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The Trace Element Geochemistry of Marine Biogenic Particulate Matter

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ABSTRACT - Plankton samples have been carefully collected from a variety of marine environments for major and trace-chemical analysis. The samples were collected and handled under the rigorous conditions necessary to prevent contamination of the trace elements. Immediately after collection, the samples were subjected to a series of physical and chemical leaching-decomposition experiments designed to identify the major and trace element composition of the biogenic particulate matter. Emphasis was placed on the determination of the trace element/major element ratios in the various biogenic phases important in biogeochemical cycling.

The majority of the trace elements in the samples were directly associated with the non-skeletal organic phases of the plankton. These associations include a very labile fraction which was rapidly released into seawater immediately after collection and a more refractory component which involved specific metal-organic binding. Calcium carbonate and opal were not significant carriers for any of the trace elements studied. A refractory phase containing aluminum and iron in terrigenous ratios was present in all samples, even from remote pelagic environments. This non-biogenic carrier contributed insignificant amounts to the other trace elements studied.

The plankton samples were collected from surface waters with a wide range in the dissolved trace element/nutrient ratios, however, the same elemental ratios in the bulk plankton samples were relatively constant in all these environments. The bulk compositions and the rapid release of the metals and nutrient elements (specifically phosphorus) from the plankton after collection were used to examine the systematics of depletions of the dissolved elements from surface waters. These elemental ratios were combined with known fluxes of the major biogenic materials to estimate the significance of the plankton in the vertical flux of the trace elements. In parallel with the major surface ocean cycles of carbon and nitrogen, significant fractions of the trace elements taken up by primary producers must be rapidly regenerated in order to explain the observed elemental compositions and fluxes.

CONTENTS

1. INTRODUCTION

The importance of marine organisms in the geochemical cycles of many elements has been recognized since the earliest work in marine chemistry. This observation has been extended, over the past decade, to include the cycles of trace elements. With the development of improved sampling and analytical techniques it has been demonstrated that many trace elements show large concentration variations in both vertical profile and areal distribution which often parallel those of the major nutrient elements involved in biological processes. These gradients are driven by the production, transport, and remineralization of particulate organic matter. The dissolved distributions in the water column and the accumulation of trace elements in the sediments are only the indirect expression of these organic processes. The direct examination of the composition of the plankton which will be discussed in this paper was made in an attempt to quantify the fluxes that drive these trace element distributions.

Most published chemical analyses of plankton and other marine particulate matter have been performed on bulk samples and include the major *or* minor element composition -- rarely both. Very few of these investigations demonstrated that the minor elements were quantitatively recovered and not contaminated during sampling or analysis. Experience gained in the collection of water samples for dissolved trace element analysis suggests that it is very likely that many of the reported plankton analyses are seriously contaminated. This fact, when considered with other sampling and analytical problems discussed below, gives one very little confidence in using currently reported plankton data in trace element geochemical models. Notable exceptions include analyses by MARTIN and KNAUER (1973) who made serious attempts to address the problem of contamination; and MARTIN, BRULAND and BROENKOW (1976), who published the only set of high-quality *bulk* plankton analyses which include major components (P, Si, Ca) along with the trace elements.

There is a large amount of data and a relatively detailed understanding of the processes controlling the flux of major biologically cycled elements. The intention here is to understand and quantify the trace element cycles by extending those of the major elements. This will be accomplished through the careful examination of the minor/major element ratios and chemical relationships between the trace elements and their biogenic carrier phases.

Numerous carrier phases and types of associations are possible between trace elements and marine particulate matter. These derive from: terrigenous material scavenged by biogenic particles; specific biochemical functions associated with metabolic processes; inclusion within structural-skeletal materials such as calcite, opal, or celestite; and scavenging processes at active surfaces such as hydrous metal-oxide precipitates or organics. Here we examine the significance of these different "carriers" in open-ocean surface plankton samples. The correlations between plankton compositions and the carrier ratios found in the water column and sediments will be linked to the known processes and fluxes determining the major element cycles.

There is a serious need for quantitative estimates of the role of organisms in determining the distributions and fluxes of trace elements in the oceans and sediments. The experiments reported here were directed at this problem and were not designed to examine specific trace element functions in the physiology or ecology of marine plankton. The complex biochemical and nutritional relationships between organisms and trace elements still need to be studied under simplified and controlled laboratory conditions; the geochemical problem is best approached through actual measurements in the field.

We present a comprehensive set of chemical analyses on a variety of plankton samples. The samples were collected from the upper 50 meters at 3 sites: the Antarctic Circumpolar Current (R/V Atlantis II, 93-04, January, 1976); the Eastern Equatorial Pacific ("Galapagos samples", R/V Melville, Pleiades II, July, 1976; R/V Knorr, K64-02, March, 1977); the Central Tropical Pacific ("MANOP samples", R/V Knorr, K79-05, May, 1979). The chemical analyses include major element compositions as well as the concentrations of trace elements. The specific trace elements were selected either because their dissolved distributions have been determined or because of anticipated relationships to particulate carriers. Immediately after collection, the samples were split for total concentration determinations and were subjected to a series of chemical leaching experiments designed to separate carrier phases and associated trace elements. Two demands were imposed on the design of all experiments: the minimization of every possibility of trace element contamination and the prevention of excessive dilution of the trace element signals in the leaching solutions. To satisfy the goal of relating the major and minor element cycles, within these necessary experimental constraints, numerous trade-offs were made between increasing the experimental complexity and decreasing the handling and splitting of the samples.

2. ANALYTICAL TECHNIQUES

Over the past five years there has been a rapid expansion of interest in trace element geochemistry. Along with this there has developed an increasing awareness of the problems of sample contamination during collection, handling, and analysis. Many of these problems have been exhaustively detailed in recent publications of high-quality trace element analyses. (BOYLE, 1976; BOYLE, SCLATER and EDMOND, 1977; SCHAULE and PATTERSON, 1978; KLINKHAMMER and BENDER, 1980; BRULAND, FRANKS, MARTIN and KNAUER, 1979). Specific methods which are uniquely important to this research will be covered in detail but it should be noted that every step in the preparation, collection, storage, and analysis of these samples has been executed with "continuous contamination consciousness".

Seawater Samples. Seawater samples used in this research include hand collected surface samples and hydrocast subsamples. The surface samples were collected in two ways: from the main research vessel and from a non-metallic raft positioned well away from the ship. In the first procedure, water was collected directly into a hot-acid-leached linear polyethylene storage bottle mounted on an all-plastic holder and lowered on a polypropylene line from the bow of a forward-moving vessel. The second procedure involved the filling of the storage bottle by hand from a Zodiac rubber raft located at least several hundred meters upwind (upstream) of the main research vessel. The hydrocasts from the Galapagos and MANOP cruises were taken with new, carefully cleaned 30-liter Niskin bottles with silicon rubber O-rings and new PVC-coated internal springs or with external butterfly-valve closures. Upon return to the ship's laboratory, the samples were moved to a filtered-air laminar-flow work station, acidified to pH 2 with Vycor-distilled 6N HCl, and stored until analysis. Thus the trace metals determined represent the total dissolvable fraction.

All nutrient concentrations were determined by standard analytical techniques outlined in RILEY (1975). Specifically, on the Antarctic and MANOP samples, the PO_4, NO_3 and Si were determined colorimetrically using modifications of methods of MURPHY and RILEY (1962), GARDNER, WYNNE and DUNSTAN (1976), and MULLIN and RILEY (1955). The nutrient chemistry at the Galapagos site was determined by colorimetric methods on a Technicon AutoAnalyser.

Determinations for Cu, Ni, and Cd in seawater were carried out by the method of BOYLE, HUESTED and JONES (1981). The metals were coprecipitated with cobaltpyrollidine dithiocarbamate from 35 ml of seawater in teflon centrifuge tubes. The precipitates were spun down, washed, digested with 6N HNO_3, and redissolved in 0.1 N HNO_3. Each sample was completely processed in a laminar-flow work station within a single centrifuge tube. The concentrated solutions were then analyzed by flameless AAS with recoveries determined by standard additions and cobalt analyses.

Plankton Samples. Collection of uncontaminated particulate matter at sea is one of the most demanding sampling tasks. No method has been devised that will provide both freedom from contamination and large quantities of sample - certain compromises have to be made. The generally low concentrations of plankton in open ocean surface water and the trace concentrations of the elements studied make it necessary to sample all of the particulate matter within a very large volume of water. This takes a fairly long time, throughout which the sample may be exposed to contamination. Therefore, the water sampled must never have been in contact with any significant source of contamination (e.g., the sampler or the research vessel). All towing equipment must be constructed of non-contaminating materials, and its handling must be equivalent to that demanded by other trace-element procedures.

Throughout this research, one set of identical plankton nets was used (Fig. 1a). These were conical, 3:1 in length-to-width ratio, with a 0.5 meter diameter mouth, and made of 44 µm Nitex nylon. The plankton were concentrated into two in-line, 1000 and 44 µm Nitex bags contained in a PVC cod end, which was tied into the end of the net with a nylon cord (Fig. 1b). The mouth ring was epoxy-coated brass and was sewn completely inside of the leading seam of the net. The net harness and all fittings were of nylon and were eye-spliced around the mouth ring. The tow line was polyproplene and was taken up on a PVC drum through nylon and PVC blocks and rigging. A 2-gallon polyethylene jug was filled with scrap lead, tightly closed and sealed in plastic, and was tied to the end of a polypropylene line as a towing weight. The net and towline were carefully cleaned before going to sea and were further cleaned before and after each use on station by towing through the surface seawater without the cod end installed.

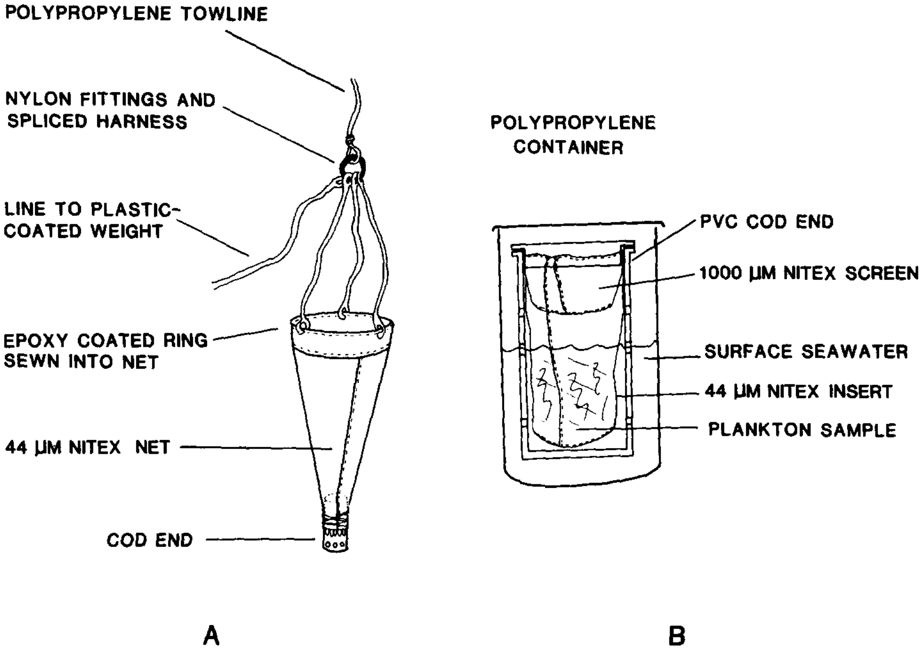


Fig. 1. Plankton sampling equipment: a) Net; b) Cod end.

Three basic towing configurations were used. Most samples (all Galapagos and most MANOP) were collected by manual vertical tows from an inflated rubber raft (Zodiac), which was moved at least several hundred meters away from the main research vessel. A motor was used to get away from the ship but was removed and stored before any of the towing equipment was set up (Fig. 2a). The complete tow was accomplished while drifting well upwind (upstream) of the ship. The net and weight were allowed to free-fall to approximately the base of the mixed layer (40-75 meters at these sites). They were then raised as rapidly as possible with the PVC hand-winch to within 5 meters of the surface, then immediately dropped back down. This raising and lowering procedure was repeated until enough sample had been collected - usually 2 to 3 hours, 30-50 lowerings - or until the operators had "expired". The procedure sampled a maximum of about 400 m^3 of seawater (not accounting for net clogging) and provided a sample of two to ten grams dry weight from productive surface waters.

The hand-towing method, although preferable to normal ship tows in eliminating possible sources of contamination, was severely limited by wind and sea-state, and by the low concentrations of plankton found in the surface waters of oligotrophic environments. Therefore some plankton tows were collected from the main research vessel. The utmost care was taken in setting up a system that would minimize the likelihood of contamination. In the Antarctic and at two of the MANOP stations the towing rig used in the Zodiac was set up with a long boom which extended away from the ship over waters which were undisturbed by the ship in its direction of travel (Fig. 2b). Airborne contamination within the ship's environment can be severe (FERGUSON, GRIFFIN and GOLDBERG, 1970) so the net was carefully protected before and after each deployment. The tows from the ship were done at 2 knots for 30 to 75 minutes at a depth of about 5 meters with a much heavier weight to limit aft-trailing of the net. The maximum volume of water sampled was 700 m^3 per hour at this towing speed. In the case where a comparison could be made between the Zodiac and ship tow (MANOP S, tow 3 (hand)

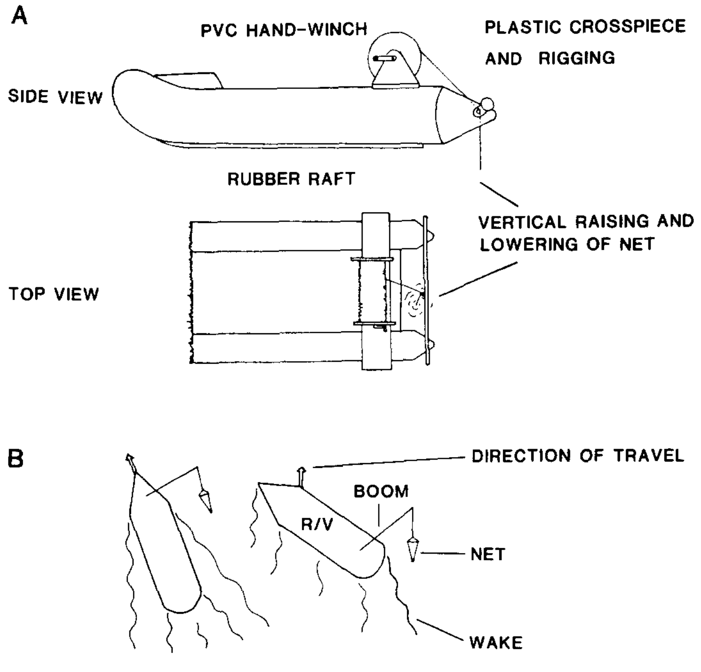


Fig. 2. Plankton towing rigs and procedures: a) Zodiac rigging; b) Ship and boom rigging

and 6 (ship), Table 7) the elemental compositions of the two samples from the same site gave no indication of any contamination due to the ship. All of the Antarctic tows were collected from the main research vessel and represent some of the lowest total metal concentrations ever reported for plankton (Table 7).

The cod end was cleaned before each use and loaded into a polyethylene container in the laminar flow hood. Immediately before deployment, the cup was carefully tied into the cleaned net. At the end of the tow, as the net was brought to the surface, it was closed off and the cod end was untied and placed in the polypropylene container with clean, freshly sampled surface seawater. The sample container was kept cool in iced water and in the dark during return to the ship for processing. There the sample was transferred from the Nitex cod-end liner to a wide-mouth polyethylene bottle in the cleanhood and stored for short periods of time in a dark refrigerator pending processing.

Sample splitting and processing. A critical step in these experiments was the subsampling of the plankton-seawater suspension. Plankton splitters were considered, and a rotating, quartered cylinder splitter was constructed out of lucite (HONJO, 1978). It was found, however, that the plankton samples were too small (<50 ml wet volume) for efficient use of this splitter, especially on a rolling ship. Also, too much handling and washing with seawater were required to effect quantitative transfer. Therefore the suspension was rendered as homogeneous as possible by a swirling agitation and then subsampled in 5 ml aliquots with an automatic pipet using wide, straight-sided polyethylene tips. Replicate analyses indicated that this method of splitting was sufficiently precise (± 10%) when compared to the uncertainties of the rest of the analyses.

Outlines of the general shipboard procedures and experiments are given in Figs. 3 and 4. For each net tow, a set of splits was immediately collected to represent the total composition of the untreated plankton. These subsamples were collected by filtration on 0.4 or 1.0 µm Nuclepore filters and by centrifugation. All filtrates and supernates were saved for analysis. The apparatus and procedures used for filtration and centrifugation are shown in Fig. 5. The filters were not washed, so they contained some volume of the seawater that the plankton were suspended in. They were placed on a teflon sheet and dried at 60°C under a clean-air environment.

A subsample of the plankton suspension was taken and preserved in buffered 7% formaldehyde for microscopic examinations. These formalin-preserved samples and some dried filter material were examined by light microscope to estimate the types and relative numbers and volumes of various organisms in each sample. The rest of the subsamples were resuspended in leaching solutions designed to selectively solubilize the particulate samples. The specific reagents and solutions used in these leaches are listed in Table 1 along with the purification procedures used to reduce contamination. The general procedure in the leaching-centrifugation experiments was as follows:

a) The splits of the seawater-plankton suspension were placed directly into 50 ml teflon centrifuge tubes and were spun down in an IEC clinical centrifuge at approximately 1700 rpm for 10 minutes.

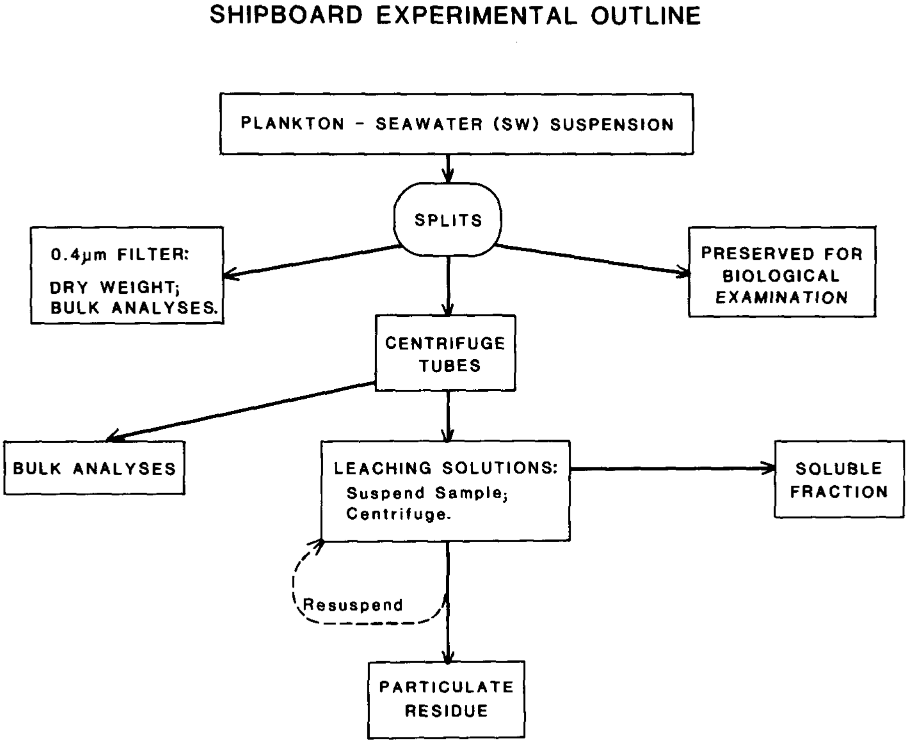


Fig. 3. General outline of shipboard experimental procedures.

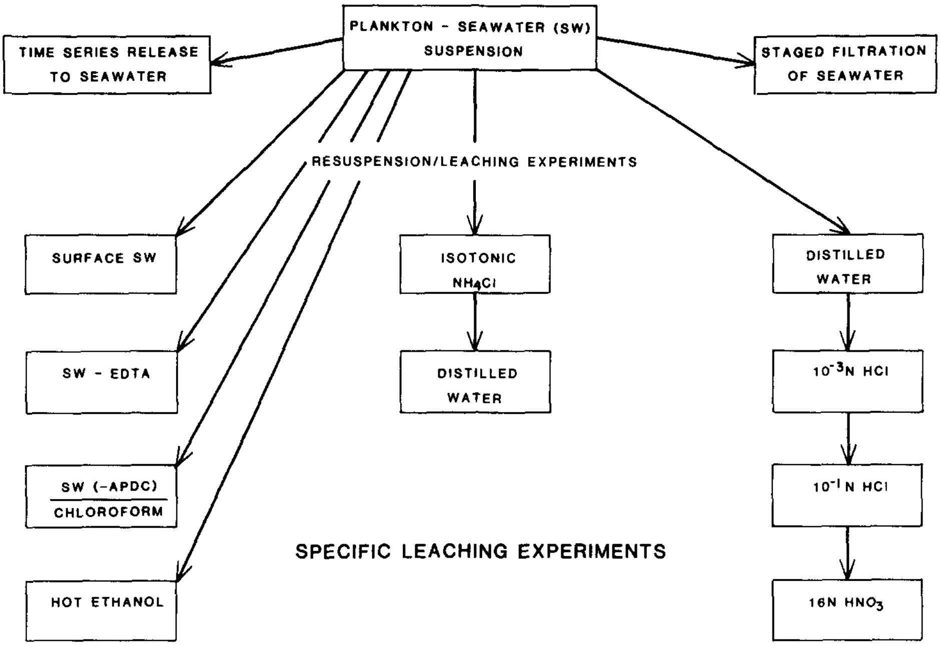


Fig. 4. Outline of specific leaching experiments.

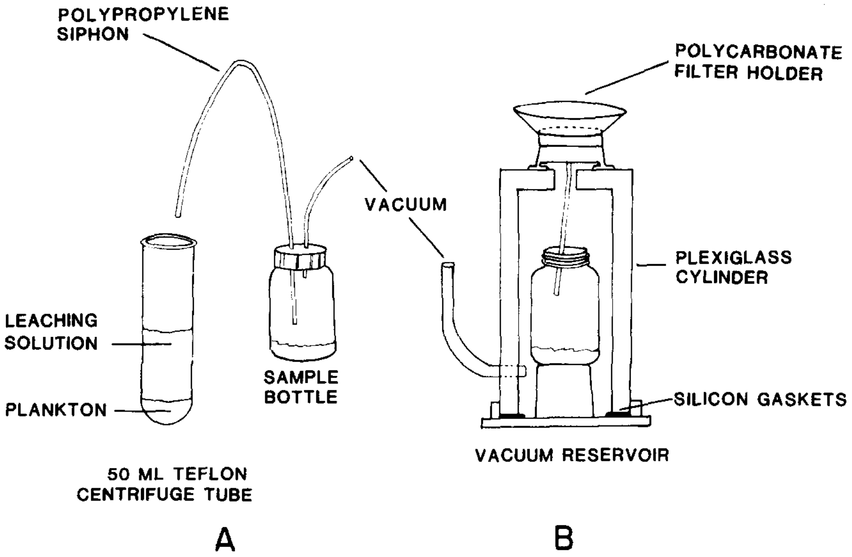


Fig. 5. Sample processing apparatus: a) Aspiration and supernate collection from centrifuged samples; b) Filtration of plankton suspensions.

TABLE 1. Chemical Reagents Used in Leaching and Analysis

Solution or reagent	
Surface Seawater	Hand collected at the time and site of the plankton tow. This water is analyzed for nutrients and trace elements and these values represent the baseline levels in seawater release experiments.
Distilled water	Distilled in the lab and transported to sea in polyethylene containers. Processing involves boiling distillation, deionization, followed by another quartz-glass distillation. Blanks were usually below detection and were never significant to these analyses.
Ammonium chloride	Synthesized from 6N HCl (Vycor distilled) which was bubbled with clean NH_3 to a pH of 5.5. The resulting solution was desiccated and the collected crystals dried at 105°C. Solutions were made 0.56 N (iso-osmotic with seawater-34.8%) and pH adjusted to 8 with NH_3.
Ethanol, chloroform	Reagent grade solvents, redistilled 2X in Vycor glass and stored in teflon.
HCl (6N)	Distilled 2X in Vycor.
HNO_3 (16N)	Reagent grade acid distilled 3X in Vycor.
HF	Baker Ultrex.
H_2O_2 (30%)	Baker Ultrex.
$HClO_4$ (70%)	GFS Co., 2X distilled from Vycor glass.
APDC	Reagent grade prepared to 2% w/w in H_2O. Solution purified by repeated extraction with chloroform.
EDTA	Aldrich Chemical, Gold Label.
Ascorbic acid	Grand Isl. Biol. Co.

b) The supernate solution was carefully removed from the top of the sample using a cleaned vacuum aspiration device (Fig. 5) which collected the solution directly in a clean storage bottle.

c) The sample was then suspended in a leaching solution, gently agitated for 5 minutes, and re-centrifuged for 5 minutes.

d) The leaching solution was aspirated from the sample tube, and the leaching process was repeated a total of three times for each solution.

The three supernates were generally combined to represent the total material leached by that solution. A typical volume of leachate was 15 ml per step (total of 45 ml over three steps), and the carry-over of solution between centrifugation steps was approximately 2-3 ml. All procedures, except for the actual centrifugation of the sealed teflon tubes, were carried out in the HEPA-filtered laminar-flow work station.

Total elemental concentrations and computation of mass balances. The total elemental concentrations in samples were computed in several ways. An assumption inherent to the sample splitting process is that the plankton mixture is basically homogeneous in species and chemical composition. The general validity of this assumption is born out by the consistency of replicate chemical analyses on different splits of one sample (Table 7).

Subsamples collected on filters were used to estimate the total mass of each split. The total elemental composition of each split was calculated as the sum of each collected fraction. In the simplest case this was the sum of the element released to the seawater supernate plus that remaining in the untreated, centrifuged plankton. For the other experiments the total is calculated as the sum in each leaching solution and in the residual particulate matter.

Shipboard Experimental Summaries. Plankton tows from three of the stations occupied on the Antarctic transect (Table 2) were subsampled onto filters and into centrifuge tubes for analysis. Leaching of the opaline material was carried out with distilled water, hydrogen peroxide, and 0.1 N HCl.

TABLE 2. Antarctic Samples - Description of Tows and Experiments

-Towed from a boom off the starboard bow of the R/V Atlantis II
Jan, 1976
-Daytime tows at approximately 5 meters depth, 1.5 knots, 30 mins.

(plankton groups listed below each station by descending numbers of individuals)

STN E (47°52'S, 22°22'E) relatively small mass.
Rhisosolenia sp.
Chaetoceros sp.
Coscinodiscineae

STN J1 (59°49'S, 27°07'E) medium density collected.
Nitzchia sp.
Rhizosolenia sp.
Corethron sp.
Coscinodiscineae

STN M (66°44'S, 30°00'E) very large mass collected.
Corethron sp. (greater than 99% of total number)
Coscinodiscineae

Surface water properties:

STN	T	PO_4	Si	Cu	Ni	Cd
E	6.0	1.26 μM	1 μM	2.4 nM	-	0.44 nM
J1	2.4	1.75	39.1	2.9	6.2	0.64
M	0.0	1.98	54.4	2.9	6.2	0.71

Experiments:
bulk determinations;
isolation of pure opaline material;
distilled water, peroxide, 0.1 N HCl washes.

Subsamples from the Galapagos tows (Table 3) were collected on filters and in centrifuge tubes for several sets of leaching experiments. These included: isotonic ammonium chloride vs. distilled water; ethanol extraction; and a series of acid leaches. All particulate residues and leaching solutions were saved and analyzed.

TABLE 3. Eastern Equatorial Pacific Samples (Galapagos) - Description of Tows and Experiments

-Towed from inflatable Zodiac, upwind of R/V Melville.
-Daytime tows, vertical hand winch, 5-30 meters depth.

TOW 1 - 3/14/77 approx.	225 ml wet volume collected.
TOW 2 - 3/17/77	100 ml
TOW 3 - 3/21/77	250 ml

All tows were similar in relative distribution of organisms and are summarized below in order of decreasing mass contribution.

I. Diatoms - Thizosolenia sp., Planktoniella sol, and a variety of discoid species.
II. Copepoda - adult Calanus sp. and numerous nauplii.
III. Acantharia - numerous and in good condition.
IV. Dinoflagellates - Ceratium sp.
V. Misc - Tintinnids and Pteropods.

Surface water properties:

T	PO_4	NO_3	Si	Cu	Ni	Cd
26°C	0.80 µM	8.0 µM	5.2 µM	2.06 nM	2.99 nM	0.08 nM

Experiments:

bulk determinations;
distilled water, isotonic ammonium chloride, ethanol washes;
acid leaching series - distilled water, .001N HCl, .1N HCl, 16N HNO_3;
timed release to seawater suspension.

The MANOP tows were collected from two sites (Table 4). At site C, two tows were collected and split between filters and leaching experiments. The several sets of experiments performed included: isotonic ammonium chloride distilled water leaching; filtration and ultrafiltration of the seawater supernate removed from the plankton suspension by centrifugation; an acid leaching series with long and short exposure times; an extraction with hot ethanol. At site S, four tows were collected: two from the Zodiac and two from the ship. The amount of plankton collected in the Zodiac tows was so small that the number of experiments performed was severely limited. Only one filter subsample was collected and processed. The two leaching experiments were: resuspension of the centrifuged plankton in a millimolar EDTA - surface seawater solution and in a chloroform-APDC extraction mixture. The tows collected by the main research vessel yielded much larger samples which were split into a series of centrifuge tubes to determine the rate of release of the various elements into the seawater in which the plankton was suspended. The first experiment separated the plankton from the seawater suspension at intervals over a 96 hour period. The samples were stored at 4°C until the time of centrifugation. The second set of samples were treated similarly but included the addition of an antibiotic mixture. The last set of samples was kept at surface seawater temperatures on the deck of the ship, exposed to sunlight (Table 4).

Analysis of Particulate Matter and Leaches. All solutions and particulate materials were analyzed in the shore-based laboratory. The particulate samples were of two general types - filters and centrifuged residues. The filters were used for mass estimation, Si determinations, and some of the total trace element determinations. Masses on the preweighed Nuclepore filters were determined using a PerkinElmer model AD-2 electromicrobalance after drying at 60°C and desiccation. Sodium analyses on the solubilized filters were eventually applied to correct for the included mass of sea salt.

Solubilization. The solubilization of particulate matter for all trace-element and most major-element analyses involved oxidative dissolution with hot HNO_3 followed by dissolution of the opal and silicate phases with HF. Because of the possibility of trace element loss due to volatilization at higher temperatures (BUCKLEY and CRANSTON, 1971), all processing steps were done at temperatures below 120°C and, when possible, in a closed system. The procedure involved the transfer of the particulate fraction from a centrifuge tube or filter split to an acid digestion bomb with long-taper sealed teflon cups (Parr Co. model 4745). The samples were digested at 120°C with five ml of HNO_3 for 24 hours. A very small amount of acid migration out of the teflon bombs was occasionally noted but blank runs indicated no significant contamination inside the bomb. On a few occasions, the residual organic matter was further digested by a heating-evaporation cycle with more HNO_3 and 100 µl perchloric acid. The digested sample was reduced to near dryness on a hotplate and spiked with 0.5 ml HF to dissolve the opal and any silicates which might have been present. After two successive spiking-volume reduction steps with 6N HCl to drive off the fluorides the sample was taken up in 5 ml 0.5N HNO_3. Table 5 shows representative values of method blanks and recoveries for the bomb decomposition steps. On the basis of these results, all recoveries were taken to be 100% except for Al which was assumed to be 90%. The loss of Al was presumably due to the formation of some volatile Al-halide compound. The most likely is $AlCl_3$ which sublimes near 180°C at atmospheric pressure. Aluminum perchlorate also is volatile near this temperature, but AlF_3 should be stable to temperatures over 1000 degrees. The temperatures in the decomposition bombs should never have reached 180 degrees, but this is harder to control during the hotplate steps. The complex matrix in these samples also makes volatility estimates using pure-substance values uncertain. A value of 90% recovery will be taken for Al, with the caution that the loss due to this type of volatilization can be variable and dependent on the precise matrix and experimental conditions. The general agreement of replicate analyses on splits of the same sample support a relatively constant Al recovery.

Particulate samples to be analyzed for Si were leached in 0.4 M $NaCO_3$ at 60°C for 5 days. After filtration and neutralization with HCl, the samples were analyzed for Si by the method of MULLIN and RILEY (1955). Particulate phosphorous analysis involved the digestion of samples in 0.5 M potassium persulfate solutions followed by colorimetric analysis of PO_4 released to the solutions (MURPHY and RILEY, 1962). The PO_4 was measured directly in the bomb decomposition solutions by the same technique.

Foraminifera from the MANOP site S filters were hand-picked to collect approximately 2.5 mg of sample. These were suspended for 3 hours in a 50:50 mixture of 0.2 N NaOH and 30% H_2O_2, heated to 60 degrees and ultrasonified occasionally. After washing in distilled water, they were subjected to a series of leaches designed to isolate the pure carbonate test and its included trace ele-

TABLE 4. Central Pacific Samples (MANOP) - Description of Tows and Experiments

-Towed from Zodiac and boom extended forward from the R/V Knorr's direction of travel.
-Daytime tows, Zodiac: vertical tows from 5-75 meters, approx. 3-4 hours; ship: horizontal tows at 20 meters depth, 1 knot, 45 minutes.

SITE C (1°N - 139°W):		
TOW 1 - 5/12/79 approx.	100 ml wet volume,	Zodiac.
TOW 2 - 5/14/79	120 ml	Zodiac.
SITE S (11°N - 138°W):		
TOW 3 - 5/19/79	50 ml	Zodiac.
TOW 5 - 5/24/79	50 ml	Zodiac.
TOW 6 - 5/25/79	90 ml	Ship.
TOW 7 - 5/26/79	100 ml	Ship.

All tows from a single site were similar in their relative distributions of organisms and are described below in order of decreasing mass contribution (estimated).

Site C - Copepoda - large variety of adults and nauplii.
Lesser numbers of Diatoms, Acantharia, Pteropods, and Forams.

Site S - Crustacea - by far the largest mass in the tow.
Much smaller numbers of Pteropods and Radiolaria.

Surface water properties:

STN	T	PO_4	NO_3	Si	Cu	Ni	Cd
C	26.5°C	0.042 μM	7.1 μM	3.2 μM	0.72 nM	2.44 nM	0.016 nM
S	27.0°C	0.027 μM	0.7 μM	1.9 μM	0.75 nM	1.94 nM	0.010 nM

Experiments:
- bulk determinations;
- distilled water, isotonic ammonium chloride, hot ethanol, and acid series (as above);
- Series filtration of seawater suspension - 1.0 μm, 0.4 μm, 0.1 μm, 0.05 μm, ultrafiltration;
- EDTA, APDC, and solvent extractions;
- timed release to seawater suspension -
  - 72 hours in dark at 4°C with and without antibiotics;
  - 72 hours on deck (in light) at surface water temp.

ments (BOYLE, 1981). A basic, reducing-complexing solution was added to remove any surface coating of Fe or Mn hydroxide phases. After a 30-minute treatment with this solution at 90°C with occasional ultrasonification, the forams were washed in hot and cold distilled water. The complete washing process caused the loss of about half of the mass of the forams through dissolution and mechanical loss but left a clean $CaCO_3$ residue. The forams were then dissolved in distilled water under 1 atm. CO_2 and the solution analyzed by flameless and flame atomic adsorption spectrometry (AAS).

TABLE 5. Representative Method Blanks and Recoveries for Acid-Bomb Particulate Decompositions

Element	Blank (nmol)	Recovery (% (std. devn.))	Element	Blank (nmol)	Recovery (% (std.devn.))
Fe	1.0	101 (5)	Cu	0.075	97 (1)
Al	0.4	90 (5)	Mn	0.025	100 (2)
Zn	0.1	99 (1)	Cd	0.005	101 (1)
Ni	0.1	101 (2)	Ba	0.025	101 (1)

Major element components. Analyses of Na, K, Ca, and Mg were done by flame AAS using a Perkin-Elmer model 403 spectrometer. Careful matrix matching, suppression of ionization and interference effects, and standardization by known additions were necessary to give good results in these varied and complex samples (SLAVIN, 1968). Carbon and nitrogen analyses on the dried splits of Galapagos filters were done using a Perkin-Elmer 240 CHN Analyser (CULMO, 1969). Methods for the analysis of phosphorous and silicon have already been discussed.

Analysis of Trace Elements. The trace elements in the solubilized plankton and leaching solutions were analyzed by atomic absorption spectrometry using electrothermal atomization. Two instrument systems were used: a Perkin-Elmer 603 with an HGA 2100 graphite furnace; and a Perkin-Elmer 5000 with an HGA 500 graphite furnace. These systems possess high dispersion monochromators, fast response peakreading electronics, and give very good sensitivity. An effective continuum-source background correcting system in both the UV and visible spectrum was important for the direct analysis of elements in the presence of significant amounts of salt and organic materials. The graphite tube furnaces and their controllers offered a high degree of flexibility in determining the sample environment and heating program. These features were very important in allowing analysis by direct injection. Model AS-1 autosamplers were used on both systems to improve the precision of each injection and allow a larger number of samples to be processed by multipoint standard additions in a single analysis run.

The wide variety of sample matrices encountered in this research required that analyses be made by the method of known additions of standards to the actual sample matrix (O'HAVER, 1976). The standard curve of absorbance vs. standard spike concentration is used to give the concentration in the sample by extrapolation. Three very important criteria must be satisfied to establish the validity of this method: 1) the linearity of the instrument response must be demonstrated throughout the measurement and extrapolation range of absorbances; 2) the absorbance of the blank matrix must be zero (or known); 3) there can be no drift in sensitivity during the analysis of a single sample set. The simplicity of these requirements often leads to their being ignored and this can cause very severe errors. The need for standard additions and some of the specific difficulties encountered in their application to these samples are detailed in COLLIER (1981).

Many of the elements under consideration form volatile chlorides as precursors to reduction of the metal in the furnace (STURGEON and CHAKRABARTI, 1978). In the presence of a great excess of chloride, the sensitivity is often reduced by the loss of the metal chloride from the furnace before reduction can occur. Addition of HNO_3 presumably forces the evaporation of HCl and subsequent precipitation of metal nitrates, not chlorides in the graphite tube. All additions to the samples contained HNO_3 and were carefully matched so that the only major variant was the analyte.

The addition of ascorbic acid was used as a matrix modification for samples containing high concentrations of dissolved salts (e.g., undiluted seawater samples). This was added to the sample such that the final concentration injected in the furnace was 1% by weight ascorbic acid. Analyses of samples treated in this manner have much better reproducibility and show sensitivities that approach those in non-salt matrices. The addition of organic acids has been investigated by numerous authors (REGAN and WARREN, 1978; HYDES, 1980), but the mechanisms of the effect are not well known. The ascorbic acid changes the wetting properties of the mixture which spreads the injected sample solution out over the inside of the graphite tube. This results in much smaller crystals of salt being formed on the surface of the tube after the sample is dried, allowing a more efficient and reproducible atomization of the sample.

Instrumental procedures. One of the critical steps in successful analysis of trace elements by flameless AAS in the presence of complicated matrices is the fine tuning of the graphite furnace operating program. This was accomplished by specifying a program of up to nine steps which was designed for the specific element and matrix. Selective volatilization of solvents and salts and the oxidation of organic phases can significantly reduce major interferences. An annotated program for the atomization of Cu from a 0.2 N ammonium chloride solution is shown in Table 6 as an example. Control of the heating rate, temperature, and internal gas flow before and during the atomization step can be used to further separate the analyte appearance from that of an interfering peak.

Graphite tubes used were of three types: normal unpyrolized tubes; tubes pyrolized in the graphite furnace; and batch-pyrolized tubes purchased from Perkin-Elmer. For elements requiring a high atomization temperature, the pyrolized tubes always give more sensitivity by at least a factor of two. The unpyrolized tubes are more porous and offer better reproducibility for low-temperature elements (Cd, Zn) and for some high-salt samples. Again, compromises must be made between sensitivity, reduction of interferences, and precision.

TABLE 6. HGA 500 Graphite Furnace Program

Analysis of Cu in 0.2N NH_4Cl

Step	Temp.	Ramp	Hold	Int.Gas	Comments
1	100°C	1sec.	0sec.	300cc/min	jump to drying temp
2	130	15	15		remove solvent w/o boiling
3	160	15	15		remove hydration water
4	340	10	0		ramp to sublimation temp
5	360	25	0		slowly sublime NH_4Cl
6	850	10	20		char, also zero baseline
7	2400	0	3	30	atomize Cu, read abs. peak
8	2600	1	4	300	cleaning step
9	20	1	4		cool, look for baseline shifts

Other important instrumental parameters include the careful overlapping of the background correction and hollow-cathode lamp image within the center of the graphite tube. The furnace must be perfectly centered in the light path to minimize the amount of stray emission picked up by the phototube. In essence, it is of the utmost importance that all instrumental parameters be carefully optimized under adverse sample matrix conditions.

3. BULK ELEMENTAL COMPOSITION OF PLANKTON

The total concentration of elements in the original plankton material was calculated from determinations on several fractions. As outlined earlier, this was represented by the sum of concentrations in an untreated subsample of plankton and in the seawater that had been separated from the plankton. For other samples it involved summing the analyses on a series of leaching solutions and particulate residues. The calculated totals for all of the analyzed plankton tows are summarized in Table 7.

Only filters and centrifuged particles were analyzed from the Antarctic plankton tows (Table 2). Analyses of filters were carried out on material from stations E, J1, and M. Analyses of several centrifuged subsamples were used from station M. The total concentrations calculated represent minimum values since they do not include the contribution of elements released to the seawater suspension (not analyzed in this series). Judging from experience gained on other samples, it is expected that these totals are reasonable estimates for Ca, Si, Cu, Fe, Zn, Al, and Ba; the values for P, Ni, Cd, and Mn may be low by a factor of two or three because of the rapid release of these elements from the plankton to the seawater suspension.

There was a significant decrease in the trace element content of bulk plankton collected at the most productive Antarctic station (M) compared to those collected north of the polar front (E, J1). This decrease (Table 7) was seen in contrast to the systematic increase in the dissolved concentrations of both nutrients and trace elements (Table 2) associated with the upwelling of deep isopycnals. The concentrations of trace elements in the plankton at station M represent the lowest levels ever reported for surface particulate matter.

The total concentrations in two of the Galapagos tows (Table 7) were calculated as the sum of all particles and solution fractions and therefore represent true totals. The total concentrations in the MANOP samples presented in Table 7 were calculated in the same manner as the Galapagos samples. The samples from Tow 7 (Site S), which were incubated at surface water temperatures in sunlight, formed a significant amount of secondary precipitates (in part due to a high rate of bacterial activity). Because of the obvious redistribution of elements in these samples, they were not used for estimates of total plankton composition (Table 7). In general, the levels of minor components in these plankton samples are similar to those reported by MARTIN and KNAUER (1973) and MARTIN and others (1976) for plankton tows in the eastern north Pacific Ocean. The levels of Ni, Mn and Cd in our samples are somewhat higher - probably due to our inclusion of the labile release products in the seawater suspensions.

There are significant compositional differences between some of the separate tows at the Galapagos and at the MANOP S site, especially for Al and Fe. In section 6.4, this will be discussed in terms of variability of the surface water masses and atmospheric transport of terrigenous matter to these sites.

4. LEACHING EXPERIMENTS

Release of elements from the plankton to the sea water suspension. One of the first results observed in the leaching experiments was that a high concentration of many elements were found in the sea water in which plankton were suspended.

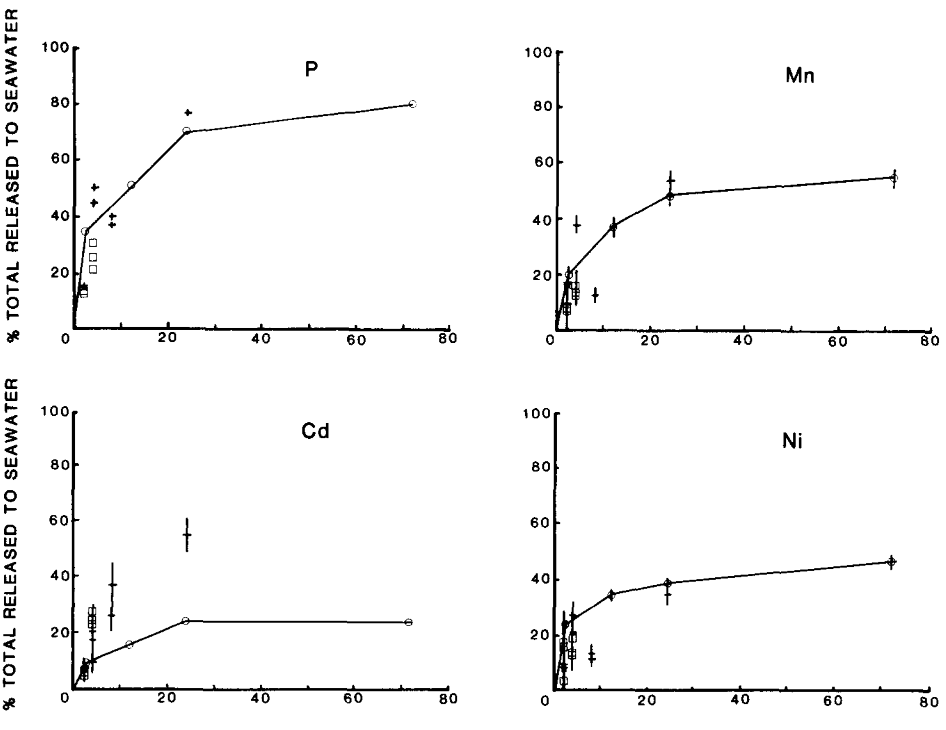
TABLE 7. Bulk Plankton Compositions, All Stations. Estimates based on averages of subsamples of each tow. Value listed immediately below the concentration is the standard deviation of the mean when several subsamples were used. If no error is listed then the concentration is based on a single subsample only. Concentration units:

Ca, P, Si, C, N -- mmol/gram dry plankton
Fe, Zn, Al -- μmol/gram dry plankton
Cu, Ni, Cd, Mn, Ba -- nmol/gram dry plankton

	ANTARCTIC			GALAPAGOS		MANOP C		MANOP S	
	STN M	STN J1	STN E	TOW 1	TOW 3	TOW 1	TOW 2	TOW 3	TOW 6
Ca	0.011	0.23	0.3	0.84 (0.03)	1.39 (0.04)	1.34 (0.27)	1.5 (0.24)	3.66 (0.26)	1.59
P	0.024		0.22	0.42 (0.04)	0.35 (0.02)	0.26 (0.03)	0.3 (0.01)	0.44 (0.01)	0.36
Si	12.3			1.28 (0.01)	0.68	0.56	0.37	0.15 (0.01)	0.1
C				33.4 (1.8)	36.8				
N				6.2 (0.2)	6.25				
Fe	0.17	2.53	2.73	6.8 (0.17)	2.93	1.31 (0.02)	1.23 (0.12)	7.4 (0.7)	1.96
Zn	0.32	6.1	3.75	1.36 (0.11)	2.26	1.02 (0.07)	0.64 (0.02)	1.35 (0.02)	1.26
Al	0.39			9	7.7	0.72 (0.09)	0.94 (0.1)	12.5 (0.3)	3.48
Cu	47	300	410	206 (33)	223 (10)	125 (4)	166 (14)	291 (17)	151
Ni	16.3	20	63	232 (5)	215 (21)	255 (25)	220 (12)	392 (16)	433
Cd	1.7	20	98	482 (48)	311 (27)	159 (7)	143 (7)	316 (11)	214
Mn				165 (17)	146 (1)	96 (7)	95 (4)	209 (11)	131
Ba	205				490		516		

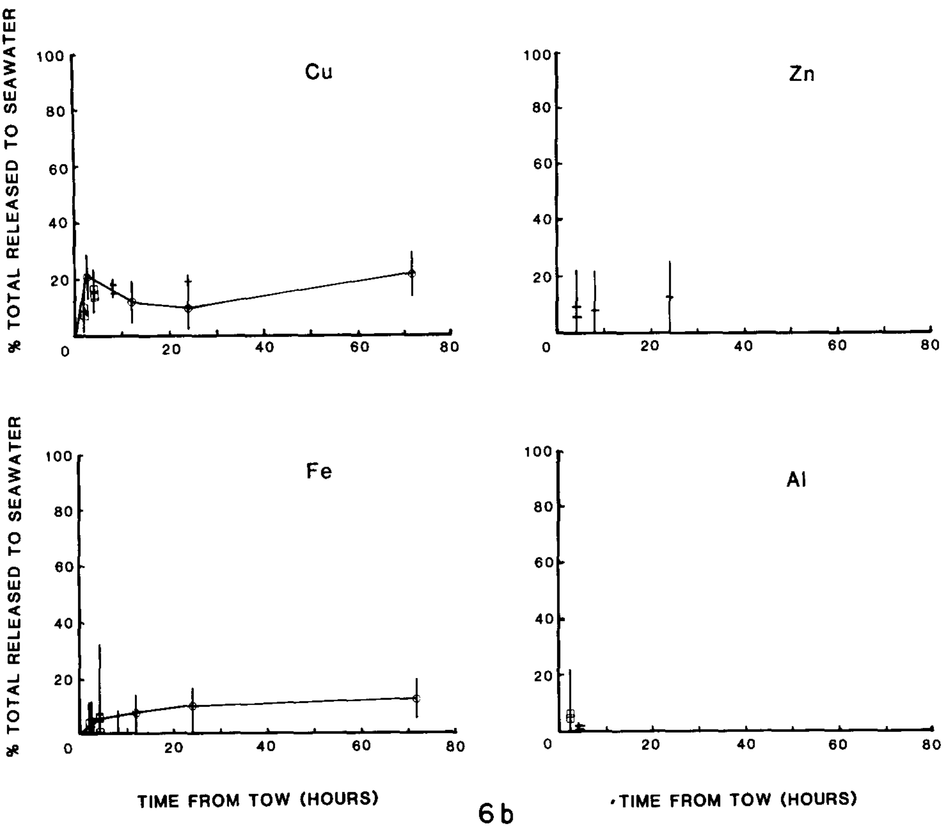
These elements were initially associated with the particles when the plankton were collected and were released to the sea water suspension during the two hours it took to get the samples into the ship's laboratory for processing. These results are summarized in Figure 6, expressed as the percentage of the total particulate element which was released to the sea water separated from the plankton sample as a function of time. All of the samples shown in the figures were stored in the dark at 4°C from the time they were collected until they were centrifuged.

The first observation of this release was in the Galapagos samples where significant amounts of the total P, Cd, Ni, and Mn were found in the sea water only six to eight hours after completion of the tow (Figure 6a). A sample stored for 24 hours (Tow 1) lost over 70% of its P, 50% of its Cd and Mn, and more than 30% of its Ni. In anticipation of these releases, several experimental changes were made at the MANOP stations: more rapid sample processing; documentation of times during processing; and several experiments following the history of regeneration of elements in solution over significantly longer time periods. The results for one of the timed experiments (MANOP S, Tow 6) are noted in Figure 6 by the five points connected by lines. The material in this experiment was handled identically to the normally processed samples. It was subsampled to a set of five centrifuge tubes, two hours after the tow and was kept cold and in the dark until the time of centrifugation.



6a

Fig. 6. Percentages of each element in the plankton released to the seawater suspension as a function of the time from collection of the tow. Data points connected by lines are replicate subsamples from one tow (MANOP S, Tow 6). Vertical lines superimposed on data points represent the 95% confidence limits in the percentages. Symbol key: plus sign - Galapagos; square - MANOP C; circle - MANOP S. a) P, Cd, Mn and Ni; b) Cu, Fe, Zn and Al.



6b

(See legend of Fig. 6 on preceding page)

As in the Galapagos experiments, P, Mn, Ni, and Cd were rapidly released from the particles to the sea water in the MANOP samples (Fig. 6a). The quantity of each element released approached a constant value within several tens of hours. The behavior of each element was similar from experiment to experiment except in Tow 6, where the relative release of Cd was lower.

In contrast to the behavior of these labile elements, significantly less of the Cu, Fe, Zn, Al, and Ba were solubilized in the sea water (Fig. 6b). There was always an initial pulse of Cu released along with the labile elements, but its concentration then decreased with time by some secondary process. The amount of Fe in the sea water was always very small with respect to its total particulate concentration. The concentrations of Zn, Al, and Ba detected in the sea water were low and non-systematic, being near their limits of detection.

Table 8 gives the atomic ratios of each of these labile elements to the P in the sea water solution. The ratios were essentially constant throughout the MANOP Tow-6 time series experiment. This would imply that these elements are being released from sites which are behaving as a single pool of labile material. Although there is some variability in the ratios between tows, the Cd/P and Ni/P ratios are similar to those of the dissolved species in the upper ocean. The initial release of Cu followed by its loss from solution can be seen in its decreasing ratio to P with time. Although the regeneration of Fe relative to its total particulate concentration is small, the fraction released has a relatively constant ratio to P.

TABLE 8. Elemental Ratios in Seawater Suspensions. (x10^{-3})

Atom ratios x10^{-3}, values in parenthesis are 95% confidence limits in the ratio.

		Cd/P	Mn/P	Ni/P	Fe/P	Cu/P
Galapagos	Tow 1	0.84 (.10)	0.12 (.02)	0.18 (.02)	0.17 (.03)	0.23 (.04)
	Tow 1	0.75 (.06)	0.23 (.02)	0.22 (.03)	0.17 (.01)	0.09 (.02)
	Tow 3	0.38 (.03)	0.34 (.02)	0.30 (.04)	0.83 (.05)	0.19 (.02)
MANOP C	Tow 1	0.52 (.02)	0.19 (.05)	0.51 (.06)	1.1 (.2)	0.26 (.06)
	Tow 2	0.25 (.01)	0.21 (.02)	0.96 (.15)	1.2 (.04)	0.40 (.04)
	Tow 2	0.15 (.01)	0.17 (.02)	0.62 (.09)	0.77 (.13)	0.34 (.04)
MANOP S	Tow 3	0.43 (.05)	0.45 (.07)	0.54 (.10)	1.8 (.4)	0.40 (.09)
	Tow 6*	0.16 (.01)	0.21 (.02)	0.82 (.15)	0.72 (.06)	0.25 (.02)
	Tow 6	0.19 (.01)	0.26 (.03)	0.81 (.08)	0.76 (.05)	0.10 (.02)
	Tow 6	0.20 (.01)	0.25 (.01)	0.66 (.05)	0.74 (.05)	0.06 (.01)
	Tow 6	0.18 (.01)	0.24 (.01)	0.69 (.07)	0.80 (.04)	0.11 (.01)
	Tow 6	0.17 (.01)	0.23 (.02)	0.75 (.06)	0.60 (.05)	0.05 (.01)
water column		0.32-0.37(1)	0.5-1.5(2)	1.0(3)	0.5-5(4)	0.5-0.8(5)

*Tow 6 - time release experiment ranging from 2.5 to 96 hours exposure.

(1) Pacific, water column (BOYLE *et al.*, 1976; BRULAND *et al.*, 1978)

(2) Pacific, oxygen minimum (KLINKHAMMER and BENDER, 1980)

(3) Pacific, upper water column (SCLATER *et al.*, 1976)

(4) Pacific, upper water column (LANDING and BRULAND, 1981)

(5) Pacific, upper water column (BOYLE *et al.*, 1977)

Several more experiments were carried out to characterize the nature of the release. An attempt was made in MANOP S, Tow 7 to assess the effect of bacterial activity, temperature, and light on the release experiments. An antibiotic mixture of chloramphenicol, penicillin, and streptomycin was added to a set of subsamples which were treated in a manner similar to the Tow 6 time series. Although these samples became contaminated for Cd, the release of Mn and Fe were similar to that observed in Tow 6. However, the total solubilized P over the same time period was only 17% (compared to over 70% in Tow 6), of which 14% had been released by the time the samples were spiked with antibiotics. Although insufficient controls were performed on this experiment, it suggests that some component of the release process is a result of bacterial metabolism.

The implications of this remineralization process must be considered during the sampling and handling of organic particulate matter by towing, filtration, and trapping. The rapid release of these elements requires careful containment of the sample and complete mass balancing from the time of collection if their chemistry in the upper oceans is to be studied. Variations in sampling techniques will surely result in large variations in the concentrations of P, Ni, Cd, Mn, and perhaps other trace species.

The form of the elements released to the sea water was examined with three sets of experiments. First, a comparison was made between the two methods of concentrating the plankton from suspension: direct filtration and centrifugation. Second, the centrifuged sea water solution was passed through a series of progressively smaller membrane filters. Third, a subsample of a sea water suspension was passed through an ultrafiltration membrane (Millipore, CX immersible, Pellicon type PTGC, nmwl 10000). The results of these experiments are summarized in Table 9, expressed as the percentage of an element in the sea water suspension which passed through each filter.

TABLE 9. Filtration Experiments

Percentage of each element in the centrifuged seawater suspension which passes through filters of various pore-sizes. Values in parenthesis are the 95% confidence limits on the percentage. Samples noted with [-] were contaminated.

Direct Filtration of Plankton:		Filtration of Seawater Supernate:			
0.4 µm		1.0 µm	0.1 µm	0.05 µm	ultrafilter
152%	P	93%	83%	80%	77%
112 (14)	Mn	96 (13)	82 (11)	69 (30)	75 (19)
135 (17)	Ni	102 (13)	71 (15)	68 (14)	[-]
116 (25)	Cu	93 (20)	39 (20)	[-]	36 (10)
112 (9)	Cd	68 (6)	12 (5)	15 (2)	25 (5)
	Fe				45 (10)

The process of filtration releases more labile material than does centrifugation. This can be seen by the excess of elements (>100%) in the filtrate compared to the centrifuged seawater suspension (Table 9). A much larger amount of P is released to the filtrate, as are larger amounts of the labile trace elements, although their enrichment is less extreme. The difference seen between the two collection methods is probably due to mechanical lysis of the cells during vacuum filtration. This releases dissolved and very small particulate cellular material, which then passes through the filter. The results of these experiments suggest that lysis and release of cell fluids is a significant process determining the observed regeneration of elements.

Filtration of the centrifuged sea water suspension gave estimates of the partitioning of the released elements between dissolved and particulate phases. Except for Cd, greater than 90% of the rapidly released elements passed through the 1.0 μm filter. This demonstrated that the metals were not associated with large, noncentrifugable organic particles which could be carried over in the aspiration procedure. As the filter pore size decreased, each element was more efficiently retained. The maximum retentions ranged from only 20% for P, to 85% for Cd. No exact estimates of the size of the materials removed from the sea water can be made, since the filters were not well characterized with respect to adsorption of metals and organic matter from solutions. Sizing by filtration is also uncertain because of clogging of the membranes as filtration proceeds (this was noticeable after only 1-2 ml of solution had been filtered). However, significant amounts of the released elements clearly passed through these membranes and met the frequently-used operational definition of dissolved components.

Releases during resuspension of plankton. Centrifuged subsamples from MANOP S, Tow 3 were resuspended two hours after the tow in fresh surface sea water collected from that site. The suspensions were left in the centrifuge tubes at room temperature for two more hours before separation of the supernatant by centrifugation. One of the subsamples was resuspended in a solution of 10^{-3}M ethylenediaminetetraacetic acid (EDTA) in the surface sea water. The releases to these solutions can be seen as a continuation of the time dependent process discussed in the last section. Most of the elements showed a solubilization (Table 10) which was equivalent to that in the previous sea water release experiments, but Cd showed a significantly higher release with an associated increase in the Cd/P ratio.

Addition of the strong metal chelator, EDTA, had no effect on the P release, which is reasonable, since there is no binding of phosphate species to the EDTA ligand. Cu and Fe did not show any significant differences in their release to the sea water with EDTA present, even though, among the metals studied, these form the strongest complexes with EDTA. The more labile elements Ni, Cd, and Mn all showed significant increases in concentration in the EDTA compared to the seawater solution alone. The deterioration of structural organic membranes exposed to EDTA solutions has been noted (HUGHES, 1972) and was attributed to the extraction of divalent cations from sites which cross-link adjacent carboxylate functions in these membranes. The increased removal of metals from the plankton to the EDTA solution may have occurred by this mechanism or by removal from other adsorbing sites on the surfaces which could not compete with the EDTA. In experiments with cultured phytoplankton, DAVIES (1970) showed that a millimolar EDTA solution solubilized freshly precipitated Fe from the surfaces of the plankton within several tens of minutes after addition of the chelator. This was not seen in the leaching experiments, and clearly very little of the Fe in these samples is present in a freshly precipitated, chelatable form. The increased removal of Ni, Cd, and Mn must be due to their association with surface sites which are less stable or physically more exposed than those sites binding Cu and Fe.

MANOP S subsamples were resuspended in surface sea water with and without the addition of the chelator - ammonium pyrrolidinedithiocarbamate (APDC).

TABLE 10. Resuspension in Seawater - EDTA Solutions.

Percentage of the total particulate element released to solution.

	Original sea water		Resuspension sea water		Resuspension sea water w/EDTA	
	%	metal/P (x10^{-3})	%	metal/P (x10^{-3})	%	metal/P (x10^{-3})
Ca	0		0		0	
P	14.9		25.9		26.9	
Cu	8.9	0.40	14.4	0.38	15.9	0.39
Ni	9.1	0.54	12.7	0.41	21.4	0.75
Cd	9	0.43	29.6	0.82	47	1.2
Fe	1.7	1.8	2.1	1.0	3.1	2.2
Mn	14.2	0.45	13.8	0.26	33.1	0.56

These samples were then directly extracted with chloroform. The small volumes involved and the difficulty of direct atomic absorption analysis in the organic matrix made quantifying the results of this experiment difficult, but several results are still significant (Table 11). The release to the simple sea water-chloroform system (without APDC) was similar to that seen in the other sea water resuspension experiments. No metals were directly extracted from this sea water suspension into the organic solvent, indicating that the majority of those released are not associated with extractable non-polar organic molecules. The extracted sea water which contained the APDC had a much lower amount of the released metals as did the residual extracted particles. These metals were easily detected in the chloroform extract. It is clear that significant amounts of the Ni, Mn, Cd, and possibly Cu bound to the particles and released to the sea-water suspension can be chelated by APDC and only then are extractable into organic solvents. The Fe released to the sea water was not extracted directly into the chloroform, nor was it extracted as the Fe-APDC chelate.

Releases to distilled water. Several of the subsamples were resuspended in a distilled water wash after separation from the plankton seawater suspension. The results of these experiments are summarized in Table 12. The elements P, Ni, Cd, and Mn, which were rapidly solubilized in the sea water suspension, were also extracted into the distilled water. The concentration of the labile elements in the distilled water was inversely related to the percentage of these elements which had already been released to the sea water before processing. The cumulative transfer of elements from the plankton to the sea water and distilled water solutions was equivalent to the maximum release seen in the long-term seawater suspension experiment (Fig. 6). The metal/P ratio was approximately the same in both the sea water and distilled water. This behavior is consistent with release or exposure of material by lysis of cell membranes. This occurs even while the sample remains in the sea-water suspension due to mechanical, bacterial, or autolytic decomposition, but is accelerated by suspension in the distilled water. The results of this experiment are significant considering the frequently used experimental practice of washing particulate matter samples with distilled water to reduce analytical interferences from sea salt. It can be expected that a significant, but variable amount of these labile elements will be lost to any distilled-water wash (Table 12). Our leaching procedure exposes the samples to distilled water for a relatively long time period when compared to the time typically taken to rinse a filter with distilled water. Therefore, the elemental losses to distilled water seen in these experiments probably represent an upper limit on the effect of lysis during filter washing.

TABLE 11. Seawater Suspension - APDC - Chloroform Extraction

Total element in each fraction (nanomols)

	Resuspension sea water	$CHCl_3$ extract*	Particulate residue
Cu w/o APDC	0.5	<0.1	10.3
w/APDC	[N.D.]	2	5.5
Ni w/o APDC	7.3	0	22.1
w/APDC	0.6	2	22.4
Cd w/o APDC	12	0	5.1
w/APDC	2	0.1	3.7
Fe w/o APDC	3	0	171
w/APDC	4	<0.5	186
Mn w/o APDC	5	0	10.7
w/APDC	0.2	0.5	5.2

* The analysis in the organic solvent was only qualitative.

In the typical leaching experiment, the total time of exposure to each leaching solution was 30 minutes (3 resuspension steps, 10 minutes each). Using two subsamples of MANOP C, Tow 2, an 8 hour exposure time was compared with the shorter period for each leaching solution. Much more of the labile components were found in the distilled water solution which was in contact with the sample for 8 hours. The net release of these elements (sea water plus distilled water) ranged from 40% to 80% for Cd, Mn, Ni, and P. Again, the relative amount of Cu in these solutions was lower than that of the labile elements, and the drop in the Cu/P ratio in the long exposure solution showed the tendency of Cu to stay associated with particulate phases or surfaces.

TABLE 12. Seawater and Distilled Water Suspensions. Percentage of each element released to each solution. Time listed in last row indicates the time that each solution was exposed to the sample.

	Galapagos Tow 3			MANOP C Tow 1		Tow 2		
	(sw)*	(dw)	(dw)	(sw)	(dw)	(sw)	(dw)	(dw)
Ca	1.2	3.8	4.6	0	1.2	0	0	0
P	47	27	29	28	36	13	33	69
Cu	14	8.9	9.7	15	16	17	38	57
Ni	23	12	13	15	32	17	38	57
Cd	19	10	10	25	17	6.7	26	34
Fe	4.6	4.0	4.3	6.3	7.1	3.7	6.8	10
Mn	38	21	22	15	30	8.7	30	54
Zn	5.8	3.3	4.1				21	22
Si	0.47	0.38	0.41					
Al	0.19	0.14	0.22			5.4	2.0	2.2
Ba	3.4		4.9					
time	4hr.	1hr.	1hr.	4hr.	1/2hr.	2hr.	1/2hr.	8hr.

* (sw) indicates the seawater suspension supernate; (dw) indicates the subsequent distilled water supernate and the two (dw) columns are replicate distilled water leaches on splits of the sample.

The effect of cell lysis was further studied by comparing an isotonic NH_4Cl solution with distilled water resuspension (Table 13). If a significant amount of the rapid release seen was due to lysis alone, then the suspension of the plankton in an iso-osmotic solution should reduce the release relative to that in distilled water. By maintaining osmotic equilibrium, the resulting releases should be equivalent to those seen in the seawater resuspension experiment (Table 10). Comparison of the P in the distilled water and NH_4Cl solutions shows the dramatic effect of lysis; only half of this element was released to NH_4Cl. In contrast to the behavior of P, noticeably more Cu, Ni, Cd, and Mn were released to the NH_4Cl solution. This apparent exchange of cations from surface sites suggests a relatively labile surface complex. This is inconsistent with the strength of the Cu particle/surface association seen in all the other experiments. Again, there was no detectable effect on the release of Fe.

A subsample of the plankton (Galapagos, Tow 1) was extracted with ethanol, removing photosynthetic pigments and low molecular weight organic acids and sugars (WALLEN and GREEN, 1971). No more than 1% of any of the trace elements was extracted by this solution and less than 5% of the P. This sample had already been stored for 24 hours and washed with distilled water, so much of the more labile material had already been released. A subsample of material from

MANOP C, Tow 2, was separated from the seawater suspension and immediately extracted with ethanol. The mixture was heated to 60°C and ultrasonified at intervals over a two hour period. The ethanol extract, which was bright green at this point, was analyzed for Cd and none was detectable beyond the small amount carried over from the seawater suspension.

Acid leaching series. Sample splits from Galapagos, Tow 3, and MANOP C, Tow 2, were processed through a series of acid leaches. The complete sample mass balance includes: the seawater supernate; distilled water; 10^{-3}N HCl; 0.1N HCl; 16N HNO_3; and the insoluble residue. The processing was done at room temperature under the normal leaching-centrifugation regimen. The Galapagos sample and one of the MANOP splits were exposed to each leaching solution for a total of 30-45 minutes. The other MANOP sample was leached for eight hours in each solution. The long and short term experiment started from splits of the same seawater suspension at 2 hours after completion of the tow. The results from the Galapagos experiment are presented in Fig. 7(a) and those from MANOP C in Fig. 7(b). The rapid release of P, Ni, Mn, and Cd to the seawater and distilled water solutions has already been discussed for these samples. The higher percentage of these elements in the seawater from the Galapagos samples can be accounted for by their longer exposure to that solution (4 hours).

TABLE 13. Isotonic Ammonium Chloride Leaches.

Percentage released to solution and metal/P ratios. (MANOP C Tow 1)

	Sea water		Distilled water		NH_4Cl	
	%	metal/P	%	metal/P	%	metal/P
Ca	0		1.2		1.6	
P	27.5		35.9		19.2	
Cu	15.5	0.26	16.1	0.14	26.9	0.75
Ni	15.2	0.51	32.2	0.50	40	2.3
Cd	24.9	0.53	17.1	0.19	28	1.0
Fe	6.3	1.1	7.1	0.68	6.3	1.7
Mn	14.6	0.19	29.8	0.23	34.2	0.63

Several additional properties of the labile group of elements can be seen in these experiments. There are two distinct fractions: one that is released to sea water and distilled water, and one which is leachable by acid. Here there is a separation in the behavior of P and the trace metals in that the more refractory component of P is soluble only in the strongly oxidizing nitric acid solution. All the metals had a significant fraction which was solubilized, along with the Ca, by 0.1N HCl. Greater than 95% of the Ni, Mn, Cd, and Ca were removed to leaching solutions before the HNO_3 leach.

There was some time dependence of the elemental release to these solutions which is seen in the MANOP C experiment (Fig. 7b). This was especially significant for P, Mn, and Ni. A fraction of these elements which was released to 0.1N HCl in the normal, short term exposure, was released to the distilled water during the 8 hour exposure. The unbuffered 10^{-3}N HCl solution was quickly neutralized by the $CaCO_3$ in the samples so that it would have behaved similarly to

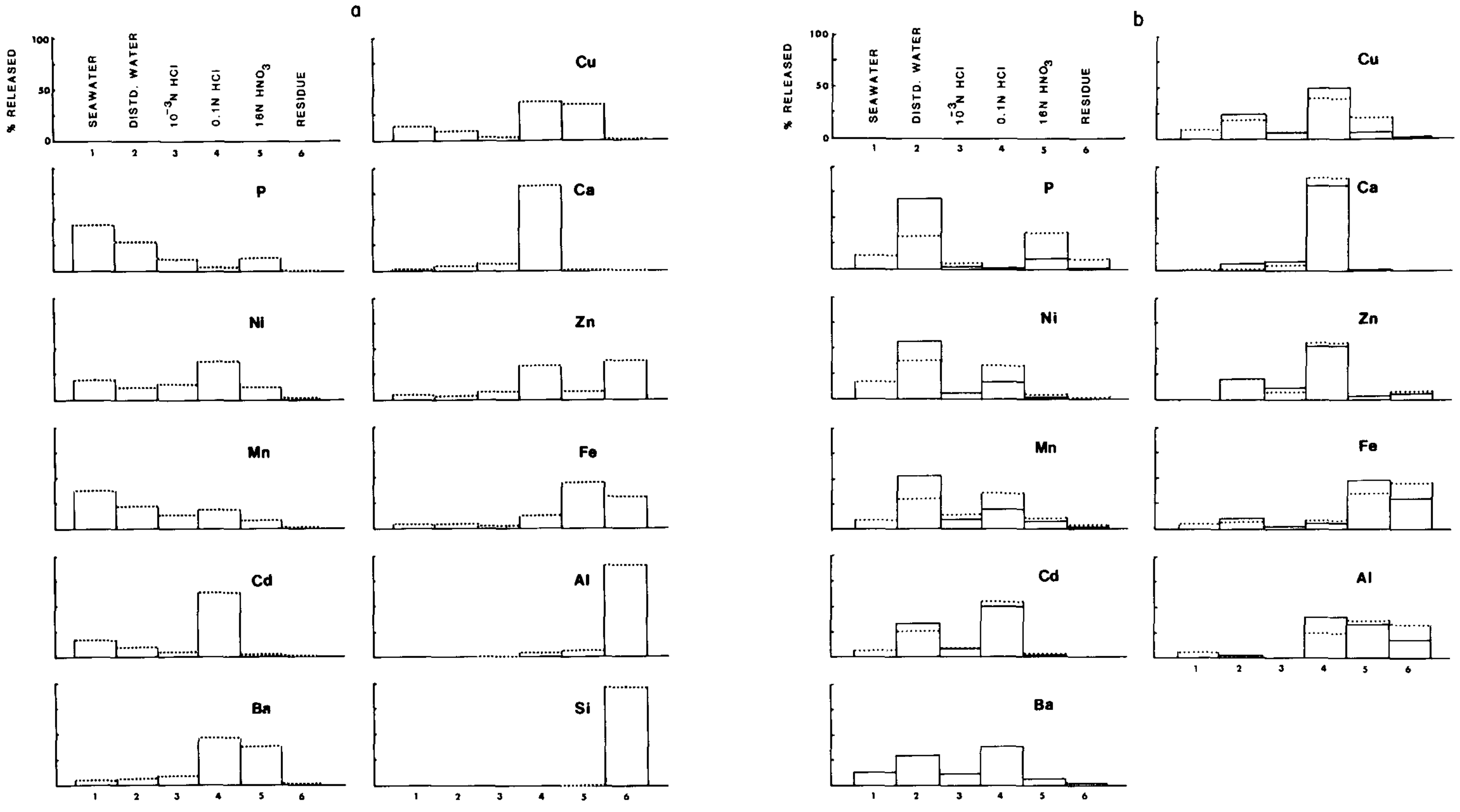


Fig. 7. Acid leaching series. Percentages of the total element released to each leaching solution in the series: seawater suspension, distilled water, 10^{-3}N and 10^{-1}N hydrochloric acid, concentrated nitric acid, and the non-leachable (residual) fraction. The dotted lines (7a and 7b) refer to the standard short-term exposures to the leaching solutions (30 minutes) and the solid lines (7b) refer to an 8-hour exposure to the solutions. a) Galapagos, Tow 3; b) MANOP C, Tow 2.

the distilled water leach preceding it. The low levels of elements released to this solution in all experiments indicated that the initial release to distilled water is largely completed during the short leaching period.

The extraction of Cu, Ni, Cd, Ba, Mn, and Zn by the 0.1N HCl, along with Ca, suggests a possible association with $CaCO_3$. To examine the known calcium carbonate phases in the plankton tows, single foraminifera were picked by hand, under a microscope, from the MANOP filters and solubilized. The metal/Ca ratios in this solution and in the bulk-plankton HCl leach are compared in Table 14. All of the ratios are two orders of magnitude greater in the acid release solution than in the pure carbonate from the same samples. Although these metals are solubilized along with the $CaCO_3$, they are not within the carbonate matrix itself.

The last empirical partition of elements defined by the acid leaching experiments is that which contains a very refractory component which is only partly released by 16N HNO_3 or remains in the residual particles after leaching. Essentially all of the Si, much of the Fe, and variable but significant amounts of Al and Zn resist even the 8-hour HNO_3 leaching. This fraction contains refractory organic matter, opaline skeletal material, and any included aluminosilicates. Variations in the percentage release of Al between the Galapagos sample (Fig. 7a) and the MANOP sample (Fig. 7b) must be examined in terms of the total amount of Al in each sample. The absolute amounts of Al released to the HCl solution, normalized to the mass of the plankton, were nearly identical in both samples. However, the total particulate Al in the Galapagos sample was more than an order of magnitude greater than that in the MANOP sample (Table 7). This suggests the existence of two separate carriers of this element--both a refractory aluminosilicate and a more easily solubilized biogenic phase.

It has often been suggested that the distribution of many elements in the water column is consistent with their incorporation into the opaline frustules of marine organisms. These skeletal materials would be included in this residual fraction. The plankton tow from the Antarctic, Station M, provided an opportunity to determine the amounts of trace elements included in marine biogenic silica. This sample was from a plankton bloom in an open-ocean upwelling region with high concentrations of dissolved trace elements and a relatively low likelihood of lithogenous contamination. Analyses of the plankton material collected (approximately 80% by weight SiO_2) are presented in Table 15. The first sample was untreated except for centrifugation to remove the suspension sea water. The second sample, was leached with peroxide and distilled water

TABLE 14. Metal/Ca Ratios in Bulk Samples and Forams.

Samples: Bulk sample - MANOP C, Tow 2, 0.1N HCl, 8 hour exposure;
Foram sample - hand picked from MANOP samples.

Ratios to Ca ($\times 10^{-6}$)	Cu	Ni	Cd	Fe	Mn	Zn	Al	Ba
Bulk	63	32	60	51	15	270	270	100
Forams	0.31	0.4	0.025	0.51	0.4	0.5	3.5	3

Deep water "regeneration" ratios ($\times 10^{-6}$):

Ni/Ca - 130	Zn/Ca - 100	Ba/Ca - 1000

washes at 60°C in the lab before analysis. A third sample was leached with distilled water and 0.1N HCl at sea. A fourth untreated sample split was digested in sodium carbonate and analyzed for total Si.

As in the pure calcite phase, the metals in this opal sample were very low. Only Al and Fe had significant percentages of their total concentrations remaining in the frustules after leaching with 0.1N HCl. The residual Fe and Al in the sample are in proportions (Fe/Al = 0.2 to 0.4) which would be consistent with their presence in an aluminosilicate phase (detrital clay Fe/Al = 0.22). Based on this ratio and total Al, this would require that the opal sample was 0.3% by weight clay. The Zn and Ba were leached from the sample by the HCl solution. Since the exact chemical nature of any coprecipitated metals is not known, it is difficult to know if this leaching could remove metals from within the opaline structure. Even if we consider the total untreated or peroxide washed material as representing the concentrations in opal, the metal/Si ratios are still very low. The Zn/Si ratio in the HCl-leached opal was an order of magnitude lower than the water column ratio (BRULAND, 1980). The ratio in the bulk, untreated sample was only a factor of two below this ratio. The Ba/Si ratio is 1 to 2 orders of magnitude below the same elemental ratio seen in the water column.

Also included in Table 15 are the results of Cu and Ni analyses on the filtered subsamples from Antarctic station M. These were unwashed and would be roughly equivalent to the material in the untreated centrifuge sample except for the lysis effects of filtration. The concentrations of these two metals are also very low in this material.

Another opal carrier - Radiolaria - was examined for the concentration of Ba. There were insufficient quantities of separable radiolaria in the surface plankton tows, so two Pacific sediment samples were used. Clean, slightly-crushed radiolaria skeletons were separated from the samples and washed with distilled water, H_2O_2 and HCl. The Ba/Si ratio in this sample was also low (Table 15) basically comparable to that in the diatom frustules.

TABLE 15. Elemental Ratios in Opal Samples.

Antarctic diatoms, Stn. M:

(Ratios to Si - x10^{-5}, Fe/Al - x1)

	Fe/Si	Zn/Si	Al/Si	Ba/Si	Fe/Al
bulk (untreated)	1.3	2.6	3.3	1.6	0.38
peroxide-water washed	0.6	1.9	2.7	1.1	0.23
HCl washed	[-]	0.28	2.5	0.2	[-]

Water column "regeneration" ratios (x10^{-5}):

Zn/Si - 5 Ba/Si - 70

Antarctic diatoms - filtered subsample (x10^{-5}):

Cu/Si - 0.38 Ni/Si - 0.13

Radiolaria hand-picked from Pacific Eocene sediment samples (x10^{-5}):

Ba/Si - 0.5

Leaching experiments - summary. A series of plankton samples, collected from a variety of environments, have been analyzed for their total major and minor elemental concentrations and were subjected to a series of decomposition experiments to identify the chemical nature and sites of the element-particle association. Major fractions of the total Ni, Cd, and Mn were found to be weakly associated with the plankton and are released back into seawater along with the rapidly recycled nutrient, phosphorus. This process occurs within a very short time after collection of samples and appears to be due to a combination of active excretion, cell lysis, and bacterial decomposition of the organic matter. The solubilized metals have major fractions which are small enough to pass through 0.4 µm filters and are not strongly bound to non-polar, extractable organic material or photosynthetic pigments. The stability of any surface organic-metal binding is low enough that significant fractions of Cd, Mn, and Ni as well as smaller fractions of the Cu and Fe are exchangeable with high concentrations of ammonium ion and are chelatable by EDTA and APDC. These results suggest that these rapidly solubilized elements should be regenerated in the water column in the dissolved fraction soon after the particulate material begins to decompose.

Significant fractions of the Cu, Ni, Cd, Ba, Mn and Zn are bound to organic sites which are not rapidly exchanged with seawater, distilled water or chelators. The elements are extracted from the organic matrix at pH 1 (0.1N HCl) along with the release of Ca, but direct analysis of the calcium carbonate demonstrates that these elements are not incorporated in that phase. These binding sites release fractions of the Ni and Mn to distilled water after several hours, but maintain their Cu complexing capacity until they are protonated or hydrolized in the acidic solution. It is likely that this fraction undergoes a much slower rate of release as the particles settle through the water column.

Lastly, there is an even more refractory group of trace elements associated with these plankton which includes large fractions of the Si, Al, Fe, and variable amounts of Zn. Examination of the major biogenic phase in this fraction, opal, shows that this is not the carrier for these elements (other than Si). Al and Fe may be present within a lithogenous phase in some samples. It is not likely that these residual components are solubilized in the water column environment, and their transport to the sediment must be a "single-pass" process.

5. TRACE ELEMENT DISTRIBUTIONS

To begin this discussion, we will examine relationships between the total concentration of trace elements in surface-ocean biogenic particulate matter and environmental factors such as the dissolved concentrations of nutrients and trace elements. Two questions can be asked: 1) To what degree does the surface environment determine the composition of the biogenic particulate matter? 2) How is the uptake of trace elements and nutrients by organisms expressed in the dissolved concentrations of those elements in surface waters? The data presented in this study do not yet uniquely answer these questions, which have both geochemical and ecological importance. However, the results of these experiments suggest several hypotheses and models which will be useful for further study and interpretation of trace element biogeochemical cycles.

5.1 Environmental control of the trace element compositions of plankton.

In discussing the relationship between biogenic particulate matter and the dissolved elements in sea water, it is useful to consider two classifications of trace elements based on their vertical distributions. The first group consists of those elements whose open-ocean surface water concentrations are depleted to less than 1% of their deep water concentrations. This group includes the micronutrient elements N, P, and Si and the trace elements Cd and Zn. These are the "bio-limiting" elements defined by BROECKER (1974). In grouping these elements together, it is not suggested that they necessarily have nutrient status or are important in growth limitation of the organisms. The other group of elements include those which are taken up by organisms but which show only partial surface depletions. This group is equivalent to BROECKER's "bio-intermediate" classification and includes Cu, Ni, and Ba. This discussion will be limited to the elements whose dissolved distributions are significantly determined by biological cycles. Other trace elements, such as Mn and Al, do not have distributions which show surface uptake or deep regenerative enrichments.

Systematics of the trace element-nutrient relationships can be expressed in terms of the element ratios to a "bio-limiting" nutrient element -- phosphorus. The total biogenic flux of a trace element out of the upper ocean is then calculated in terms of its ratio to P in the particles and the total flux of particulate P. This makes no assumptions about a functional relationship between these elements (other than their common association with the planktonic particles), nor any assumptions about the regenerative fractionation of the particulate elements. Phosphorus is chosen as the reference element representing the organic matter because PO_4 uptake continues in oligotrophic surface waters well after the apparent depletion of NO_3 (VACCARO, 1963; THOMAS, 1966; RYTHER and DUNSTAN, 1971) and because it was more easily followed (analytically) through the plankton sampling and leaching experiments described above. BOYLE and others (1981) and COLLIER (1981) and have investigated variations in the horizontal distributions of surface Cu, Ni, Cd and PO_4 in terms of inferred ratios in biogenic particles formed in the mixed layer. The elemental ratio in the plankton is compared to that in the surrounding surface water:

$$\alpha = \frac{\text{metal/P}_{\text{(plankton)}}}{\text{metal/P}_{\text{(water)}}}$$

Differential regeneration of nutrients and trace elements within the surface ocean will result in different element ratios in the settling particles described by:

$$\beta = \frac{\text{metal/P}_{\text{(sinking)}}}{\text{metal/P}_{\text{(plankton)}}}$$

As long as this regeneration is taking place within the mixed layer, the product of the ratios, $\alpha \cdot \beta$, compares the relative enrichment or depletion of the particulate trace element flux with respect to the dissolved ratios; α represents the particulate formation step by primary producers and β represents all of the heterotrophic and physical processes which modify the ratio before the particulate matter settles out of the upper ocean. In calculating these parameters, α and β, it is not implied that they are constant in space or time. In fact, it will be demonstrated that they do vary.

For these samples, the relative sea water release percentages from the leaching experiments are used as first-order estimates of the magnitude of β. This is calculated as the percentage of the total element not released to the sea-water suspension after collection of the plankton divided by the same percentage for P (Fig. 6). The plankton collected for these experiments were a mixture of phytoplankton and microzooplankton collected by the 44 μm net. This mixture does not directly represent the composition of the primary producers. However, the coefficient β is derived directly from the experiments on this intermediate material. Therefore, the product of the sample composition and β should still give a consistent estimate of the settling composition. This estimate of β could still be subject to significant error since the relationship between rapid regeneration in the upper ocean and the sea water suspension experiment has not been established. The relative importance of active excretion, autolysis, or bacterial and other heterotrophic activity in contributing to a net value of β has not been quantified.

The models of trace element cycles presented in this paper are necessarily based on our relatively limited data set. These plankton samples cannot truely represent the whole surface community and all of its inherent variability. Significantly more sampling of microorganisms, fecal material, and detrital material must eventually be included in this type of analysis. The fluxes which will be predicted using these plankton data generally support the values of β derived from the leaching experiments for the "bio-intermediate" trace elements but do not work well for Cd or Zn.

The total metal and phosphorous concentration data for the Pacific plankton samples and surface waters are shown in Figures 8 and 9 and the elemental ratios are calculated in Table 16. The dissolved concentrations of the "bio-limiting" elements all decrease, more or less simultaneously, from high values in upwelling environments to nearly zero in oligotrophic waters, and the ratios between them remain relatively constant. The ratios between the "bio-intermediate" elements and P show a large range due to the specific depletion of the nutrient. In contrast to this range in the dissolved ratios, the "bio-intermediate" element ratios to P in the plankton samples are nearly constant and show little relationship to the large dissolved variations. These ratios are constant for Cu, Ni, Mn and Cd (Zn shows little relationship to P in the plankton Table 7). Clearly, these plankton trace compositions are not determined in simple proportion to the surface water concentration ratios to nutrients. This emphasizes the relatively specific nature of the organic association of these trace elements and implies that the "available sites" are saturated. In a general sense, these ratios (Table 16b) can be compared to those describing the major-element compositions of the plankton, or "Redfield ratios" (REDFIELD, KETCHUM and RICHARDS, 1963), which are relatively constant when compared to large variations in the ratios of dissolved inorganic C, N, and P.

5.2 Horizontal distributions of dissolved trace elements.

A great deal of information about the biogeochemical cycles of trace elements has been derived in recent years through the examination of their horizontal distributions in surface waters (BOYLE and EDMOND, 1975; BRULAND, 1980; BOYLE and others, 1981). The regions of transition between upwelled waters at ocean margins or divergences and the oligotrophic central gyres can be especially useful in formulating models describing the development of surface water depletions through biogenic particle fluxes. These regions are important in that a significant fraction of the total vertical flux of materials between the surface and deep oceans occurs near the ocean margins. Although the central oligotrophic regions cover nearly 50% of the world oceans, they contribute less than 10% of the total vertical flux of biogenic particulate matter (KOBLENTZ-

Horizontal transects away from the eastern margins of the Pacific Ocean which include high-quality surface trace element and nutrient analyses have been reported and discussed by BRULAND (1980) and BOYLE and others (1981). A simple model describing the history of surface water along such a horizontal section can be examined. It suggests that the thermocline water is brought to the surface near the coastal divergence and then mixes radially into the central gyre, along isopycnals, without significant new inputs from below. As biological production proceeds in this nutrient-rich surface water, the total dissolved fraction of each element is depleted according to the element ratios present in the settling particles. This closed system model is analogous to a laboratory batch culture (DROOP, 1975) except for the removal of the particulate phases by settling. Starting with this crude model, we can compare the dissolved depletion ratios along a horizontal section with the plankton data presented in this paper. The surface water samples of BRULAND (1980) were taken from a transitional environment and the data set includes both nutrients and

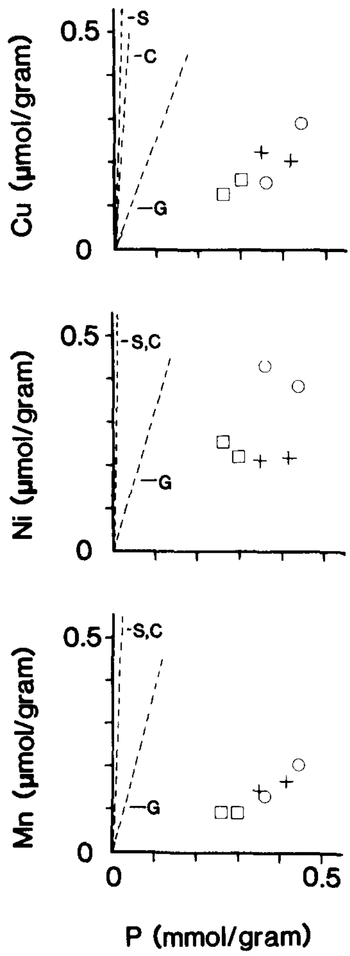


Fig. 8. Bulk plankton compositions: Cu, Ni, Mn vs. P. Symbol key: plus sign - Galapagos(G); square - MANOP C(C); circle - MANOP S(S). Dotted lines represent the ratio of metal to phosphorus in the surface water at the different tow sites.

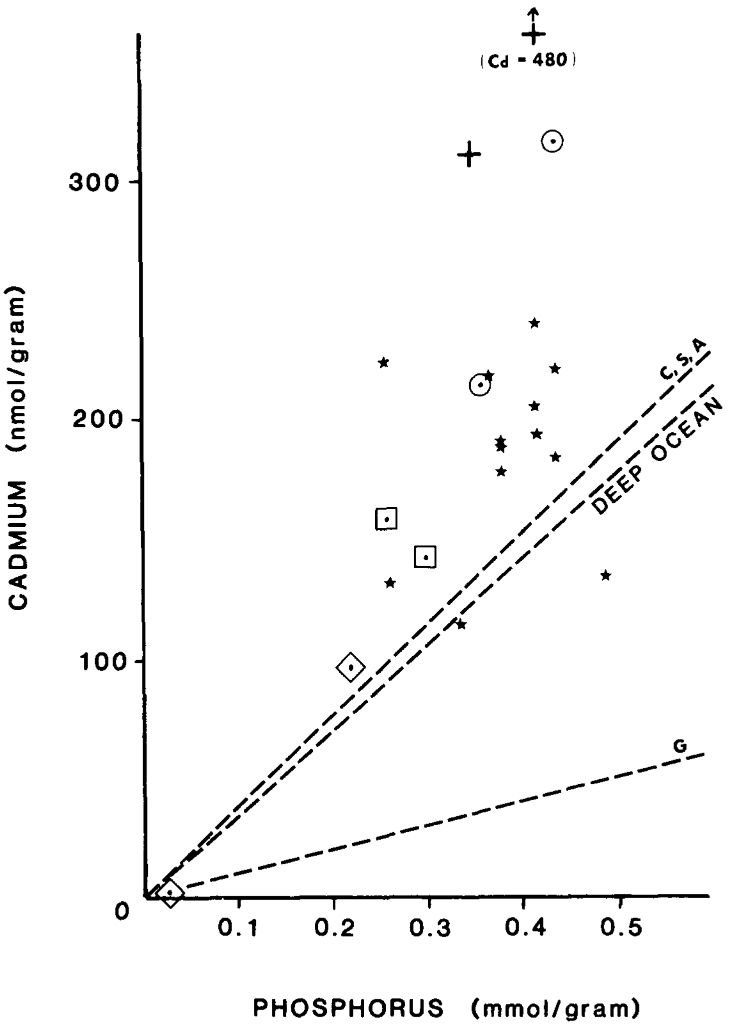


Fig. 9. Bulk plankton compositions: Cd vs. P. Symbol key: plus sign - Galapagos(G); square - MANOP C(C); circle - MANOP S(S); star - data from Martin and others (1976) recalculated to a salt-free plankton mass. Dotted lines represent the ratio of Cd to P in surface water at the different sites and in the deep Pacific.

TABLE 16. Total Concentration Ratios.

Sites	Surface water dissolved: PO_4 (µM)	$Si(OH)_4$ (µM)
G - Galapagos	0.8	5.2
C - MANOP C	0.04	3.2
S - MANOP S	0.03	1.9

RATIOS:

Sites:		G	C	S		G	C	S
	Cd	0.10	0.38	0.37		0.89	0.55	0.66
a) Surface Water Ratios to P	Zn*	.35	2.4	3.0	b) Plankton Ratios to P	5	3	3.3
		--	--	--		--	--	--
($x10^{-3}$)	Cu	2.6	17	28	($x10^{-3}$)	0.56	0.52	0.54
	Ni	3.7	58	72		0.58	0.86	1.1
	Mn*	3.8	29	52		0.40	0.34	0.42
	Ba*	45	830	1300		1.2	1.7	
	Cd	9	1.5	1.8		1.6	1.6	3.0
c) Plankton Ratio/ Seawater Ratio	Zn	14	1.3	1.1	d) Relative Seawater Release Ratio		6	
		--	--	--		--	--	--
						t		
α	Cu	.22	.03	.02	β		3.4	
	Ni	.16	.01	.02			2.4	
	Mn	.11	.01	.01			2	
	Ba	.03	.002				6	

*Dissolved trace element concentrations estimated from BRULAND (1980), KLINKHAMMER and BENDER (1980), and EDMOND (unpublished).

high-quality trace element data. Dividing BRULAND's (1980) surface water metal-phosphate plots into three consecutive horizontal sections and taking the slope over each section allows us to calculate the predicted elemental ratios for the particles causing the depletion along each section (Table 17). For Cu and Ni, the depletion ratios are relatively constant but significantly higher than those measured in the bulk surface plankton. Modifying the measured plankton ratios by the parameter β (as defined in the previous section and estimated from the seawater release fractions) predicts flux ratios for Cu and Ni which are consistent with the dissolved depletion ratios.

When this analysis is applied to a "bio-limiting" element, Cd, several difficulties arise. The dissolved Cd concentration reported by BRULAND (1980) drops to near the detection limit within the first four stations away from the coast while the PO_4 concentration drops more slowly (Fig. 10). The resulting depletion ratios are not at all constant and approach zero rapidly. Using the crude horizontal transport model, these observations would require a large range in Cd/P ratios in the settling particles. The high initial ratio (when compared to the deep ocean Cd/P ratio) is consistent with the higher Cd/P ratios measured in surface plankton (Figures 9 and 10). However in order to maintain the relatively constant deep water Cd/P ratio of 0.35-0.40 X 10^{-3}, the particulate material must preferentially lose its excess Cd before settling into the thermocline. As PO_4 uptake continues after the depletion of Cd, the model requires the flux of low-Cd/P particulate matter (which has never been sampled). Since there is no clear relationship between Zn and P in the plankton samples and since there is no significant variation in dissolved Zn across BRULAND's (1980) horizontal transect, these plankton composition and surface water depletion models can not be applied.

Only a small fraction of the total particulate matter produced in the surface ocean is actually transported out of that environment into the deep ocean (EPPLY and PETERSEN, 1979). The majority of the "bio-limiting" elements are rapidly recycled and these cyclic fluxes are many times greater than the settling flux which determines the deep regeneration ratios. If the uptake/regeneration ratios in the surface cycle are at all different from the elemental ratios in the settling material then various dissolved ratios will be expressed in mixtures of

TABLE 17. Surface Water Depletion vs. Plankton Ratios. ($\times 10^{-3}$).

North Pacific surface water transect (BRULAND, 1980)	ΔCu/ΔP	ΔNi/ΔP
Stations 13 - 18	1.9	3.2
17 - 21	1.4	2.4
20 - 25	2.2	8
	Cu/P	Ni/P
Pacific plankton ratios (this work)	0.54	0.6-1.1
plankton ratios x β	1.8	1.4-2.6
(β) used from Table IV-3:	(3.4)	(2.4)

water from these different environments. More specifically in the case of Cd, particulate formation in nutrient-rich environments occurs at a Cd/P ratio in the range of $0.4-0.7 \times 10^{-3}$, which is almost always significantly higher than the dissolved ratio. Cadmium may be regenerated preferentially from these particles as they settle out of the mixed layer such that the residual composition approaches the deep ratio. This is in general agreement with the results of Pacific sediment trap experiments (KNAUER and MARTIN, 1981) but not with the seawater release experiments. Water which has been recently upwelled from the thermocline and mixed with depleted gyre water would follow the deep-water Cd/P mixing line, in a manner similar to the deep water "Redfield" N/P ratios displayed in "new" upwelled water (TRAGANZA, CONRAD and BREAKER, 1981). This effect can be seen for Cd in the western North Pacific near the Kuroshio (BOYLE and others, 1981), and in Antarctic surface waters (COLLIER, 1981). Older surface water which has either moved away from its source of upwelling or is derived fro the slower vertical exchange through the upper thermocline will tend to express the preferential uptake of Cd over P. To better constrain this system, we need simultaneous measurements of plankton uptake and regeneration, near-surface particle compositions and fluxes, and a better physical description of the mixing and transport regime. A horizontal transect away from a eutrophic environment is still one of the best laboratories for this type of experiment. is

In contrast to the wide variations in dissolved ratios, the particulate trace element/carrier ratios have been shown to be relatively constant and this will allow the direct prediction of the biogenic flux of each element in terms of the major organic cycles. These biogenic fluxes can then be compared to other known fluxes for each trace element to determine their significance in the total geochemical cycle.

6. BIOGENIC TRACE ELEMENT CARRIERS

The nature of the biogenic carriers of trace elements can only be inferred from the results of the leaching experiments and from metal-carrier distributions in the marine environment. Identification of the precise metal-organic compounds or functions in these heterogeneous, chemically unstable particulate samples is beyond the scope and intention of this investigation. The plankton leaching experiments have quantified the trace element associations with various carriers in surface-ocean particulate material. The known cycles of these carriers will be used to examine the significance of the biogenic associations in the geochemical cycles of the trace elements.

Most of the trace elements studied were associated with the non-skeletal organic phases of the particulate samples. The three basic partitions of elements defined by the leaching experiments were: extremely labile release products; the HCl-soluble fraction; and the refractory components which were only released by concentrated nitric acid or remained in the particles throughout the experiments. These classes do not represent mechanistic definitions but rather provide useful distinctions between the behavior of the trace elements along with their major carriers.

6.1 Labile Organic Associations.

The dominant particulate fraction of several of the elements studied was very weakly associated with the particles and covaried with P during leaching. The rapid release of P and N to seawater by marine organisms has been documented during zooplankton excretion (BUTLER, CORNER and MARSHALL, 1970) and with decomposing phytoplankton (GRILL and RICHARDS, 1964). HARRISON (1980) has outlined laboratory decomposition processes releasing C, N, and P following three stages: autolysis; microbial colonization; and very slow degradation of refractory organics. The rapid loss of N and P from particles in the upper oceans has been demonstrated for suspended material (BISHOP, COLLIER, KETTEN and EDMOND, 1980), and settling material collected in sediment traps (KNAUER, MARTIN and

BRULAND, 1979). Evidence from the rates of total primary production in the euphotic zone (EPPLEY and PETERSON, 1979; KING and DEVOL, 1979) and from the relationship of the chemical composition of phytoplankton to their growth rates and nutritional states (GOLDMAN, MCCARTHY and PEAVEY, 1979) all suggest that N and P are rapidly recycled within the euphotic zone.

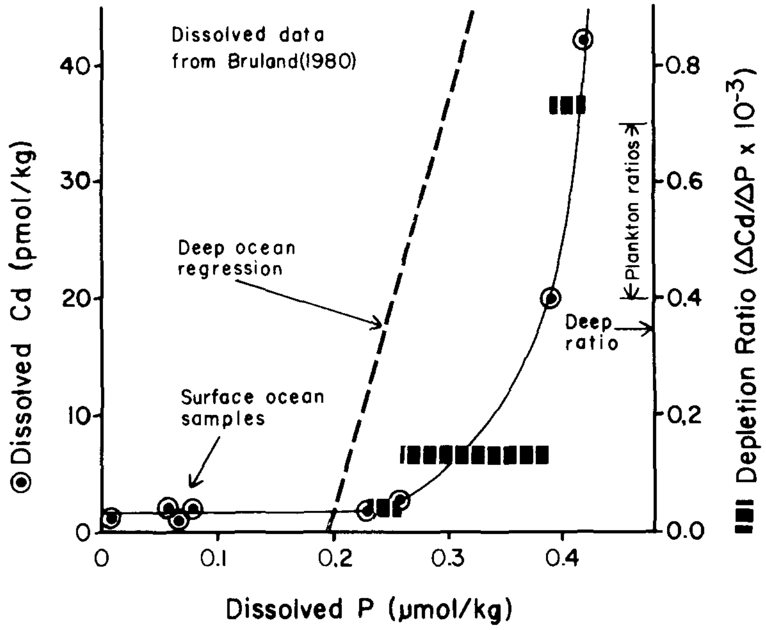


Fig. 10. Cd-P systematics in the North Pacific. Dissolved Cd vs. PO_4 in surface water (Bruland, 1980) along a horizontal transect extending from the coast of California into the oligctrophic central gyre. Depletion of Cd occurs rapidly while the depletion of phosphorus continues well out into the gyre. Estimates of the compositon of particulate matter required to remove Cd and P between the surface stations are compared with the observed range in Cd/P ratios in plankton.

The experiments reported here show that a group of labile trace metals are released along with the micronutrients. Major fractions of the total Cd, Ni, and Mn are found in the sea water and distilled water leaching solutions. This is the first quantitative documentation of this process occurring in open-ocean biogenic particles, although it had been predicted from the water column distribution of the dissolved species (BOYLE, 1976). In every experimental examination of Cd in laboratory cultures of marine organisms, its labile association with the cell contents or organic surfaces has been noted, but the nature and function of this association is not known (COSSA, 1976; KREMLING, PIUZA, VON BROCKEL and WONG, 1978; SICK and BAPTIST, 1979). More recently, KNAUER and MARTIN (1980, 1981) have reported a significant release of Cd, Mn and P to the hyper-saline collection fluid in a sediment trap, however the effects of osmotic pressure and exchange in this release are difficult to evaluate. No specific references to a labile behavior for Ni have been reported.

The various leaching experiments indicate that this regenerated material is derived from several different sites within the plankton particles. Significant acceleration of the release by lysis due to osmotic shock suggests the presence of these elements in a dissolved pool within cell structures. Direct excretion by the zooplankton in the tows can account for a portion of the release products. The initial and rapid release of P was higher than reported rates of zooplankton excretion (BUTLER and others, 1979), but this active process is accelerated by the physical shock of the plankton tow and concentration process (HELLEBUST, 1974).

Several other experiments demonstrated the dissolved nature of the released products. Large fractions of the released elements were not filterable, they were not directly extractable into a non-aqueous solvent, and they were in a form which is available to chelation by APDC followed by extraction of the complex into chloroform.

Increased amounts of trace metals were extracted from the particles by iso-osmotic solutions containing APDC, EDTA, and NH_4Cl indicating that a fraction of the labile elements were weakly bound to exchangeable surface sites. In EDTA-leaching experiments with plankton samples, MOPPER and DEGENS (1972) reported the release of significant fractions of the total hydrolyzable monosaccarides and amino acids. This was attributed to the extraction of metals functioning as binding bridges between these organic ligands and other organic surface sites.

The role of bacterial activity in the observed regenerations can not yet be quantified. HELLEBUST (1974) has noted the difficulty in separating heterotrophic bacterial activity from active excretion or autolysis and the general ineffectiveness of antibiotic treatments in stopping bacterial decomposition in collected plankton samples. However, a significant decrease in the release of P after the addition of antibiotics was noted. Because these samples were contaminated with Ni, Cu and Cd, the direct effects of antibiotics on the metal releases was not determined.

In summary, a significant fraction of the biogenic Cd, Mn, and Ni are weakly bound to surface planktonic particulate matter. This fraction is most likely regenerated as dissolved material in the upper ocean, along with the nutrient P, through active excretion, cell lysis, and heterotrophic activity. The geochemical cycles of P, Cd, Mn, and Ni will be discussed in section 7.3 as they reflect the sites of regeneration and the significance of the release products in the total fluxes of these elements.

6.2 HCl-soluble material.

Most of the remaining fractions of the non-silicate associated trace elements were solubilized by 0.1N HCl. Although $CaCO_3$ was specifically solubilized in this acid, that phase was shown by direct analysis to be an insignificant carrier of the metals found in the particles. This result is consistent with recent trace element analyses of the $CaCO_3$ in core-top foraminifera (BOYLE, 1981).

Several lines of evidence suggest that hydrous metal-oxide precipitates are unlikely to be significant carriers of these trace elements in biogenic particles. Fe is the only metal present in sufficient quantities to be considered as a possible carrier of this type. The proposed mechanisms of association with Fe include surface adsorption (MURRAY, 1975; JAMES and MACNAUGHTON, 1977) and homogenous incorporation as a solid solution within a freshly-formed precipitate. Adsorption at metal oxide surfaces has been modeled as the formation of surface hydroxyl complexes with the metal or hydrated metal (JAMES and MACNAUGHTON, 1977). The maximum number of these surface adsorbing sites in an FeOH precipitate must be less than or equal to the total number of moles of Fe in the precipitate. The plankton samples contain approximately 2 µmol Fe/gram which results in 0.01 µmol Fe/ml in the sea water-plankton suspension. EDTA was added to the sample to make a concentration of 1.0µmol EDTA/ml suspension: at least, 100-times more concentrated than the maximum numbe of Fe sites. At pH 8, the formation constants for the metal-EDTA complexes are at least 10 orders of magnitude larger than those for the formation of the metal-surface complexes (SILLEN and MARTEL, 1971; BALISTRIERI, BREWER and MURRAY, 1981). If adsorption at the surface of a hydrous iron-oxide precipitate was quantitatively important in these samples, then a larger percentage of the metals would have been exchanged from the surfaces by the addition of EDTA.

It has been demonstrated that metal oxides and hydroxides adsorb dissolved organic material from natural waters (DAVIS and LECKIE, 1978; DAVIS, 1980). If these hydrous metal oxides are present in the plankton samples, they are very likely to be coated with adsorbed organic material. The metal adsorption properties of these systems take on the properties of the exposed organic ligands rather than those of the surface hydroxide groups.

It has been suggested that a hydrous iron-oxide phase with coprecipitated metals could be a significant carrier of trace elements associated with biogenic particulate matter (MARTIN and KNAUER, 1973; TUREKIAN, KATZ and CHAN, 1973; BOSTROM, JOENSUU and BROHN, 1974). If such a carrier were significant in these samples, then there should have been a simultaneous release of the minor elements and the iron carrier to the 0.1N HCl solution. Although the bulk-plankton metal/Fe ratios were on the order of 0.1, the ratios in the material released to 0.1N HCl were approximately 1 and the total metal/Fe ratio was 3-5. Therefore, it is not reasonable to describe this matrix as an iron hydroxide coprecipitate.

Elimination of the two acid soluble mineral carriers - $CaCO_3$ and hydrous iron oxides, leaves fixed organic ligands as the likely site of metal binding for the HCl-soluble fraction. There is little surprise in this result, although the characterization of these metal complexes has hardly begun. Approximately one quarter to one third of all proteins and enzymes that have been purified contain metals or require metal ions for their biological activity (IBERS and HOLM, 1980). These are generally classified into two groups: metalloproteins and metal-activated proteins or complexes (HUGHES, 1972). In the first group the metal is firmly bonded as part of the structure of the protein. In the second, the metal ion - binding group interaction is much weaker. The metalloproteins and enzymes are relatively resistant to chemical attack and are bound to the metals through multi-dentate associations at their more basic residues such as the imidazole ring of histidine and the thiol group in cysteine. These complexe are usually metal-specific and the metals function as structural templates or redox catalysts. The metal-activated proteins and complexes are lower in stability, are less metal-specific, and can be reversibly disassociated from their metal ions by acid or prolonged exposure to low metal activities (e.g., through dialysis). The metals in these systems usually function as Lewis Acids in their catalysis and their association with the donor sites usually follows the Irving-Williams order of stability for divalent cation complexes. Typical ligands involved include carboxyl, hydroxyl, and amino groups.

The solubilization of the trace elements from the plankton samples is generally consistent with the stability of metal-organic complexes. The fractions of the Cu and Fe that were released by the HNO_3 solution may have been bound within stable metalloproteins. These metals have been studied in numerous enzymes involved in electron transport, oxygen transport, and storage. Zn is also functional in numerous hydrolytic enzymes. Only small fractions of the total Cu, Fe, and Zn were released to the non-acidic leaching solutions consistent with metalloprotein associations and with their stable organic ligand complexes. At the other extreme, the rapid release of Cd and Mn can be interpreted in terms of the low stability of their organic complexes (HUGHES, 1972). In general, due to its large ionic radius, Ba forms very weak organic complexes. The relative stability of the particulate Ba in these samples suggests that it is not bound in organic complexes.

It has been shown that a large fraction of most of the particulate trace elements studied here are either dissolved in cell fluids, loosely bound to organic surfaces, or more specifically associated with metalloproteins and complexes. A precise knowledge of the regenerative behavior and transport of these metals will require specific knowledge of the binding sites and the fate of the organic matter involved. Although we are still a long way from both of these goals, having established the ratios of the trace elements to major elements representing the carriers allows the examination of the element cycles in the water column and sediments.

6.3 Refractory Carriers.

The total fraction of each trace element which was not solubilized by the leaching solutions was generally small. Significant fractions of Fe and Al were resistant -- most likely associated with small amounts of clay scavenged by the biogenic material. This carrier, which will be discussed in section 6.4, was not significant for other elements in these plankton samples.

Variable amounts of P, Mn, Fe, Cu, and Zn were also resistant to acid leaching and may have been associated with refractory metalloproteins and storage products. The solubilization of these elements in concentrated nitric acid occurred very slowly through oxidative decomposition of the resistant organic structures.

The primary Si-phase in these samples was opal which is also resistant to acid leaching. Analyses of bulk opaline material from the Antarctic sample demonstrated that this phase was not a major carrier for trace elements other than Zn. The HCl-washed opal had a very low Zn/Si ratio (2.8×10^{-6}) suggesting that this phase may not even be a significant carrier for Zn.

6.4 Particulate Aluminum in Biogenic Samples.

The concentration of Al was determined as an indicator of the presence and significance of lithogenous particulate matter. Aluminum has both a terrigenous and biogenic component and its bulk concentration varies by more than an order of magnitude between different plankton samples. Results discussed in this section will show that aluminosilicate contributions to the trace elements (other than Al and Fe) in these plankton are insignificant. The experiments demonstrate the presence of a chemically-resistant lithogenous Al and Fe carrier and a trace fraction of Al that behaves similarly to several of the more labile trace elements. Variations in the concentration of refractory Al were consistent with inferred variations in the input of lithogenic particles and with dilution and scavenging of these inputs by biogenic materials in regions of high productivity.

6.4.1 Terrigenous sources of Al. The emphasis of this research was to study the effects of biogenic particulate matter on trace element geochemistry. The sampling of surface particulate matter does not necessarily provide the pure biogenic end-member, even in highly productive regions since there is usually some admixture of terrigenous materials. Examination of the average composition of the detrital fraction of pelagic clay (Table 18), taken as representing the lithogenous end-member, shows a relatively high enrichment in several metals over levels found in biogenic material. Since mixtures of biogenic and terrigenous material are, at best, difficult to separate mechanically or chemically, every attempt was made to sample biogenic material which was not significantly contaminated by lithogenous particles. Sampling sites were chosen for their distance from terrigenous sources and for their relatively high organic productivity.

The remoteness from land is not a sufficient criterion to establish the absence of suspended aluminosilicates. Long-range transport of these materials and their presence in the water column and sediments below remote mid-ocean areas are well documented (FERGUSON and others, 1970; WINDOM, 1975; BREWER, NOZAKI, SPENCER and FLEER, 1980; DUCE, UNNI, RAY and ARIMOTO, 1982). Estimates of the terrigenous contribution to the trace element composition of these plankton

TABLE 18. Element/Al Ratios

Tabulated for each sample are the total Al and the element/Al ratios in the bulk material as well as the maximum contribution of a clay carrier to the total trace element in the sample assuming all the Al is present in clay.

Sample		Total Al µm/gram	Fe/Al (x1)		Mn/Al (x10^{-2})		Ni/Al (x10^{-2})		Cu/Al (x10^{-2})		Zn/Al (x10^{-2})	
Detrital pelagic clay (1)		3100	.22		1.2		.03		.09		.08	
Antarctic plankton	Stn.M	0.39	.44	51%							80	0.1%
Galapagos plankton	Tow 1	9	.54	40%	1.7	70%	2.2	1%	1.7	5%	13	0.6%
	Tow 3	7.8	.36	60%	1.2	100%	1.7	2%	2.2	4%	27	0.3%
MANOP plankton C	Tow 1	0.72	1.8	12%	13	9%	35	0.1%	17	0.5%	140	0.1%
	Tow 2	0.94	1.3	17%	10	12%	23	0.1%	18	0.5%	68	0.1%
S	Tow 3	12.5	.59	37%	1.7	71%	3.1	1.0%	2.3	4%	11	0.7%
	Tow 6	3.5	.56	39%	3.7	32%	12	0.3%	4.3	2%	36	0.2%

(1) KRISHNASWAMI (1976), TUREKIAN and WEDEPHOL (1961), CRONAN (1969).

samples will be based on two properties of aluminosilicates found in the marine environment: they are relatively constant in their composition and they are generally resistant to chemical attack by acids (GOLDBERG and ARRHENIUS, 1958; CHESTER and HUGHES, 1967).

The method most frequently used to identify terrigenous materials within a complex matrix involves the assumption that one of the measured elements is present *only* in the terrigenous component, and that all other terrigenous elements are present in known proportions. The most frequently used indicator of the terrigenous carrier phase is Al, but other elements, such as Sc, Ti, and Th-232, have also been used. SPENCER and SACHS (1970) and PRICE and CALVERT (1973) have shown, using this approach, that a silicate component becomes the dominant part of the sampled particulate metals with increasing depth and decreasing productivity in coastal marine environments. BREWER and others, (1980) have studied the chemistry of particulate fluxes into sediment traps in the North Atlantic. The fluxes of Ti, K, V, La, Co, and Th-232 all correlate with the flux of Al, and inter-element ratios are close to those in crustal materials. The estimated terrigenous component accounts for 10 to 45% of the total mass flux collected by the traps. It cannot, however, be simply assumed that these elements are carried by terrigenous matter in all environments. Depending on the relative importance of terrigenous sources and biological productivity, the dominant carrier for, and chemical behavior of an element in the bulk suspended particles can change dramatically.

To estimate the maximum contribution of terrigenous trace elements to the plankton composition, the metal/Al ratios were calculated for each sample and compared to lithogenous metal/Al ratios (Table 18). The lithogenous ratios chosen were those of KRISHNASWAMI (1976); these are estimates of the *detrital* fraction of pelagic clay and should represent the input composition of the lithogenous component. The end-member model assumes that all Al in suspended particles is lithogenous and that other terrigenous elements are present in known proportions to Al. For each element, the maximum contribution of the model terrigenous component to the total measured concentration is calculated. Only Fe and Mn have concentrations in the plankton samples which could be significantly accounted for by a lithogenous component. All of the other elements have concentrations which are at least 1 to 2 orders of magnitude in excess of that predicted from the metal/Al ratio.

The acid leaching experiments performed on the Galapagos plankton tows (Fig. 7a, Table 19) showed that the relatively high concentration of Al in that sample was resistant to acid leaching. In low-temperature, short-term acid leaching experiments with sedimentary clay, it has been shown that most of the Al (>90%) and a significant fraction of the Mn resist acid leaching by 0.5N HCl (CHESTER and HUGHES, 1967; AGEMIAN and CHAU, 1976). Although the ratio of Mn/Al in the plankton is similar to that reported for lithogenous material, the labile behavior of Mn during leaching is totally inconsistent with its presence in a refractory silicate. From 40 to 60% of the total particulate Mn was always released to the seawater and distilled water solutions, and most of the rest was solubilized in 0.1N HCl. The *absence* of refractory Mn in the plankton conflicts with the assumption that all of the Al is present in terrigenous material with a *known* Mn/Al ratio. There is an increasing body of data which questions the refractory nature of the atmospheric input of Mn. Water column profiles of Mn (KLINKHAMMER and BENDER, 1980; JONES and MURRAY, 1980; LANDING and BRULAND, 1980) show a surface maximum in total Mn which is mostly accounted for in the dissolved fraction. This requires some amount of dissolution of Mn from the atmospherically-transported particulate input. HODGE, JOHNSON and GOLDBERG (1978) have shown that 50% of the Mn filtered from air samples at a coastal site was solubilized when suspended in seawater even though the particulate matter possessed a crustal Mn/Al ratio. Clearly, more work needs to be done on the nature of the lithogenous particulate Mn inputs. The labile behavior of Mn in the plankton rules out its direct association with a refractory aluminosilicate.

The slow solubilization of Fe from these samples by HNO_3 is consistent with its presence within a silicate carrier. Samples with high particulate Al (Galapagos tows and MANOP S, Tow 3) also have high particulate iron although the converse relationship is not always true.

The total Al concentration in surface particulate material has been shown to co-vary with the inferred rate of atmospheric input of crustal material (KRISHNASWAMI and SARIN, 1976, 1981; WALLACE, HOFFMAN and DUCE, 1977). The variations in Al concentrations seen in the plankton samples from this study are consistent with this observation. In regions of high biological productivity, the terrigenous component will be diluted by the biogenic particles and more rapidly scavenged from the surface via incorporation in and settling of fecal material and large organic aggregates (BISHOP, EDMOND, KETTEN, BACON and SILKER, 1977; HONJO, 1980). No direct measurements of clay deposition rates are available for any of the plankton sampling regions, so inferences must be drawn from the meteorological, oceanographic, and sedimentary descriptions of the areas. The Galapagos samples have the highest Al concentrations and were collected relatively close to the American continent. This region has been shown to have sediment compositions reflecting aeolian transport of quartz by the south-east trades (MOLINA CRUZ and PRICE, 1975). Excursions of equatorial surface-water fronts, discussed by WYRTKI (1967), affect the organisms and flux of particulate matter out of the surface (BISHOP and others, 1980). Changes were noted in the weather and currents while on station at the Galapagos. There wasa a significant intensification of winds and change in current direction between Tow 1 and 3, which might account for compositional differences between the two tows (Table 7).

TABLE 19. Acid Leaching Series - Results for Al, Fe and Mn

Percentage of total particulate element released to each solution.

Sample	Total Al	Element	Leaching solutions: S.W.	Dist. Water	HCl	HNO_3	Residual
Galapagos Tow 3	7.8 µm/gram	Al	0.2%	0.2	4	6	90
		Fe	5	4	14	46	32
		Mn	41	16	35	9	0
MANOP C Tow 2 8-hour exposure	0.75 µm/gram	Al	5	2	40	34	19
		Fe	3	10	7	48	32
		Mn	9	54	29	7	1

The MANOP sites are significantly further away from land and the samples show lower levels of particulate Al. Differences in the Al between the two MANOP sites can be understood in terms of their relative productivity and the trajectories and intensities of winds over them. The mean annual productivity at site C is estimated to be on the order of 250 mg C/m^2/day (KOBLENTZ-MISHKE and others, 1970). At site S the estimate is less than 100 mg C/m^2/day (EL-SAYED and TAGUCHI, 1979) and may have been lower during sampling due to the annual weakening of the front between the Countercurrent and the North Equatorial Current. The surface water concentration of biogenic material was much higher at site C than at S based on the plankton yield per unit towing time.

In June, when the samples were collected, the northeast trades at site S were well developed and could carry dust from the arid regions of North America. The southeast trades over site C were much weaker and have a much longer trajectory back to a terrigenous source. The winds over the two sites are normally separated by the intertropical convergence zone - ITCZ, (WYRTKI and MEYERS, 1975). SILKER (1972) has shown that Be-7 concentrations in the Central Pacific surface waters are more than an order of magnitude higher at 10°N than at the equator. This is attributed to equatorial upwelling of older water and a much higher aerosol washout at, and north of, the intertropical convergence zone. These processes could further increase the relative concentration differences of particulate Al at the two sites.

Site S lies at a latitude which experiences short-term and seasonal variations in surface currents and winds (HALPERN, 1979). The front between the Equatorial Countercurrent and the North Equatorial Current moves through this zone as does the ITCZ (WYRTKI and MEYERS, 1975). Two tows collected at site S showed significant differences in the total concentration of Al and Fe which could be associated with variations in the atmospheric delivery of terrigenous materials to the surface waters in this region. Tows 3 and 6, which contained 12 and 3 µmol Al/gram, respectively, were separated by 6 days of high wind and rain, possibly indicating the passage of a frontal system. Surface hydrocasts at the site indicated the presence of a very shallow layer of low oxygen water at the end of the cruise that was not present at the beginning. This water mass was probably of eastern Pacific origin as opposed to the more oxygenated waters of western origin in the Countercurrent (TSUCHIYA, 1968).

All of these factors suggest that control of the concentration of refractory particulate Al is a function of variations in atmospheric input of lithogenic particulates and of the dilution and scavenging of these materials by biogenic particles. These effects appear to be significant even in central Pacific stations such as MANOP C and S. This result is consistent with the recent data of DEUSER, BREWER, JICKELLS and COMNEAU (1983) suggesting that the amount of aluminum found in surface water suspended particulate matter was related to short-term variations in the input of aeolian materials. The vertical flux was controlled by production of biogenic material which carried the terrigenous material out of the surface ocean.

6.4.2 Non-terrigenous Particulate Al. Dissolved Al profiles of HYDES (1979) display surface and bottom maxima with broad mid-depth minima. Scavenging of dissolved aluminum is indicated by curvature in the salinity - Al relationship through a region of linear potential temperature - salinity relationship. It is presumed that the surface maximum is supported by an atmospheric input of lithogenous material. Significant dissolution of Al from these particles and the formation of new particulate phases through scavenging are both processes which, if quantitatively significant, violate the assumption that all of the particulate Al is associated with refractory lithogenous material.

There is no evidence or reason to suppose that Al is not taken up or scavenged by plankton. RILEY and ROTH (1971) were able to measure particulate Al in plankton cultured in the laboratory where the only source of Al to the cultures was a small level of dissolved contamination in the media. MARTIN and KNAUER (1973) reported relatively large variations in the concentration of Al in their Pacific plankton samples which were consistent with those determined in this study. Significant fractions of the Al in their samples were leachable into HNO_3-especially from samples with low total Al concentrations. Although their hot-nitric reflux method would also have removed some of the Al from clays, their results suggest that a component of the Al was carried in a more labile phase than a silicate. The Al in the Galapagos plankton was resistant to chemical leaching and was most likely present as a refractory aluminosilicate. The distilled water - acid leaching experiments on material from MANOP C (Fig. 7b, Table 19) clearly show Al behavior which is different than that expected from a terrigenous carrier. This sample contained a very low concentration of total Al, 40% of which was solubilized by the 8 hour-0.1N HCl suspension and another 30% by the 16N HNO_3. The absolute amounts of Al released by HCl from the Galapagos and MANOP samples were essentially the same and probably represent a component of Al taken up or scavenged by the organisms from Al dissolved in seawater.

Another possible biogenic carrier for Al is the siliceous tests of diatoms and radiolarians. The proposed associations include adsorption (LEWIN, 1961; HYDES, 1979) and actual incorporation within the opaline lattice - in solid solution or as an authigenic phase (van BENNEKOM and van der GAAST, 1976). To test the importance of structural incorporation of Al in opal, the diatom samples from Antarctic station M were analyzed (Table 15). The concentration of Al was found to be very low ($Al/Si = 3x10^{-5}$), as were the concentrations of Fe, Ba, and Zn. Both the Al and the Fe were resistant to HCl leaching and the Fe/Al ratio was 0.44 - only a factor of two above the lithogenous ratio. Even at these low concentrations of Al, its association with opal cannot be clearly distinguished from terrigenous material based on element ratios.

6.4.3 Particulate Aluminum - Summary. The aluminum in these plankton samples demonstrated both a terrigenous and biogenic carrier. The terrigenous component varied as a function of the inferred rates of atmospheric input and of the production of biogenic matter which dilutes and scavenges the lithogeous material. This component was the major carrier of Al in most samples and may have been a significant source for the particulate iron. The terrigenous material did not contribute significantly to the concentrations of other minor elements studied. At low levels of total Al, a labile ("biogenic") fraction of Al was seen in the leaching experiments. Although this fraction is usually a small contributor to the total particulate Al, its autochthonous origin suggests that it may be important to the cycle of dissolved Al in seawater.

7. BIOGENIC PARTICULATE FLUXES

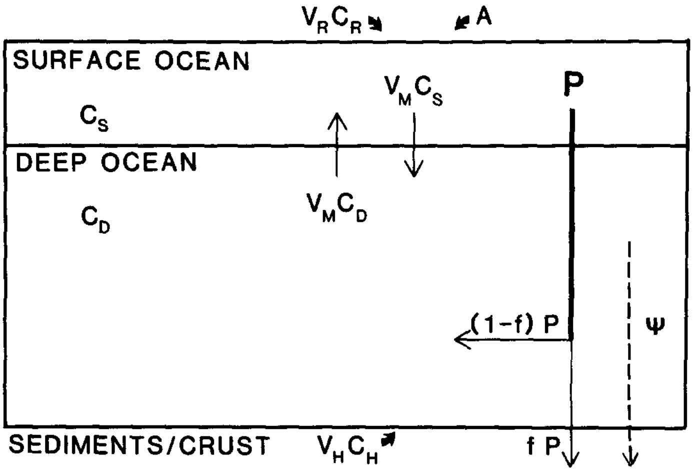
7.1 Models.

Marine geochemical cycles of the trace elements can be examined in terms of box models describing exchanges between reservoirs which are assumed to be homogeneous. The complexity of such models varies in proportion to the knowledge we have of the distribution of chemical tracers in the system; of the rates of inputs, outputs, and internal chemical processes; and of the movement of water masses between the reservoirs by advection and diffusion.

The particulate fluxes driving the vertical segregation of elements involved in the biogeochemical cycles of uptake and regeneration have been interpreted with a simple two-box ocean model with surface and deep reservoirs (BROECKER, 1971). The deep circulation between the ocean basins (STOMMEL and ARONS, 1960; REID and LYNN, 1971), coupled with the continuous production of organic matter in the surface ocean, create significant horizontal enrichments of the nutrient elements between the deep Atlantic, Indian, and Pacific oceans. In spite of this, a simple two-box model of the oceans will be used as a starting point in the examination of the trace element geochemical cycles. The amount of data on the distribution of these elements does not warrant any further complexity at this time. The focus of this discussion will be to demonstrate the significance of the biogenic flux of trace elements from the surface ocean based on the plankton data. A simple two-box model is best suited to that goal.

Application of the model involves defining the dissolved distributions, the mixing rates of water between the reservoirs, and the primary input or output fluxes for the elements. The box model fluxes are then compared with biogenic carrier fluxes and independent measurements of fluxes within and between the reservoirs. A schematic representation of the box model used, and the appropriate mass-balance equations are given in Fig. 11. The terminology is basically the same as that of BROECKER (1971). A similar model was used by BENDER and others (1977) to discuss the marine Mn balance.

Dissolved distributions. The horizontal heterogeneity of the deep-ocean nutrient and trace elements must be considered when choosing an average deep-reservoir composition. The concentrations in the deep northeast Pacific are not representative of the average ocean and using these values for biologically-cycled elements will overestimate the flux required to maintain their deep enrichment. A volume-weighted factor of 1:4 will be used to average deep Atlantic and Pacific+Indian deep-ocean concentrations (BROECKER and LI, 1970). At all Pacific stations where plankton were collected, standard hydrographic, nutrient, and trace element profiles of Cu, Ni, and Cd were determined. These are combined with GEOSECS profiles (BAINBRIDGE, 1981; BROECKER, SPENCER and CRAIG, 1982) and with others from the literature, to give estimates of the oceanic concentration of these elements in the surface and deep reservoirs.



$$P = V_M(C_D - C_S) + V_RC_R + A$$

Fig. 11. Two-reservoir box model (surface and deep ocean). Symbols for the model parameters are essentially the same as in BROECKER (1971): V_r, C_r- volume and concentration of an element in river water; A - atmospheric input; C_S, C_D dissolved concentrations in the surface and deep reservoirs; V_M - volume mixing rate between the surface and deep reservoirs; P - particulate matter flux out of the surface ocean; f fraction of particulate matter preserved in sediments; - additional particulate matter flux due to scavenging within the deep ocean; V_H,C_H volume and concentration of an element in hydrothermal solutions. The particulate matter flux (P) is calculated by the mass balance of all other inputs and outputs to the surface ocean reservoir.

Reservoir mixing rates. The volume rate of exchange between the deep and surface reservoirs has generally been estimated using versions of a similar two-layer box model applied to ^{14}C distributions (BROECKER, GERARD, EWING and HEEZEN, 1960; BROECKER and LI, 1970). The early models assumed that the ^{14}C mixed into the deep ocean was derived from the warm surface layer and was equilibrated with the atmosphere. The detailed data on the hydrography of the Atlantic, Antarctic, Indian and Pacific oceans obtained during the GEOSECS program, emphasize that deep waters formed at high latitudes through the thermohaline circulation have not equilibrated isotopically with atmospheric $^{14}CO_2$ (STUIVER, 1976). Also, these source waters are not completely depleted in the biologically cycled elements to the degree seen in most of the surface ocean. Physical mixing parameters for simple box models based on different elements having a variety of boundary conditions must, therefore, be used with caution. Water exchange rates based on ^{14}C will be used here as the best first-order estimates of mixing rates between the surface and deep ocean. A ^{14}C residence time of 930 years (BROECKER, 1979) and a mean deep-reservoir thickness of 3200 meters yield a mixing flux, V_m, of 3.5 meters/year.

Primary inputs and outputs. We will consider rivers and atmospheric deposition as the main primary inputs to the surface oceans. Hydrothermal circulation will also be considered in a few cases where data is available but these fluxes act directly on the deep reservoir. For most elements, rivers will be the only important source. Estimation of the magnitude of all of these fluxes is extremely difficult and, in the case of many of the trace elements, is currently impossible.

The flux of river water to the oceans, V_r, is taken to be 10.3 to 12.7 cm/year, distributed over the entire surface area of the oceans (BAUMGARTNER and REICHEL, 1975; KORZUN, SOKOLOV, BUDYKO, VOSKRESENSKY, KALIMIN, KONOPLYANTSER, KOROTKEVICH, KUZIN and LVOVICH, 1974). The composition of this flow, C_r, is poorly known - its estimation involves extrapolation from very few data of questionable coverage and quality (LIVINGSTONE, 1963; MARTIN and MAYBECK, 1979). Problems include separation of particulate from dissolved materials, contamination of many of the trace elements, estimation of pre-anthropogenic levels, and characterization of physical, chemical, and biological processes at the estuarine and coastal interface which affect the eventual transport of elements into the open ocean. Therefore, the river flux, although the dominant input for most elements, must be given carefully guarded weight in consideration of the rest of the trace elemental cycles.

Atmospheric inputs of trace elements, A, are even more difficult to estimate and relatively few attempts to do so have been published. Most of the higher-quality atmospheric particulate estimates have been made over the Atlantic Ocean. These might be biased by the high density of land masses surrounding the Atlantic, compared to that around the Pacific Ocean. Flux estimates used for this model will generally be taken from WALLACE and others (1977) and BUAT-MENARD and CHESSELET (1979). A new data set for atmospheric fluxes in the Pacific Ocean will soon be available from the NSF-SEAREX program. Some preliminary SEAREX data from the North Pacific will also be used (DUCE and others, 1982). Estimates of the percentage of the total input which is soluble in the surface reservoir will be taken from leaching experiments published by HODGE and others (1978).

Hydrothermal inputs of minor elements, V_hC_h, will be based on data collected at vents along the Galapagos and East Pacific Rise spreading centers (EDMOND, MEASURES, MCDUFF, CHAN, COLLIER, GRANT, GORDON and CORLISS, 1979; EDMOND, VON DAMM, MCDUFF and MEASURES, 1982). A great deal of uncertainty exists in the extrapolation of the minor element fluxes from these systems due to the effects of the subsurface mixing on the removal of high-temperature mobilized elements to secondary precipitates (EDMOND, MEASURES, MANGUM, GRANT, SCLATER, COLLIER, HUDSON, GORDON and CORLISS, 1979). The global significance of this source (sink) of elements in the deep ocean reservoir remains uncertain. But this uncertainty does not directly affect the estimation of the surface particulate flux.

The major output for elements considered in the model is through their burial in the sediments. The global inventory of the composition and accumulation rate of sediments is not well known and the separation of the various genetic sources of the bulk material is very difficult (GOLDBERG and ARRHENIUS, 1958; PRICE and CALVERT, 1970; KRISHNASWAMI, 1976; HEATH and DYMOND, 1977). One of the major motivations in this study of the biogenic trace element cycles is to independently establish the nature and magnitude of the biogenic inputs to the sediments, so other inputs such as hydrothermal and authigenic precipitates can be resolved (DYMOND, 1981).

Internal Fluxes. Several other estimates of chemical fluxes within the marine system can be used in comparison to the predicted box model fluxes. We will introduce a "carrier model" to estimate biogenic trace element fluxes based on plankton compositions and independent estimates for the flux of biogenic materials. The relative magnitude of primary production can be estimated and global inventories of carbon fixation rates have been published (KOBLENTZ-MISHKE and others, 1970; PLATT and SUBBA RAO, 1973). These will be used to make first-order estimates of the total production of biogenic particulate carriers. The marine productivity estimates generally range between 550 and 650 µmol C/cm^2/year averaged over the area of the oceans (3.62×10^{18} cm^2). It has been recognized that the mixing-flux of dissolved NO_3 from the deep ocean accounts for only 20-25% of the total amount of N fixed into particles (EPPLY and PETERSON, 1979). The balance is made up with recycled organic-N and NH_3 released directly from the plankton and by rapid heterotrophic activity within the surface reservoir. Assuming a C:N ratio of 6.6, the primary NO_3 flux yields an estimate of "new production" which is approximately 110 µmol C/cm^2/year. Trace elements which are rapidly recycled with P and N in the surface layer (Cd, Ni, Mn) should be transported out of the mixed layer in proportion to this "new productivity" flux. Elements which are fixed into biogenic particles but are not regenerated during this cyclic process (Cu, Zn, Ba, Fe) could be enriched in the resulting particles such that their flux is proportional to the total productivity estimate.

The variation of the elemental ratios in the settling particulate matter, due to differences in the extent of surface recycling of nutrients, has been described in section 4.1 by an enrichment parameter, β. This parameter will be taken as a first-order estimate of the ratio of total/new production for each element. The plankton collected for these experiments were composed of a mixture of phytoplankton and zooplankton and can not represent the "true" primary producer's composition. However, the experimental parameter β was derived from these bulk samples - which must represent some intermediate composition between the produced and settling end-members. Therefore, the use of this parameter is still consistent with the recycling model. An outline of the carrier model is given in Figure 12.

Because of the definition of the homogeneous reservoirs, box models can not distinguish between chemical processes occurring throughout the whole reservoir and those concentrated at a boundary. This has been a serious problem in considering the sites of regeneration of the biogenic particulate matter - the deep water column or the surface sediments (EDMOND, 1974). When available, several different independent data and models will be considered to address this specific question. These are: one-dimensional advection-diffusion models of the distribution of dissolved tracers in applicable sections of the deep ocean; comparisons of suspended and settling particulate material with surface sediment accumulations; and fluxes from the sediments based on dissolved distributions in pore waters.

7.2 Major component elements of the biogenic carriers.

The cycles of biogenic particulate material will be traced through the elemental cycles of some of its major components: organic carbon, phosphorus, calcium carbonate, and opal. The box model will first be applied to these major particulate elements and their dissolved remineralization products. The carrier fluxes derived from the model are compared with independent estimates. These fluxes will then be used with the trace element carrier ratios deduced from the leaching experiments to estimate trace element fluxes.

Unless otherwise noted, the river input data in the following sections are calculated from KORZUN and others (1973), LIVINGSTONE (1963) and MARTIN and MAYBECK (1979). Hydrothermal inputs were estimated from EDMOND and others (1979b,c; 1982). Dissolved distributions were taken from hydrographic data reports of the GEOSECS expedition (BAINBRIDGE, 1981; BROECKER and others, 1982).

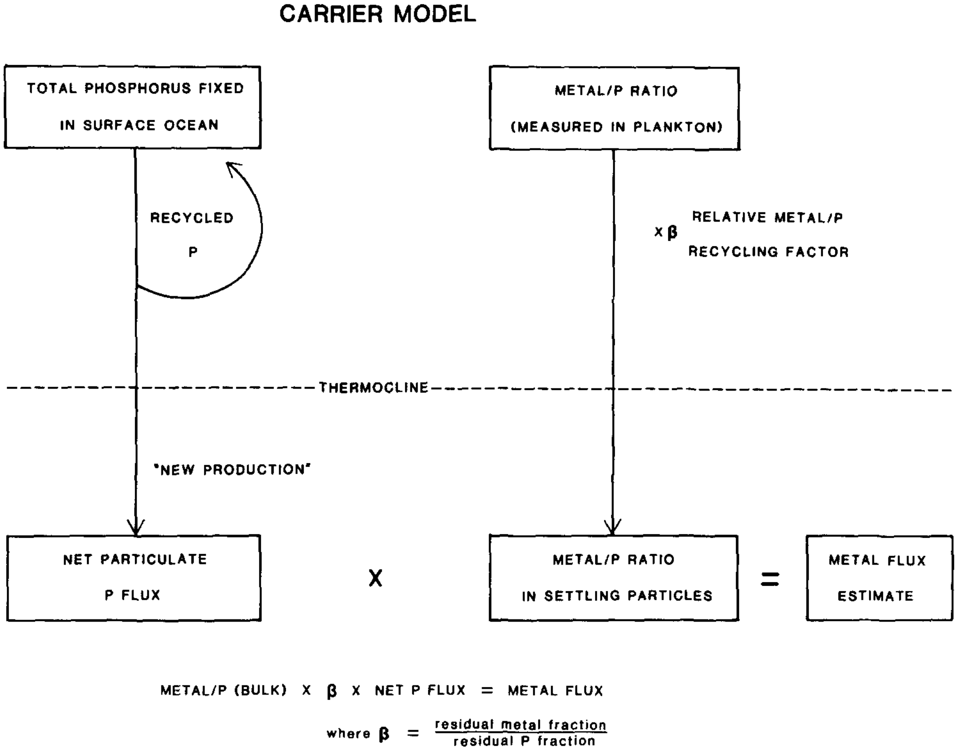


Fig. 12. Outline of the "carrier model". Metal flux estimates are based on independent phosphorus flux estimates, the metal/P ratio in the surface plankton, and an estimate (β - derived from the seawater release experiments) of the relative efficiency of recycling of P vs. the metal from the plankton within the surface ocean.

Organic carbon. Estimates of total primary production in the oceans average near 550 μmol C/cm^2/year (KOBLENTZ-MISHKE and others, 1970; PLATT and SUBBA RAO, 1973). Values in different environments range by at least an order of magnitude. The "new production" estimate of EPPLY and PETERSON (1979) is 20-25% of the total - approximately 100 μmol C/cm^2/year. The box model estimates for organic carbon flux can be developed based on changes in the total dissolved CO_2 concentration between the surface and deep reservoirs and are summarized in Table 20. The box model suggests a carbon flux of approximately 100 μmol C/cm^2/year which is in good agreement with the "new production" model. The burial flux of this carbon is only 1-2% of the surface particulate flux and less than 0.5% of the total primary production (HEATH, MOORE and DAUPHIN, 1977). Sediment trap collections

TABLE 20. Organic Carbon Cycle

- Primary input fluxes:

Rivers (C_r) and Atmosphere (A) - Concentration unknown but low compared to marine primary production (DeVOOYS, 1979).

- Distribution of $\Sigma CO_2$$^{(1)}$:

Surface C_s = 2.02 µmol/cm³

Deep Atlantic - 2.18

C_d = 2.38 µmol/cm³

Pacific - 2.43

75-85% of change in ΣCO_2 is from oxidation of organic carbon:$^{(2)}$

$\Delta\Sigma CO_2$ (oxidative) = (0.75 to 0.85) x (2.38 - 2.02)

= 0.26 to 0.31 µmol/cm³

- Box model for surface particulate flux:

$P = V_m(C_d - C_s) + V_rC_r + A$ (from figure IV-3)

$P_{C_{org}}$ = (350 cm/year) x (0.26 to 0.30 µmol/cm³)

= 91 to 109 µmol C/cm²/yr

- Independent estimates:

Primary production - Total production: 550 to 650 µmol/cm²/yr$^{(3)}$

"New production": 95 to 125 µmol/cm²/yr$^{(4)}$

(1) TAKAHASHI et al. (1980)

(2) KROOPNICK (1974), LI et al. (1969)

(3) KOBLENTZ-MISHKE et al. (1970), PLATT and SUBBA RAO (1973)

(4) EPPLY and PETERSON (1979)

also indicate that >95% of the "new production" is remineralized before reaching the sediments (KNAUER and others, 1979; COBLER and DYMOND, 1980; HONJO, MANGANINI and COLE, 1982; FISCHER, DYMOND, MOSER, MURRAY and MATHERNE, 1983).

Phosphorus. Fluxes of P predicted by the box model are given in Table 21. The flux out of the surface reservoir is calculated to 0.8 to 0.9 µmol P/cm²/year. Using a ratio of C:P of 106:1 combined with the total and "new" productivity estimates suggests total and "new" P fluxes of 5.7 and 1.0 µmol/cm²/year, respectively. Suspended particulate samples and sediment trap samples demonstrate a significant loss of P relative to C as particles settle out of the

TABLE 21. Phosphorus Cycle

- Primary input fluxes:

  Rivers (C_r) = 1.0 nmol/cm³$^{(1)}$

  V_rC_r = 10 to 13 nmol P/cm²/yr.

- Distribution of dissolved PO_4:

  Surface C_s = .05 nmol/cm³

  Deep Atlantic - 1.4

  Pacific - 2.8 C_d = 2.5 nmol/cm³

- Box model for surface particulate flux:

  P_p = (350 cm/yr) x (2.5 - .05 nmol/cm³) + 13

  = 0.87 μmol P/cm²/yr.

- Independent estimates:

  Primary production -

  Total organic C production x Redfield ratio (1:106)

  = 5.7 μmol P/cm²/yr.

  from "new production" = 1.0 μmol P/cm²/yr.

(1) FROELICH (1979)

surface layer - with C/P ratios in large particles climbing above 800 (KNAUER and others, 1979; BISHOP and others, 1980; KNAUER and MARTIN, 1981). The dissolved distribution of P, and its sediment and porewater inventories (FROELICH, 1979; EMERSON, JAHNKE, BENDER, FROELICH, KLINKHAMMER, BOWSER and SETLOCK, 1980) demonstrate that most of the particulate P is remineralized above 1500 m and very little survives transit to the sediments.

Because P was determined in all of the plankton samples and leaches, it will be used (as opposed to organic carbon or nitrogen) to represent the organic carrier in trace element flux calculations.

Calcium Carbonate. The distribution and fluxes of $CaCO_3$ in terms of the box model are outlined in Table 22. Even for the major element, Ca, the primary river and hydrothermal fluxes are uncertain by at least ± 30%. However, as in the case of P, the cyclic flux required to maintain even the slight deep enrichment of Ca is much larger than any primary inputs to the surface ocean. The box model predicts that this flux should range between 26 and 40 μmol Ca/cm²/year.

TABLE 22. Calcium Carbonate Cycle

- Primary input fluxes:

Rivers (C_rV_r) = 4.7 µmol Ca/cm²/yr.

Hydrothermal (C_hV_h) = 0.6 to 1.1 µmol Ca/cm²/yr.

- Distribution of normalized Ca:(1)

$C_d - C_s$ = .06 to .10 µmol Ca/cm³

- Box model for surface particulate flux:

P_{Ca} = (350 cm/yr) x (.06 to .10 µmol/cm³) + 4.7 µmol/cm²/yr.

= 26 to 40 µmol Ca/cm²/yr.

- Independent estimates:

Primary production: (neglects foraminifera)
assuming Ca/C = 0.33(2)

Total production - 180 to 215 µmol Ca/cm²/yr.

"new" production - 33 µmol Ca/cm²/yr.

(1) HORIBE *et al.* (1974); SHILLER and GIESKES (1980); CHEN *et al.* (1982)

(2) LISITZIN (1972)

The relatively large error has its source in the high variability of the surface water concentration of salinity-normalized Ca compared to the small magnitude of (C_d-C_s) (HORIBE, ENDO and TSUBOTA, 1974; BREWER, WONG, BACON and SPENCER, 1975; SHILLER and GIESKES, 1980; CHEN, PYTKOWICZ and OLSON, 1982). A total $CaCO_3$ production of 200 µmol Ca/cm²/year is estimated based on the total primary production of 550-650 µmol C/cm²/year with a mean Ca/C ratio of 0.33 (LISITZIN, 1972). The same estimate, based on the "new production" of carbon (33 µmol Ca/cm²/year), is in agreement with the box model prediction. However, the degree to which $CaCO_3$ is produced and regenerated in parallel to the total primary production of organic carbon is unknown. HONJO (1980) and HONJO and others (1982) have reported that material collected in sediment traps shows little sign of dissolution within the water column - even in the highly corrosive deep Pacific; however, the measured $CaCO_3$ flux in these and other Pacific traps (FISCHER, 1983) are a factor of 2 to 5 below the estimated surface production. Advection-diffusion models of alkalinity profiles indicate highly variable remineralization within the water column and do not constrain the site of dissolution (EDMOND, 1974). A significant decrease in $CaCO_3$ flux occurs between the deep traps and bottom accumulations at the Galapagos and MANOP sites (COBLER and DYMOND, 1980; FISCHER, 1983) demonstrating the importance of dissolution of $CaCO_3$ at the sediment interface.

Opal. The geochemical box model of biogenic Si is outlined in Table 23. The input fluxes (2.3-2.5 μmol/cm²/year) are again a small fraction of the total particulate flux (43-47 μmol/cm²/year) needed to drive the deep-water enrichment. The particulate Si formed can be estimated using the primary production and Si/C ratio of 0.42 (LISITZIN, 1972). The total production of Si is 250 μmol/cm²/year and the "new production" equivalent is 42 μmol/cm²/year. Again, this assumes that this bulk ratio can be directly applied to both total and "net" production. The new production estimate is closer to that predicted by the other models and suggests that a large fraction of the Si uptake by organisms is recycled in the surface ocean. NELSON and GORDON (1982) demonstrated that an average of 32% (range 18-58%) of the particulate Si produced in the photic zone of the Southern Pacific - Antarctic dissolves *in situ*.

TABLE 23. Biogenic Silica Cycle

- Primary input fluxes:

Rivers(1) (C_rV_r) = 1.5 to 2.3 μmol Si/cm²/yr.

Hydrothermal (C_hV_h) = 0.8 μmol Si/cm²/yr.

- Distribution of dissolved Si:

Surface C_s = 1 nmol/cm³

Deep Atlantic - 30
Pacific -150
C_d = 126 nmol/cm³

- Box model for surface particulate flux:

P_{Si} = (350 cm/yr) x 126 nmol/cm³ = 1.9 μmol/cm²/yr.
= 46 μmol Si/cm²/yr.

- Independent estimates:

Primary production - (neglects radiolarians)

assume Si/C = 0.4(2)

Total production - 250 μmol Si/cm²/yr.

"new" production - 42 μmol Si/cm²/yr.

(1) DEMASTER (1981)

(2) LISITZIN (1972)

Sediment traps reflect the variability of surface production and significant remineralization in the water column. Traps deployed in the low and mid latitudes of the Atlantic and Pacific collect less than 25% of the box model value and most frequently collect between 1 and 5 µmol Si/cm²/year (HONJO and others, 1982; FISHER and others, 1983; FISCHER, 1983). However, the Antarctic high-productivity regions dominate the global production and sedimentation of biogenous silica (LISITZIN, 1972; DEMASTER, 1981) and recent sediment trap data of WEFER, SUESS, BALZER, LIEBEZEIT, MULLER, UNGERER and ZENK (1982) in the Drake Passage show Si fluxes of 200 µmol Si/cm²/year and an estimated surface production of 600 µmol Si/cm²/year. This extreme range in fluxes demonstrates the inadequacy of a simple vertical box model in accounting for some of the important variations in production of biogenic particulate matter in different environments.

Dissolution of biogenic Si at the sediment-seawater interface can be seen by significant differences between deep trap and surface sediment accumulations. This is also consistent with estimated porewater fluxes of between 1 and 10 µmol/cm²/year (HURD, 1973; SCHINK, GUINASSO and FANNING, 1975). Advection-diffusion models for the Pacific generally predict in situ remineralization between 10 and 20 µmol/cm²/year. The quality of the fits is poor and the validity of the one-dimensional model applied to Si distributions is questionable since strong horizontal gradients exist in the north Pacific, apparently driven by the bottom dissolution flux (EDMOND, JACOBS, GORDON, MANTYLA and WEISS, 1979).

7.3 Biogenic fluxes of trace elements.

In the previous section we have developed several models for the flux of major biogenic particulate materials out of the surface ocean. The two-box model for the dissolved distribution of elements was shown to be consistent with independent estimates of the flux of these materials based on primary productivity. These major component or "carrier" fluxes will now be coupled with the trace element composition of the plankton to predict fluxes of the minor elements. These will be compared to fluxes predicted with the box model using the dissolved distributions of trace elements to examine the role of biogenic particles in the specific trace element cycles.

Cadmium. A summary of the distribution and fluxes of Cd estimated from various sources is presented in Table 24. In describing this cycle, we encounter a difficulty common to all of the trace elements - the nature and magnitude of the primary inputs are poorly known. Both the river and atmospheric data are based on very few quality measurements and will no doubt undergo significant refinement as more data become available.

The distribution of dissolved Cd in the Pacific is relatively well known (BOYLE, SCLATER and EDMOND, 1976; BRULAND, KNAUER and MARTIN, 1978; BRULAND, 1980; BOYLE and others, 1981). The Atlantic value is taken from BENDER and GAGNER (1976) and from a preliminary profile from GEOSECS station 54, analysed by F. SCLATER at Massachusetts Institute of Technology.

The magnitudes of the various components of the total particulate Cd flux demonstrate that, as in the case of P, the cyclic component completely dominates the total flux. The product of the Cd/P ratio in plankton and the box model flux of P predicts a Cd flux which is too high compared with the flux calculated using the box model for dissolved Cd. A fraction of the total Cd measured in the plankton samples must be recycled more rapidly than P, such that the elemental ratio of the particulate flux into the deep box is lower by a factor of β. To balance the box-model Cd flux with the C:P carrier flux requires a value of β between 0.5 and 0.9. KNAUER and MARTIN (1981) presented sediment trap data from the Northeast Pacific which clearly demonstrate the labile behavior of Cd and P in settling particles. At all depths in their profile, the Cd/P ratio in the labile solution fraction was always greater than the bulk sample. In agreement

TABLE 24. Cadmium Cycle

- <u>Primary input fluxes:</u>

Rivers(1) - $C_r \sim 0.2$ pmol/cm³

$C_rV_r \sim 0.002$ nmol/cm²/yr.

Atmospheric(2) - A = .004 to .017 nmol/cm²/yr.

- <u>Distribution of dissolved Cd</u>(3):

Surface $C_s = 0.01$ pmol/cm³

Deep Atlantic - 0.35
Pacific - 1.0
$C_d = 0.9$ pmol/cm³

- <u>Box model for surface particulate flux:</u>

$$P_{Cd} = (350 \text{ cm/yr}) \times (0.9 \text{ pmol/cm}^3) + (<0.02 \text{ nmol/cm}^2\text{/yr})$$

$$= 0.34 \text{ nmol Cd/cm}^2\text{/yr.}$$

- <u>Independent estimates:</u>

<u>Using carrier ratios</u> -

<u>Total organic matter</u> as P flux (0.87 μmol/cm²/yr);

plankton Cd/P ratios - 0.4-0.7 x 10^{-3}:

Cd flux = 0.35-0.61 nmol/cm²/yr

to balance deep enrichment requires β = 0.5-0.9

<u>$CaCO_3$</u> (30 μmol Ca/cm²/yr);

ratio of Cd/Ca in forams - .025 x 10^{-6}:

Carbonate carrier flux < .001 nmol Cd/cm²/yr.

<u>Sediment traps</u> -

California Current(4)	Depth	Particulate	Total	β
	35m	0.6 nmol/cm²/yr.	4	0.4
	1500m	0.05	0.3	0.7

Eastern Tropical N. Pacific(5)

MANOP Site M	0.01 - 0.03 nmol/cm²/yr.
Site H	0.02 - 0.04

TABLE 24. (continued)

Advection-diffusion models of deep Cd distribution - regeneration of 0.02-0.05 nmol $Cd/cm^2/yr$.

Sediment accumulation,(5) MANOP sites M and H ~ 0.0006 nmol Cd/cm^2yr.

(1) Based on averages for Mississippi, Amazon, Yangtze and Orinoco Rivers, GRANT et al. (1982); BOYLE et al. (1982); SHILLER et al. (1982)

(2) Atlantic, WALLACE et al. (1977); Pacific, DUCE et al. (1982)

(3) BOYLE et al. (1976); BENDER and GAGNER (1976); BRULAND (1980); BOYLE et al. (1981)

(4) KNAUER and MARTIN (1981)

(5) FISCHER (1983)

with the box-model, these data suggest a value of β ranging between 0.4 at 35 meters to 0.7 at 1500 meters. The bulk plankton compositions and the model for the evolution of surface water depletions of Cd, presented earlier, both suggest that the particulate Cd in surface plankton samples must be regenerated "faster" than the phosphorus.

The residual particulate flux of Cd (not including the trap solubilized fraction) to sediment traps deployed below 1000 m in the North Pacific ranges between 0.01 and 0.05 $nmol/cm^2/year$ - less than 10% of the estimated surface flux (KNAUER and MARTIN, 1981; FISCHER and DYMOND, unpublished). The preservation of Cd in the sediments of the eastern tropical North Pacific is approximately 0.0006 $nmol/cm^2/year$ (FISCHER and DYMOND, unpublished) roughly equivalent to the estimated river flux. The Cd/P ratio in these sediments is less than 0.1×10^{-3} demonstrating that the diagenesis of the residual fractions of Cd and P is quite different when compared to the upper-ocean cyclic components.

Nickel. The box model geochemical cycle and carrier fluxes for Ni are outlined in Table 25. Again, the river input estimates are limited and the atmospheric value is derived from the Atlantic stations of WALLACE and others (1977). EDMOND and others (1979c) have shown that hydrothermal circulation can act as a source or sink for Ni and other sulfide-forming transition elements.

The box model calculations predict that approximately 90-95% of the total particulate Ni leaving the surface is regenerated. An inventory of the carrier fluxes demonstrates that Ni fluxes in $CaCO_3$ and opal are insignificant. The organic flux represented by the bulk plankton Ni/P ratio and the total P flux is too low to account for the deep-water enrichment. Using a value of 2.5 for β, derived from the leaching experiments, brings the total estimated carrier flux in closer agreement with the box model value. The Ni/P ratio in the material settling into the deep ocean must be higher than the measured plankton values by a factor of 2-4. Water column profiles of Ni do show a component of shallow regeneration like P, but the surface reservoir recycling must be significantly less than that for P.

The site of regeneration of the Ni flux to the deep ocean can be examined from several independent estimates. The water column profiles and rapid release of Ni with P in the leaching experiments suggest that Ni begins to be regenerated calculated for much of the deep reservoir by the application of advection-diffu-

TABLE 25. Nickel Cycle

- Primary input fluxes:

Rivers(1) – C_r = 5 pmol/cm³

V_rC_r = 0.06 nmol/cm²/yr.

Atmospheric(2) – A = 0.04 nmol/cm²/yr.

(40% soluble)

- Distribution of dissolved Ni(3):

Surface C_s = 2 pmol/cm³

Deep Atlantic – 7
C_d = 9 pmol/cm³
Pacific –10

- Box model for surface particulate flux:

P_{Ni} = (350 cm/yr) x (9 – 2 pmol/cm³) + 0.1 nmol/cm²/yr.

= 2.6 nmol/cm²/yr.

- Independent flux estimates:

Using carrier ratios –

Total organic matter as P flux (0.87 μmol P/cm²/yr);

plankton Ni/P ratio – 0.6–1.1 x 10^{-3}:

Ni flux = 0.5–1.0 nmol Ni/cm²/yr.

for β = 2.4, Ni flux = 1.2–2.3 nmol Ni/cm²/yr.

$CaCO_3$ (30 μmol Ca/cm²/yr);

Ni/Ca ratio in forams – 0.4 x 10^{-6}:

Carbonate carrier flux = 0.01 nmol Ni/cm²/yr

Opal (45 μmol Si/cm²/yr);

Ni/Si ratio (unwashed diatoms) – 1.3 x 10^{-6}:

Sediment traps(4)–

Tropical North Pacific 0.3 – 2 nmol/cm²/yr.

Regeneration (advection-diffusion modeled) in the deep Pacific:

0.6 nmol/cm²/yr.

TABLE 25. (continued)

Porewater fluxes(5) into the deep Pacific:

< 0.04 nmol/cm²/yr.

Sediment accumulation(4)-

Eastern tropical north Pacific: 1.0-1.4 nmol/cm²/yr.

(1) SCLATER *et al.* (1976); GRANT *et al.* (1982); SHILLER *et al.* (1982)

(2) Atlantic, WALLACE *et al.* (1977)

(3) SCLATER *et al.* (1976); BRULAND (1980); BOYLE *et al.* (1981)

(4) FISCHER (1983)

(5) KLINKHAMMER (1980)

sion models ranges from 10 to 50% of the total surface flux. The estimated pore water flux is less than 5% of the surface flux (KLINKHAMMER, 1980) so the balance requires that 50-95% of the surface flux must be regenerated above 1500 meters.

Copper. An outline of the biogeochemical cycle of copper is given in Table 26. Again, the primary input estimates are based on very few data, but these suggest that the river input is the major source with atmospheric inputs of less than or equal to one-half of the river flux. Again, the significance of hydrothermal activity is unknown (EDMOND and others, 1979c).

The surface water distribution of Cu generally shows increases of Cu near the continents (BOYLE and others, 1981; BRULAND, 1980). A lack of covariation with ^{210}Pb (BRULAND, 1980) suggests that this increase in Cu is not from direct atmospheric input, and BOYLE and others (1981) have suggested an input from shelf sediments at the continental margins. The deepwater concentration of Cu (BOYLE and others, 1977; BRULAND, 1980) generally increases into the bottom and demonstrates scavenging by particulate matter throughout the water column. This requires that the site of regeneration of Cu accounting for its general deep enrichment must occur near or within the sediment water interface.

The complexity of the distribution and inputs of Cu in the ocean are especially difficult to include within the simple two-box model. However, Cu *is* depleted in surface water with respect to its deep water concentration, demonstrating that biogenic particulate matter is a carrier of a significant Cu flux. The box model requires a particulate flux of 1.2 to 1.6 nmol Cu/cm²/year to balance the upward mixing of regenerated Cu.

Estimates of this flux, based on the carrier model are given in Table 26. The leaching experiments demonstrated the unique behavior of Cu as compared to several other regenerated trace elements. The association of Cu with the particulate organic matter was very strong such that relatively little of it was released along with P. The expected enrichment (β) of Cu with respect to P in the remaining (settling) particles was calculated to be 3.4. When applying this factor to the total organic matter flux we predict a net Cu flux equivalent to the box model result. The significance of $CaCO_3$ as a carrier is very small and opal may carry about 10% of the flux.

TABLE 26. Copper Cycle

- Primary input fluxes:

Rivers(1) - C_r = 23 pmol/cm³

V_rC_r = 0.3 nmol/cm²/yr.

Atmospheric - A: Atlantic(2) = 0.15 nmol/cm²/yr.

Pacific(3) = .01 nmol/cm²/yr.

- Distribution of dissolved Cu(4):

Surface C_s = 1-1.5 pmol/cm³

Deep Atlantic - 2
C_d = 4.0 pmol/cm³
Pacific - 4-5

- Box model for surface particulate flux:

P_{Cu} = (350 cm/yr) x (2.7 pmol/cm³) + 0.4 nmol/cm²/yr.

= 1.2 to 1.5 nmol Cu/cm²/yr.

- Independent estimates:

Using carrier ratios -

Total organic matter as P flux (0.87 μmol/cm²/yr);

plankton Cu/P ratio - 0.5-0.6 x 10^{-3}:

Cu flux = 0.44-0.52 nmol/cm²/yr.

with β = 3.4, Cu flux = 1.5-1.8 nmol Cu/cm²/yr.

$CaCO_3$ (30 μmol Ca/cm²/yr);

ratio of Cu/Ca in forams - 0.3 x 10^{-6}:

Carbonate carrier flux = 0.01 nmol Cu/cm²/yr.

Opal (45 μmol Si/cm²/yr);

ratio of Cu/Si in unwashed diatoms - 3.8 x 10^{-6}:

Opal carrier flux = 0.17 nmol Cu/cm²/yr.

Sediment Traps(5)-

Eastern Tropical Pacific, flux through 500m: 0.3-0.5 nmol/cm²/yr

TABLE 26. (continued)

Scavenging Fluxes estimated from advection-diffusion models:

Pacific stations range from 0.3 to 1.7 nmol/cm²/yr.

Porewater Fluxes$^{(6)}$-

MANOP M,H,S - 1-2 nmol/cm²/yr.

MANOP C - 6 nmol/cm²/yr.

(1) GRANT *et al.* (1982); BOYLE *et al.* (1982); SHILLER *et al.* (1982)

(2) WALLACE *et al.* (1977)

(3) Estimated based on DUCE *et al.* (1982)

(4) BOYLE *et al.* (1977); MOORE (1978); MANGUM and EDMOND (1979); BRULAND (1980);

BOYLE *et al.* (1981)

(5) FISCHER (1983)

(6) KLINKHAMMER (1980) personal communication

The flux of Cu through 500 m into sediment traps in the tropical Pacific ranges between 3 and 5 times less than the box and carrier model estimates but there is still very little data available (FISCHER and DYMOND, unpublished). The increase in Cu flux due to scavenging throughout the deep water column accounts for an additional 1 nmol/cm²/year. The flux of Cu back into bottom water from the sediments has been estimated by KLINKHAMMER (1980) based on pore water gradients and it is roughly equivalent to the surface flux estimate (see Table 26).

Two components of the Cu cycle are of particular interest based on the results of this work - the deep scavenging rate and the preservation of the Cu particulate carrier in the sediments. This element is one of the better-studied trace metals in the oceans and very high quality data are available on its distribution, especially in the North Pacific (BOYLE and others, 1977; MANGUM and EDMOND, 1979; BRULAND, 1980; BOYLE and others, 1981). The application of steady-state, one-dimensional (vertical) advection-diffusion models to these profiles demonstrates systematic differences of scavenging rate which vary by a factor of 5. It was shown in the plankton leaching experiments that the association of Cu with the particulate organic matter is very strong - even after the release of the other metals (Cd, Ni and Mn) is complete. BALISTRIERI and others (1981) have suggested, based on equilibrium models, that the scavenging (adsorption) properties of settling particles in the ocean are controlled by organic surfaces. The net scavenging flux of Cu should, therefore, be related to the flux of these particles through the water column. DUESER and ROSS (1980) and FISCHER and others (1983) have demonstrated variations in particulate organic carbon fluxes throughout the water column which are very tightly coupled to the primary productivity. Since we believe this material is the main scavenger, then the removal of Cu from the water column should vary with the mean regional productivity. In Figure 13, estimates of surface production are compared with the values of J/w (the scavenging rate normalized to the net upwelling rate) derived from the dissolved Cu profiles. Assuming that w does not vary widely (approximately 3.5 meters/year), there is a striking correlation between the scavenging rate and production (and therefore flux) of organic particulate matter. Due to the magnitude of the uncertainties involved in these productivity data (PETERSON, 1980) and one-dimensional models (FIADERO and CRAIG, 1978; TOGGWEILER, 1983), it is impossible at this point to further quantify this relationship. However, this result emphasizes the importance of the areas of high productivity in driving much of the total vertical transport of elements in the oceans. This is caused by the combination of the rapid vertical mixing of nutrients which sustain the high rates of net particulate production, the rapid settling of the original organic carriers, and the increased scavenging of specific elements throughout the water column by these particles.

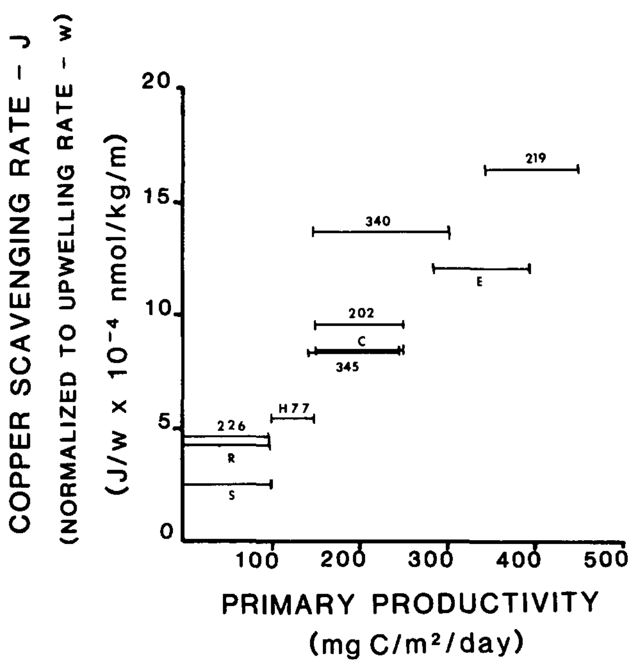


Fig. 13. Estimates of the primary production of carbon in the surface ocean (^{14}C-uptake) vs. the relative scavenging rate of Cu in the deep ocean. Scavenging rates (normalized to the vertical advection parameter, w) were derived by multiple linear regression of a steady-state vertical advection-diffusion model on dissolved Cu, depth, and temperature within the linear T-S region (BOYLE and others, 1977). Dissolved distributions from the North Pacific include: GEOSECS data [numbered stations - BOYLE and others (1977)]; MANOP data [C,S,R - MANGUM and EDMOND (1979)]; H77 - BRULAND (1980). Scavenging rate at E (North Atlantic) was estimated from sediment trap data (BREWER and others, 1980). Primary productivity estimates are from: KOBLENTZ-MISHKE and others (1970), BOGOROV (1968), EL SAYED and TAGUCHI (1979), MOORE and others (1973), BEERS and others (1968), McCOY and GOERING (1975), LOVE and ALLEN (1974).

The deepwater distribution of dissolved Cu requires that it must be regenerated at or near the sediments (BOYLE and others, 1977) and the porewater distributions (KLINKHAMMER, 1980) suggest a significant flux of Cu out of the sediments. The eventual preservation of Cu in the sediments is dependent on a variety of complex diagenetic processes. Many authors have noted a general correlation of Cu with carbonate-rich sediments (ARRHENIUS, 1963; TUREKIAN and IMBRIE, 1966; BURNETT, 1971). However, it has been demonstrated here and elsewhere (HARTMANN, MULLER, SUESS and VAN DER WEIJDEN, 1976; BOYLE, 1981) that the pure biogenic calcium carbonate phase is not the carrier of the Cu flux to the sediments. The highest porewater flux measured in the North Pacific (see Table IV-12) is at MANOP Site C - a carbonate sediment (KLINKHAMMER, unpublished). Several diagenetic processes can be hypothesized which explain many of these observations.

There is a correlation between the accumulation of organic carbon in sediments and the bulk sedimentation rate (MUELLER and SUESS, 1979). The burial of organic matter in rapidly accumulating carbonate sediments is a good example of this relationship. The critical Cu-organic carrier(s) might similarly become buried (mixed) deeper into the sediment column. In other, more slowly accumulating pelagic sediments, the Cu-organic association is probably destroyed during its relatively long residence time at the sediment water interface within the "benthic transition layer" (HONJO and others, 1982). Decomposition of this carrier does eventually occur, as evidenced by both the porewater distributions and the lack of direct correlation of Cu and organic carbon in these sediments (HARTMANN and others, 1976). Therefore, other diagenetic phases must exist for Cu in the carbonate sediments to preserve a fraction of that released from its organic carrier. A variety of such phases are possible including apatite (KRAUSKOPF, 1956; HARTMANN and others, 1976), manganese carbonates (PEDERSEN and PRICE, 1982), and hydrous metal-oxide overgrowths (BOYLE, 1981).

The complexity of the Cu sedimentary cycle is probably related to and at least as complicated as that controlling $CaCO_3$ preservation (EMERSON and BENDER, 1981). However, since we have not identified the specific Cu-organic carrier or its diagenetic behavior, we cannot yet constrain these hypotheses. The plankton composition and leaching experiment reported here serve to emphasize the importance of the Cu-organic carrier in these sedimentary processes.

Manganese. The dissolved distributions and the biogenic particulate components of the Mn cycle are outlined in Table 27. This trace element is unique among those discussed so far in that its dissolved profile shows little or no resemblance to the nutrient distributions. Surface concentrations of Mn are almost always greater than deep water concentrations and, instead of regeneration, scavenging of Mn throughout the deep water column dominates its distribution (BENDER and others, 1977; KLINKHAMMER and BENDER, 1980; LANDING and BRULAND, 1980). Another significant difference in the Mn cycle is the major importance of hydrothermal input to the total budget (EDMOND and others, 1979c). This source is injected within the deep ocean and has a short residence time with respect to scavenging (WEISS, 1977).

The particulate flux predicted by the box model is completely dependent on the values chosen for the riverine and atmospheric inputs. As mentioned earlier, these estimates are still quite crude and therefore so is the box model estimate of the Mn flux. The organic carrier flux is lower than the box model estimate by a factor of 2 or 3, but is in the same range as the Mn fluxes in North Pacific sediment traps (KNAUER and MARTIN, 1980; FISCHER, 1983).

The concentration of dissolved Mn displays a maximum within the oxygen minimum zone of the tropical Pacific and this has been attributed to: the regeneration of a Mn-organic particulate carrier; lateral transport from strong ocean margin inputs; or equilibrium with a mixed-solid manganese oxyhydroxide phase (KLINKHAMMER and BENDER, 1980). Although the Mn/P ratio at some of these stations is equivalent to that seen in the plankton samples, the range of Mn/P

TABLE 27. Manganese Cycle

- Primary input fluxes:

Rivers(1) - $C_r = 0.13$ pmol/cm³

$V_rC_r = 1.7$ nmol/cm²/yr.

Atmospheric(2) - $A = 0.3\text{-}0.8$ nmol/cm²/yr.
(30-50% soluble)

Hydrothermal(3) - $V_hC_h = 16\text{-}40$ nmol/cm²/yr.

- Distribution of dissolved Mn(4):

Surface $C_s = 0.8\text{=}3.0$ pmol/cm³

Deep Atlantic - 1.8
Pacific - 0.2-1.0
$C_d = 0.5\text{-}1.2$ pmol/cm³

- Box model for surface particulate flux:

$P_{Mn} = (350 \text{ cm/yr}) \times (-0.5 \text{ to } -1.0 \text{ pmol/cm}^3) + 2 \text{ to } 2.5 \text{ nmol/cm}^2\text{/yr.}$

$= 2$ nmol/cm²/yr. (estimate completely driven by surface input choices)

- Independent estimates:

Using carrier ratios -

Total organic matter as P flux (0.87 µmol P/cm²/yr);

plankton Mn/P ratios - $0.35\text{-}0.43 \times 10^{-3}$:

Mn flux = 0.3 to 0.4 nmol/cm²/yr.

with $\beta = 2$, Mn flux = 0.6 to 0.8 nmol/cm²/yr.

$CaCO_3$ (30 µmol Ca/cm²/yr);

ratio of Mn/Ca in forams - 0.4×10^{-6}

Carbonate carrier flux = 0.01 nmol/cm²/yr.

Sediment traps -

North Pacific(5), fluxes through 500 m: 0.1 to 1 nmol/cm²/yr.

(1) BENDER *et al.* (1977)
(2) WALLACE *et al.* (1977); DUCE *et al.* (1982)
(3) EDMOND *et al.* (1979c)
(4) KLINKHAMMER and BENDER (1980); LANDING and BRULAND (1980)
(5) MARTIN and KNAUER (1980); FISCHER (1983)

ratios between stations suggests that the organic carrier is not the sole factor determining the subsurface maximum of Mn. The pure $CaCO_3$ carrier was shown to be insignificant to these fluxes.

Barium. Barium has been studied for many years as a chemical analog for ^{226}Ra and was the first systematically determined trace element whose distribution indicated involvement in biological cycling (CHOW and GOLDBERG, 1960; TUREKIAN and JOHNSON, 1966; BACON and EDMOND, 1972; CHAN, EDMOND, STALLARD, BROECKER, CHUNG, WEISS and KU, 1976; CHAN, DRUMMOND, EDMOND and GRANT, 1977). The primary input fluxes and distribution of Ba used in the box model are given in Table 28. The box model presented here is essentially identical (in form) to that of LI, KU, MATHIEU and WOLGEMUTH (1973) except we use a higher estimate for the deep ocean concentration of Ba, a somewhat higher vertical mixing rate, and modified estimates of primary inputs. These Ba inputs are slightly higher due to the process of desorption from suspended material in estuaries (HANOR and CHAN, 1977; EDMOND, BOYLE, DRUMMOND, GRANT and MISLICK, 1978; GRANT, HU, BOYLE and EDMOND, 1982) and to new estimates of hydrothermal inputs to the deep oceans (1 to 2 nmol/cm^2/year - EDMOND and others 1979b). In spite of the higher primary input estimates, the cyclic flux required by the deep enrichment completely dominates the total surface particulate flux. Examination of all of the known carriers, outlined in Table IV-14, indicates a serious deficit in accounting for the magnitude of the deep Ba enrichment. This unique situation requires a closer examination of the various carrier estimates.

The flux of Ba with particulate organic matter was estimated based on the bulk plankton ratio ($Ba/P = 1.4$ to 1.8×10^{-3}) and a cyclic enrichment factor ($\beta = 6$) based on its relatively refractory behavior in the plankton leaching experiments. The resulting flux estimate accounts for no more than 25% of the required Ba flux. The form of Ba within this carrier is not resolved by these plankton experiments, but it has been demonstrated that barite ($BaSO_4$) may account for a significant fraction (DEHAIRS, CHESSELET and JEDWAB, 1980). This specific carrier will be discussed in more detail below. Strong organic complexes with Ba are very unlikely in the presence of nearly any other divalent cation (HUGHES,1972), however, simple ion exchange of cations (electrostatic) frequently favors this weakly-hydrated element. Some fraction of the total Ba in surface particulate matter may be bound by ion exchange as is the case for Ca and Sr (BISHOP and others, 1977). These same authors showed an increase in the total ion exchange capacity of fine particles (<53μm) with increasing depth. As these particles fall into the thermocline (where the dissolved Ba concentration increases) they would become relatively enriched in Ba with respect to other adsorbed cations (esp. Ca and Sr). However, this effect is not likely to change the composition by more than a factor of two, and another major carrier phase or a dramatic change in the surface properties of the particles is required to carry enough Ba to supply the deep enrichment.

Examination of pure biogenic calcite phases (foraminifera - this study, BOYLE, 1981; coccoliths - GOLDBERG and ARRHENIUS, 1958) demonstrate Ba/Ca ratios less than 10^{-5}. All other reports of higher values are from sediments where the separation of the pure calcite is in doubt. At these low ratios, biogenic calcite can account for no more than a few percent of the required flux.

The general correlation of dissolved Ba with Si in the oceans has suggested its possible involvement in the uptake and regeneration of opal. However, several investigations have failed to directly identify sufficient Ba in biogenic Si phases to account for the ratio of 7×10^{-4} seen in the water column correlations (MARTIN and KNAUER, 1973; Ng, 1975; LIBICKI, 1976; DEHAIRS and others, 1980). The data presented in this work further support this and demonstrate that a significant fraction of the Ba which is present in the particles does not co-vary with Si during leaching. The Ba/Si ratio in the bulk and HCl-washed Antarctic diatom samples was 1.5×10^{-5} and 0.2×10^{-5}, respectively.

TABLE 28. Barium Cycle

- Primary input fluxes:

Rivers(1) - C_r = 0.3 - 0.45 nmol/cm^3

V_rC_r = 4 - 6 nmol Ba/cm^2/yr.

- Distribution of dissolved Ba(2):

Surface C_s = 35 pmol/cm^3

Deep Atlantic - 70
Pacific -150
C_d = 135 pmol/cm^3

- Box model for surface particulate flux:

P_{Ba} = (350 cm/yr) x (100 pmol/cm^3) + 4 to 6 nmol/cm^2/yr.

= 40 nmol Ba/cm^2/yr.

- Independent estimates:

Using carrier ratios -

Total organic matter as P (0.87 μmol P/cm^2/yr);

ratio of Ba/P in plankton - 1.4-1.8 x 10^{-3}:

Ba flux = 1.2-1.6 nmol/cm^2/yr.

with β = 6, Ba flux = 7-10

Barite(3)

Atlantic production estimate - 5.8 nmol Ba/cm^2/yr

$CaCO_3$ (30 μmol Ca/cm^2/yr);

ratio of Ba/Ca in forams - 3 x 10^{-6}:

Carbonate carrier flux = 0.1 nmol Ba/cm^2/yr.

Opal (45 μmol Si/cm^2/yr);

ratio of Ba/Si in diatoms - 1.5-5.0 x 10^{-5}:

Opal carrier flux = 0.7-2.3 nmol Ba/cm^2/yr.

Acantharia ($SrSO_4$ - 220 nmol Sr/cm^2/yr)(4);

ratio of Ba/Sr(5)- 7 x 10^{-3}:

Celestite carrier flux 1.5 nmol Ba/cm^2/yr.

TABLE 28. (continued)

Sediment traps -

Eastern Tropical Pacific$^{(6)}$, flux through 500 m: 5-7 nmol Ba/cm^2/yr.

Tropical Atlantic$^{(7)}$, flux through 900 m: 9 nmol Ba/cm^2/yr.

Deep-water regeneration (from advection-diffusion models),

Pacific GEOSECS stations$^{(2)}$: 4-11 nmol Ba/cm^2/yr.

Pore water fluxes -

Tropical Pacific$^{(8)}$ 1 nmol Ba/cm^2/yr. (minimum estimate)

South Pacific, Antarctic$^{(9)}$ 5-12 nmol Ba/cm^2/yr.

(1) HANOR and CHAN (1977); EDMOND *et al.* (1978); GRANT *et al.* (1982)

(2) CHAN *et al.* (1977); EDMOND *et al.* (1978)

(3) DEHAIRS *et al.* (1980)

(4) BRASS (1980)

(5) ARRHENIUS (1963)

(6) FISCHER and DYMOND, unpublished

(7) BREWER *et al.* (1980)

(8) CHURCH and WOLGEMUTH (1972)

(9) SUESS *et al.* (1980); SUESS, unpublished

These phases, coupled with the surface biogenic Si flux, fall short of providing the required particulate Ba flux by *at least* an order of magnitude. The only estimate of Ba in the opaline tests of Radiolaria are those given in Table III-9. These were handpicked from Pacific (Eocene) sediments and carefully cleaned. The Ba/Si ratio was equivalent to that in the Antarctic diatoms. Assuming that the relative production of Radiolaria with respect to diatoms is equivalent to their relative preservation in sediments (less than 10% of diatoms, LISITZIN, 1972; TAKAHASHI and HONJO, 1980) then Radiolarian opal cannot be a significant carrier of Ba.

The celestite ($SrSO_4$) skeleton of Acantharia has also been suggested as a possible carrier of Ba (MARTIN and KNAUER, 1973; BRASS, 1980). The total production estimate of celestite (220 nmol Sr/cm^2/year, BRASS, 1980) coupled with a Ba/$SrSO_4$ analysis (5400 ppm) reported by ARRHENIUS (1963) still accounts for less than 5% of the required flux.

In summary, the surface production of particulate Ba by the carriers outlined above is insufficient, by at least a factor of two, to account for the flux maintaining the upper ocean depletion of dissolved Ba. Several possible resolutions exist. We do not feel that our estimates of the composition or flux of the major biogenic carriers could be in sufficient error to account for this difference. However, our sampling techniques for the biogenic particulate matter (44 μm net) do not sample an important component of the nano- and pico-plankton which might be responsible for production of the small barite crystals (0.5 - 1.5 μm) reported by DEHAIRS and others (1980). Finally, there is evidence in the dissolved Ba distributions (CHAN and others, 1977; CHAN and EDMOND, unpublished) and in suspended particulate matter distributions (DEHAIRS and others, 1980; and presented below) that a significant uptake of Ba from the water column occurs below the surface zone of nutrient depletion by an uncharacterized (active or passive) enrichment process.

Particulate barite ($BaSO_4$) has been identified in suspended material (CHESSELET and others, 1976; DEHAIRS and others, 1980) throughout the water column, even though the water is clearly undersaturated with respect to that phase (CHURCH and WOLGEMUTH, 1972). The particulate Ba concentrations determined on 0.4 μm filters by DEHAIRS and others (1980) and BREWER and SPENCER (unpublished GEOSECS data) frequently show subsurface maxima. Even more dramatic is the relative enrichment of Ba over other components of the particles. Figure 14 shows a set of particulate and dissolved data from GEOSECS station 331 (Eastern Tropical Pacific). The striking features of the particulate data are the near-absence of Ba in the mixed layer and its dramatic increase in the upper thermocline. There is not sufficient Ba in the surface material to create this Ba enrichment simply by the loss of other regenerated components. This can be checked by normalizing Ba to Al which, assuming a steady state input, should be conservative through this settling/regeneration process. The Ba/Al ratio still displays the same distinct maximum demonstrating that the Ba enrichment represents a significant Ba uptake.

The dissolved distributions at this station further demonstrate that Ba is not removed from surface waters in parallel to any of the "biolimiting" nutrients. The dissolved Ba concentration is nearly constant from the surface down to 200 meters depth, while the nutricline is well developed by 100 meters. The distinct difference between the surface cycle of Ba and the nutrients (in this case Si) is clearly seen in the pronounced "hook" in the near-surface dissolved Ba-Si plot and is also seen in many of the Atlantic GEOSECS stations (CHAN et al., 1977).

These particulate materials are collected from 30 liter water samples on 0.4 μm filters and may not represent a significant settling flux (BISHOP and others, 1977). However, we have now determined particulate Ba in >53 μm particulate matter and can estimate the vertical flux of these particles. Figure 15 shows the total suspended Ba data from a profile collected in the Eastern Equatorial Pacific in 1976 (BISHOP and others, 1980) and again in 1979 (COLLIER and others, in preparation). The same increase in total suspended Ba is seen and the Ba content of the deeper particles increases by a factor of 5 in the 1976 data and by 30 in 1979. Fluxes through 500 meters are estimated to be between 30 and 50 mol $Ba/cm^2/year$ in 1976 (1979 flux estimates are not yet available). Other Ba fluxes can be estimated for the Cape Basin off S.W. Africa (BISHOP and others, 1978; KURZ, unpublished) and those range between 20 and 50 nmol $Ba/cm^2/year$ through 400 meters depth. These fluxes are much closer to those predicted by the box model, and if significant over larger areas, may resolve the apparent anomaly. Still, the exact carrier of this Ba remains unresolved - is it an unknown biogenic carrier or do barites form within decomposing biogenic debris as originally proposed by CHOW and GOLDBERG (1963)?

There is evidence of Ba regeneration in both the deep water column and the sediments. If the carrier phase is barite then subsequent exposure of the barite, possibly through the oxidation of protective organic coatings, will allow dissolution to begin. DEHAIRS and others(1980) noted barite grains from deep samples which displayed significant signs of dissolution.

The regeneration fluxes predicted within the linear T-S sections of the deep water column by the advection-diffusion models range from 4 to 11 nmol

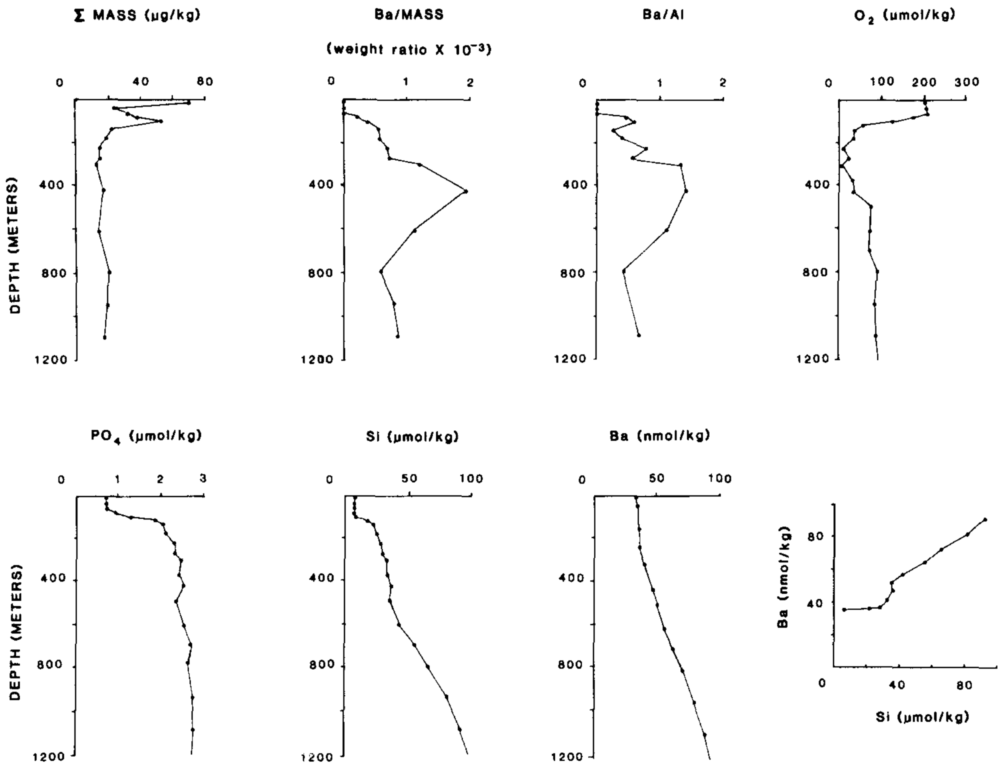


Fig. 14. Particulate and dissolved distributions of Ba at GEOSECS station 331 (4°35'S, 125°10'W). Dissolved data from CHAN and others (1976) and BROECKER and others (1982). Particulate data from BREWER and SPENCER, unpublished

Ba/cm²/year. The maximum value is at site 331 and the increased regeneration here could be related to the increased flux of settling particles which, in the case of Ba, are slowly dissolving.

Independent flux estimates from sediment traps (BREWER and others, 1980; DYMOND and FISCHER, unpublished) vary with the productivity of waters above them and fluxes in the upper 1000 meters generally range between 4 and 10 nmol Ba/cm²/year.

A pore water profile of Ba was reported by CHURCH and WOLGEMUTH (1972) from a core taken in the Eastern Tropical Pacific. It shows a gradient of Ba, implying a flux into the bottom water. Their coarse sampling interval (30 cm) would obscure any sharp concentration gradients which might have been present (similar to those seen for Cu in the upper 3 cm of other cores). Therefore, the estimated flux (approximately 1 nmol Ba/cm²/year) represents only a minimum value.

The porewaters in Pacific sediments south of New Zealand have been analyzed with much more detailed sampling and sensitive methods (SUESS and others, 1980 SUESS, unpublished). These samples always have an excess of Ba in the pore waters of the upper-most core section (0-2 cm). These data suggest a flux to bottom water ranging between 5 and 12 nmol Ba/cm²/year. The release of Ba to these porewaters appears to be more closely related to the nitrification of sedimentary organic matter than to the dissolution of opaline skeletal phases (SUESS, personal communication).

In summary, portions of the biogeochemical cycle of Ba are constrained by the large amount of available data - more so than any other trace element. However, this cycle is unique and in many ways more complex. The surface ocean is depleted by 100 nmol/kg with respect to water upwelled from the deep ocean. We have not yet been able to fully account for the biogenic particulate carriers providing the large vertical flux necessary to maintain this depletion.

Zinc. The biogeochemcial fluxes of Zn are outlined in Table 29. Among the elements discussed here, Zn is one of the most prone to contamination and very little quality data exists to constrain its cycle. All available river input estimates yield Zn residence times which are less than 1000 years. As discussed

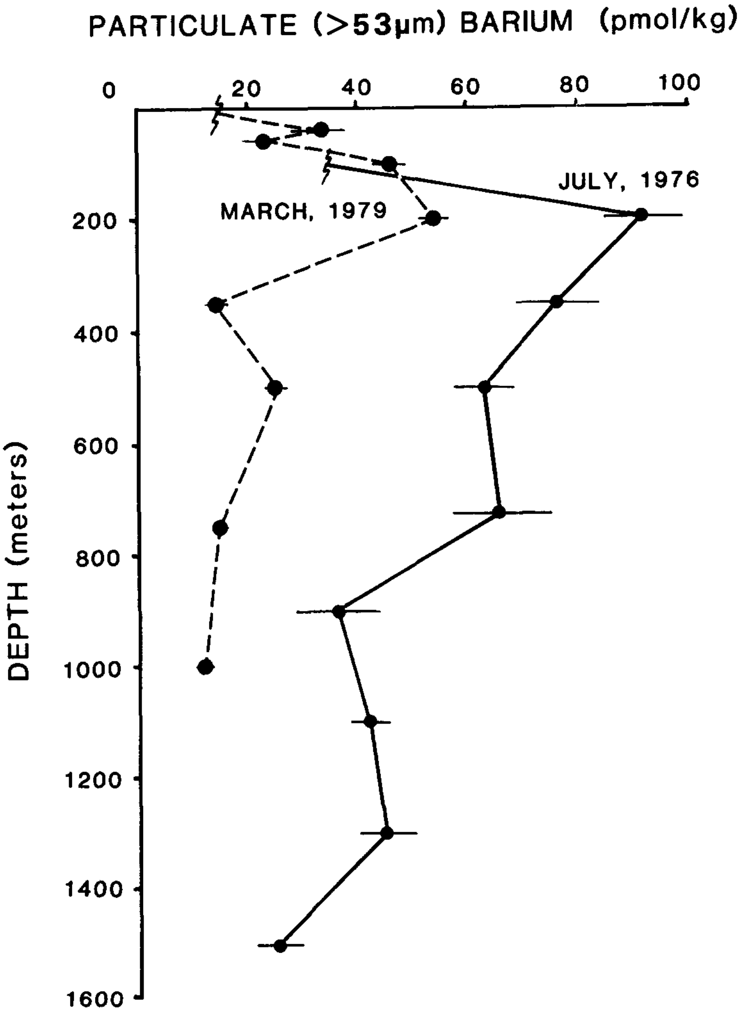


Fig. 15. Particulate (>53μm) Ba distributions in the eastern equatorial Pacific ("Galapagos" plankton station). The chemistry, biology and vertical flux of particulate matter at this station have been described by BISHOP and others (1980).

TABLE 29. Zinc Cycle

- Primary input fluxes:

Rivers(1) - C_r = unknown, probably <0.1 nmol/cm^3

Atmospheric - A, Atlantic(2) = 0.33 nmol/cm^2/yr.

Pacific(3) = 0.2 nmol/cm^2/yr.
(sum of primary surface inputs probably <0.5 nmol Zn/cm^2/yr.

- Distribution of dissolved Zn(1):

Surface C_s = 0.8 pmol/cm^3

Deep Atlantic - (1.6)
Pacific - 8.2
C_d = 7 pmol/cm^3

- Box model for surface particulate flux:

P_{Zn} = (350 cm/yr) x (7 pmol/cm^3) + (<0.5 nmol/cm^2/yr)
= 2.5 to 3.0 nmol/cm^2/yr.

- Independent estimates:

Using carrier ratios -

Total organic matter as P flux (0.87 µmol/cm^2/yr);

plankton Zn/P ratio - 2-5 x 10^{-3}:

Zn flux = 1.7-4.4 nmol/cm^2/yr.

with β = 6, Zn flux = 10 - 25 nmol Zn/cm^2/yr.

$CaCO_3$ (30 µmol Ca/cm^2/yr);

ratio of Zn/Ca in forams - 0.5 x 10^{-6}:

Carbonate carrier flux = 0.02 nmol Zn/cm^2/yr.

Opal (45 µmol Si/cm^2/yr);

ratio of Zn/Si in diatoms - 1.9-2.6 x 10^{-5}:

Opal carrier flux = 0.9-1.2 nmol Zn/cm^2/yr.

Sediment traps -

Eastern Tropical Pacific(4), flux through 500 m: 5 nmol Zn/cm^2/yr.

(1) BRULAND (1980)
(2) WALLACE et al. (1977) (3) Estimated from DUCE et al. (1982) (4) FISCHER and DYMOND, unpublished

by BRULAND (1980), this is inconsistent with an element which shows significant regeneration along with organic material within the deep ocean, further emphasizing that these river data should not be used for primary input estimates. Output flux estimates based on sediment inventories (TUREKIAN and WEDEPOHL, 1961) range between 0.2 and 0.4 nmol Zn/cm^2/year which would result in more reasonable residence times of at least several thousand years. The net output term includes the unknown hydrothermal flux (+ or -) and, therefore, does help in estimating the primary surface inputs. The box model is based on high quality dissolved distributions - but from only four stations in the N.E. Pacific (BRULAND and others, 1978; BRULAND, 1980). The value chosen for the deep Atlantic Zn is based on the Pacific Zn-Si relationship and the Si concentration in the deep Atlantic. The box model calculation requires a surface flux of approxiamtely 2-3 nmol Zn/cm^2/year.

Application of the carrier model using the P flux is difficult because there is essentially no relationship between P and Zn in the plankton samples (in contrast to the behavior of Cu, Ni, Mn and Cd figures 8, 9). The initial flux predicted based on the range of Zn/P ratios is between 2 and 5 nmol Zn/cm^2/year. In the plankton leaching experiments, very little of the Zn was released along with P which would suggest a relatively high regenerative enrichment factor ($\beta \sim 6$). When we include this factor in the Zn flux, we calculate a value which is nearly an order of magnitude larger than the box model flux. This problem cannot be reconciled within the current model and the possibility of Zn contamination of the bulk plankton samples cannot yet be dismissed.

The hand picked and cleaned foraminifera (Table 14) give very low Zn/Ca ratios (0.5×10^{-6}) which yield carrier flux estimates equivalent to only 1% of the box model values. BOYLE (1981) has measured Zn in cleaned forams from sediment cores and calculates Zn/Ca ratios between less than 10 to 70×10^{-6}. These would suggest that $CaCO_3$ may be a significant carrier of Zn. The Zn/Si ratio in the Antarctic diatoms (Table 15), coupled with the opal flux suggest a Zn flux of approximately 1 nmol/cm^2/year. This is equivalent to 20-50% of the box model value. Sediment trap collections from the Eastern Tropical Pacific (FISCHER and DYMOND, unpublished) predict a flux of approximately 5 nmol Zn/cm^2/year. This is also somewhat higher than the box model flux. Considering all these data and understanding the possibilities of contamination that exist, we are still not able to uniquely identify the specific carrier of Zn in the oceans.

Iron. The biogeochemical cycle of iron is even less well constrained. Very little quality data exists on its distribution or primary inputs. One of the most difficult elements analytically due to contamination, it also has a complex redox-chemistry, organic chemical functions, and colloidal properties. All of these factors have worked together to obscure the validity or systematics of most data or models on the marine distribution of Fe. Recent work by LANDING and BRULAND (1981, 1982) and GORDON, MARTIN and KNAUER (in press) shows very low concentrations of dissolved iron with a surface depletion over deep water values. A unique feature of the distribution of this trace metal is that particulate iron concentrations are several times higher than the dissolved concentrations.

From examination of the box model presented in Table 30, it is immediately clear that the total flux of iron out of the surface ocean is dominated by the primary inputs as opposed to the upwelling flux of "regenerated" iron. These inputs are largely atmospheric particulate matter and are introduced at crustal Fe/Al ratios (DUCE and others, 1982). The relatively refractory nature of this material and the variability of its input are supported by the plankton compositions and leaching experiments. The range of fluxes predicted from the plankton data are consistent with these input fluxes. The fluxes of Fe collected by sediment traps generally support the lower end of the box model estimates for open-ocean regions. As expected, much higher fluxes of iron are seen near the

TABLE 30. Iron Cycle

- Primary input fluxes:

Rivers(1) - C_r <1 nmol Fe/cm²/yr. (dissolved)

V_rC_r <13 nmol Fe/cm²/yr.

Atmospheric(2) - A = 20-60 nmol/cm²/yr.

Hydrothermal - maximum estimate based on 21°N data(3) -

V_hC_h <70 nmol/cm²/yr.

- Distribution of dissolved Fe (N.E. Pacific)(4):

C_s - 0.1 to 0.4 nmol/kg

C_d - 1 to 3 nmol/kg

- Box model for surface particulate flux:

P_{Fe} = (350 cm/yr) x (0.6 to 2.9 nmol/kg) + (20 to 70 nmol Fe/cm²/yr)

- Independent estimates:

Using carrier flux ratios -

Total organic matter flux as P (0.87 μmol P/cm²/yr);

plankton Fe/P ratios - 5-15 x 10^{-3}:

Fe flux = 4-13 nmol Fe/cm²/yr.

with β = 6, Fe flux = 25-80 nmol/cm²/yr.

Sediment traps(5)-

From upper 1000 meters (pelagic) - 10 to 35 nmol Fe/cm²/yr.

Other values range over 100 nmol Fe/cm²/yr.

(1) BOYLE, EDMOND and SHOLKOVITZ (1977).

(2) Atlantic, WALLACE et al. (1977); Pacific, DUCE et al. (1982)

(3) EDMOND et al. (1982)

(4) LANDING and BRULAND (1981), (1982); GORDON et al. (in press)

(5) BREWER et al. (1980); LANDING and BRULAND (1982); FISCHER (1983).

continents where the atmospheric inputs and horizontal transport are stronger. In all cases, the flux of iron increases with increasing depth, suggesting scavenging and/or additional horizontally-derived inputs at depth.

A great deal more work must be done on the chemistry of iron in the oceans before we can truly constrain its cycle. Iron is an extremely important nutrient for the metabolism of marine organisms and its availability in the open ocean may have as much ecological significance as the depletion of the major plant nutrients.

Aluminum. It was suggested in section 4.2.4 that most of the Al in these and other reported plankton samples was associated with included lithogenous material. However, a small fraction of the total Al was identified that was associated with the biogenic material formed in situ. Here we will examine the possible significance of this biogenic fraction with respect to the geochemical cycle of dissolved Al in seawater. It is essential, in using these box models, to separate the biogenic (autochthonous) particulate component from the lithogenous material. Among the trace elements studied, it was shown that this distinction was only quantitatively important for particulate Al and perhaps Fe. The non-critical use of bulk plankton compositions will seriously over-estimate the biogenic flux of particulate Al (and hence the uptake of dissolved Al).

Details of the dissolved distribution of Al and its primary inputs are outlined in Table 31. As with the other trace metals, the inputs of Al are not well known. Reported river water concentrations vary and its behavior during estuarine mixing is not well characterized (ECKERT and SHOLKOVITZ, 1976). The dissolution of Al in surface seawater from the large input flux of terrigenous material is also not known. Although it is expected that very little of this refractory material will dissolve (less than 1%, HODGE and others, 1978) the maxima of dissolved Al in surface waters observed by HYDES (1979) suggest this is occurring.

The dissolved distribution of Al in open-ocean surface seawater does not show any systematic depletion with respect to the deep ocean and frequently shows an enrichment. Scavenging of Al throughout the deep water column is also indicated. Maximum limits on the biogenic flux can be set using the carrier model and the box model. Taking the sum of the biogenic carrier fluxes estimated in Table 31 (2 to 5 nmol Al/cm^2/year) and neglecting the primary inputs of dissolved Al to the surface ocean, we calculate a maximum depletion of 3 to 15 nmol/kg. The lower end of this range is barely detectable by the current techniques. The biogenic fraction (non-opal) of Al carried by the plankton was estimated based on the HCl-soluble fraction, and is a maximum estimate. Inclusion of any primary inputs of dissolved Al in the box model further lowers the predicted surface depletion. Although there is clearly some fraction of Al associated with biological cycles, its dissolved distribution is largely controlled by other processes.

Summary of biogenic trace element fluxes. A summary of the results from the organic matter carrier model is presented in Table 32. These are also compared to the fluxes predicted by the box model. In cases where the regenerated component of the biogenic flux is a large fraction of the total flux (leading to a surface-depletion and deep-enrichment of the dissolved element) the carrier model and the box model predictions are similar. Elements whose total flux is dominated by their primary inputs to the surface ocean (especially those associated with terrigenous materials) are not described well by either model. In any case, these simplified global ocean models can only roughly quantify these complex biogenic particulate matter cycles. They have been constructed here taking advantage of this new data set on the major and minor element compositions of plankton and the increasing availability of high-quality dissolved distribituons of trace elements.

TABLE 31. Aluminum

- Primary input fluxes:

Rivers⁽¹⁾ - C_r = 0.5 to 2 nmol Al/cm^3

V_rC_r = 5 to 25 nmol Al/cm^2/yr.

Atmospheric⁽²⁾ -

Terrigenous particulate matter = 10 to 200 nmol Al/cm^2/yr.;

Less than 1% soluble: A < 0.1 to 2 nmol soluble Al/cm^2/yr.

- Distribution of dissolved Al⁽³⁾:

C_s = 20-50 nmol/kg (no systematic depletion; more often a surface enrichment)

C_d = 20-40 nmol/kg

- Independent flux estimates:

Using carrier ratios -

Total organic matter as P flux (0.87 μmol P/cm^2/yr);

plankton ratio of HCl-soluble Al/ΣP = 1×10^{-3}:

Al flux = 0.9 nmol Al/cm^2/yr.

with $\beta = 6$, Al flux = 5 nmol Al/cm^2/yr.

$CaCO_3$ (30 μmol/cm^2/yr);

ratio of Al/Ca in forams - 3.5×10^{-6}:

Al flux = 0.1 nmol Al/cm^2/yr.

Opal (45 μmol/cm^2/yr)

ratio of Al/Si in diatoms - 3.3×10^{-5}:

Al flux = 1.5 nmol Al/cm^2/yr.

Sediment traps - Mostly terrigenous material consistent with atmospheric inputs. Horizontal transport causes increase in flux with depth.

(1) MARTIN and MEYBECK (1979); STALLARD (1980)

(2) WALLACE *et al.* (1977); BUAT-MENARD and CHESSELET (1979); DUCE *et al.* 1982; HODGE *et al.* (1978)

(3) HYDES (1979); STOFFYN and MACKENZIE (1982)

TABLE 32. Carrier Model, Box Model Results

Element	Metal/P (measured) x 10^{-3}	X	Cyclic enrichment factor(β)	=	Metal/P (settling) x 10^{-3}	$C_s^{(1)}$ (nmol/kg)	C_d (nmol/kg)	Flux Estimates (nmol/cm^2/yr)	
								via organic carrier	box model estimate
P						50	2500		870
Cd	0.4-0.7		1.6		0.6-1.1	0.0	0.9	0.5-1.0	0.34
Ni	0.6-1.1		2.4		1.4-2.6	2	9	1.2-2.3	2.6
Cu	0.5-0.6		3.4		1.7-2.0	1.2	4	1.5-1.8	1.2-1.5
Mn	0.35-0.43		2		0.7-0.9	0.8-3.0	0.5-1.2	0.6-0.8	2
Ba	1.4-1.8		6		8-11	35	135	7-10	40
Zn	2-5		6		12-30	0.8	7	10-25	2.5-3.0
Fe	5-15		6		30-90	0.1-0.4	1-3	25-80	20-70

The carrier model has allowed us to specifically examine the relative significance of skeletal versus organic components in the biogenic flux. Extension of this model will allow us to estimate plankton compositions and biogenic fluxes as a function of the large range of productivity in specific environments. Further, it provides a conceptual framework to couple the production of particulate matter (and its required uptake of dissolved materials) to the flux of these elements collected by sediment traps.

8. CONCLUSIONS - MARINE BIOGEOCHEMISTRY OF TRACE ELEMENTS

Surface ocean plankton samples have been carefully collected and analyzed for major and trace element composition. It was shown that significant fractions of some elements are very weakly associated with the plankton and that their loss during sampling is very likely. Unless extreme care is taken to contain all fractions and avoid washing the sample, errors will result in estimating the role of plankton in the surface cycles of these elements.

Relationships between the dissolved and particulate trace elements in surface waters. Systematic variations in the surface water concentrations of nutrients and trace elements have been noted (BOYLE and EDMOND, 1975; BRULAND, 1980; BOYLE et al., 1981). Plankton samples taken from the Antarctic upwelling regions demonstrated a decrease in their total trace element concentrations as the dissolved concentration of nutrients and trace elements increased. The concentrations of the non-terrigenous trace elements were relatively constant in the Pacific plankton, when normalized to P as compared to the same ratios in surface water. These particulate compositions are primarily determined and limited by the properties of the organic materials and metabolism of the plankton and do not appear to be very sensitive to the dissolved concentrations in the surface water. This emphasizes the importance of specific metal-organic complexes as carriers.

Variations in the dissolved concentrations in surface waters as a function of the production of the biogenic material were also noted. The concentrations of Zn and Cd are depleted to very low levels in surface waters along with P. The ratios of these metals to P in the plankton samples are always greater than, or equal to, the surface water values. In the case of Cd, this may be responsible for its rapid depletion (before that of P) as upwelled waters evolve into nutrient-depleted surface waters. The metal/P ratios for the "biointermediate" elements (eg. Cu, Ni, Ba) in the plankton are always much less than the surface water ratios. The dissolved concentrations of these metals are never totally depleted.

Biogenic Carriers. The primary carrier for most of the elements studied was the non-skeletal organic fraction of the particulate material. Direct examination of $CaCO_3$ and opal demonstrated that these phases contained only small percentages of the trace elements in the plankton.

The organic association included an extremely labile fraction containing P, Cd, Ni, and Mn which was rapidly released into sea water and distilled water. Cell lysis, active excretion, and bacterial decomposition effect the rapid release of 40 to 60% of the initial concentration of these elements. The box models for these elements suggest that this recycling must occur very near to, or within the surface reservoir, and results in a change in the ratio of metal/P in the settling particles. Near-surface sediment trap experiments and suspended particulate sampling should detect this process. The ratio of Ni and Cu to P should increase by a factor of 2-4 and the Cd/P ratio should be 60-90% of the ratio determined in the fresh surface plankton. Since bacterial activity and osmotic shock have been identified as variables in this process, special care must be taken to determine the effects of trap poisoning, length of deployment, and the loss of cell fluids during collection or storage.

The other major biogenic fraction of the trace elements in the plankton samples was more strongly bound to fixed organic sites. The regeneration of this fraction appears to be more metal-specific and related to the stability of the organic complexes involved. The nature of these specific metal-organic complexes needs to be investigated. Although the metal-organic biochemistry is still poorly characterized, the carrier relationships can still be used to quantify trace element fluxes and identify major processes affecting their distribution.

Terrigenous Carriers. The refractory behavior and element ratios of Al and Fe demonstrated the presence of an aluminosilicate phase within the plankton samples. This was present in all samples - even from the more remote regions of the central equatorial Pacific and Antarctic. In no case did this refractory phase contribute significantly to the other trace elements in the samples. The flux estimate for terrigenous Al carried within the biogenic samples ranged between 0.005 and 0.1 μmol Al/cm^2/year, based on the range of compositions detected. This variation was a function of the input flux of terrigenous materials and of the biological production rate at the sampling site.

A trace level of Al was detected that was directly associated with the biogenic material. This was identified by its solubility in dilute HCl and most likely was derived from dissolved Al in the surface water. The flux of this phase was estimated to be on the order of 1-5 nmol Al/cm^2/year - significantly less than the estimated river input of dissolved Al. To quantify the complete geochemical cycle of Al, particulate trace element studies need to determine the chemical nature of the total particulate Al before it is simply assigned to silicate phases.

Geochemical cycles. The trace element-major element ratios determined in the plankton samples and their regeneration products have provided a basis for outlining the marine geochemical cycles of these elements. A simple, two-reservoir box model has been used to predict the averge flux of each element out of the surface ocean and those were compared to fluxes estimated by a carrier model.

Several specific experiments need to be pursued in support of the predictions made by the carrier models. There are differences between the ratios of Cd, Cu and Ni to P measured in surface plankton compared to those predicted by the carrier-box model. These have been interpreted as evidence of rapid cyclic regeneration of the organic material within the surface ocean which results in changes in the element/P ratios in the residual settling material. These changes should be measurable in carefully-collected, near-surface settling particles.

The depletion of Cd and P in the eastern North Pacific suggests that there should be a significantly lower Cd/P ratio in plankton sampled from surface waters in oligotrophic environments. Again, a series of plankton and water samples collected on transect between an upwelling region and central gyre are needed.

The production of a sub-surface Ba carrier, such as barite or an increase in surface-exchanged Ba is necessary to balance the magnitude of that element's deep enrichment. The eastern equatorial Pacific displays a dramatic increase in particulate Ba within the upper thermocline and appears to be one of the best places to study this process.

The average fluxes estimated by the carrier-box model must now be supported by direct suspended-matter and sediment-trap measurements in the near-surface and deep ocean. The release of labile elements continues to occur within the sediment traps, and this must be considered in their design, handling and in data interpretation. The flux of biogenic material to sediment traps is directly dependent on the magnitude of the total surface productivity. This varies by more than a factor of ten between different surface-ocean environments. Until many more trap experiments can quantify these variations, available trap results must still be extrapolated using carrier models to describe the total fluxes of trace elements to the deep ocean and sediments.

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REFERENCES

AGEMIAN, H. and A.S.Y. CHAU (1976) Evaluation of extraction techniques for the determination of metals in aquatic sediments. The Analyst, 101, 761-767.

ARRHENIUS, G.S. (1963) Pelagic sediments. In: The Sea, M.N. HILL, editor, Wiley, 3, pp. 655-727.

BACON, M.P. and J. M. EDMOND (1972). Barium at GEOSECS III in the southwest Pacific. Earth and Planetary Science Letters, 16, 66-74.

BAINBRIDGE, A.E. (1981). GEOSECS Atlantic Expedition, Vol. 1, Hydrographic Data. National Science Foundation, 121 pp.

BALISTRIERI, L., P.G. BREWER and J.W. MURRAY (1981) Scavenging residence times of trace metals and surface chemistry of sinking particles in the deep ocean. Deep-Sea Research, 28A, 101-121.

BAUMGARTNER, A. and E. REICHEL (1975). The World Water Balance. Elsevier, New York, 179pp.

BEERS, J.R., D.M. STEVEN and J.B. LEWIS (1968) Primary production in the Caribbean Sea off Jamaica and the Tropical North Atlantic off Barbados. Bulletin of Marine Science, 18, 86-104.

BENDER, M.L. and C. GAGNER (1976). Dissolved Cu, Ni, and Cd in the Sargasso Sea. Journal of Marine Research, 3, 327-339.

BENDER, M.S., G.P. KLINKHAMMER and D.W. SPENCER (1977). Manganese in seawater and the marine manganese balance. Deep-Sea Research, 24, 799-812.

BISHOP, J.K., J.M. EDMOND, D.R. KETTEN, M.P. BACON and W.B. SILKER (1977). The chemistry, biology and vertical flux of particulate matter from the upper 400 meters of the equatorial Atlantic Ocean. Deep-Sea Research, 24, 511-548.

BISHOP, J.K.B., D.R. KETTEN and J.M. EDMOND (1978). The chemistry, biology and vertical flux of particulate matter from the upper 400 m of the Cape Basin in the southeast Atlantic Ocean. Deep-Sea Research, 25, 1121-1161.

BISHOP, J.K., R.W. COLLIER, D.R. KETTEN and J.M. EDMOND (1980). The chemistry, biology and vertical flux of particulate matter from the upper 1500 m of the Eastern Equatorial Pacific. Deep-Sea Research, 27, 615-640.

BOSTROM, K., O. JOENSUU and I. BROHN (1974). Plankton: its chemical composition and its significance as a source of pelagic sediments. Chemical Geology, 14, 255-271.

BOYLE, E.A. (1976). The marine geochemistry of trace metals. Doctoral dissertation, WHOI-MIT Joint Program in Oceanography.

BOYLE, E.A. (1981). Cadmium, Zinc, Copper and Barium in Foraminifera tests. Earth and Planetary Science Letters, 53, 11-35.

BOYLE, E.A. and J.M. EDMOND (1975). Copper in the surface waters south of New Zealand. Nature, 253, 107-109.

BOYLE, E.A., F. SCLATER and J.M. EDMOND (1976). On the marine geochemistry of Cd. Nature, 263, 42-44.

BOYLE, E.A., J.M. EDMOND and E.R. SHOLKOVITZ (1977a). The mechanism of iron removal in estuaries. Geochimica Cosmochimica Acta, 41, 1313-1324.

BOYLE, E.A., F. SCLATER and J.M. EDMOND (1977b). The distribution of dissolved copper in the Pacific. Earth and Planetary Science Letters, 37, 38-54.

BOYLE, E.A., S.S. HUESTED and S.P. JONES (1981). On the distribution of copper, nickel and cadmium in the surface waters of the North Atlantic and North Pacific Ocean. Journal of Geophysical Research, 86, 8048-8066.

BOYLE, E.A., S.S. HUESTED and B. GRANT (1982). The chemical mass balance of the Amazon Plume - II. Copper, nickel, and cadmium. Deep-Sea Research, 29, 1355-1364.

BRASS, G.W. (1980). Trace elements in Acantharian skeletons. Limnology and Oceanography, 25, 146-149.

BREWER, P.G., G.T.F. WONG, M.P. BACON and D.W. SPENCER (1975). An oceanic calcium problem Earth and Planetary Science Letters, 26, 81-87.

BREWER, P.G., Y. NOZAKI, D.W. SPENCER and A.P. FLEER (1980). Sediment trap experiments in the Deep North Atlantic: Isotopic and elemental fluxes. Journal of Marine Research, 38, 703-728.

BROECKER, W.S. (1971). A kinetic model for the chemical composition of seawater. Quaternary Research, 1, 188-207.

BROECKER, W.S. (1974). Chemical oceanography. Harcourt Brace Jovanovich, 214pp.

BROECKER, W.S. (1979). A revised estimate for the Radiocarbon age of the North Atlantic deep water. Journal of Geophysical Research, 84, 3218-3226.

BROECKER, W.S., R. GERARD, M. EWING and B.C. HEEZEN (1960). Natural radiocarbon in the Atlantic Ocean. Journal of Geophysical Research, 65, 2903-2931.

BROECKER, W.S. and Y.H. LI (1970). Interchange of water between the major oceans. Journal of Geophysical Research, 75, 3545-3552.

BROECKER, W.S., D.L.O. SPENCER and H. CRAIG (1982). GEOSECS Pacific Expedition, Vol. 3, Hydrographic Data. National Science Foundation, 137 pp.

BRULAND, K.W., G.A. KNAUER and J.H. MARTIN (1978). Cadmium in northwest Pacific waters. Limnology and Oceanography, 23, 618-625.

BRULAND, K.W. (1980). Oceanographic distributions of Cd, Zn, Ni, and Cu in the North Pacific. Earth and Planetary Science Letters, 47, 177-198.

BRULAND, K.W., R.P. FRANKS, G.A. KNAUER and J.H. MARTIN (1979). Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in seawater. Analytica Chimica Acta, 105, 233-245.

BUAT-MENARD, P., R. CHESSELET (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. Earth and Planetary Science Letters, 42, 399-411.

BUCKLEY, D.E. and R.E. CRANSTON (1971). Atomic absorption analysis of 18 elements from a single decomposition of alumunosilicate. Chemical Geology, 7, 273-284.

BURNETT, W.C. (1971). Trace element variations in some central Pacific and Hawaiian sediments. M.S. Thesis, University of Hawaii.

BUTLER, E.I., E.D.S. CORNER and S.M. MARSHALL (1970). On the nutrition and metabolism of zooplankton. VII. Seasonal survey of nitrogen and phophorus excretion by Calanus in the Clyde Sea-area. Journal Marine Biological Association U.K., 50, 525-560

CHAN, L.H., J.M. EDMOND, R.F. STALLARD, W.S. BROECKER, Y.C. CHUNG, R.F. WEISS and T.L. KU (1976). Radium and Barium at GEOSECS stations in the Atlantic and Pacific. Earth and Planetary Science Letters, 32, 258-267.

CHAN, L.H., D. DRUMMOND, J.M. EDMOND and B. GRANT (1977). On the Barium data from the Atlantic GEOSECS Expedition. Deep-Sea Research, 24, 613-649.

CHEN, C.-T., R.M. PYTKOWICZ and E.J. OLSON (1982). Evaluation of the calcium problem in the South Pacific. Geochemical Journal, 16, 1-10.

CHESSELET, R., J. JEDWAB, C. DAROURT and F. DEHAIRS (1976). Barite as discrete suspended particles in the Atlantic Ocean. EOS, Transactions, American Geophysical Union, 57, 255 (abstract).

CHOW, T.J. and E. GOLDBERG (1960). On the marine geochemistry of Barium. Geochimica Cosmochimica Acta, 20, 192-198.

CHESTER, R. and M.J. HUGHES (1967). A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. Chemical Geology, 2, 249-262.

CHURCH, T.M. and K. WOLGEMUTH (1972). Marine barite saturation. Earth and Planetary Science Letters, 15, 35-44.

COBLER, R. and J. DYMOND (1980). Sediment trap experiment on the Galapagos aspreading Center, Equatorial Pacific. Science, 209, 801-803.

COLLIER, R.W. (1981). The Trace Element Geochemistry of Marine Biogenic Particulate Matter. Ph.D. Thesis. Massachusetts Institute of Technology/Woods Hole Oceanographic Institution, WHOI-81-10.

COSSA, D. (1976). Sorption of Cd by a population of the diatom Phaeodactylum tricornutum in culture. Marine Biology, 34, 163-167.

CRONAN, D.S. (1969). Average abundances of Mn, Fe, Ni, Co, Cu, Pb, Mo, V, Cr, Ti, P in Pacific pelagic clays. Geochimica Cosmochimica Acta, 33, 1562-1565.

CULMO, R. (1969). Automatic microdetermination of carbon, hydrogen, and nitrogen: improved combustion-train and handling techniques. Mikrochimica Acta, WIEN, 175-180.

DAVIES, A.G. (1970). Iron, chelation and the growth of marine phytoplankton. I. Growth kinetics and chlorophyll reduction under iron limiting conditions. Journal Marine Biology Association, U.K., 50, 65-86.

DAVIS, J.A. (1980). Adsorption of natural organic matter from freshwater environments by aluminum oxide. In: Contaminants and Sediments, R.A. BAKER, editor, 2, pp.279-304.

DAVIS, J.A. and J.O. LECKIE (1978). Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environmental Science and Technology, 12, 1309-1315.

DEHAIRS, F., R. CHESSELET and J. JEDWAB (1980). Discrete suspended particles of barite and the Barium cycle in the open ocean. Earth and Planetary Science Letters, 49, 528-550.

DEMASTER, D.J. (1981). The supply and accumulation of silica in the marine environment. Geochimica Cosmochimica Acta, 45, 1715-1732.

DEUSER, W.G., P.G. BREWER, T.D. JICKELLS, R.F. COMNEAU (1983). Biological control of the removal of abiogenic particles from the surface ocean. Science, 219, 388-391.

DEUSER, W.G. and E.H. ROSS (1980). Seasonal change in the flux of organic carbon to the deep Sargasso Sea. Nature, 283, 364-365.

DROOP, M.R. (1975). The nutrient status of algal cells in batch culture. Journal of Marine Biology Association, U.K., 55, 22-36.

DUCE, R.A., C.K. UNNI, B.J. RAY, R. ARIMOTO (1982). Atmospheric deposition of trace metals to the Tropical North Pacific. Transactions, American Geophysical Union (E.O.S.), 63, 987. (Abstract).

DYMOND, J. (1981). Geochemistry of Nazca Plate surface sediments: evaluation of hydrothermal, biogenic, detrital, and hydrogenous sources. In: Studies of the Nazca Plate and Andean Convergence Zone, L.D. COOMBE, editor, Geological Society of America, memoir, 154, pp. 133-173.

ECKERT, J.M. and E.R. SHOLKOVITZ (1976). The flocculation of iron aluminum and humates from river water by electrolytes. Geochimica Cosmochimica Acta, 40, 847-848.

EDMOND, J.M. (1974). On the dissolution of carbonate and silicate in the deep ocean. Deep-Sea Research, 21, 455-480.

EDMOND, J.M., E.D. BOYLE, D. DRUMMOND, B. GRANT and T. MISLICK (1978). Desorption of Ba in the plume of the Zaire River. Netherlands Journal of Sea Research, 12, 324-328.

EDMOND, J.M., S.S. JACOBS, A.L. GORDON, A.W. MANTYLA and R.F. WEISS (1979a). Water column anomalies in dissolved silica over opaline pelagic sediments and the origin of the deep Si maximum. Journal of Geophysical Research, 84, 7809-7826.

EDMOND, J.M., C. MEASURES, R. MCDUFF, L.H. CHAN, R. COLLIER, B. GRANT, L. GORDON and J. CORLISS (1979b). Ridge crest hydrothermal activity and the balances of major and minor elements in the oceans: the Galapagos data. Earth and Planetary Science Letters, 46, 1-18.

EDMOND, J.M., C. MEASURES, B. MANGUM. B. GRANT, F.R. SCLATER, R. COLLIER, A. HUDSON, L.I. GORDON and J.B. CORLISS (1979c). On the formation of metal--rich deposits at ridge crests. Earth and Planetary Science Letters, 46, 19-30.

EDMOND, J.M., K.L. VON DAMM, R.E. MCDUFF and C.I. MEASURES (1982). Chemistry of hot springs on the East Pacific Rise and their effluent dispersal. Nature, 297, 187-191.

EL-SAYED, S.Z. and S. TAGUCHI (1979). Phytoplankton standing crop and primary productivity in the Tropical Pacific. In: Marine Geology and Oceanography of the Pacific Manganese Nodule Province, J.L. BISCHOFF, D.Z. PIPER, editors, Marine Science, Vol. 9, pp. 241-286.

EMERSON, S. and M. BENDER (1981). Carbon fluxes at the sediment-water interface of the deep-sea: calcium carbonate preservation. Journal of Marine Research, 39, 139-162.

EMERSON, S., R. JAHNKE, M. BENDER, P. FROELICH, G. KLINKHAMMER, C. BOWSER and G. SETLOCK (1980). Early diagenesis in sediments from the eastern equatorial Pacific, I. Porewater nutrient and carbonate results. Earth and Planetary Science Letters, 49, 57-80.

EPPLEY, R.W. and B.J. PETERSON (1979). Particulate organic matter flux and planktonic new production in the deep ocean. Nature, 282, 677-680.

FERGUSON, W.S., J.J. GRIFFIN and E.D. GOLDBERG (1970). Atmospheric dusts from the North Pacific - A short note on long-range eolian transport. Journal of Geological Research, 75, 1137-1139.

FIADERO, M. and H. CRAIG (1978). Three-dimensional modeling of tracers in the deep Pacific Ocean: I. Salinity and Oxygen. Journal of Marine Research, 36, 323-355.

FISCHER, K. (1983). Particle fluxes to the eastern tropical Pacific Ocean -- sources and processes. Ph.D. Dissertation, Oregon State University.

FISCHER, K., J. DYMOND, C. MOSER, D. MURRAY and A. MATHERNE (1983). Seasonal variations in particulate flux in an offshore area adjacent to coastal upwelling. In: Coastal Upwelling: Its Sediment Record, E. SUESS and J. THIEDE, editors, Vol. I. Plenum.

FROELICH, P.N. (1979). Marine phosphorus geochemistry. Doctoral dissertation, University of Rhode Island.

GARDNER, W.S., D.S. WYNNE and W.M. DUNSTAN (1976). Simplified procedure for the manual analysis of nitrate in seawater. Marine Chemistry, 4, 393-396.

GOLDBERG, E.D. and G.O.S. ARRHENIUS (1958). Chemistry of Pacific pelagic sediments. Geochimica Cosmochimica Acta, 13, 153-212.

GOLDMAN, J.C., J.J. MCCARTHY and D.G. PEAVEY (1979). Growth rate influence on the chemical composition of phytoplankton in oceanic waters. Nature, 279, 211-215.

GORDON, R.M., J.H. MARTIN and G.A. KNAUER (1983). Iron in north-east Pacific waters. Nature, in press.

GORSUCH, T.T. (1970). The destruction of organic matter. Pergamon Press, p. 151.

GRANT, G., M.-H. HU, E. BOYLE and J.M. EDMOND (1982). Comparison of the trace metal chemistry in the Amazon, Orinoco, and Yangtze plumes. Transactions, American Geophysical Union (E.O.S.), 63, 48.

GRILL, E.V. and F.A. RICHARDS (1964). Nutrient regeneration from plankton decomposing in seawater. Journal of Marine Research, 22, 51-69.

HALPERN, D. (1979). Observations of upper ocean currents at DOMES sites A, B, and C in the tropical central North Pacific Ocean during 1975 and 1976. In: Marine Geology and Oceanography of the Pacific Manganese Nodule Province, J.L. BISCHOFF, D.Z. PIPER, editors, Marine Science, Vol. 9.

HARRISON, W.G. (1980). Nutrient regeneration and primary production in the sea. In: Primary Production in the Sea, P.G. FALKOWSKI, editor, Plenum, pp. 433-460.

HARTMANN, M., P.J. MULLER, E. SUESS and C.H. VAN DER WEIJDEN (1976). Chemistry of Late Quaternary sediments and their interstitial waters from the NW African continental margin. "Meteor" Forsch.-Ergebnisse C, No. 24, 1-67.

HANOR, J.S. and L.H. CHAN (1977). Non-conservative mixing of Ba during mixing of Mississippi River and Gulf of Mexico waters. Earth and Planetary Science Letters, 37, 242-250.

HEATH, G. R. and J. DYMOND (1977). Genesis and transformation of metalliferous sediments from the East Pacific Rise, Bauer Deep, and Central Basin, northwest Nazca plate. Geological Society of America Bulletin, 88, 723-733.

HEATH, G.R., T.C. MOORE and J.P. DAUPHIN (1977). Organic carbon in deep sea sediments. In: The fate of Fossil Fuel CO2 in the Oceans. N.R. ANDERSEN and A. MALAHOFF, editors, pp. 605-625.

HELLEBUST, J.A. (1974). Extracellular products. In: Algal Physiology and Biochemistry, W.D.P. STEWART, editor, University of California, pp. 838-863.

HODGE, V., S.R. JOHNSON and E.D. GOLDBERG (1978). Influence of atmospherically transported aerosols on surface ocean water composition. Geochemical Journal, 12, 7-20.

HONJO, S. (1978). Sedimentation of materials in the Sargasso Sea at a 5367m deep station. Journal of Marine Research, 36, 469-492.

HONJO, S. (1980). Material fluxes and modes of sedimentation in the mesopelagic and bathypelagic zones. Journal of Marine Research, 38, 53-97.

HONJO, S., S.J. MANGANINI, J.J. COLE (1982). Sedimentation of biogenic matter in the deep ocean. Deep-Sea Research, 29, 609-625.

HORIBE, Y., K. ENDO and H. TSUBOTA (1974). Calcium in the South Pacific, and its correlation with carbonate alkalinity. Earth and Planetary Science Letters, 23, 136.

HUGHES, M.N. (1972). The Inorganic Chemistry of Biological Processes. Wiley and Sons, pp. 306.

HURD, D.C. (1973). Interaction of biogenic opal, sediment and seawater in the central equatorial Pacific. Geochimica Cosmochimica Acta, 37, 2257-2282.

HYDES, D.J. (1979). Aluminum in seawater: Control by inorganic processes. Science, 205, 1260-1262.

HYDES, D.J. (1980). Reduction of matrix effects with soluble organic acid in the carbon furnace atomic absorption spectrometric determination of Co, Cu, and Mn in seawater. Analytical Chemistry, 52, 959-963.

IBERS, J.A. and R.H. HOLM (1980). Modeling Coordination sites in metallobiomolecules. Science, 209, 223-235.

JAMES, R.O. and M.G. MACNAUGHTON (1977). The adsorption of aqueous heavy metals on inorganic minerals. Geochimica Cosmochimica Acta, 41, 1549-1555.

JONES, C.J. and J.W. MURRAY (1980). The distribution of Mn in the Cascadia Basin. E.O.S., Transactions, American Geophysical Union, 61, 269.

KING, F.D. and A. DEVOL (1979). Estimates of vertical eddy diffusion through the thermocline from phytoplankton nitrate uptake rates in the mixed layer of the eastern tropical Pacific. Limnology and Oceanography, 24, 645-651.

KLINKHAMMER, G.P. (1980). Early diagenesis in sediments from the eastern equatorial Pacific. II. Porewater metal results. Earth and Planetary Science Letters, 49, 81-101.

KLINKHAMMER, G.P. and M.L. BENDER (1980). The distribution of Mn in the Pacific Ocean. Earth and Planetary Science Letters, 46, 361-384.

KNAUER, G.A., J.H. MARTIN and K.W. BRULAND (1979). Fluxes of particulate carbon, nitrogen, and phosphorus in the upper water column of the northwest Pacific. Deep-Sea Research, 26, 97-108.

KNAUER, G.A. and J.H. MARTIN (1980). Manganese cycling in northeast Pacific waters. Earth and Planetary Science Letters, 51, 266-274.

KNAUER, G.A. and J.H. MARTIN (1981). Phosphorus and cadmium cycling in northeast Pacific waters. Journal of Marine Research, 39, 65-76.

KOBLENTZ-MISHKE, O.J., V.V. VOLKOVINSKY and J.G. KABANOVA (1970). Plankton primary production of the world ocean. In: Scientific Exploration of the South Pacific, W.S. WOOSTER, editor, National Academy of Science, pp. 183-193.

KORZUN, V.E., A.A. SOKOLOV, M.I. BUDYKO, K.P. VOSKRESENSKY, G.P. KALIMIN, A.A. KONOPLYANTSER, E.S. KOROTKEVICH, P.S. KUZIN and M.I. LVOVICH (1974). World water balance and water resources of the earth. USSR Committee for the International Hydrologic Decade published by UNESCO, Studies and Reports in Hydrology No. 25, Unesco Press, Paris, Table 150, p. 492.

KRAUSKOPF, K.B. (1956). Factors controlling the concentrations of thirteen rare metals in sea water. Geochimica Cosmochimica Acta, 9, 1-32.

KREMLING, K., J. PIUZA, K. VON BROCKEL and C.S. WONG (1978). Studies on the pathways and effects of cadmium in controlled ecosystem enclosures. Marine Biology, 48, 1-10.

KRISHNASWAMI, S. (1976). Authigenic transition elements in Pacific pelagic clays. Geochimica Cosmochimica Acta, 40, 425-434.

KRISHNASWAMI, S. and M.M. SARIN (1976). Atlantic surface particulates: composition, settling rates, and dissolution in the deep sea. Earth and Planetary Science Letters, 32, 430-440.

KRISHNASWAMI, S. and M.M. SARIN (1981). Chemical and radiochemical investigations on surface and deep particulates of the Indian Ocean. Earth and Planetary Science Letter, 54, 81-96.

KROOPNICK, P. (1974). The dissolved O_2-CO_2-^{13}C system in the eastern equatorial Pacific. Deep-Sea Research, 21, 211-227.

LANDING, W.M. and K.W. BRULAND (1980). Manganese in the North Pacific. Earth and Planetary Science Letters, 49, 45-56.

LANDING, W.M. and K.W. BRULAND (1981). The vertical distribution of iron in the Northeast Pacific (Abstract). Transactions, American Geophysical Union (E.O.S.), 62, 906.

LANDING, W.M. and K.W. BRULAND (1982). The biogeochemistry of Fe and Mn at VERTEX-II. (Abstract). Transactions, American Geophysical Union (E.O.S.), 63, 960.

LEWIN, J.C. (1961). The dissolution of Si from diatom walls. Geochimica Cosmochimica Acta, 21, 182-198.

LI, Y.H., T. TAKAHASHI and W.S. BROECKER (1969). The degree of saturation of $CaCO_3$ in the oceans. Journal of Geophysical Research, 74, 5507-5525.

LI, Y.H., T.L. KU, G.G. MATHIEU and K. WOLGEMUTH (1973). Barium in the Antarctic Ocean and implications regarding the marine geochemistry of Ba and Ra-226. Earth and Planetary Science Letters, 19, 352-358.

LIBICKI, C.M. (1976). Barium uptake by marine diatoms. M.S. Thesis, Massachusetts Institute of Technology.

LISITZIN, A.P. (1972). Sedimentation in the World Oceans. Society of Economic Paleontologists and Mineralogists, Special Publication No. 17.

LIVINGSTONE, D.A. (1963). Chemical composition of rivers and lakes. U.S. Geological Survey Professional Paper, 440-G.

LOVE, C.M. and R.M. ALLEN (1974), editors. EASTROPAC Atlas, Vols. 2,4,6,8,10, NOAA-NMFS Circular 330, 1971-1974.

MANGUM, B.J. and J.M. EDMOND (1979). Trace metal profiles from MANOP sites M, H, C and S. Transactions, American Geophysical Union (E.O.S.), 60, 858. (Abstract).

MARTIN, J.H. and G.A. KNAUER (1973). The elemental composition of plankton. Geochimica Cosmochimica Acta, 37, 1639-1653.

MARTIN, J.H., K.W. BRULAND and W.W. BROENKOW (1976). Cadmium transport in the California Current. In: Marine Pollutant Transfer, H.L. WINDOM and R.A. DUCE, editors, Lexington Books, pp. 159-184.

MARTIN, J.M. and M. MEYBECK (1979). Elemental mass-balance of material carried by major world rivers. Marine Chemistry, 7, 173-206.

MCROY, C.P. and J.J. GOERING (1975). Primary production budget for the Bering Sea. In: Bering Sea Oceanography - an update, 1972-1974. D.W. HOOD and Y. TAKEMONTI, editors, Report 75-2, Institute of Marine Science, University of Alaska, pp. 97-108.

MOLINA-CRUZ, A. and P. PRICE (1977). Distribution of opal and quartz on the ocean floor of the subtropical southeastern Pacific. Geology, 5, 81-84.

MOORE, R. (1978). The distribution of dissolved Cu in the eastern Atlantic Ocean. Earth and Planetary Science Letters, 41, 461-468.

MOPPER, K. and E.T. DEGENS (1972). Aspects of the biogeochemistry of carbohydrates and proteins in aquatic environments. W.H.O.I. Technical Report, 72-68, Woods Hole Oceanographic Institution, pp.118.

MUELLER, P.J. and E. SUESS (1979). Productivity, sedimentation rate, and sedimentary organic matter in the oceans - I. Organic carbon preservation. Deep-Sea Research, 26A, 1347-1362.

MULLIN, J.B. and J.P. RILEY (1955). The colorimetric determination of silicate with special reference to sea and natural waters. Analytica Chimica Acta, 12, 162-176.

MUNK, W. (1966). Abyssal recipes. Deep-Sea Research, 13, 707-730.

MURPHY, J. and J.P. RILEY (1962). A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, 27, 31-36.

MURRAY, J.W. (1975). The interaction of metal ions at the manganese dioxide - solution interface. Geochimica Cosmochimica Acta, 39, 505-519.

NELSON, D.M. and L.I. GORDON (1982). Production and pelagic dissolution of biogenic silica in the Southern Ocean. Geochimica Cosmochimica Acta, 46, 491-501.

NG, A. (1975). Barium uptake by diatoms and the Ra-226-Ba-Si system in the oceans. M.S. Thesis. Massachusetts Institute of Technology.

O'HAVER, T.C. (1976). Analytical considerations. In: Trace Analysis; Spectroscopic Methods for Elements. J.D. WINEFORDNER, editor, Wiley, pp. 15-62.

PEDERSEN, T.F. and N.B. PRICE (1982). The geochemistry of manganese carbonate in Panama Basin sediment. Geochimica Cosmochimica Acta, 46, 59-68.

PETERSON, B.J. (1980). Aquatic primary productivity and the $^{14}C-CO_2$ method: A history of the productivity problem. Annual Reviews of Ecological Systems, 11, 359-385.

PLATT, T. and D.V. SUBBA RAO (1973). Fisheries Research Board of Canada, Technical Report, No. 370.

PRICE, N.B. and S.E. CALVERT (1970). Compositional variation in Pacific Ocean ferromanganese nodules and its relationship to sediment accumulation rates. Marine Geology, 9, 145-171.

REDFIELD, A.C., B.H. KETCHUM and F.A. RICHARDS (1973). The influence of organisms on the composition of seawater. In: The Sea, M.N. HILL, editor, Wiley, 2, pp. 26-77.

REGAN, J.G.T. and J. WARREN (1978). The effect of graphite tube condition and of ascorbic acid on load peak shapes obtained by flameless atomic absorption spectroscopy using low temperature atomization. Atomic Absorption Newsletter, 17, 89-90.

REID, J.S. and R.J. LYNN (1971). On the influence of the Norwegian-Greenland and Weddell seas upon the bottom waters of the Indian and Pacific oceans. Deep-Sea Research, 18, 1063-1088.

RILEY, J.P. (1975). Analytical chemistry of seawater. In: Chemical Oceanography, second edition, J.P. RILEY and G. SKIRROW, editors, 3, pp. 193-514.

RILEY, J.P. and I. ROTH (1971). The distribution of trace elements in some species of phytoplankton grown in culture. Journal of the Marine Biological Association, U.K., 50, 63-72.

RYTHER, J.H. and W.M. DUNSTAN (1971). Nitrogen, phosphorus, and eutrophication in the coastal marine environment. Science, 171, 1008-1013.

SCHAULE, B. and C. PATTERSON (1978). The occurrence of lead in the northeast Pacific and the effects of anthropogenic inputs. In: Proceedings of an International Experts Discussion of Lead: Occurrence, Fate, and Pollution in the Marine Environment, Roving Yugoslavia, October 1977, M. BRANICA, editor, Pergamon Press.

SCHINK, D.R., N.L. GUINASSO and K.A. FANNING (1975). Processes affecting the concentration of silica at the sediment-water interface of the Atlantic Ocean. Journal of Geophysical Research, 80, 3013-3031.

SCLATER, F.R., E.A. BOYLE and J.M. EDMOND (1976). On the marine geochemistry of Ni. Earth and Planetary Science Letters, 31, 119-128.

SHILLER, A., K. BUESSELER and E.A. BOYLE (1982). Trace metals in the Mississippi Plume. EOS, Transactions American Geophysical Union, 63, 1009 (Abstract).

SHILLER, A.M. and J.M. GIESKES (1980). Processes affecting the oceanic distributions of dissolved calcium and alkalinity. Journal of Geophysical Research, 85, 2719-2727.

SICK, L.V. and G.J. BAPTIST (1979). Cadmium incorporation by the marine copepod Psuedodiaptomus coronatus. Limnology and Oceanography, 24, 453-462.

SILKER, W.B. (1972). Berylium-7 and fission products in the GEOSECS II water column and applications of their oceanic distributions. Earth and Planetary Science Letters, 16, 131-137.

SILLEN, L.G. and A.E. MARTELL (1971). Stability constants supplement #1. The Chemical Society, Special Publication 25, London.

SLAVIN, W. (1968). Atomic Absorption Spectroscopy. Wiley, Chemical Analysis Series, Vol. 25.

SPENCER, D.W. and P.L. SACHS (1970). Some aspects of the distribution, chemistry, and mineralogy of suspended matter in the Gulf of Maine. Marine Geology, 9, 117-136.

STALLARD, R.F. (1980). Major element geochemistry of the Amazon River System. Ph.D. Thesis, Massachusetts Institute of Technology/Woods Hole Oceanographic Institute. WHOI-80-29.

STOFFYN, M. and F.T. MACKENZIE (1982). Fate of dissolved aluminum in the oceans. Marine Chemistry, 11, 105-127.

STOMMEL, H. and A.B. ARONS (1960). On the abyssal circulation of the world ocean II. An idealized model of the circulation pattern and amplitude in ocean basins. Deep-Sea Research, 6, 217-233.

STUIVER, M. (1976). The ^{14}C distribution in West Atlantic abyssal waters. Earth and Planetary Science Letters, 32, 322-331.

STURGEON, R.E. and C.L. CHAKRABARTI (1978). Recent advances in electrothermal atomization in graphite furnace atomic absorption spectrometry. Progress in Analytical Atomic Spectroscopy, 1, 5-199.

SUESS, E., P.J. MULLER, H.S. POWELL and C.E. REIMERS (1980). A closer look at nitrification in pelagic sediments. Geochemistry Journal, 14, 129-137.

TAKAHASHI, K. and S. HONJO (1980). Vertical flux of sedimentary Radiolaria: A taxon-quantitative sediment trap study from the Western Tropical Atlantic. Micropaleontology, 27, 140-190.

TAKAHASHI, T., W.S. BROECKER, A.E. BAINBRIDGE and R.F. WEISS (1980). Carbonate chemistry of the Atlantic, Pacific and Indian Oceans: The Results of the GEOSECS Expeditions 1972-1978. TR 1, CU-1-80, Lamont-Doherty Geological Observatory.

THOMAS, W.H. (1966). Surface nitrogenous nutrients and phytoplankton in the northeastern tropical Pacific Ocean, Limnological Oceanography, 11, 393-400.

TOGGWEILER, J.R. (1983). A multi-tracer study of the hydrography and geochemistry of the deep Bering Sea. Ph.D. Thesis, Columbia University.

TRAGANZA, E.D., J.C. CONRAD and L.C. BREAKER (1981). Satellite observations of a cyclonic upwelling system and giant plume in the California Current. In: Coastal Upwelling, F.A. Richards, editor, American Geophysical Union, pp. 228-241.

TSUCHIYA, M. (1968). Upper Waters of the Intertropical Pacific Ocean. Johns Hopkins Oceanographic Studies, No. 4.

TUREKIAN, K.K. and J. IMBRIE (1966). The distribution of trace elements in deep-sea sediments of the Atlantic Ocean. Earth and Planetary Science Letters, 1, 161-168.

TUREKIAN, K.K. and D.G. JOHNSON (1966). The barium distribution in seawater. Geochimica Cosmochimica Acta 30, 1153.

TUREKIAN, K.K., A. KATZ and L. CHAN (1973). Trace element trapping in pteropod tests. Limnological Oceanography, 18, 240-249.

TUREKIAN, K.K. and K.H. WEDEPOHL (1961). Distribution of the elements in the major units of the earth's crust. Geological Society of America Bulletin, 72, 175.

VACCARO, R.F. (1963). Available nitrogen and phosphorus and the biochemical cycle in the Atlantic off New England. Journal of Marine Research, 21, 284-301.

VAN BENNEKOM, A.J. and S.J. VAN DER GAAST (1976). Possible clay structures in the frustules of living diatoms. Geochimica Cosmochimica Acta, 40, 1149-1152.

WALLACE, G.T., G.L. HOFFMAN and R.A. DUCE (1977). Influence of organic matter and atmospheric deposition on the particulate trace metal concentration of northwest Atlantic surface seawater. Marine Chemistry, 5, 143-170.

WALLEN, D.G. and G.H. GREEN (1971). The nature of the photosynthate in natural phytoplankton populations in relation to light quality. Marine Biology, 10, 44-59.

WEFER, G., E. SUESS, W. BALZER, G. LIEBEZEIT, P.J. MULLER, C.A. UNGERER and W. ZENK (1982). Fluxes of biogenic components from sediment traps deployment in circumpolar waters of the Drake Passage. Nature, 299, 145-147.

WEISS, R.F. (1977). Hydrothermal manganese in the deep sea: Scavenging residence time and Mn/^{3}He relationships. Earth and Planetary Science Letters, 37, 257-262.

WEISS, R.F., H.G. OSTLUND and H. CRAIG (1979). Geochemical studies of the Weddell Sea. Deep-Sea Research, 26, 1093-1120.

WINDOM, H.L. (1975). Eolian contributions to marine sediments. Journal of Sedimentary Petrology, 45, 520-529.

WYRTKI, K. (1967). Circulation and water masses in the eastern equatorial Pacific Ocean. International Journal of Oceanology and Limnology, 1, 117-147.

WYRTKI, K. and G. MEYERS (1975). The trade wind field over the Pacific Ocean, Part I. Hawaii Institute of Geophysics, Report No. HIG-75-1.