{++}, $CoCl^{+}$, and perhaps $Co(OH)^{+}$ also. No data have been found for nickel, but its behavior is probably similar to that of cobalt. The available information about bismuth, as summarized by Latimer (1952, p. 122) and by Babko and Golub (1953), indicates that BiO^+ is predominant over $BiCl_4^-$ and that Bi^{+3} is very minor. Chromium in aerated sea water would exist as CrO_4^{--}; molybdenum and tungsten are doubtless also present as anions, but the formulas are unknown. Vanadium, according to the data of Ducret (1951), should be present almost entirely in the quinquevalent form, chiefly as $H_2VO_4^-$ but perhaps in part as $H_3V_2O_7^-$. The ions and molecules discussed in this paragraph are listed as the first column of table 2.

Effect of sea water on solubility products

Solubility products given in the literature are measured in dilute solutions or extrapolated to infinite dilution, hence are not directly applicable to so complex and concentrated a solution as sea water. The effect of electrolytes on a solubility product can be calculated by the formulas of the Debye-Hückel theory, but only up to an ionic strength of about 0.1. (The ionic strength of a solution is a measure of its total concentration; it is defined as half the sum of the concentrations of the ions present, each concentration being mulitplied by the square of the valence of the ion.) For sea water, with an ionic strength about 0.7 direct calculation is impossible. A rough idea of the factor by which solubility products must be modified can nevertheless be obtained by inspection of tables of activity coefficients for various salts (Latimer, 1952, p. 354). For uni-univalent salts activity coefficients in solutions of ionic strength 0.7 cluster around 0.7; for di-divalent salts around 0.12; and for uni-divalent and di-univalent salts around 0.4. There are notable exceptions, but the values are sufficiently uniform to justify their use as tentative approximations. The solubility products as given for dilute solutions should accordingly be multiplied by the following factors.

for 1-1 salts, by 1 divided by $(0.7)^2$, or 2
for 2-2 salts, by 1 divided by $(0.12)^2$, or 70
for 2-1 salts, by 1 divided by $(0.4)^3$, or 16

Results

The results of using these factors are shown in table 2. The first column lists the metals for which pertinent solubility data are available and shows the form in which each metal most probably exists in sea water. The second column shows for each metal the compound with a major ion of sea water which, according to existing data, gives the lowest concentration of the metal in solution. Solubility products for these compounds are listed in the third column; all are from Latimer except the ones for cadmium (from Feitknecht and Reinmann, 1951) and vanadium (from Ducret, 1951), and one of the two for strontium (from Wattenberg and Timmermann, 1937). The fourth column shows the factors used to multiply the solubility products to correct for the ionic strength of sea water. The fifth column gives the calculated equilibrium concentrations, for sea water at 25° containing 10^{-6}M OH^-, 0.55M CL^-, 0.0002M CO_3^{--}, and 0.028M SO_4^{--}.

The metals Ag, Hg, and Co require more complicated calculations than do the others. Ag exists chiefly as the complex ion $AgCl_2^-$, for which slightly different dissociation constants are given by Jonte and Martin (1952), Shchigol (1952), and Berne and Leden (1953); figures for $AgCl_2^-$ calculated from the two extreme values are given in the table. Hg also exists chiefly as a chloride complex, and the amount of this complex that can form is limited by the solubility of HgO; the calculation thus involves the dissociation constant of the complex and the solubility product of HgO, both given by Latimer. The amount of Co^{++} is limited either by the oxidation potential of its reaction with oxygen and the solubility of $Co(OH)_3$, or by the solubility of $CoCO_3$; the two processes give the same equilibrium concentration. No attempt was made to correct for ionic strength in the calculations for these metals.

The limitations of these calculations should be emphasized. The correction for ionic strength is extremely rough; the compounds for which solubility products are recorded may not be the ones actually formed in sea water (copper, for instance, forms a basic carbonate rather than the simple carbonate); and solubilities of some metals may be affected by the formation of complex ions.

Discussion

The general lack of agreement between calculated concentrations and actual concentrations in sea water is shown by table 3, where the calculated values are repeated in the second column and concentrations in the sea are given in the fourth column. (Figures in the third and fifth columns are discussed in the next section.) The last three metals in the table (Ca, Sr, Ba) show about as much agreement as could be expected, in view of the assumptions involved, and the agreement suggests that these metals may indeed have concentrations controlled largely by solubilities.

The calculated figure for Mg has little meaning, since this metal would most likely be controlled by the solubility of dolomite rather than the simple carbonate; a figure for the solubility product of dolomite has been given by Halla (1935), but the correction for ionic strength is so uncertain that calculation seems pointless. For all other metals in the table the calculated figures exceed the observed amounts, and for all except Pb and Bi the discrepancy exceeds a factor of 100. This could mean that the assumptions underlying the calculations are grossly inaccurate; but the fact that the discrepancies are all in one direction, together with the fact that the assumptions appear to be justified for Ca, Sr, and Ba, suggests the alternative interpretation that amounts of these rare metals in the sea are not controlled by solubilities of the compounds listed in table 2.

Another possibility for the control of concentrations would be the solubility of compounds of the rare metals with some of the less abundant ions of sea water. Nickel, for example, is obviously not dependent on the solubility of $NiCl_2$, $NiSO_4$, $NiCO_3$, or $Ni(OH)_2$; but conceivably it might form a very insoluble compound with F^-, Br^-, I^-, BO_2^-, PO_4^{-3}, AsO_4^{-3}, or SeO_4^{--}. A study of this possibility requires calculating the amount of Ni^{++} that could exist in sea water with the known amounts of each of these anions. To give all the calculations for each metal would be tedious, but the method may be illustrated with $PbCO_3$ and $Pb_3(PO_4)_2$. The concentration of Pb^{++} in equilibrium with the CO_3^{--} of sea water (0.0002M) is given by

$$Pb^{++} = \frac{\text{solbty. prod. of } PbCO_3}{CO_3^{--}} = \frac{1.5 \times 10^{-13}}{2 \times 10^{-4}} = 0.8 \times 10^{-9} \text{ mole/l.}$$

and that in equilibrium with PO_4^{-3} (using the maximum value for total phosphate given by Sverdrup and others (1946), 0.0035M, and using 8.5×10^{-12} as the dissociation constant of HPO_4^{--}):

$$Pb^{++} = \sqrt[3]{\frac{\text{solbty. prod. } Pb_3(P)_4)_2}{(PO_4^{-3})^2}} = \sqrt[3]{\frac{1.5 \times 10^{-32}}{(3 \times 10^{-6})^2}} = 1.2 \times 10^{-7} \text{ mole/l.}$$

Thus more lead could exist in the presence of the PO_4^{-3} in sea water than in the presence of the CO_3^{--}, despite the greater insolubility of the phosphate. Similar calculations have been carried out for all compounds of the other metals for which solubility data are known, and the result in each case is the same: equilibrium concentrations of metal ions permitted by the less abundant ions of sea water are larger than the concentrations permitted by the major ions. This statement refers only to ions normally present in aerated sea water, but not to ions which may exist locally in reducing environments, such as S^{--}; the possible influence of such ions will be considered later. The statement is also subject to limitations imposed by the scarcity of accurate solubility data. Nevertheless, a tentative generalization seems justified that according to calculation, normal aerated sea water is undersaturated with respect to rare metals, except possibly for Sr and Ba.

EXPERIMENTS WITH NORMAL, AERATED SEA WATER

Experiment offers another approach to the problem of how effectively concentrations may be controlled by equilibrium with slightly soluble compounds. Rigidly controlled experiments in a medium as complex as sea water would be prohibitively time-consuming, but much suggestive information can be obtained from rapid semi-quantitative work. The procedure adopted was to add a solution of each metal ion to a sample of sea water until a precipitate formed and then allow the mixture to stand until the metal ion concentration became constant, making the necessary adjustments throughout to keep the pH of the solution constant. This should give, in favorable cases, an equilibrium value for the metal ion concentration in contact with the precipitate, and in any case a maximum value. The equilibrium was then approached from the opposite direction by filtering off some of the precipitate and adding it to a new sample of sea water, again adjusting the pH and measuring the metal ion concentration at intervals until it became constant. This should give a minimum value for the equilibrium concentration, and in cases where the two values did not coincide the equilibrium figure was assumed to lie between. Great accuracy was not attempted, and the nature of the various precipitates was not investigated. Whatever the precipitates are, they must be the ones formed in places where metal ions enter the sea in quantity (disregarding the possibility of very slow reactions); if such compounds play any role in holding metal concentrations at particular values, the experimental figures should have at least the same order of magnitude as the concentrations found in nature.

To analyze the sea water samples, Sandell's (1950) colorimetric procedures were used. Colors were evaluated by visual comparison with standards. The validity of the analytical method was checked in each case by a series of tests on solutions of known metal concentration but otherwise identical with the solutions to be analyzed. Slight modifications were necessary in some of the procedures, but less difficulty was found than anticipated in applying Sandell's methods to sea water. Sufficient duplicate runs were made to insure reproducibility within at least a factor of 2. Examples of the kind of data obtained are given in table 4.

Many of the experiments were tried both in artificial sea water prepared by the Lyman-Fleming formula (Sverdrup and others, 1946, p. 186) and in natural sea water. The natural water was obtained through the courtesy of Professor Bjørn Føyn, director of the marine biological station of the University of Oslo, from the Oslo Fjord at Drøbak, about 40 km south of Oslo and 60 km north of the mouth of the fjord. It was obtained from a depth of 26 meters by pumping through lead pipes, so of course could not be used in the experiments on this metal. The water had a salinity of about 30 parts per thousand, a little less than that in water from the open sea. Determinations of copper and zinc (after extraction from 200 ml with dithizone) in the water gave 0.0025 ppm and 0.008 ppm respectively, values in the low part of the ranges generally reported for these metals; no other direct measurements of metal content were attempted, but these two suggest that there has been little contamination of the water beyond slight dilution. One series of experiments was run on water acidified with HNO_3, immediately after collection, in order to prevent adsorption of ions or organic matter on the glass walls of the containing vessel. Comparison of results obtained in sea water of various kinds--artificial sea water, fresh natural sea water, natural water which had stood in a soft-glass container for several weeks, and natural water treated with

HNO_3--showed no differences in results greater than a factor of 2, which is within the accuracy attempted; hence for most experiments natural sea water was used directly.

Thirteen metals were used in the experiments: Cu, Zn, Pb, Cd, Hg, Ag, Co, Ni, Bi, Mo, W, Cr, V. The metals were chosen primarily on the basis of ease of analysis. Many runs of several days' duration were necessary for each metal, and complicated analyses would have prolonged the work unduly. The group selected is a representative sample from the middle of the periodic system; it is hoped that the work can be extended to metals on either side, such as the rare earths, Ba, Sb, and Se.

Results of the experiments are given in the third column of table 3. The two figures listed for most of the metals show the concentrations obtained in approaching the solubility equilibrium from different directions. The wide gap between the figures for some of the metals is unexplained. Comparison of the second, third, and fourth columns of table 3 shows that the measured equilibrium concentrations are uniformly larger than observed concentrations in sea water but have the same order of magnitude as the calculated concentrations (except Co). Some of the agreement with the calculated figures may be fortuitous; it certainly is in the case of copper, since the compound formed on adding Cu^{++} to sea water is a basic chloride or a basic carbonate rather than the normal carbonate (Harvey, 1945, p. 33). Nevertheless, the agreement is as close as could be expected in view of the assumptions underlying the calculations and, hence, gives some basis for relying on these adsumptions.

Only two figures have been found in the literature which can serve as checks on the measurements of equilibrium concentration. One is Harvey's (1945, p. 33) statement that the amount of copper remaining in sea water of pH 8 after a precipitate (basic chloride changing to basic carbonate) has been formed by the addition of $CuSO_4$ in 0.18 ppm. This is somewhat lower than the range (0.4 - 0.8) obtained in the present experiments. The second previously reported figure in Shibasaki's (1952) measurement of the copper remaining in solution after addition of $CuSO_4$, 1.9 ppm (average of 1.65 and 2.1) at a pH of 7. Shibasaki's data do not permit a reliable extrapolation to pH 8, but his measurements at the lower pH agree fairly well with the result of similar experiments to be described in the next section, 2.5 ppm.

The ratios between experimental concentrations and those observed in sea water are listed in the last column of table 3. For four metals (Cu, Zn, Bi, Pb) the ratio is in the neighborhood of 100, for all others (excluding the alkaline earths) greater than 1,000. The uniformly high values corroborate the conclusion of the last section that the concentrations of these metals in aerated, moderately warm sea water cannot be controlled by solubility equilibria with ions ordinarily present in such water.

EFFECT OF TEMPERATURE, PRESSURE, AND pH

The experiments just described were conducted at room temperature (18°-23° C)* and at the normal pH of sea water (7.8 - 8.2). Equilibrium concentrations would of course be different in parts of the sea with

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* Centigrade temperatures are used throughout this paper.

different temperatures, pressures, and pH's, and conceivably the difference might be sufficient so that locally the concentrations would be reduced to the values actually observed. Then if circulation in the oceans is sufficiently rapid, the precipitation of rare metals in such local areas might control concentrations elsewhere--just as calcium in the sea is probably controlled by the formation of $CaCO_3$ in shallow tropical water, and phosphorus by the precipitation of carbonate-fluorapatite in areas of upwelling currents.

Calculation shows that an increase of one pH unit should diminish the solubility of simple divalent carbonates by a factor of 10, and that of divalent hydroxides by a factor of 100; these are the maximum expectable effects of pH changes. The effect of temperature is less easily calculated, but a survey of tabulated solubilities shows very few salts (and these unusual ones) whose solubility changes by a factor of more than 100 for a temperature change of 100° ; hence the effect of temperature in the range found in sea water will be relatively slight. A change in pressure, according to the study of Owen and Brinkley (1941) should also have little effect. Thus theoretically the four metals with the smallest ratios in table 4 (Cu, Zn, Pb, Bi), provided that their precipitates are basic salts and provided that the temperature effect aids the pH effect, might just possibly have their equilibrium concentrations reduced to the neighborhood of the observed ones by a pH of 9, the maximum figure expectable in the sea.

To test this deduction, equilibrium concentrations of copper were measured at pH's of 7, 9, and 10 and at temperatures of 0° and 55° (table 5). The concentration decreases by a factor of about 4 for each unit increase in pH, and by a factor of about 2 for each 20-degree rise in temperature (why the change with pH should be so small is not obvious; theoretically it should be greater for either a basic chloride or a basic carbonate). Hence the concentration would be lowered on the order of 100 times at a pH of 10 and a temperature of 60°-- but these are impossibly high values for natural sea water. Tests were not run on Zn, Pb, or Bi, but the results for Cu together with the theoretical deductions make it most unlikely that pH and temperature extremes in the sea are responsible for the observed concentrations. Such effects would be even less capable of controlling the concentrations of the other nine elements studied.

PRECIPITATION OF SULFIDES

Up to this point only aerated sea water has been considered. This includes by far the greater part of the water in the oceans, for circulation is effective enough to keep an excess of dissolved oxygen even in water at great depths. In some parts of the ocean, however, notably in stagnant basins, in areas of upwelling currents, and within some of the bottom sediments, the water is depleted of its oxygen by decaying organic matter and the chemical environment becomes reducing rather than oxidizing. Under such conditions two additional factors may affect rare metal concentrations: the presence of sulfide ion, which is capable of forming very insoluble sulfides with some metals; and the presence of reducing agents powerful enough to change the valence of some metals and so to make possible other kinds of precipitation reactions.

If the sea water circulates fast enough, the reduction of metal ion concentrations by these factors locally might be sufficient to maintain the low observed metal concentrations in the sea (W. W. Rubey, personal communication).

To test this possibility, solubilities in sea water of sulfide precipitates of several of the thirteen metals were measured (table 6), Conditions were used which roughly duplicate the most stagnant water found by Strøm (1936) in his study of Norwegian fjords--pH about 7 and H_2S concentration about 0.005M. As before, the measurements were made by approaching equilibrium from two directions--adding H_2S to solutions of each metal ion in sea water, and placing the freshly precipitated metal sulfide in contact with sea water. Again only rough values bracketed between maxima and minima could be obtained, but they are accurate enough for the purpose. Calculated concentrations for the experimental conditions (using Kolthoff and Sandell's (1952, page 68) figures for the solubility products and multiplying by a correction factor for ionic strength) are given in the second column of table 6.

For ZnS both calculation and experiment show a concentration comparable with that found in nature. For Cu, Pb, Hg, and Ag, the experimental concentrations are below the limit of detection by the analytical methods used, but the maximum possible concentrations differ from concentrations in the sea only by factors of 2-20; the calculated concentrations for these metals are much lower than concentrations in the sea. No tests were made on Cd or Bi, but results would doubtless be similar since these metals also form very insoluble sulfides. The sulfides of Ni, Co, W, Mo, and V, on the other hand, are far too soluble to explain the concentrations of these metals. Chromium forms no sulfide, but H_2S slowly reduces chromate to the tervalent form which precipitates as the hydroxide; and this reduces the amount of the metal below the concentration detectable colorimetrically. Hence the same conditions in the ocean that produce H_2S could control Cr by causing it to precipitate as the hydroxide.*

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*A similar mechanism would be a possible control for vanadium, provided that the hydroxide of either the quadrivalent form, $VO(OH)_2$, or the tervalent form $V(OH)_3$, is sufficiently insoluble. For quadrivalent V Ducret (1951) gives the following activity products:

$$VO(OH)_2 = VO^{++} + 2OH^-, \qquad K = 7 \times 10^{-23}$$

$$VO^{++} + H_2O = VO(OH)^+ + H^+, \qquad K = 1.7 \times 10^{-5}$$

$$2VO(OH)_2 = H_2O + H^+ + HV_2O_5^-, \qquad K = 5 \times 10^{-11}$$

from which it follows that the principal ion in equilibrium with $VO(OH)_2$ at pH 7 is $HV_2O_5^-$, with a concentration of about 5×10^{-4}M, equivalent to 50 ppm of V. Hence $VO(OH)_2$ cannot possibly hold the V concentration low enough, regardless of any equilibrium with H_2S. For $V(OH)_3$ the equilibrium to be considered is

$$HV_2O_5^- + H_2S + 2H_2O = 2V(OH)_3 + S + OH^-$$

The free energy of formation of $HV_2O_5^-$ can be found from the first and third reactions above, together with Latimer's figure of -109 kcal for VO^{++}; it is approximately -357 kcal. Garrels (1953) estimates -221 kcal as the free energy of formation of $V(OH)_3$. From these and the free energies for H_2S, H_2O, and OH^- given by Latimer the standard free energy for the reaction turns out to be -2.4 kcal. For a pH of 7 and a concentration of H_2S 0.005M, this gives as an equilibrium concentration of $HV_2O_5^-$ 3×10^{-7}M, or 0.03 ppm of V. This figure is certainly a minimum, since it includes no correction for ionic strength or for possible complexes with other ions in sea water; even so, it is 100 times greater than the usual figure for V in sea water, 0.0003. It is 30 times smaller than the measured figure, 1 ppm, but such a discrepancy is expectable when ionic strength is not considered. Hence there seems to be no possibility, experimentally or theoretically, that vanadium can be controlled by precipitation in a sulfide-rich environment.

These data suggest that sulfide ion is a possible control for some of the metals. Against this conclusion is the fact that the concentrations of the metal ions have no apparent relation to the calculated solubilities of the sulfides; thus if Cu and Zn are both governed by the solubilities of their sulfides, the amount of Cu in sea water should be a million million times smaller than the amount of Zn instead of almost equal to it. A possible answer to this objection is that the less soluble sulfides may form sulfide complexes, as has been demonstrated for Hg by Treadwell and Schaufelberger (1946), for Ag by Treadwell and Hepenstrick (1949), and for Pb by Hemley (1953).

To make this mechanism of control effective, it must be further demonstrated that sea water circulation is rapid enough to bring all parts of the ocean in contact with H_2S at reasonably frequent intervals.

Some light has been thrown on this question by the work of Kulp (1951), whose measurements of the C^{14} content of ocean water from various depths indicate that circulation of large masses of water in the open sea is measured in thousands of years. This is probably fast enough for unusual conditions in local areas to exert a considerable influence on the ocean as a whole.

The rare metals, which do not form very insoluble sulfides in sea water (Ni, Co, Mo, W, V), and which therefore are not subject to direct control by sulfide ion, might still be removed from the sea in a sulfide-rich environment if they were appreciably coprecipitated with another sulfide. In order to test this possibility, experiments were tried in which ferrous sulfide (probably the most abundant sulfide formed in the sea) was precipitated in samples of sea water to which solutions of each of the five metals had been added. Only vanadium, however, showed any lower concentrations than would have been obtained by precipitating the metal sulfide without added iron. Even for vanadium the decrease is not large: the equilibrium concentration of either the quadrivalent or quinquevalent form is about 1 ppm in the presence of vanadium sulfide alone, and 0.23 and 0.12 ppm if iron sulfide is present also. Thus coprecipitation with ferrous sulfide can play little part in maintaining the low concentration of vanadium in sea water, 0.0003 ppm.

To summarize, the precipitation of sulfides in local areas is a possible explanation for the observed low concentrations of Cu, Zn, Cd, Bi, Hg, Pb, Ag, and Cr in sea water. The complete lack of parallelism, however, between sulfide solubilities and observed concentrations is not satisfactorily explained. For the metals V, Mo, W, Co, and Ni, equilibrium with sulfide ion cannot be responsible for observed concentrations.

ADSORPTION

General

The efficacy of adsorption in controlling metal ion concentrations is much more difficult to determine quantitatively than is the solubility of metal compounds. The amount of adsorption in any particular case depends not only on temperature, pH and salinity (as does solubility), but on time of standing, amount and physical state of the adsorbent, and concentration of the adsorbed ions as well. Despite the addition of these new variables to an already complex system, it seemed worthwhile to compare the effectiveness of different adsorbents on the various metal ions under similar conditions.

In some experiments the metal ion was removed from solution almost completely, while in others its concentration remained almost unaffected by the adsorbent. The question then arises, how effective must adsorption appear in such experiments to indicate large-scale removal of a metal from the sea? Obviously, even moderate adsorption repeated often enough as the ocean circulates could ultimately reduce the concentration of an adsorbed ion to a very small figure. Although the question cannot be answered completely with present data, one circumstance indicates that more than moderate adsorption is required. When zinc, for example, is adsorbed on montmorillonite from a 2-ppm solution, some 99 per cent of the ion is removed within a few hours, while only about 20 percent of silver ion is removed under the same conditions. Now if the adsorptive process in sea water is equivalent to many repetitions of the laboratory process, as it would have to be in order to control the concentration of Ag^{+}, the concentration of Zn^{++} would at the same time be lowered far below the observed amount in the sea. Hence the fact that zinc can be reduced almost to the concentration in nature by a single adsorption experiment with montmorillonite suggests that ions not so effectively removed in the laboratory are also less effectively controlled by adsorption on this material in the sea. It is on this basis that the laboratory experiments are considered to have at least a qualitative application to natural conditions.

Previous work

Some recent experimental and theoretical work by Kurbatov, Wood, and Kurbatov (1951) on the adsorption of cobalt by iron oxide provides an excellent background for this discussion. These authors employed a radioactive tracer technique to analyze for cobalt, which enabled them to work with concentrations 1,000 times lower than those used in the present experiments. Equilibrium in the adsorption process was reached within 24 hours when iron oxide was precipitated in a solution containing cobalt; when iron oxide was not precipitated in the same solution but added from the outside, the same equilibrium was eventually reached but required six or seven days. In general Kurbatov and others found that adsorption increases with increasing amounts of adsorbent and adsorbate, with increasing pH, with decreasing temperature, and with decreasing concentrations of NH_4CL. Log-log plots of cobalt adsorbed against cobalt in the original solution showed two regions: at low concentrations the graphs are straight lines, showing that the amount adsorbed is proportional to the concentration ("Henry's law region"), while at higher concentrations the amount adsorbed falls off. The position of the break in the curve depends on the conditions of the experiment, particularly on the amount of adsorbent. The experimental conditions were not exactly comparable to those of the present work, but enough data are given to permit extrapolation; values so obtained are in satisfactory agreement with results of the present study.

Kurbatov and others go on to show that their experimental results can be explained by a simple adsorption mechanism following a mass-law equation, the Co ions taking the place of H ions on the surface of the adsorbent. From the mass-law expression the following equation is derived:

$$\frac{y}{1 - y} \cdot \frac{(H^{+})^{x}}{(\text{amt. of adsorbent})^{x}} = K$$

in which y is the fraction of cobalt adsorbed, 1 - y the fraction left in solution, and x an empirical constant. For the Henry's Law part of the adsorption curves, $y/(1 - y)$ is constant as the total cobalt changes; above this part of the curve the amount of adsorbent left is significantly affected by the amount of Co, so that the value of the fraction falls off. The constant x has a value of 1.2 for cobalt, and plays the role of an "effective valence", indicating that the cobalt is present in solution partly as Co^{++} and partly as $CoCl^{+}$ or $Co(OH)^{+}$. The role of NH_4Cl in decreasing the amount of adsorption is not described by the above equation, but is attributed by Kurbatov and others to interference by Cl^{-} in the adsorption of Co.

In a later paper, Duval and Kurbatov (1952) compare the adsorption of barium and cobalt on ferric oxide. Barium shows a markedly smaller adsorption than cobalt, which the authors explain by the greater hydrolysis of Co^{++}.

One other set of experiments has a bearing on the present work. Correns (1924) determined the adsorption on kaolin of copper out of very dilute $CuSO_4$ solutions and of lead out of $Pb(NO_3)_2$ solutions. The concentrations of metal ions used by Correns were similar to those in the present experiments, but other conditions were markedly different: the pH was lower, the amounts of adsorbent and of other ions in solution were smaller, and kaolinite was used instead of montmorillonite. These differences are ample explanation for the fact that Correns obtained much smaller values for the amounts of copper and lead adsorbed. Correns found that adsorption of the two ions was roughly similar, in agreement with the present work; his data for low concentrations of copper (0.1 - 0.5 ppm) permit calculation of the quotient $y/(1 - y)$, which is approximately constant in agreement with Kurbatov's results.

Experimental details

The present experiments are extremely crude in comparison with the careful work of Kurbatov and others, and have only the virtue of permitting many ions and several different adsorbents to be tested within a reasonable time. To samples of sea water (usually 25 or 50 ml) amounts of a metal ion were added to give concentrations in the range 0.1 -10 ppm; then a measured amount of adsorbent was added (or precipitated) and the mixtures were shaken; at various times thereafter, up to a few days for most experiments, samples of the supernatant liquids were pipetted out and analyzed colorimetrically. The pH was adjusted to 8.0-8.2 after addition of the metal ion and also after addition of the adsorbent; in some experiments repeated adjustments of pH were necessary while the adsorption was coming to equilibrium. Filtering was required in some cases to obtain samples for analysis free from particles of the adsorbent. The temperature ranged from 18° to 23°. Blank tests were made to determine the amount of adsorption on glass and filter paper, and also to make sure that the colorimetric tests were not affected by the presence of the various adsorbents. Blank corrections were necessary in some cases but were never large.

Adsorbents were chosen to duplicate as closely as possible the principal adsorbing materials in the sea: iron oxide, manganese oxide, carbonate-fluorapatite, clay, and organic material. Other substances such as colloidal silica and calcium carbonate might have been added to the list, but the small concentrations of rare metals in silica and carbonate sediments is an indication that adsorption on these would be relatively minor. The degree of correspondence between the laboratory adsorbents and those in nature is of course open to question. In nature the adsorbents are doubtlessly formed by different processes, and their concentrations are generally less than in the experiments. Furthermore, the far longer times available for adsorption processes in nature perhaps make possible slow reactions which would not be detected in the laboratory. Despite these obvious shortcomings of the experiments, the laboratory work should provide in a general exploratory way some indication of what behavior is to be expected from various ions and various adsorbents in the sea.

Ferric oxide, manganese dioxide, and apatite in most of the experiments were precipitated in the sample itself rather than being added from outside. Ferric oxide was obtained simply by adding 0.1M $FeCl_3$ in small amounts, and adjusting the pH to 8.2 with NaOH solution after each addition. Apatite was precipitated by adding Na_2HPO_4 solution (containing 0.01 g P_2O_4 per ml), again adjusting the pH at frequent intervals. Manganese dioxide was formed by adding 0.1M $MnSO_4$ and a slight excess of bromine water, then removing excess bromine by bubbling air through the solution and adjusting the pH. This procedure could not be used for Ni and Co because the divalent ions may be partly oxidized by free bromine; so MnO_2 was precipitated in sea water in a separate flask, the bromine was bubbled out, and the suspension was added to sea water containing the ion to be tested. Runs made with ferric oxide added from outside rather than precipitated verified the conclusion of Kurbatov and others that the adsorptive capacity is the same but that a longer time is needed for adsorption equilibrium to be reached.

For clay, two samples of montmorillonite (bentonite) were used, one from Coalinga, California and the other from Kinnekulle, Sweden. Montmorillonite was selected not because it is especially typical of marine environments, but because it should show the maximum adsorptive effect of which clay minerals are capable. Before use, both samples were washed with artificial sea water until the wash water failed to give tests for the metals under investigation.

Two kinds of organic matter were tried, ordinary commercial peat moss and dead plankton suspended in sea water obtained from the Oslo Fjord through the courtesy of Professor Bjørn Føyn. One, it was hoped, would simulate terrestrial organic matter carried into the sea by streams, while the other would represent a common type of organic matter produced in the sea itself. Probably neither is very similar to the actual organic material with which the ions of sea water are usually in contact, and experiments with them can serve only to give a rough idea of the efficacy of organic substances as adsorbents. The plankton was used without treatment, since the sea water in contact with it showed no unusual concentration of metals; the peat moss was washed with artificial sea water until the wash water was free of rare metals.

Results

Results of the adsorption experiments are shown in table 7. The last column of the table gives for each run the percent of metal adsorbed, i.e., the difference between the numbers in the fifth and sixth columns divided by the number in the fifth column. The striking difference between adsorbabilities of some of the ions is shown, for example, by comparison of the figures for copper and silver; the dependence of adsorption on concentrations of adsorbent and adsorbate is particularly well shown by the data for cobalt and ferric oxide; the attainment of adsorption equilibrium in one or two days is illustrated by many of the runs, although the behavior of mercury is an outstanding exception.

The data of table 7 are obviously incomplete, and some of the figures are not as self-consistent as could be desired. The discrepancies arise in part from failure to keep temperature, pH and concentrations strictly uniform, and in part from the fact that experimental objectives and methods changed as the work progressed, so that earlier data are not entirely comparable with later data. The results could certainly be made more presentable by repeating the earlier experiments using procedures adopted toward the end, and by making additional measurements to fill gaps in the table. The effort hardly seemed justified in view of the facts that the theoretical basis for comparing one element with another is uncertain, that correspondence with actual conditions in the sea is not very close, and that complete reproducibility was not attained even in runs carried out with meticulous care to insure constant conditions. The experiments, be it repeated once more, were intended only to provide gross comparison between different metals, and for this purpose the data seem accurate enough.

Significant relationships among the various adsorbents and adsorbates are not well displayed in table 7. Some selection of data for comparison is clearly needed, and several possibilities suggest themselves as to how the selecting should be carried out. One may choose figures obtained with similar initial concentrations of metal ions and similar amounts of the different adsorbents, or one may pick figures corresponding to similar final concentrations of the different metals left in solution when adsorption has reached equilibrium; or (following Kurbatov and others) one may try to establish a "Henry's law" part of the adsorption curve for each metal and then compare values of $y/(1-y)$. Which procedure theoretically will give the most meaningful comparison is not immediately obvious, but practically with present data the first procedure proves to be the only feasible one. The third procedure is ruled out because for several of the metals a constant $y/(1-y)$ could be reached only at dilutions inaccessible to the simple methods of analysis employed. The second procedure is not applicable to as many of the data as is the first, and results of using it where possible show that in any event the relations obtained would not be very different. The selection of data according to the first procedure, i. e., for similar initial concentrations of adsorbents and adsorbates, leads to the compilation in table 8.

In this table each adsorbent-adsorbate combination is represented by a single number, or at most a pair of numbers. The numbers selected (indicated by asterisks in table 7) are in general maximum values obtained for the combination of concentrations used, except where a lower value was clearly the more trustworthy experimental result. Parentheses indicate values obtained for lower concentrations of adsorbate, and underlining denotes higher concentrations of adsorbent. The numbers in table 8 obviously have little quantitative meaning but provide a basis for rough qualitative comparisons.

Discussion

Copper, zinc, and lead, according to table 8, are adsorbed more strongly and more consistently than the other metals. All the adsorbents except plankton reduce the concentrations of these three within a few hours nearly to the range found in sea water. Cobalt and nickel, although likewise divalent elements, are much less effectively adsorbed. For these two metals manganese dioxide is by far the best adsorbent; adsorption on other materials can be greatly increased by increasing the amount of adsorbent and reducing the concentration of the metal ions, as is shown by the figures in parentheses. Mercury shows the greatest adsorption of any metal on plankton, strong adsorption by montmorillonite, notably weak adsorption by apatite; its behavior is peculiar in that adsorption equilibrium is apparently reached only slowly, especially with iron oxide and clay (table 7). Silver is surprisingly little affected by any of the adsorbents except organic materials, even in dilute solutions containing large amounts of adsorbents. Chromium and tungsten are adsorbed readily by manganese dioxide, molybdenum somewhat less so; tungsten shows moderate adsorption by iron oxide, chromium and molybdenum very little. In contrast to these three, vanadium is adsorbed much more strongly by iron oxide than by manganese oxide; other adsorbents affect it only slightly.

Of the various adsorbents, manganese dioxide appears to be most effective and iron oxide next. The other adsorbents are relatively inactive unless they are present in large amounts, except toward Cu, Zn, Pb, and Hg.

The tables show little apparent correlation between the adsorptive behavior of the metals and their other chemical properties. Colloidal manganese dioxide is commonly thought to carry a negative charge and hence to attract cations, while colloidal iron oxide normally has a positive charge and should attract anions. In the tables, however, the anion-forming elements Cr and W are as effectively adsorbed by manganese dioxide as are the cation-forming elements Ni and Co. These results provide no explanation for Goldberg's (1954) conclusion that Co is concentrated with iron and Ni and Cu with manganese in manganese nodules. The markedly smaller adsorption of Ni and Co as compared with Cu, Zn, and Pb, despite the similarity of their ions in sea water, may possibly be correlated with the greater polarizing ability (greater chalcophile tendency) of elements with complete 18-electron shells. The very weak adsorption of Ag and V by most of the materials used may be connected with the fact that they form univalent anions.

The elements Bi and Cd were not studied in this part of the work because of analytical difficulties with the small concentrations remaining after adsorption has taken place. Both might be expected to behave like Cu, Zn, and Pb, since they are chalcophile elements existing in sea water partly as positive ions. The adsorption of Cd may be lessened by the fact that much of it in the sea would form neutral $CdCl_2$ molecules; the extent of adsorption of Bi is unpredictable, since the proportion of it in the form of undissociated BiOCl is not known.

ORGANIC PROCESSES

Another possible way in which metal concentrations may be controlled is by reactions in living organisms. If metals taken up in biologic processes are returned to the sea shortly after the death of the organism, the control will be only temporary; but the possibility remains that some metal-containing compounds may survive partial decay and burial of the organisms, and so may help to remove metals permanently from the sea. The well-known fact that rare metals are often notably enriched in organic sediments is an indication that this process may be of considerable importance.

To evaluate the role of organic processes even qualitatively seems all but impossible. A wealth of data exists on the rare metal content of individual organisms (for a comprehensive tabulation see Vinogradov, 1953), but the content ranges so widely from species to species and from season to season that over-all averages have little meaning. Even if such averages could be obtained, data are completely lacking on the relative importance of different organisms in the rare-metal economy of the sea and on the relative stabilities of metal-organic compounds. The problem can also be approached from the other end, by analyzing organic sediments for rare metals, but the obvious difficulty here is that an unknown fraction of the metal content owes its presence to adsorption and possibly to sulfide precipitation rather than to biologic reactions.

As examples to show how important the enrichment of rare metals in organisms can be, data from two recent detailed studies are brought together in table 9. The second column shows enrichment factors (ratios of concentrations in organisms to concentrations in sea water) obtained by Black and Mitchell (1952) for brown algae, and the fourth column gives similar figures for nine representative marine animals analyzed by I. and W. Noddack 1939). Both of these investigators also measured concentrations of the metals in sea water; some of the figures obtained are widely different, so it seemed reasonable to include also enrichment factors recalculated with concentrations obtained by the other investigators (third and fifth columns). The high enrichment factors for some metals and the great diversity in values are especially notable. Tentatively one might conclude from the table that the six elements Ni, V, Zn, Cd, Co, and Ag show more enrichment in these particular organisms than do the other five elements listed, but this is hardly an adequate basis for assuming that such a relationship is universal among marine organisms.

COMPARISON OF POSSIBLE CONTROL MECHANISMS

Three processes survive this inquiry into possible control mechanisms for rare metal concentrations in sea water. One is the precipitation of sulfides within bottom sediments or in isolated areas of reducing conditions, a second is adsorption, and the third is biologic processes. The relative effectiveness of the first two can be roughly evaluated from the experimental results; no pertinent data exist regarding the third, so that it can be safely assigned a primary role only for metals for which the first two processes are inadequate.

The precipitation of sulfides, as pointed out previously, is capable of reducing the concentrations of eight of the thirteen elements under discussion to values within or lower than the ranges found in sea water. As a major control of concentration the mechanism is questionable because observed concentrations bear no apparent relation to solubilities of the sulfides. The validity of this objection is not altogether certain, because the experimental work could not be carried to low enough concentrations and because calculated solubilities may be modified by the formation of complex ions.

To evaluate adsorption processes as a control of concentrations requires a different basis of comparison. Adsorption processes, unlike precipitation processes, are cumulative; no matter how small the concentration of an ion may be, addition of fresh adsorbent will reduce it further. In other words, if addition of rare metal ions to the sea were suddenly to cease altogether, an adsorption mechanism would ultimately lower metal ion concentrations below any assigned limit, while a precipitation process would maintain the concentrations at values fixed by the solubility products. This means that absolute values of the concentrations can give little information about the effectiveness of adsorption processes. A more significant measure would be the rate of removal of the various metals from the sea, a quantity which cannot itself be easily measured but which can be compared for different elements in an indirect way. The efficiency of removal of a metal is evidently related to (1) the steady-state concentration and to (2) the rate of supply. If the concentration is low with respect to the rate of supply, removal must be rapid; if the ratio of concentration to rate of supply is large, removal must be sluggish. These two factors, concentration and rate of supply, have already been listed in table 1. The last column of this table, which shows ratios of concentration to supply, should be a measure of relative efficiencies of removal and hence of relative amounts of adsorption--provided that adsorption is indeed the controlling factor in determining concentrations.

To test the efficacy of adsorption processess, the percentages in table 1 will now be compared with predictions based on the experimental data of table 8. Underlying such a comparison are several assumptions. With regard to table 1, the chief assumptions are (1) the rate of supply of rare metals to the sea has been constant through geologic time, (2) rare metals go entirely into solution during weathering, and (3) the analytical data on rare metal concentrations are reliable. None of these assumptions is strictly true, of course, but they are probably not too far wrong to invalidate qualitative comparisons. Regarding table 8, one must make some sort of guess as to the relative importance of the different adsorbents in the ocean. Presumably ferric oxide would play a greater role than manganese oxide, since more iron is brought to the sea than manganese; apatite probably has less effect than the other adsorbents, since its amount in sediments is smaller; clay should be more important near the shore than far from shore. But such statements do not permit quantitative evaluation, so the simplest assumption will be used--that the adsorbents are of roughly equal importance, and that therefore an average of the figures for each element gives a crude measure of its adsorbability. A further convention will be adopted, that adsorption in the more concentrated solutions (figures without parentheses in table 8) amounting to 40 per cent or more will be considered "strong" adsorption.

The percentages in table 1 divide the elements into three groups: those least effectively removed from sea water, with percentages 0.2 and over (Ag, Bi); an intermediate group with percentages between 0.005 and 0.2 (Cd, Pb, Cu, Zn, Mo, Hg); and a group showing the most effective removal, with percentages less than 0.005 (Ni, Co, V, Cr, W).

The adsorption experiments give at once a basis for predicting the extent of removal of elements which are supplied to the sea in roughly equal amounts. Copper, zinc, and lead, for example, are probably added to the sea in about the same quantities and are all strongly adsorbed by several different materials, so that a general similarity in their ratios would be expected. On the other hand an element supplied in much smaller amounts might be removed to the same extent, even though its measured adsorbability is less, simply because the percentage adsorption increases as the concentration of metal decreases. Mercury, for example, shows less net adsorption than Cu, Zn, and Pb, at high concentrations, but comparable adsorption at low concentrations (table 8), so that the similarity in percentages shown in table 1 is understandable. The difficulty is that the effect of concentration on adsorbability is not quantitatively predictable with present data, so that agreement of the percentages may be fortuitous.

For molybdenum a similar explanation can be suggested, although it is less plausible because molybdenum even at low concentrations is much less adsorbed than is mercury. The data of table 8, in fact, suggest that removal of molybdenum should be scarcely more effective than that of silver. The data concerning molybdenum are so diverse, both with respect to its crustal abundance and to its concentration in sea water (table 1) that a satisfactory test of this prediction is impossible. The generally accepted concentration range would put the element in the second group with Pb, Cu, and Zn; but the recent much higher figures given by Black and Mitchell (1952) and by Ishibashi (1953) would place it ahead of silver.

For silver the agreement between prediction from table 8 and data from table 1 is excellent. It is the metal least subject to adsorption in the laboratory, and likewise the metal least effectively removed from the sea.

Bismuth and cadmium were not studied experimentally. For bismuth a guess may be hazarded that its relatively slight removal from sea water is due to the fact that it probably exists as a univalent ion (BiO^+ or $BiCl_4^-$) and the undissociated molecule $BiOCl$, neither of which would be strongly adsorbed. Cadmium, by similar reasoning, should also be in the first group, since it would form chiefly $CdCl^+$ and $CdCl_2$ in sea water; it is not seriously out of place, however, inasmuch as its ratio is next to the highest among the elements in the second group.

For the elements Ni, Co, V, W and Cr adsorption fails to provide a complete explanation. These metals are supplied to the sea in amounts comparable to those of Cu, Zn, and Pb (table 1); they are much less affected by most adsorbents (table 8); yet their removal from sea water is more effective by factors of 10-100. It is true that their adsorption increases with dilution, and that data were not obtained at concentrations close to those in natural sea water; still it seems highly improbable that any adsorption process at lower concentrations would become <u>more</u> effective for those elements than for Cu, Zn, and Pb. Stated another way, any imagined adsorption process that could control the concentrations of Ni and Co should at the same time reduce the amounts of Cu and Zn far below their observed values.

The possible alternative control by precipitation in sulfide-rich environments is not feasible for Ni, Co, V or W, but may account for removal of Cr. Not even sulfide is required for this element; any reducing environment capable of changing it to the tervalent form will cause its removal as the insoluble $Cr(OH)_3$.

The very efficient removal of V, Ni, Co, and W from sea water seems most plausibly explained by organic reactions. Admittedly this is an hypothesis justified principally by the failure of alternative hypotheses; yet there is some indirect evidence for such a mechanism, at least for V and Ni. These elements are usually the two that show greatest enrichment in organic sediments (e.g., Goldschmidt, Krejci-Graf, and Witte, 1948; Erickson, Myers, and Horr, 1954), and also are among those most strongly enriched in marine organisms (table 9). Cobalt is also prominent among the elements concentrated by organisms (table 9), but its enrichment in organic sediments is less marked and less consistent than that of V and Ni. Tungsten has been noted as present in marine organisms and in organic sediments, but nothing is known about its degree of enrichment in either; to ascribe its removal from the sea to organic agencies is accordingly a pure assumption.

In summary, adsorption provides the most satisfactory general explanation for the observed concentrations of rare metal ions in the sea. It must be supplemented with biologic processes to account for the low concentrations of V and Ni, and probably also for Co and W. The small figure for Cr is most plausibly explained by reduction in parts of the sea where organic matter accumulates. Local precipitation of sulfides cannot be ruled out as a contributing factor, but it is certainly not the major control.

CORRELATION WITH RARE ELEMENTS IN MARINE SEDIMENTS

The mechanism by which rare metal concentrations are controlled in the sea should be reflected both in the abundance and in the mode of occurrence of the metals in various marine sedimentary rocks. Unfortunately, neither the data of this report nor existing data on rare metal occurrences in sedimentary rocks (summarized in Krauskopf, 1955) are sufficiently accurate or complete to make correlations more than tentative.

Although sulfide precipitation is a possible means of limiting the concentrations of Ag, Cu, Pb, Zn, Cd, and Hg, sulfides of these metals are not common in sedimentary rocks nor are the metals notably concentrated in sedimentary pyrite. Even where the presence of rare-metal sulfides has been established in sediments, there is no assurance that the metals were originally deposited in this form. Hence evidence from sedimentary rocks does not support the hypothesis that insoluble sulfides are a controlling factor in the sea, but on the other hand offers no convincing disproof.

The adsorption experiments suggest that Cu, Zn, and Pb, which are strongly adsorbed by many different substances, should be widely distributed in minor amounts in marine sediments. Moderate concentrations of these elements might be expected in sediments deposited slowly, with little addition of coarse clastic material; large concentrations should be uncommon but might be associated with various kinds of adsorbents in places where the local supply of metals was abnormally great. These predictions accord well with experience. Mercury and cadmium might well be included in this group, but too little is known about their occurrence to test the prediction. Silver, little affected by most adsorbents but strongly held by organic matter, would be expected in large amounts in carbonaceous sediments, which again corresponds with observation. The strong adsorption of Co and Ni on the hydrated oxides of iron and manganese is a convenient explanation for the frequent presence of these elements in iron and manganese ores. The observed concentration of V in sedimentary iron oxides and of Mo in manganese oxides agrees with the adsorption experiments. Data on rare-metal concentrations in marine hydroxide and oxide sediments are so fragmentary, however, that a satisfactory check against the experimental work is not possible.

Apatite precipitated from sea water (table 8) is not an effective adsorbent for the metals considered in this study, with the exception of the three (Cu, Zn, Pb) which are strongly adsorbed by all the other adsorbents as well. Accordingly there is no reason to expect notable amounts of any of these metals to be found in phosphorites. In agreement with this prediction, analysis of existing data on phosphorites (Krauskopf, 1955) shows that most of the metals sometimes enriched in these rocks owe their presence to organic matter rather than to apatite, and that the few metals which are associated with apatite itself are not among those included in this study.

Black shales and asphalts often contain, in addition to silver, notable concentrations of V, Ni, Mo, and Pb, less commonly also Cu, Co, Zn, and Cr (also Au, As, and Sn, which are not under discussion here). The enrichment in V and Ni can be ascribed reasonably to their uptake in biologic reactions, as discussed in the preceding section. Cobalt can be explained in similar fashion, but less convincingly. Moderate enrichment of Pb, Zn, and Cu can be attributed to adsorption, if the carbonaceous sediments are assumed to represent unusually slow deposition; all three are also known to play specific roles in some organisms (Noddacks, 1939; Marks, 1938). Local extremely large concentrations of these elements (as in the Kupferschiefer and occasional beds in the Phosphoria formation) are difficult to explain without some abnormality of supply. The presence of Cr in organic sediments is expectable from the fact that no process is known which might limit the concentration of this element except reduction to the tervalent state in environments where carbonaceous material would be deposited. A good reason for the great enrichment of Mo in black shales and asphalts is difficult to find; it is not conspicuously adsorbed by organic material, and seems to show only modest enrichment in marine organisms (table 9). Despite the lack of confirmatory evidence, the enrichment of Mo is most plausibly ascribed to a biologic process.

It is worth emphasizing that four of the rare metals most characteristic of black shales and asphalts (V, Ni, Co, Mo) belong to the group which, according to the experiments, cannot possibly be controlled in sea water by precipitation of sulfides. The first three are also in the group for which adsorption is an inadequate explanation and are among the metals known to be greatly concentrated in some marine organisms. Such a combination of facts is difficult to explain without assuming that biologic processes play an important role in the enrichment of these metals in sedimentary rocks.

In summary, the conclusion from the experimental part of this work that adsorption processes are the most important controls of rare metal concentrations in the sea is in general agreement with available data on the distribution of elements in sedimentary rocks of marine origin. But neither the data on distribution nor the experimental results are sufficiently accurate and inclusive to make the test of hypothesis against observation wholly convincing.

SUMMARY

Factors controlling the concentrations of Cu, Zn, Cd, Hg, Pb, Ag, Bi, Cr, Mo, W, Ni, Co, and V in the sea were studied. The principal conclusions are as follows:

1. The concentrations are not controlled by the low solubility of compounds formed with the ions present in normal aerated sea water; in other words, sea water is far from saturated with any of these metals. This conclusion is suggested by calculations and confirmed by experiment.

2. Variations in the pH and temperature of sea water affect the solubilities of rare metal compounds locally, but in aerated sea water the variations are not sufficient to make solubilities an effective control of concentration. In other words, aerated sea water is unsaturated with respect to any of the thirteen metals even in places where the pH and temperature have extreme values.

3. In sea water containing H_2S (and therefore depleted in oxygen), Zn is reduced to a concentration similar to that in nature, and the amounts of Cu, Pb, Hg, Ag, and Cr (probably also Bi and Cd) become too small to measure by simple methods. Amounts of these metals in the sea, therefore, could be controlled at least in part by the precipitation of sulfides locally in reducing environments, provided that circulation of ocean water is sufficiently rapid. (Chromium is not precipitated as a sulfide but is reduced and precipitated as the hydroxide.) The concentrations of these metals, however, have no discernible relation to the solubilities of their sulfides, so that precipitation of sulfides is probably not a major controlling factor.

4. Sulfide precipitation cannot be a control for Co, Ni, Mo, W, or V. Even co-precipitation with FeS does not bring the concentration of these metals into the range found in sea water.

5. Adsorption is a possible control for all the metals except V, Co, Ni, W and Cr. Relative efficiencies of adsorption of the various metals are in rough agreement with observed rates of removal from the sea.

6. The metals V and Ni (possibly also Co, W and Mo) are probably controlled largely by organic reactions. The control of Cr is most reasonably ascribed to local reduction and precipitation as $Cr(OH)_3$.

7. Of the various common adsorbents in sea water, hydrated manganese dioxide appears to be most efficient (weight for weight), and hydrated ferric oxide next. The three metals, Cu, Zn, and Pb, are strongly adsorbed on all the adsorbents tried; other metals show marked differences in the effects of different adsorbents.

8. The occurrence of rare metals in marine sedimentary rocks is in rough agreement with predictions made from the hypothesis that metal concentrations in the sea are controlled chiefly by adsorption, supplemented by organic reactions and by precipitation in sulfide-rich environments.

These conclusions, established for 13 elements only, can probably be extended to other metals in the central part of the periodic system, i.e., to those elements which have a complete or nearly complete 18-electron shell in their atoms and only a few valence electrons outside this shell. To extend the conclusions to metals at the extremes of the system, such as Sr, Cs, Y, As, or Se, would be unwarranted.

Table 1. Effectiveness of removal of rare metals from the sea.

Metal	Calculated amount supplied to the sea during geologic time(ppm)	Concentration in sea water at present (ppm)	Percentage remaining in solution
Ag	0.06	0.00015-0.0003	0.25-0.5
Bi	0.12	0.0002	0.2
Mo	0.6-9	0.0003-0.0007 (0.012-0.016)	0.003-0.12 (0.1-2.7)
Cd	0.09	0.000032-0.000075	0.04-0.08
Pb	9.6	0.003-0.008	0.03-0.08
Hg	0.046-0.3	0.00003	0.01-0.07
Cu	42	0.001-0.015	0.002-0.04
Zn	79	0.005-0.021	0.006-0.03
W	0.9-41	0.00009-0.0001	0.0002-0.01
Co	14	0.0001	0.0007
Ni	48	0.0001-0.0005 (0.0015-0.006)	0.0002-0.001 (0.003-0.012)
V	90	0.0003 (0.0024-0.007)	0.0003 (0.003-0.008)
Cr	120	0.00004-0.00007 (0.001-0.0025)	0.00003-0.00006 (0.0008-0.002)

Data chiefly from Mason (1952) and Rankama and Sahama (1950). Data for Mo partly from Kuroda and Sandell (1954); for Cd from Mullin and Riley (1954); for W and Cr from Ishibashi (1953). Numbers in parenthesis for Mo, Ni, V, and Cr are spectrographic determinations by Black and Mitchell (1952); for these same four elements Ishibashi (1953) gives values between those of Mason and those of Black and Mitchell.

Table 2. Calculated concentrations of metal ions in saturated solutions.

Chief metal ion or ions	Insoluble compound	Solubility product	Factor	Calcd. concn. of metal in satd. soln. (ppm)
Zn^{++}, $ZnCl^{++}$, $Zn(OH)^{+}$?	$ZnCO_3$	2×10^{-10}	70	4.6
Cu^{++}, $CuCl^{+}$, $Cu(OH)^{+}$?	$CuCO_3$	2.5×10^{-10}	70	5.7
$PbCl^{+}$, Pb^{++}	$PbCO_3$	1.5×10^{-3}	70	0.01
BiO^{+}, BiOCl?, $BiCl_4^{-}$?	BiOCl	7×10^{-9}	2	0.006
$CdCl^{+}$, $CdCl_2$, $Cd(OH)^{+}$?	Cd(OH) Cl	3.2×10^{-11}	16	105
Ni^{++}?, $NiCl^{+}$?, $Ni(OH)^{+}$?	$Ni(OH)_2$	1.6×10^{-16}	16	150
Co^{++}, $CoCl^{+}$?, $Co(OH)^{+}$?	$CoCO_3$ $Co(OH)_3$	8×10^{-13}	70	0.02 0.01-0.08*
$HgCl_4^{--}$	HgO			high
$AgCl_2^{-}$	AgCl			0.5- 6
CrO_4^{--}	$CaCrO_4$?	7.1×10^{-4}	70	high
$H_2VO_4^{-}$, $H_3V_2O_7^{-}$	$V_2O_5 \cdot nH_2O$	5×10^{-4}	2	high
Mg^{++}	$MgCO_3 \cdot H_2O$	1×10^{-5}	70	84,000
Ca^{++}	$CaCO_3$	5×10^{-9}	70	70
Sr^{++}	$SrCO_3$	$3\text{-}16 \times 10^{-10}$	70	9 - 44
Ba^{++}	$BaSO_4$	1×10^{-10}	70	0.03

Table 2. Calculated concentrations of metal ions in saturated solutions--Continued.

In the first column, ? following a formula indicates that the ion is probably present, but quantitative data are lacking. An ion underlined is the most abundant species present.

Concentrations in the last column are calculated for sea water with $Cl^- = 0.55M$, $OH^- = 10^{-6}M$, $CO_3^{--} = 0.0002M$, $SO_4^{--} = 0.028M$, temperature 25° C and pressure 1 atmosphere.

Data on Ca, Sr, Ba, and Mg included for comparison purposes only.

Solubility product for Cd from Feitknecht and Reinman (1951), for V from Ducret (1951), for Sr from Wattenberg and Timmermann (1937); all others from Latimer (1952).

*Concentration of Co is 0.01 ppm for $pO_2 = 0.2$ atm. and 0.08 ppm for $pO_2 = 10^{-4}$ atm.

Table 3. Comparison of calculated and measured concentrations of metals in saturated solutions with observed concentrations in sea water.

Metal	Concentration in satd. soln.		Concn. in sea water(ppm)	Ratio of <u>measd. concn. to</u> concn. in sea
	Calculated(ppm)	Measured(ppm)		
Zn	4.6	1.2-2.5	0.005-0.021	60-500
Cu	5.7	0.4-0.8	0.001-0.015	30-800
Pb	0.01	0.3-0.7	0.003-0.008	25-200
Bi	0.006	0.04	0.0002	200
Cd	105	4 - 1000	$32 - 75 \times 10^{-6}$	$10^{5} - 10^{7}$
Ni	150	20-450	0.0001-0.0005 (0.0015-0.006)	$4\times10^{4} - 5\times10^{6}$ ($3\times10^{3} - 3\times10^{5}$)
Co	0.01-0.08	25-200	0.0001	$2.5\times10^{5} - 20\times10^{5}$
Hg	high	100 - 1000	0.00003	$3\times10^{6} - 30\times10^{6}$
Ag	0.5 - 6	2.0 - 2.5	0.00015-0.0003	$0.7\times10^{4} - 1.7\times10^{4}$
Cr	high	high	$4-7\times10^{-5}$ (0.001-0.0025)	$>10^{6}$ ($>10^{4}$)
Mo		25 - 750	0.0003-0.0007 (0.012-0.016)	$3.5\times10^{4} - 2.5\times10^{6}$ ($1.6\times10^{3} - 62\times10^{3}$)
W		2 - 200	0.0001	$2\times10^{4} - 2\times10^{6}$
V^{IV}	high	4 - 150	0.0003 (0.0024-0.007)	$>10^{4}$ ($>10^{3}$)
V^{V}	high	>400		$>10^{6}$
Mg	84,000	36,000	1272	0.035
Ca	70	100-480	400	0.8 - 4
Sr	9 - 44	22	13	0.6
Ba	0.03	0.11	0.05	0.5

Parentheses indicate data from Black and Mitchell (1952).
Data on Sr, Ba, Ca, and Mg from Wattenberg and Timmermann (1937).

Table 4. Averages of solubility measurements.

Under each metal the first row of figures shows (in parts per million) the concentration of metal remaining in solution after the compound indicated has been added to sea water until a precipitate forms. The second row shows the concentration of metal in solution obtained by adding some of the precipitate to a fresh sample of sea water. Times of standing were different in different runs, hence are given as ranges rather than specific numbers of days. Most of the numbers are averages from several runs. In all experiments pH = 7.8-8.2 and temperature = 18°-23°.

	1-20 hr	1-3 da	4-8 da	10-17 da	21-28 da	37-63 da
Zinc						
$ZnCl_2$		1.3	5(?)		2.5	2.5
Zn ppt		1.2	1.7		1.2	
Copper						
$CuSO_4$		0.59	0.76		0.75	
Cu ppt		0.87	0.61		0.65	
Lead						
$Pb(NO_3)_2$		0.33	0.29			
Pb ppt		0.4	0.67	0.71		0.53
Bismuth						
$Bi(NO_3)_3$	1.3	0.05	0.05			
Bi ppt	<0.02		0.03			
Cadmium						
$CdCl_2$		400			3000(?)	1000
Cd ppt		0.5			2.5	4
Nickel						
$NiCl_2$			405		455	
Ni ppt			35		23	
Cobalt						
$CoCl_2$			153	218	196	
Co ppt			33		26	28
Mercury						
$HgSO_4$			118			
Hg ppt	500				700	
HgO				1000		
Silver						
$AgNO_3$	2.0	2.2				
Ag ppt			2.5			

Table 4. Averages of solubility measurements--Continued.

	1-20 hr	1-3 da	4-8 da	10-17 da	21-28 da	37-63 da
c Chromium:	No ppt even after massive additions of K_2CrO_4.					
Molybdenum						
$(NH_4)_2MoO_4$	1950	1000	750			
Mo ppt		32		25		
MoO_3	1800	1200		1000		
Tungsten						
Na_2WO_4		400		280		
W ppt		<1		2		
WO_3		43		160		
Vanadium						
V^{+4} ppt				4.3	3.9	

If $VOSO_4$ is added slowly to sea water, a precipitate forms when about 16 ppm of V is present, but the precipitate appears to dissolve on standing over a period of hours. A permanent precipitate forms only after enough has been added to give more than 150 ppm of V in solution. Quinquevalent vanadium gives no precipitate even after massive additions.

Table 5. Equilibrium concentrations of copper as a function of temperature and pH.

Solutions allowed to stand one day in contact with copper precipitate. Solutions with different pH's kept in tightly corked flasks; frequent adjustments of pH necessary because of exchange of CO_2 with the atmosphere at pH's different from 8

	pH = 7	pH = 8	pH = 9	pH = 10
0°C		1.1 ppm		0.03 ppm
18-20°	2.5 ppm	0.65	0.17 ppm	0.03 ppm
ca. 55°		0.15		

Table 6. Calculated and measured concentrations of metals in equilibrium with HS^- and S^{--}.

Metal	Concn. in equilibrium with HS^- and S^{--}		Concentration in sea water
	Calculated	Measured	
Zn	0.02 ppm.	0.008-0.07 ppm.	0.005-0.021 ppm.
Cu	7×10^{-14}	<0.003	0.001-0.015
Pb	0.0006	<0.02	0.003-0.008
Bi	6×10^{-18}	n.d.	0.0002
Cd	0.0002	n.d.	$32 - 75 \times 10^{-6}$
Ni	0.002	0.06-0.2	0.0001-0.0005 (0.0015-0.006)
Co	0.003	0.02-0.6	0.0001
Hg	2×10^{-29}	<0.005	0.00003
Ag	3×10^{-11}	<0.006	0.00015-0.0003
Cr	10^{-34}?	<0.004	$4 - 7 \times 10^{-5}$ (0.001-0.0025)
Mo	0.002 ?	6	0.0003-0.0007 (0.012-0.016)
W	no data	large	0.0001
*V	0.03	1	0.0003 (0.0024-0.007)

Parentheses indicate data from Black and Mitchell (1952).
Calculated concentrations for Cr and Mo based on free energy data from Latimer (1952); for V on data from Ducret (1951) and Garrels (1953); others on solubility products of the sulfides in Kolthoff and Sandell (1952), p. 68.

Concentration of H_2S about 0.005M; pH ca. 7; temperature 18°-23°.

*H_2S was added to solutions of both quadrivalent and quinquevalent vanadium. The resulting brownish-black precipitate appeared to be the same in each. Whether it is V_2S_3, VS_2 or a mixture (possibly with V_2S_5 also for V^V) is uncertain. The equilibrium concentration of V in the solution was 1.0 ppm for V^{IV} and 1.3 ppm for V^V.

Table 7. Adsorption experiments Temperature 18°-23°, pH 7.7-8.2.

Adsorbent	Concn. of adsorbent (gm./liter)	Volume of sol'n (ml.)	Time (days)	Concn. of adsorbate		Per cent adsorbent
				Initial (ppm.)	Final (ppm.)	
Zinc						
$Fe_2O_3 \cdot nH_2O$	0.03	25	1	2.0	0.1	95*
	0.03	25	8	2.0	0.15	93
Apatite	0.1	25	1	2.0	0.28	86*
	0.5	20	1	2.0	0.03	99
Clay	20	50	3	2.0	0.02	99*
Plankton	dilute	40	2	0.99	0.59	40*
	concd.	40	2	0.50	0.26	48*
Peat Moss	20	50	3	2.0	0.01	99*
Copper						
$Fe_2O_3 \cdot nH_2O$	0.03	25	2	0.65	0.014	98
	0.03	25	13	0.65	0.024	96
	0.03	25	14	0.65	0.025	96*
$MnO_2 \cdot nH_2O$	0.1	50	7	0.65	0.028	96*
Apatite	0.1	25	1	0.65	0.25	62
	0.1	25	6	0.65	0.15	77*
	0.5	20	1	0.65	0.015	98
Clay	15	20	1	0.65	0.07	89
	15	20	2	0.65	0.04	94*
Plankton	dilute	40	4	0.65	0.38	42
	concd.	40	6	0.65	0.30	54*
Lead						
$Fe_2O_3 \cdot nH_2O$	0.03	25	2	0.5	0.07	86*
Apatite	0.1	25	1	0.5	0.05	90
	0.1	25	6	0.5	0.02	96*
Clay	20	50	3	0.5	<0.02	>96*
Peat moss	20	50	3	0.5	<0.02	>96*

Table 7. Adsorption experiments Temperature 18°-23°, pH 7.7-8.2--Continued.

Adsorbent	Concn. of adsorbent (gm./liter)	Volume of sol'n (ml.)	Time (days)	Concn. of adsorbate Initial (ppm.)	Final (ppm.)	Per cent adsorbed
Nickel						
$Fe_2O_3 \cdot nH_2O$	0.03	25	1	2.0	1.5	25
	0.03	25	9	2.0	1.35	33*
	0.3	50	2	1.92	0.12	94*
	0.3	50	2	0.49	0.033	93
	0.3	50	2	0.095	c. 0.01	c. 90
$MnO_2 \cdot nH_2O$	0.1	50	6	1.95	0.01	99*
	0.1	50	6	0.5	c. 0.002	c. 99
Apatite	0.1	25	2	2.0	1.9	5
	0.1	25	6	2.0	1.85	8*
	0.5	20	1	2.0	1.35	33
	0.7	50	2	0.19	0.06	69*
	0.7	50	7	0.19	0.06	69
Clay	12	25	2	2.0	1.8	10*
Plankton	dilute	40	8	1.95	c. 1.8	c. 8
	dilute	40	14	1.95	1.8	8*
Cobalt						
$Fe_2O_3 \cdot nH_2O$	0.3	50	3	1.92	0.22	89
	0.3	50	3	0.49	0.055	91*
	0.3	50	3	0.1	c. 0.01	c. 90
	0.03	50	3	1.92	1.25	35*
	0.03	50	3	0.49	0.27	45
	0.03	50	3	0.1	0.035	65
	0.003	50	3	0.1	0.07	30
	0.03	25	1	2.0	1.4	30
	0.03	25	9	2.0	1.6?	20?
$MnO_2 \cdot nH_2O$	0.1	50	5	1.95	0.13	93*
	0.1	50	5	0.5	0.031	94*
Apatite	0.1	25	2	2.0	1.7	15*
	0.5	20	1	2.0	0.8	60
	0.7	50	9	0.19	0.035	82*
Clay	12	25	2	2.0	1.65	18*
Plankton	dilute	40	3	1.95	1.6	18
	dilute	40	15	1.95	1.8	8*

Table 7. Adsorption experiments Temperature 18°-23°, pH 7.7-8.2--Continued.

Adsorbent	Concn. of adsorbent (gm./liter)	Volume of sol'n (ml.)	Time (days)	Concn. of adsorbate		Per cent adsorbed
				Initial (ppm.)	Final (ppm.)	
Mercury						
$Fe_2O_3 \cdot nH_2O$	0.3	50	3	1.9	1.7	10
	0.3	50	9	1.9	1.9	<5
	0.3	50	12	1.9	1.9	<5
	0.3	50	16	1.9	1.5	20
	0.3	50	9	0.2	0.18	10
	0.3	50	12	0.2	0.1	50
	0.3	50	16	0.2	0.06	70
	0.03	50	3	1.95	1.85	5
	0.03	50	9	1.95	1.95	<5
	0.03	50	12	1.95	2.1	<5
	0.03	50	16	1.95	0.9	50*
	0.03	50	2	0.2	0.19	5
	0.03	50	6	0.2	0.02	90
	0.03	50	9	0.2	<0.04	>80
	0.03	50	12	0.2	<0.01	>95*
Apatite	0.5	50	3	1.9	1.9	< 5
	0.5	50	9	1.9	2.0	< 5*
	0.5	50	9	0.2	0.15	25*
Clay	7	50	3	1.95	1.8	8
	7	50	9	1.95	0.08	96*
	7	50	9	0.2	<0.02	>90
	20	50	3	2.0	1.2	40
	20	50	25	2.0	0.2	90
Plankton	dilute	40	3	2.4	0.08	98*
Peat Moss	20	50	4	4	0.05	99*
Silver						
$Fe_2O_3 \cdot nH_2O$	0.3	50	3	1.92	1.50	22*
	0.3	50	3	0.59	0.50	15
	0.3	50	3	0.20	0.16	20*
	0.03	25	2	2.2	1.2	45?
	0.03	25	13	2.2	1.3	41?
$MnO_2 \cdot nH_2O$	0.1	50	7	0.5	0.46	8*
Apatite	0.1	25	1	2.0	1.1	45?
	0.1	25	6	2.0	1.55	23*
	0.5	20	1	2.0	1.3	35
	0.7	50	2	0.48	0.45	6*

Table 7. Adsorption experiments Temperature 18°-23°, pH 7.7-8.2--Continued.

Adsorbent	Concn. of adsorbent (gm./liter)	Volume of sol'n (ml.)	Time (days)	Concn. of adsorbate		Per cent adsorbed
				Initial (ppm.)	Final (ppm.)	
Clay	20	50	4	1.0	0.8	20*
Plankton	dilute	40	8	1.95	1.00	49*
	concd.	40	2	0.49	0.02	96*
Peat moss	20	50	4	1.0	0.46	54*
Chromium						
$Fe_2O_3 \cdot nH_2O$	0.3	50	2	1.94	1.71	12*
	0.3	50	2	0.49	0.38	22
	0.3	50	2	0.095	0.050	47
	0.3	50	9	1.94	1.75	10*
	0.3	50	9	0.49	0.38	16
	0.3	50	9	0.095	0.048	49*
	0.04	20	2	10	c. 7	c. 30?
	1.0	15	1	10	c. 6	c. 40?
$MnO_2 \cdot nH_2O$	0.1	50	4	1.75	0.13	94*†
	0.1	50	4	0.5	0.05	90
	0.1	50	8	0.5	0.055	89
Apatite	0.1	25	2	4	3.5	12*
	0.1	25	6	4	3.5	12
	0.5	20	2	4	3.4	15
Clay	12	25	3	4	3.7	8
Plankton	dilute	40	7	1.95	1.71	12
	dilute	40	14	1.95	1.75	10*
Molybdenum						
$Fe_2O_3 \cdot nH_2O$	0.3	50	2	4.7	2.9	38
	0.3	50	2	1.45	0.66	54
	0.3	50	2	0.39	0.16	59
	0.3	50	7	4.7	3.0	36
	0.3	50	7	1.45	0.8	45
	0.3	50	7	0.39	0.17	56*
	0.03	25	2	4	3	25*
	0.03	25	12	4	4	< 5?
	1.0	15	1	1.0	0.35	65?

Table 7. Adsorption experiments Temperature 18°-23°, pH 7.7-8.2--Continued.

Adsorbent	Concn. of adsorbent (gm./liter)	Volume of sol'n (ml.)	Time (days)	Concn. of adsorbate		Per cent adsorbed
				Initial (ppm)	Final (ppm)	
$MnO_2 \cdot nH_2O$	0.1	50	3	1.95	1.7	13
	0.1	50	3	0.5	0.45	10
	0.1	50	8	1.95	1.7	13
	0.1	50	8	0.5	0.13	74?*
	0.02	50	1	4	2	50*
	0.2	50	1	1.0	0.2	80?†
Apatite	0.1	25	2	4	3.6	10*
	0.5	20	2	4	3.2	20
Clay	20	50	4	2	1.3	35*
	20	50	4	8	6	25
Plankton	dilute	40	4	1.95	1.65	15*
Peat moss	20	50	4	8	c. 3.8	c. 53*
Tungsten						
$Fe_2O_3 \cdot nH_2O$	0.03	25	2	8	1.6	80*
	0.03	25	9	8	1.8	78
	0.03	25	12	8	1.1	86
$MnO_2 \cdot nH_2O$	0.02	25	2	4	0.05	99*
Apatite	0.1	25	2	4	4	< 2
	0.5	20	2	4	3.8	5*
Plankton	dilute	40	7	1.95	c. 1.8	c. 8*
Vanadium^{IV}						
$Fe_2O_3 \cdot nH_2O$	0.03	25	2	2.6	0.2	92
	0.03	25	9	2.6	0.1	>96*
Apatite	0.1	25	2	2.6	2.5	4
	0.5	20	1	2.6	2.1	19*
Clay	12	25	2	2.6	1.9	27*
Plankton	dilute	40	6	2.5	2.1	16*
	dilute	40	17	2.5	2.2	12

Table 7. Adsorption experiments Temperature 18°-23°, pH 7.7-8.2—**Continued**

Adsorbent	Concn. of adsorbant (gm./liter)	Volume of sol'n (ml.)	Time (days)	Concn. of adsorbate Initial (ppm.)	Concn. of adsorbate Final (ppm.)	Per cent adsorbed
<u>Vanadium</u>^{V}						
$Fe_2O_3 \cdot nH_2O$	0.03	25	1	4	0.8	80
	0.03	25	5	4	0.2	95*
$MnO_2:nH_2O$	0.1	50	7	0.5	0.3	40*
	0.03	50	4	4	3.1	23*
Apatite	0.1	25	2	4	3.3	17*
	0.1	25	6	4	3.8	5
	0.5	20	1	4	2.8	30*
Clay	12	25	2	4	2.7	33*
Plankton	dilute	40	6	1.93	1.78	8?
	dilute	40	17	1.93	2.0	<3*
	dilute	40	11	0.81	0.85	<3

Notes on table 7: Asterisks designate numbers repeated in table 8. Question marks indicate values which seem markedly inconsistent with other data; some of these are older results obtained before the analytical methods had been fully explored. Daggers indicate two runs in which the pH dropped to 7.3 before the analysis was made.

Table 8. Summary of results of adsorption experiments,

Concentration of adsorbate: 0.6-2.5 ppm for first seven elements, 2-10 ppm for last five. A second number in parentheses is the per cent adsorption for lower concentrations of adsorbate, in the range 0.1-0.7 ppm.

Concentrations of adsorbent: for Fe_2O_3, MnO_2, and apatite, 0.02-0.1 gram/liter, except for underlined figures which have 0.3-0.7 gram/liter; for clay and peat moss, 7-20 gram/liter; for plankton, not measured.

All values are given as per cent of metal adsorbed. Figures are the same as figures marked with an asterisk in table 7.

Temperature 18°-23°, pH 7.7-8.2

Metal	Hydrated Fe_2O_3	Hydrated MnO_2	Apatite	Clay	Plankton	Peat moss
Zn	95		86	99	40 (48)	99
Cu	96	96	77	94	54	
Pb	86		96	>96		>96
Ni	33 (94)	99	8 ($\underline{69}$)	10	8	
Co	35 (91)	93 (94)	15 ($\underline{82}$)	18	8	
Hg	50 (>95)		<$\underline{5}$ ($\underline{25}$)	96	98	99
Ag	$\underline{22}$ ($\underline{20}$)	(8)	23 ($\underline{6}$)	20	49 (96)	54
Cr	$\underline{10}$ ($\underline{49}$)	94	12	8	10	
Mo	25 ($\underline{56}$)	50 (74?)	10	35	15	53?
W	80	99	$\underline{5}$		c. 8	
V^{IV}	>96		$\underline{19}$	27	16	
V^{V}	95	23 (40)	17	33	<3	

Table 9.--Representative data on concentrations of rare metals in marine organisms

Metal	Enrichment factor for brown algae, fresh weight (data of Black and Mitchell, 1952)	Same, using Noddacks' values (1939) for concentrations in sea water	Average enrichment factor for 9 marine animals, dry weight (data of I. and W. Noddack, 1939)	Same, using Black and Mitchell's values (1952) for concentrations in sea water
Ni	200-1,000	1,600-8,000	41,000	5,000
V	10-300	>160-5,000	>280,000	17,000
Zn	400-1,400	400-1,400	32,500	32,500
Mo	2-15	60-420	6,000	200
Cr	100-500	3,000-15,000[α]	>1,400	200
Co	(>4,500)	(13,000)	21,000	>7,000
Ag	(10->150)	(600)	22,000	1,000->7,000
Pb	(>410)	(410)	2,600	2,600[β]
Cu		(410)	7,500	2,600[β]
Cd			>4,500	27,000-67,000[γ]
Bi			1,000	1,000[β]

[α] Calculated from concentration in sea water given by Ishibashi (1953).

[β] Calculated from concentration in sea water given by Mason (1952).

[γ] Calculated from concentration in sea water given by Mullin and Riley (1954).

Numbers in parentheses are not given explicitly by Black and Mitchell (1952), but are estimated from their data.

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