

Distribution of elements in marine sediments: a review and synthesis*

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Abstract: The importance of Fe-Mn oxides in scavenging minor elements from the water column and fixing them in marine sediments is re-evaluated.

1) Dissolved elements in seawater are taken up by phytoplankton and transported to the sea-floor as settling particles. Biogenous components in settling particles are regenerated during sinking through the water column and the proportion of terrigenous aluminosilicate fraction increases with depth. Below the oxygen minimum zone, Fe-Mn oxides are precipitated on settling particles by microbial mediation and play an important role in scavenging minor elements from seawater.

2) The chemical compositions of oxic deep-sea sediments can be simulated by admixtures of aluminosilicates with average shale composition and Fe-Mn oxides with ferromanganese nodule compositions of four different origins (hydrogenous, oxic diagenetic, suboxic diagenetic and hydrothermal).

3) Near-shore sediments in which neither manganese oxides nor iron sulfides are present have the chemical composition of average shale, because elements transported by settling particles are released during early diagenesis from the sediments as benthic fluxes.

4) In anoxic environments where iron sulfides are formed, chalcophile elements are enriched in the sediments.

5) The present concentrations of many minor elements in seawater and their mean oceanic residence times may be controlled by their ultimate incorporation into Fe-Mn oxides, because anoxic sediments are restricted within narrow limits.

1. Introduction

WHITFIELD and TURNER (1979) established the correlation between the concentration ratios of elements in crustal rocks relative to seawater and the mean oceanic residence times of elements, which are a measure of reactivity of elements in the marine environment. On the other hand, LI (1982a) discussed the mean oceanic residence times on the basis of both the concentration ratios of elements in pelagic clays to seawater and those in river water to seawater. WHITFIELD and TURNER (1979) also found a linear correlation between the concentration ratios of elements in the crustal rocks relative to seawater and the electronegativity function

($Q_{MO} = (\chi_M - \chi_O)^2$, where χ is the electronegativity of the subscripted element). In their discussion on the composition of river water and seawater, they emphasized the importance of the electrostatic interaction of elements with oxygen-dominated mineral lattices during the weathering of the crustal rocks, which produces dissolved solids in river water and clay minerals, and during reverse weathering in marine environments where authigenic silicates, iron and manganese oxides are formed from seawater. On the other hand, LI (1981a) observed a relationship between the concentration ratios of elements in the pelagic sediment to seawater and their first hydrolysis constants for cationic elements and for oxyanionic elements an inverse relationship between the concentration ratios of elements and the first or second dissociation constants of their oxyacids. These relationships

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are in accordance with the surface complex formation model (SCHINDLER, 1975; BALISTRERI *et al.*, 1981). Although there was a debate on the two concepts (WHITFIELD and TURNER, 1982; LI, 1982b), WHITFIELD and TURNER (1983) and LI (1991) recognized the two concepts as different ways of expressing the chemical bonds between adsorbed elements and oxygen atoms of hydrolyzed solid phases (silicate minerals, oxides, etc.). The surface complex formation model is more mechanistic than the electronegativity function model, although hydrolysis constants for cationic elements and dissociation constants for oxyanionic acids are not necessarily available for all the elements.

In the oceans, many dissolved elements are taken up by phytoplankton and transported to the sea-floor as biogenic settling particles. The elements associated with settling particles are fixed into sedimentary components and otherwise recycled into overlying bottom water during diagenesis. In oxic sediments, the most important adsorbents of elements are iron and manganese oxides, which occur as coatings on sedimentary components (silicate minerals, biogenic silica and calcium carbonates), manganese micro- and macro-nodules (ELDERFIELD *et al.*, 1972; CHESTER *et al.*, 1973; GLASBY, 1975; LI, 1981a; STOFFERS *et al.*, 1981; GLASBY *et al.*, 1987; PIPER, 1988; KUNZENDORF *et al.*, 1989). In anoxic environments, iron sulfides and humic substances play an important role in fixing elements into sediments (VINE and TOURTELOT, 1970; BRUMSACK, 1980; LEVENTHAL *et al.*, 1982; CALVERT and PRICE, 1983; JACOBS *et al.*, 1987).

In this study, ferromanganese concretions are chosen as the representative hydrogenous product of oxic marine environments and black shales as that of anoxic environments, and the behavior of elements in marine environments is discussed in relation to the mean oceanic residence time.

2. Enrichment of elements in oxic pelagic sediments relative to the crustal rocks

Pelagic sediments are considered to be the ultimate sink of many elements as well as ferromanganese concretions (LI, 1981a). However, ferromanganese concretions are better models

than sediments to investigate the removal mechanisms of minor elements in oxic marine environments, because most constituents of ferromanganese concretions are of marine origin. On the other hand, pelagic sediments are the mixture of aluminosilicate minerals transported from land, biogenic calcium carbonate and silica, humic matter, and manganese and iron oxides which occur as coatings on the sedimentary components and as manganese micronodules. The chemical composition of the hydrogenous fraction of pelagic clays is similar to that of the associated ferromanganese concretions (PIPER *et al.*, 1979; APLIN and CRONAN, 1985; PIPER *et al.*, 1987).

As described above, WHITFIELD and TURNER (1979) established the correlation between the concentration ratios of elements in the crustal rocks relative to seawater and their mean oceanic residence times. The concentration ratios of elements in ferromanganese concretions relative to seawater are plotted against those in the crustal rocks relative to seawater (Fig. 1). In the abscissa, elements are therefore roughly arranged in decreasing order of their mean oceanic residence times. The concentration data of ferromanganese concretions, the crustal rocks and seawater are mainly from the compilations given by BATURIN (1988), MASON and MOORE (1982) and BRULAND (1983), respectively. In Fig. 1, elements plotted above the 1: 1 line indicate that they are concentrated in ferromanganese concretions more than in the crustal rocks. Elements located along the 1: 1 line are elements which are contained in aluminosilicate minerals transported from land or elements of which concentration ratios in ferromanganese concretions are similar to those in the crustal rocks.

Cationic minor elements are adsorbed on iron and manganese oxides and some of them are substituted for manganese in edge-shared $[\text{MnO}_6]$ octahedra (BURNS and BURNS, 1976; BURNS *et al.*, 1983). According to LI (1981a), adsorption affinities of cationic elements on oxides depend on their first hydrolysis constants. In Fig. 2, concentration ratios of cationic elements in ferromanganese concretions are plotted against their first hydrolysis constants. The hydrolysis constants are mainly from the compilation given by SMITH and MARTELL (1976). The most

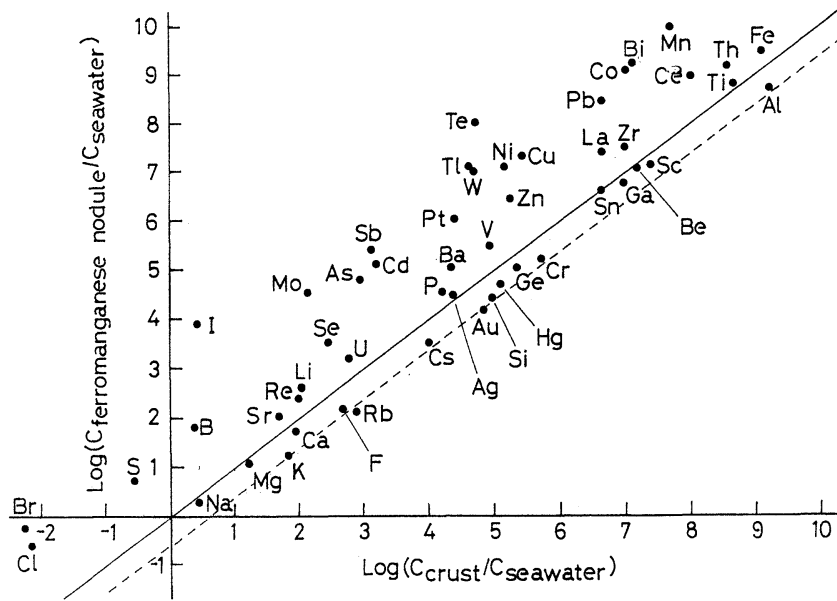


Fig. 1. Concentration ratios of elements in ferromanganese nodules relative to seawater versus those in the crustal rocks to seawater. A dashed line shows the case where the lithogenous fraction is 25% in concretions and the oxide fraction is only a diluent.

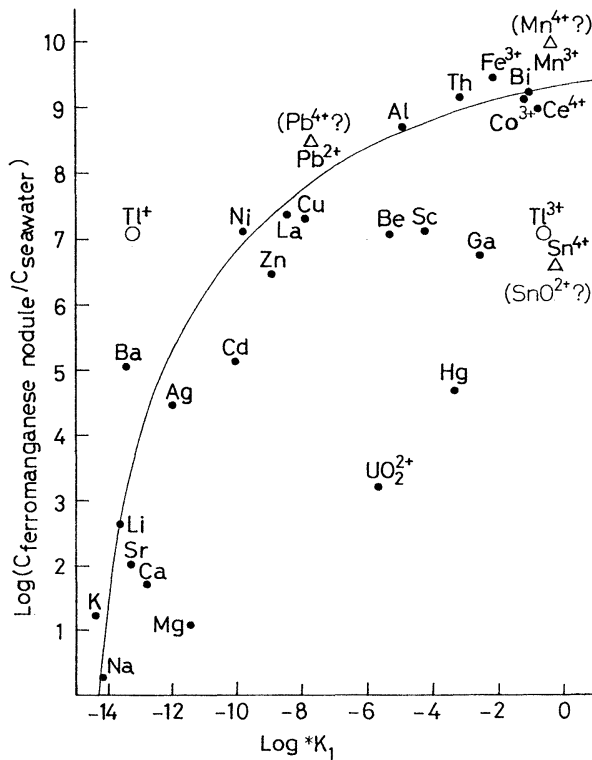


Fig. 2. Concentration ratios of elements in ferromanganese nodules relative to seawater versus the first hydrolysis constants of elements.

enriched elements such as Mn, Fe, Co, Ce and Pb are oxidized to higher valence states after adsorption and are present as oxides in concretions (GOLDBERG, 1965; GLASBY, 1975). The large negative deviations of Ga, Sn, Hg and U from the main trend are attributed to their speciation in seawater. The species of Ga, Sn, Hg and U in seawater are considered to be $\text{Ga}(\text{OH})_4^-$, $\text{SnO}(\text{OH})_3^-$, HgCl_4^{2-} and $\text{UO}_2(\text{CO}_3)_3^{4-}$, respectively (BRULAND, 1983). Such anionic species may not be effectively adsorbed on oxides. Silver does not deviate negatively to a great extent, although it occurs as AgCl_2^- in seawater. The first hydrolysis constant of Au is not available but the low content of Au in ferromanganese concretions relative to the crustal rocks is attributed to the presence of AuCl_2^- in seawater (GOLDBERG, 1987). Platinum is present in seawater as PtCl_4^{2-} but it is markedly enriched in ferromanganese concretions because Pt(II) is oxidized to Pt(IV) on manganese oxides (GOLBERG, 1987). The oxidation state of thallium is unknown but mixed valence states of Tl^+ and Tl^{3+} may occur in ferromanganese concretions judging from its concentration ratio and the first hydrolysis constants of mono- and tri-valent thallium. The positive deviation of Ba may be attributed to the presence of barite in concretions (BOSTROM *et al.*, 1973; LYLE *et al.*, 1977; DEHAIRS *et al.*, 1980), while the negative deviations of Mg and Ca remain unexplained.

Oxyanionic elements (B, Si, P, S, V, Cr, Ge, As, Se, Mo, Sb, Te, I, W, Re, etc) except Te and W are generally low in their concentration ratios and have long mean oceanic residence times, compared with cationic transition metals (Fig. 1). The low concentration ratios of oxyanionic elements in ferromanganese concretions have been explained in terms of a lack of lattice substitution in edge-shared $[\text{MnO}_6]$ octahedra after adsorption (TAKEMATSU, 1987). Adsorption affinities of oxyanionic elements are inversely dependent on the first or second dissociation constants of their acids (LI, 1981a). For some elements occurring in seawater as oxyanions, there is a correlation between their concentration ratios in ferromanganese concretions and the first or second dissociation constants of their acids (TAKEMATSU *et al.*, 1990). An exception to this is

tungsten which may form manganese or iron compounds of tungstate on the Fe-Mn oxide surface (LI, 1981a). Tellurium has been considered to be present in seawater as HTeO_3^- or TeO_3^{2-} (BRULAND, 1983). However, according to LEE and EDMOND (1985), Te(VI) is more abundant than Te(IV) in seawater and would be present as $\text{Te}(\text{OH})_6$. The reactivity of Te in seawater is similar to that of Po, which occurs as $\text{Po}(\text{OH})_4$ and has a short residence time, reflecting the position of neighbors in Group VIb of the Periodic Table. The high reactivity of Te in the water column is consistent with the high concentration ratio of Te in ferromanganese concretions.

The above concept is not applicable to fully hydrolyzed elements which occur in seawater as undissociated acids or hydrolyzed anions. Among them, B, Si, Ge and Sb are included, whose predominant species in seawater are considered to be $\text{B}(\text{OH})_3$, $\text{Si}(\text{OH})_4$, $\text{Ge}(\text{OH})_4$ and $\text{Sb}(\text{OH})_6^-$, respectively (BRULAND, 1983). Antimony in the water column exhibits little variations in concentrations with depth (MIDDELBERG *et al.*, 1988) and has a residence time of ca. 10^5 yr (LI, 1982a). In accordance with this, Sb has a relatively weak adsorption affinity for marine sediments, although the distribution coefficient of Sb for manganese oxides (ca. 5×10^4 ml/g) is relatively high (LI *et al.*, 1984; SANTSCI *et al.*, 1984). The species of Sb in seawater is considered to be $\text{Sb}(\text{OH})_6^-$ but its adsorption mechanism on oxides is unknown. Boron is conservative in the water column and has the oceanic residence time of ca. 10^7 yr (LI, 1982a). According to GOLDBERG and GLAUBIG (1985), boric acid exhibits an adsorption maximum on iron oxides at about pH 8 and the distribution coefficient is ca. 10^2 (ml/g), which is almost equal to the concentration ratio of B in ferromanganese concretions (Fig. 1). The adsorption affinity of silicate on iron oxides is somewhat lower than that of arsenate (BALISTRERI and CHAO, 1987). This is consistent with the fact that the concentration ratio of silicate in ferromanganese concretions is a little lower than that of arsenate (Fig. 1). However, the most of Si in ferromanganese concretions is present as aluminosilicate minerals. The average lithogenous (alumino-silicates) fraction of concretions is about 25% (CALVERT *et al.*, 1978;

TAKEMATSU, 1979; BISCHOFF *et al.*, 1981). In Fig. 1, the case where the lithogenous fraction is 25% in concretions and the oxide fraction is only a diluent is shown by a dashed line. Inorganic germanium exhibits the same vertical distribution as Si in the water column (FROELICH and ANDREAE, 1981) and probably behaves like Si in marine environments.

It is interesting to investigate whether elements located around the line of 25% lithogenous fraction are in the aluminosilicate phase or in the oxide phase. There are two methods to distinguish them: investigation of relationships between Si or Al and elements in nodules, and selective dissolution of the oxide phase using an acid-reducing agent (CHESTER and HUGHES, 1967). By selective dissolution, BISCHOFF *et al.* (1981) claimed the presence of Al, Si, K and Na in the authigenic phillipsite fraction, and MOORBY and CRONAN (1981) suggested the association of Al, Ti, Cr and some Ca with aluminosilicates. The elements reported to be associated with aluminosilicates from inter-element relationships are K, Ca, Rb, Sr and Zr (CALVERT and PRICE, 1977; CALVERT *et al.* 1978). LI (1982c) concluded that Al, Si, Sc, Ga, Cr, Be, Na, K, Rb and Cs are preferentially concentrated in aluminosilicates. However, this conclusion was derived from the fact that the enrichment factors of these elements in nodules, relative to pelagic clays are close to one. PIPER *et al.* (1979) found by selective dissolution that the concentration of Sc in the lithogenous fraction is 2.5 times higher than that in the bulk nodules. This indicates that the abundance ratio of Sc in the lithogenous and oxide fractions is about 3:2 if the lithogenous fraction of nodules is 25%. According to BISCHOFF *et al.* (1981), 42% of Al, 12% of Si, 84% of Na, 47% of K, 72% of Mg, 66% of Ca and 51% of Ti in nodules are leached by acid-reducing agent attack. SATO *et al.* (1989) measured the contents of Na, K, Mg and Ca in almost pure manganese oxides precipitated from seawater, and concluded that a considerable part of Na, Mg and Ca in marine ferromanganese concretions are in the oxide fraction as charge-balancing cations and that the most of K is associated with aluminosilicates. In short, major parts of Al, Si, K, Rb, Ti and Cr in nodules are associated with

aluminosilicates. Sodium, Mg, Ca and probably Sc are in the oxide phase as well as in the aluminosilicate phase. However, it is necessary to investigate whether the soluble fraction of Al and Ti in nodules by acid-reducing agent attack (BISCHOFF *et al.*, 1981) is leached from authigenic aluminosilicates or from the oxide phases or from aluminosilicates transported from land.

LI (1981b) assumed that aluminosilicate minerals transported to the ocean by rivers and through the atmosphere have the composition of average shale. If this is the case, pelagic sediments are a mixture of silicate minerals with typical shale composition and authigenic components in marine environments. If ferromanganese oxides play a major role in fixing trace elements transported by settling particles in the deep-sea sediment, elements enriched in ferromanganese concretions have higher contents in pelagic sediments than in shales. In Fig. 3, the concentration ratios of elements in pelagic sediments and average shale relative to seawater are plotted against those in the crustal rocks relative to seawater. The concentrations of elements in pelagic sediments and average shale are from the compilations given by BATURIN (1988) and MASON and MOORE (1982), respectively. The elements having higher contents in pelagic sediments relative to average shale are Mn, Cu, Mo, W, Ba, Co, Pb, Ni, La, Ce, P, Zn, Sr, Ba and I. All of them are concentrated in ferromanganese concretions, although Ba and Sr occur in pelagic sediments as barite and carbonates, respectively. The contents of As, Sb and Bi in pelagic sediments are almost equal to those in average shale, although these elements are enriched in ferromanganese concretions relative to the crustal rocks, because the contents of these elements in shales are high relative to the crustal rocks.

Boron, S, As, Se, Sb, I and Bi are much enriched in shales relative to the crustal rocks. The enrichment of these elements in shales are primarily attributed to the so-called magmatic volatiles, which include H₂O, CO₂, H₂S, HCl, HBr, HI, B, As, Se, Sb, Bi, Hg and so forth (WEDEPOHL, 1969) but secondarily to their incorporation into organic-rich reducing sediments, as described below.

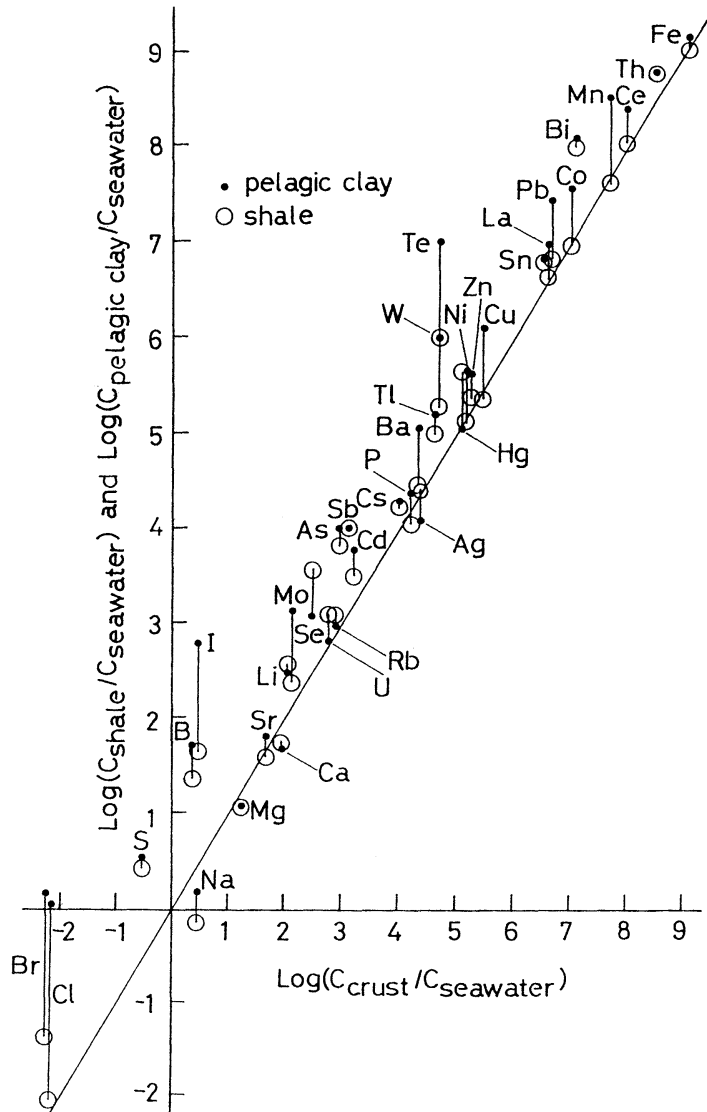


Fig. 3. Comparison between concentration ratios of elements in pelagic clay relative to seawater and those in average shale to seawater.

3. Enrichment of elements in anoxic sediments relative to the crustal rock

In near-shore environments, sediments are more reducing than in deep-sea waters, because settling particles reach the bottom before the decomposition of organic matter, and anoxic diagenesis occurs in the near-shore sediments. On the Southwest Africa (Namibia) shelf and in the Gulf of California, organic-rich reducing diatomaceous sediments occur as a result of high plankton productivity by intense upwelling

of nutrient-rich deep water. In the sediments, As, Se, Br, Mo, Cd, Sb, I, Hg, Bi and V are concentrated relative to average shale (Fig. 4) (BRONGERSMA-SANDERS *et al.*, 1980; CALVERT and PRICE, 1983; BRUMSACK, 1986). These are the elements enriched in shales relative to the crustal rocks, as shown in Fig. 3. In restricted basins such as the Black Sea, the Cariaco Trench and Saanich Inlet (British Columbia), where the O_2/H_2S boundary lies within the water column, metal sulfides are further added to the

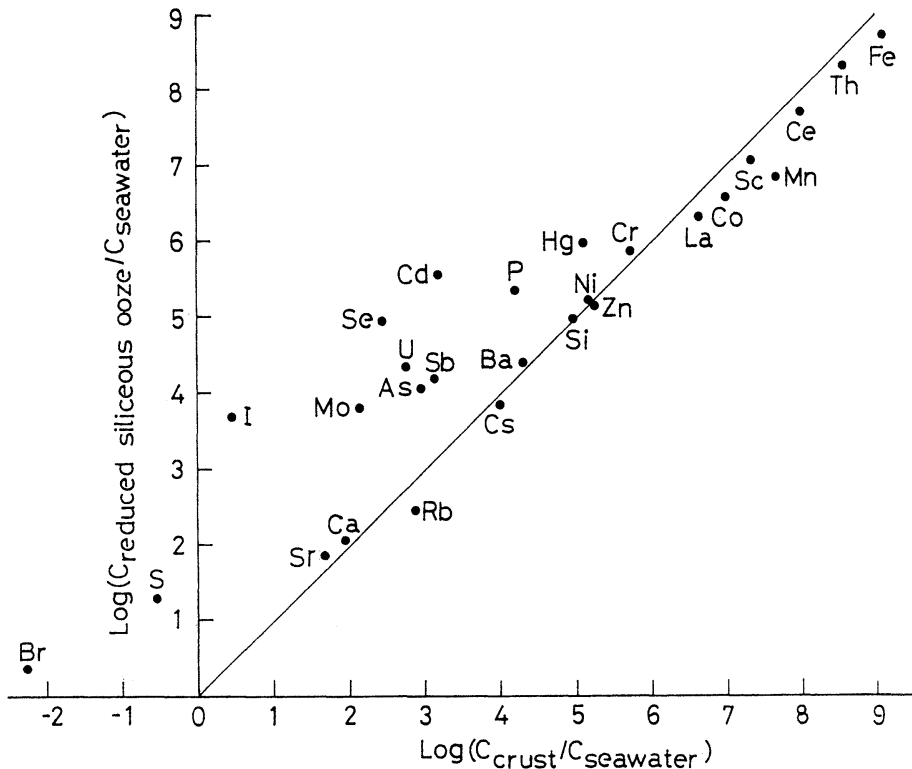


Fig. 4. Concentration ratios of elements in reduced siliceous ooze relative to seawater versus those in the crustal rocks to seawater.

sediments from the water column (JACOBS *et al.*, 1987). The products as a result of anoxic diagenesis in the area where the supply of biogenic settling particles is large relative to that of detrital aluminosilicates have the chemical composition similar to black shales (BRUMSACK, 1980). As there is no adequate compilation of elements in the marine reducing sediment, a near-shore sediment and organic-rich shales are chosen from Geostandards. In Fig. 5, the concentration ratios of elements in Geostandards of a near-shore sediment (MAG-1) and shales (SCo-1, SGR-1 and SDO-1) relative to seawater are plotted against those in the crustal rocks relative to seawater, except some elements of which concentrations are within a factor of 2, compared to the crustal rocks. MAG-1 is a gray-brown fine-grained clayey mud from the is the Wilkinson Basin of the Gulf of Maine; SCo-1 is the Upper Cretaceous silty marine shales; SGR-1 is an oil shale from the

Mahogany zone of the Green River Formation of Eocene age (carbonate lake) and SDO-1 is an organic-rich silt shale representative of the relatively radioactive, metalliferous Devonian age black shales (GOVINDARAJU, 1989). The organic carbon contents of MAG-1, SCo-1, SGR-1 and SDO-1 are 2.15, 0.81, 3.16 and 9.95%, respectively, and those of CO₂ are 7.88, 2.97, 11.58 and 1.01%, respectively. The trend of elemental enrichments in these Geostandards is similar to that in modern organic-rich reducing marine sediments (Fig. 4). Arsenic, Se, Sb, Te and Bi are enriched relative to the crustal rocks. These elements are chalcophile and positioned in Groups Vb and VIb of the Periodic Table. The cause of the enrichment of As, Se and Sb has been well documented concerning the Cretaceous-Tertiary boundary problem (KEITH, 1982; SCHMITZ, 1985, 1988; STRONG *et al.*, 1987; GILMOUR and ANDERS, 1989). Arsenic, Se, Sb and probably Te and Bi are scavenged from the

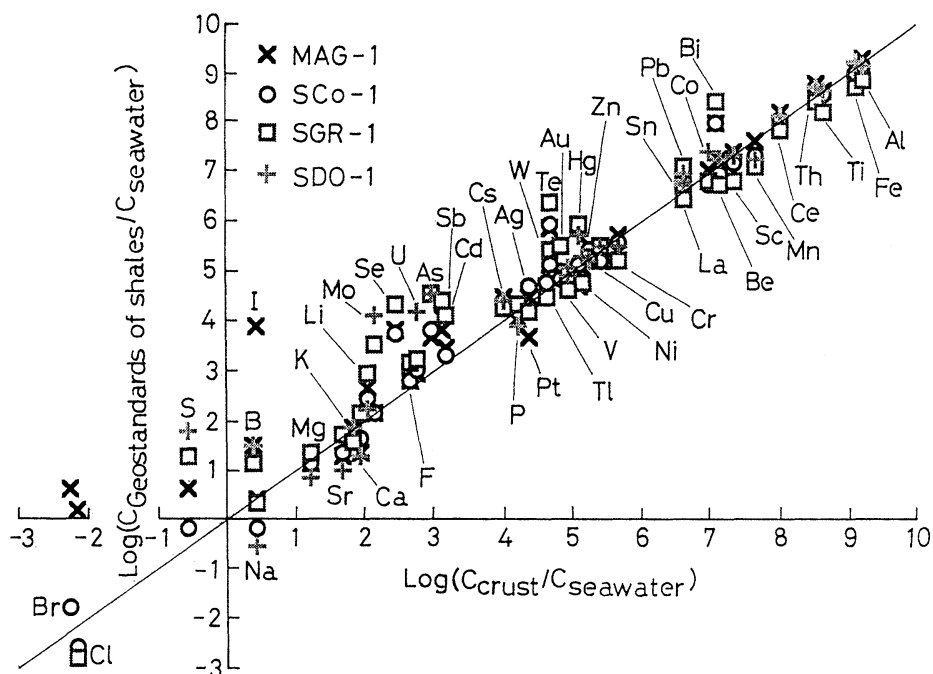


Fig. 5. Concentration ratios of elements in Geostandards of shales relative to seawater versus those in the crustal rocks to seawater.

water column by degraded organic matter (KNAUSS and KU, 1983; MASUZAWA *et al.*, 1989) and fixed in organic-rich reducing sediments as sulfides and organometallic compounds (HOWARD, 1977; CUTTER, 1985; BELZILE and LABEL, 1986; EDENBORN *et al.*, 1986; TAKAYANAGI and BELZILE, 1988).

Molybdenum is enriched more than an order of magnitude in modern organic-rich reducing sediments than in average shale (Fig. 4) and in ancient black shales (VINE and TOURTELOT, 1970; BRUMSACK, 1980; LEVENTHAL and HOSTERMAN, 1982). Molybdenum in organic-rich reducing sediments is considered to be either coprecipitated with Fe sulfides (MANHEIM, 1961; BERTINE, 1972; PILIPCHUK and VOLKOV, 1974; MALCOLM, 1985) or associated with organic matters (NISSENBAUM and SWAINE, 1976; BRUMSACK and GIESKES, 1983). However, Mo is little concentrated in plankton in spite of its high concentration in seawater ($11 \mu\text{g}/\text{l}$) (MARTIN and KNAUER, 1973; LI, 1984; FRANCOIS, 1988). Therefore, it is assumed that Mo diffuses from the sea water column into reducing sediments and is incorporated into organic

matter or sulfides after reduction to the +5 or +4 valence state (BRONGERSMA-SANDERS *et al.*, 1980; BRUMSACK *et al.*, 1983; FRANCOIS, 1988).

Uranium is also extremely enriched in organic-rich reducing sediments, especially in phosphatized sediments (MANHEIM, 1961; VEEH, 1967; VEEH *et al.*, 1974; RONA and JOENSU, 1974; BRONGERSMA-SANDERS *et al.*, 1980; CALVERT and PRICE, 1983) and in ancient black shales (VINE and TOURTELOT, 1970; LEVENTHAL and HOSTERMAN, 1982). The proposed mechanism for uranium enrichment is as follows. Hexavalent uranium is supplied from the water column into the sediment via pore water or with settling particles and reduced to tetravalent uranium which is incorporated into organic matter or carbonate fluoroapatite formed diagenetically (VEEH *et al.*, 1974; CALVERT and PRICE, 1983; YAMADA and TSUNOGAI, 1983/1984).

Vanadium is slightly concentrated in organic-rich reducing sediments such as Black Sea sediments (HIRST, 1974; VOLKOV and FOMINA, 1974), Saanich Inlet sediments (FRANCOIS, 1988)

and upwelling sediments from the Gulf of California (BRUMSACK, 1986). It is extremely enriched in ancient black shales from Atlantic Ocean (BRUMSACK, 1980) and the United States (VINE and TOURTELOT, 1970; LEVENTHAL and HOSTERMAN, 1982). Although the vanadium content is a little low in living plankton compared to average shale (KNAUSS and KU, 1983), most of vanadium in ancient sediments of marine origin are in the kerogen fraction and its chemical species is largely vanadyl porphyrin (PREMOVIC *et al.*, 1986). In reducing environments, vanadate anions are reduced to vanadyl cations (VO^{2+}), which form stable complexes with organic chelates such as humic substances, and is strongly adsorbed on particles such as clays and oxides (WEHRLI and STUMM, 1989). Chromium is slightly enriched in organic-rich reducing sediments (BRONGERSMA-SANDERS *et al.*, 1980; FRANCOIS, 1988) and in black shales (VINE and TOURTELOT, 1970; BRUMSACK, 1980). Chromium supplied with biogenic particulates is reduced to Cr^{3+} in anoxic sediments, and Cr^{3+} is readily adsorbed and incorporated in the sediments (ELDERFIELD, 1970; FRANCOIS, 1988; SHAW *et al.*, 1990).

Iodine is much more concentrated in organic-rich oxidizing sediments than in organic-rich reducing sediments (PRICE and CALVERT, 1973, 1977). This is attributed to that iodine is concentrated in living plankton within the euphotic zone and taken up additionally by organic matter at the sediment-seawater interface under oxidizing conditions, where the concentration of total iodine in interstitial water is much higher than that in seawater (PRICE and CALVERT, 1977; HARVEY, 1980; KENNEDY and ELDERFIELD, 1987a). However, sorption of iodine on Mn and Fe oxyhydroxides is not ruled out (SUGAWARA *et al.*, 1958; ULLMAN and ALLER, 1985; KENNEDY and ELDERFIELD, 1987b). The enrichment of B in shales relative to the crustal rocks is due to its incorporation into clay minerals (WEDEPOHL, 1970).

Manganese is less concentrated in organic-rich reducing sediments than in normal shales. Manganese has a weak affinity for organic matter and sulfides, although it is sometimes enriched in reducing sediments as carbonates (MANHEIM, 1961; PEDERSEN and PRICE, 1982; JAKOBSEN

and POSTMA, 1989). Sodium, Mg, Ca, Sr and Cl are washed off from sediments after uplift above sea level or during weathering.

4. The behavior of elements in marine environments

As the result of weathering of the crustal rocks, dissolved solids are supplied to the oceans by rivers, and solid products by rivers as suspended matter and through the atmosphere as eolian dust. The partitioning of elements between weathered silicate minerals and river water is controlled by the electrostatic interaction between elements and oxygen in silicate mineral lattices, and can be related to their electronegativity function (Q_{MO}) (WHITFIELD and TURNER, 1979; MARTIN and WHITFIELD, 1983). Further, the concentration ratios of elements in river water to seawater show a linear relationship with their mean oceanic residence times (LI, 1982a). Suspended matter in river water and eolian dust have the chemical composition of average shale (LI, 1981b; MARTIN and WHITFIELD, 1983). These terrigenous aluminosilicates will suffer only a little alteration during settling through the water column and during diagenesis after deposition on the seafloor.

Dissolved elements in seawater are taken up by phytoplankton and removed from surface water as settling particles. They are divided into fecal pellets and large amorphous aggregates (marine snow), and composed of organic matter, biogenic calcium carbonate and opal (see FOWLER and KNAUER, 1986). The biogenic components of settling particles are partially regenerated during sinking through the water column and the fluxes decrease with depth. However, a mid-water increase of the fluxes has been observed and has been attributed to *in situ* repacking of suspended matter into fecal pellets by zooplankton (URRERE and KNAUER, 1981) or *in situ* production of new particulate organic carbon by bacterial chemolithotrophy (KARL *et al.*, 1984, 1988). Further, Fe and Mn depositing bacteria are present in settling particles and Fe-Mn oxides contribute to scavenging trace elements from seawater (COWEN and SILVER, 1984; COWEN and BRULAND, 1985; COWEN *et al.*, 1986). Aluminosilicate minerals of eolian origin

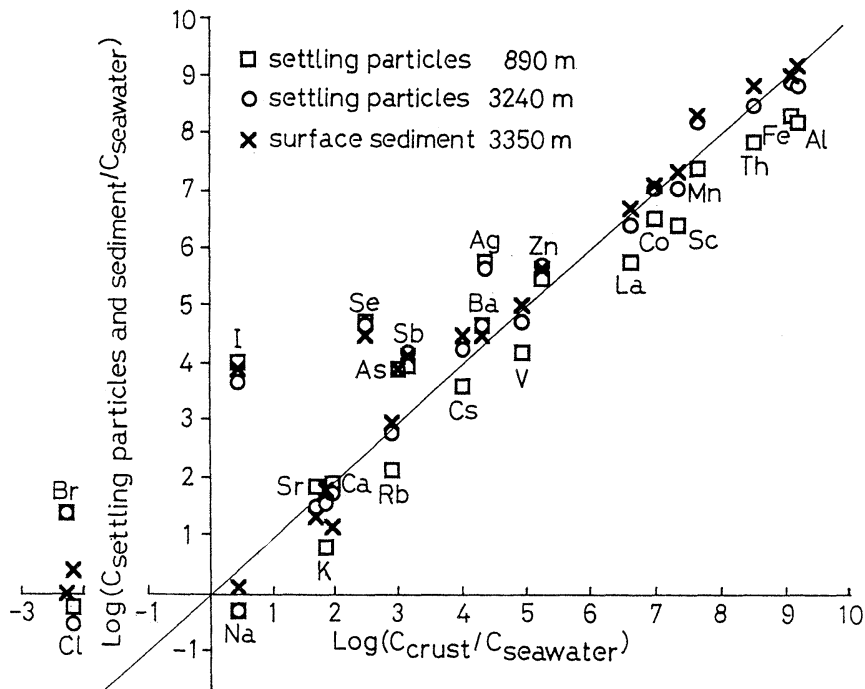


Fig. 6. Comparison between concentration ratios of elements in settling particles relative to seawater and those in the underlying surface sediment to seawater.

and transported laterally from continental slopes are entrapped by settling particles, and the flux of the lithogenous portion increases with depth (HONJO *et al.*, 1982a).

Settling particles on the sea-floor undergo early diagenesis mainly by the oxidation of organic matter (FROELICH *et al.*, 1979). Most of biogenic calcium carbonate and opal is dissolved during diagenesis. The composition of settling particles collected within a few hundred meters above the bottom is extremely different from that of the bottom surface sediment (HONJO *et al.*, 1982b; GARDNER *et al.*, 1985; WALSH *et al.*, 1988a, b). During diagenesis, the accompanying elements with settling particles are incorporated into sedimentary components and otherwise recycled into overlying bottom water as benthic fluxes.

A linear relationship is found between the mean oceanic residence time of elements and their concentration factors for marine organisms, which are concentration ratios of elements in marine organisms relative to seawater (YAMAMOTO, 1972; YAMAMOTO *et al.*, 1983; FISHER, 1986). FISHER (1986) explained the

relationship mainly by the interaction between metals and hydroxyl groups in biological systems. CHERRY *et al.* (1978) also found the linear relationship between the mean oceanic residence times of elements and their concentration factors for fecal pellets of zooplankton. However, the concentrations of elements in settling particles collected in sediment traps change with depth (BREWER *et al.*, 1980; ANDERSON, 1982; GARDNER *et al.*, 1985; MASUZAWA *et al.*, 1989).

In Fig. 6, the concentration ratios of elements in settling particles at two different depths and the underlying sediment from Japan Sea (MASUZAWA *et al.*, 1989) are plotted against those in the crustal rocks. The concentrations of elements enriched in oxidizing sediments (Mn, Fe, Co, Th, etc.) increase with depth, while those enriched in reducing sediments (As, Se, Sb, I, etc.) decrease slightly or change little. As the lithogenous fraction increases with depth. Brewer *et al.* (1980) divided elements into three groups on the basis of Me/Al ratios. Lithogenous components, whose Me/Al ratios are constant with depth, involve Al, Ti, V, K, La, ²³²Th, etc. Biogenic components, whose Me/Al

ratios decrease with depth, involve Ca, Sr, Ba, ^{226}Ra , Si, Br, I, As, Se, Sb, Ag, Cd, U, etc. Scavenged components, whose Me/Al ratios increase with depth, involve Mn, Fe, Co, Cu, $^{230,234}\text{Th}$, etc.

The concentrations of elements classified into biogenic components are higher in fecal pellets than in the crustal rocks (FOWLER, 1977). However, biogenic elements are not necessarily enriched in fecal pellets than scavenged elements with respect to their concentration factors (CHERRY *et al.*, 1978). The difference between the two groups is attributed to the fact that biogenic elements are less adsorbed on hydrogenous components such as *in situ* produced Fe-Mn oxides than scavenged elements. Arsenic, Se and Sb, which are present as oxyanions in oxygenated seawater, are usually reduced after uptake by organisms and transformed into organometalloid compounds (ANDRAE and KLUMP, 1979; WILLIAMS, 1981; WOOD and WANG, 1983). These organometalloid compounds in settling particles are regenerated to oxyanions during vertical transport in the water column (CUTTER and BRULAND, 1984). Oxyanions are less adsorbed on hydrogenous oxides than so-called scavenged elements, and have relatively long mean oceanic residence times (Fig. 1). On the other hand, scavenged elements in settling particles are also solubilized with the decomposition of biogenic components but adsorbed on *in situ* produced hydrogenous components. The concentrations of scavenged elements in settling particles increase with that of manganese, which is mostly present as oxides in settling particles (CHESTER and ASTON, 1976; JICKELLS *et al.*, 1984; COWEN and BRULAND, 1985; MASUZAWA *et al.*, 1989). In sediment traps, Fe-Mn oxides in settling particles are probably reduced to the readily leachable form during deployment (MARTIN and KNAUER, 1983, 1984).

The classification of elements according to their behavior in settling particles is sometimes inconsistent with that on the basis of their distribution in sediments. CHESTER and HUGHES (1967) developed a chemical technique to separate ferromanganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments using an acid-reducing agent. On the basis of the method, V, Cr and Fe are classified into the lithogenous category, and Mn, Co, Ni

and Cu into non-lithogenous (hydrogenous + biogenous) category (CHESTER and HUGHES, 1969; CHESTER and MESSIHA-HANNA, 1970; ELDERFIELD, 1972). This means that although non-lithogenous iron behaves as a scavenged element, most of iron in marine environments is incorporated in aluminosilicate minerals. TOYODA and MASUDA (1990) measured the concentrations of many elements in surface sediments along the longitude of 170° W and observed that Co, Ni, Cu, Y and La have concentration maxima around the equatorial area together with Mn, while V and Cr have almost constant concentrations along the entire profile. This means that La is a scavenged element in contrast with the classification from settling particles. However, it is difficult to classify elements into a certain group because some elements have intermediate characteristics. It is necessary to know the non-lithogenous portion of elements in the sediment for the calculation of their mean oceanic residence times if we use the mean oceanic residence times as the measure of reactivity. When the total accumulation rates of lithogenous elements such as Fe, V and Cr are used for calculation, their mean oceanic residence times are underestimated.

Any of the elements in settling particles except for lithogenous ones are more or less recycled at the sediment-water interface as the benthic fluxes (COBLER and DYMOND, 1980; DYMOND and LYLE, 1985; FISCHER *et al.*, 1986). The benthic fluxes of elements depend upon the supply rate and composition of settling particles, sediment redox conditions, bioturbation and other factors. In the area where the penetration of oxygen into the sediment is enough to oxidize organic matter accumulated via settling particles, oxic diagenesis occurs and the benthic fluxes of trace elements are relatively small, judged from their concentrations in interstitial water of the surface sediment (KLINKHAMMER *et al.*, 1982; SAWLAN and MURRAY, 1983). During diagenesis of settling particles, Fe-Mn oxides are formed and occur as coatings on sedimentary components, microneules dispersed in the sediment and ferromanganese nodules (CALVERT and PRICE, 1977; CALVERT *et al.*, 1978; KUNZENDORF *et al.*, 1989). Authigenic Fe-Mn oxides readily adsorb trace

elements released from settling particles, although the adsorption affinity is different from element to element as is evident from Fig. 1.

In the oxic-diagenetic environment such as DOMES Sites A, B and C, and MANOP Site S, the chemical composition of the leached fraction with an acid-reducing agent from the sediments (sediment oxyhydroxides) is similar to that of δ -MnO₂-rich nodules (CHESTER *et al.*, 1973; PIPER *et al.*, 1979; APLIN and CRONAN, 1985; PIPER *et al.*, 1987). Further, the composition of micronodules in the sediments is similar to that of associated macronodules (SUGISAKI *et al.*, 1987; KUNZENDORF *et al.*, 1989). The aluminosilicate fraction after leaching has the chemical composition similar to average shale (PIPER *et al.*, 1979; PIPER, 1988).

In the suboxic diagenetic regions such as MANOP Sites H and M where the flux of organic carbon is more than that in the oxic diagenetic regions, cationic transition metal contents in the surface sediments are rather higher than those from the oxic diagenetic regions because manganese and iron, which are remobilized from the suboxic deeper layer, are precipitated as oxides in the oxic surface layer (GRAYBEAL and HEATH, 1984; LYLE *et al.*, 1984). However, cationic transition metal contents in manganese nodules from the suboxic diagenetic regions are lower than those from the oxic diagenetic regions (DYMOND *et al.*, 1984). A partial decoupling of the sediment-nodule system can be explained by the non-steady-state model for the formation of suboxic diagenetic manganese nodules (TAKEMATSU *et al.*, 1989). Calcareous oozes in suboxic diagenetic regions have the chemical composition similar to suboxic diagenetic siliceous sediments on a carbonate-free basis, and therefore carbonates are only a diluent (STOFFERS *et al.*, 1981).

In deep-sea regions where the flux of biogenic components is small and continentally derived aluminosilicates are the major components, red clay occurs, whose non-lithogenous components are directly from seawater. Cationic transition metal contents in red clay are almost constant with depth (EL-WAKEEL and RILEY, 1961; CHESTER and HUGHES, 1969), and are generally low relative to those in the oxic and suboxic diagenetic surface sediments. The ratios of Ce

/La and Co/Mn are the good indicators of the different sediment types. The order of their ratios is red clay > oxic diagenetic sediments > suboxic diagenetic sediments (GLASBY *et al.*, 1987; PIPER *et al.*, 1988; KUNZENDORF *et al.*, 1989).

In hydrothermal areas, metalliferous sediments occur and have high contents of cationic transition metals, especially of Fe, on a carbonate-free basis (BOSTROM and PETERSON, 1969; DYMOND *et al.*, 1977; HEATH and DYMOND, 1977, 1981; DYMOND, 1981; MARCHIG and GUNDLACH, 1982; SHEARME *et al.*, 1983; BACKER *et al.*, 1985; MARCHIG *et al.*, 1985; STOFFERS *et al.*, 1985; BARRETT *et al.*, 1987). However, the contents of minor cationic transition metals in metalliferous sediments are rather low relative to those in pelagic clays when their contents are normalized to non-lithogenous Fe and Mn oxides. Buoyant hydrothermal emanations containing particulate Fe and dissolved Mn trail several hundred meters above the sea-floor and are advected away from vent fields (KLINKHAMMER and HUDSON, 1986; KLINKHAMMER *et al.*, 1986). Fe and Mn oxides of hydrothermal origin scavenge minor elements from seawater together with settling particles and settle on the sea-floor (TROCINE and TREFRY, 1988; FEELY *et al.*, 1990). The validity of this scenario is evident from the fact that hydrothermal sediments have the negative Ce anomaly which is the reflection of rapid scavenging of REE from seawater by hydrothermal Mn-Fe oxides as well as biogenous carbonates (RUHLIN and OWEN, 1986).

Hydrothermal massive sulfides of Fe, Zn and Cu are almost free of Ni, reflecting the composition of hydrothermal fluids (BISCHOFF *et al.*, 1983; BOWERS *et al.*, 1985; RONA *et al.*, 1986). However, even suspended particles in black smoke within 20m above hydrothermal vents contain 20–220 ppm of Ni (MOTTL and MCCONACHY, 1990) in spite that hydrothermal fluids contain little Ni (VON DAMM *et al.*, 1985). The content of Ni in metalliferous sediments on the crest of the East Pacific Rise (ERR) is rather low relative to that on the flanks of EPR (BOSTROM and PETERSON, 1969). This phenomenon is attributed to the scavenging of minor transition elements from seawater by hydro-

thermal Fe-Mn oxides or sulfides (RUHLIN and OWEN, 1986; METZ *et al.*, 1988; TROCINE and TREFRY, 1988). Therefore, the concentration ratio of Cu to Ni in sediments can be used as a measure of hydrothermal influence. Metalliferous sediments in which the contents of Cu and Zn are much higher than that of Ni are restricted to the proximity of hydrothermal vent fields (DYMOND *et al.*, 1977; HEATH and DYMOND, 1977; SHEARME *et al.*, 1983; BARRETT *et al.*, 1987; METZ *et al.*, 1988).

The chemical composition of EPR crest sediments is equivalent to that of micronodules in them within a factor of two with respect to Mn, Fe, Co, Ni, Cu and Zn (STOFFERS *et al.*, 1985). The micronodules have the chemical composition similar to that of hydrothermal manganese crusts. Hydrothermal manganese crusts have more than an order of magnitude lower contents of cationic transition metals (Co, Ni, Cu, Zn, etc.) relative to and oxyanionic element contents comparable to the nodules of other origins (CORLISS *et al.*, 1978; LALOU *et al.*, 1983; MOORBY and CRONAN, 1983; RONA *et al.*, 1984; THOMPSON *et al.*, 1985; TAKEMATSU *et al.*, 1989, 1990), although their chemical composition is highly variable. The low contents of cationic transition metals in hydrothermal manganese crusts are attributed to insufficient scavenging by rapid growth of crusts (EDMOND *et al.*, 1979). As described before, the enrichment of cationic transition metals in manganese nodules is due to lattice substitution after adsorption, and that of oxyanionic elements only to adsorption (TAKEMATSU, 1987). It takes long time for the incorporation of cationic transition metals into manganese nodules.

This is the reason why cationic transition metals are depleted and oxyanionic elements are enriched in rapidly growing hydrothermal manganese crusts (MOORBY and CRONAN, 1983; MOORBY *et al.*, 1984; TAKEMATSU *et al.*, 1990). Therefore, the contents of cationic transition metals in metalliferous sediments increase with the distance from mid-ocean ridges, when their contents are normalized to those of non-lithogenous iron and manganese oxides, as is evident from the sediments of the East Pacific Rise-Tahiti transect (STOFFERS *et al.*, 1985). In the case of the Bauer Deep sediments, Fe and Mn

are of hydrothermal origin and the other minor elements are mainly from seawater (DYMOND, 1981). This is because the concentrations of Fe and Mn in hydrothermal fluids are ca. 10^6 times higher than those in deep seawater, those of Co, Cu and Zn are ca. 10^4 times, and Ni is less than 10 times (BRULAND, 1983; VON DAMM *et al.*, 1985). The sediments from the Bauer Basin have the minor element composition similar to those from EPR-Tahiti transect when the contents of manganese and iron oxides are similar (HEATH and DYMOND, 1981; STOFFERS *et al.*, 1985).

In brief, the chemical composition of oxic deep-sea sediments is expressed as admixtures of aluminosilicate minerals with average shale composition and ferromanganese oxides with the end-member compositions of different origins (hydrogenous, oxic diagenetic, suboxic diagenetic and hydrothermal), although metalliferous sediments contain Al-poor Fe-smectite, of which minor transition metal contents are lower than those of average shale (MOORBY and CRONAN, 1983; RONA *et al.*, 1984).

In the more reducing environments such as continental margins, concentrations of transition metals such as Mn, Co, Ni, Cu and even Fe are high in interstitial water and these elements are released from the sediments as the benthic fluxes (SAWLAN and MURRAY, 1983; HEGGIE *et al.*, 1987; JOHNSON *et al.*, 1988; SHAW *et al.*, 1990). Therefore, the chemical composition of mildly reducing continental margin sediments is similar to that of average shale (WEDEPOHL, 1960; CHESTER and MESSIHA-HANNA, 1970; ELDERFIELD, 1972). Cationic transition elements released from reduced continental margin sediments are transported laterally to the central parts of the ocean through oxygen minima (KLINKHAMMER and BENDER, 1980; MARTIN and KNAUER, 1984; MARTIN *et al.*, 1985). However, the behavior of oxyanionic elements such as V, Cr and Mo to redox conditions is in contrast to that of cationic transition metals such as Mn, Ni and Co. According to SHAW *et al.* (1990), in suboxic diagenetic sediments (The Patton Escarpment), concentrations of V, Cr and Mo in interstitial water of the oxidizing surface layer where Mn-oxides are present are high, while those of Mn, Ni and Co are extremely low. High concentrations of oxyanionic

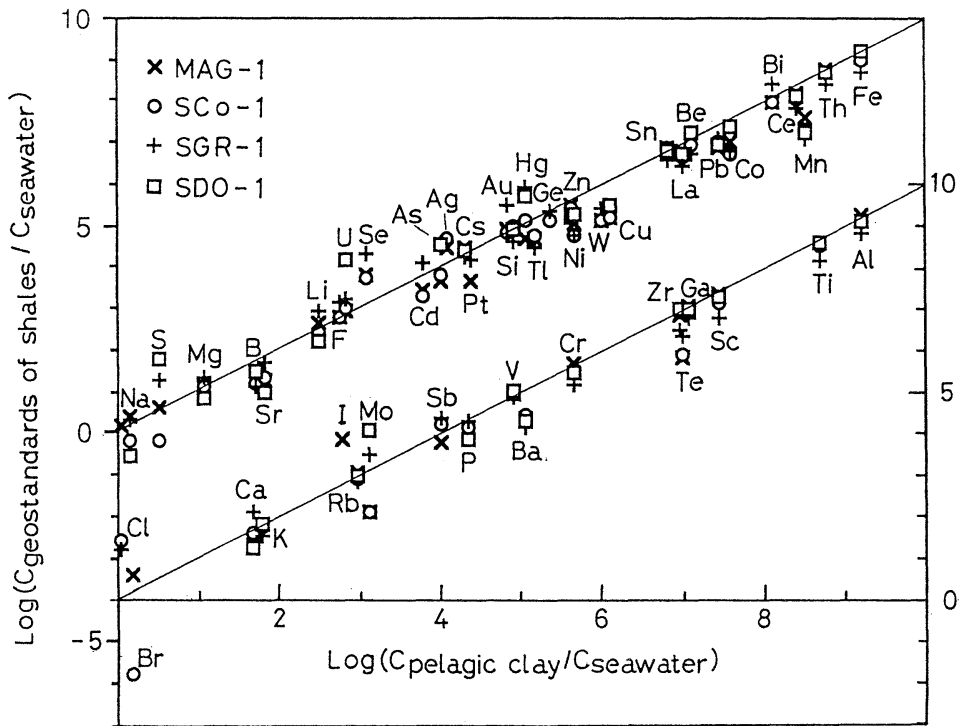


Fig. 7. Comparison between concentration ratios of elements in reducing shales relative to seawater and those in oxidizing pelagic clay to seawater. To avoid overlapping, elements are arbitrarily divided into two parts.

elements in the oxidizing interstitial water are the result of the adsorption affinity of these oxyanions on oxides which is weaker than that of cationic transition metals as is evident from Fig. 1. On the other hand, in more reducing sediments of the California Borderland, concentrations of cationic transition metals in interstitial water are high, while those of oxyanionic elements decrease as conditions become more reducing. The oxyanions are transformed to their reduced species and incorporated into the sediments. The contents of V, Cr and Mo are high in the most reducing sediments investigated, although high contents of Mo are also observed in the most oxidizing Mn-rich sediment. Such contrasting behavior of cationic transition metals and oxyanionic elements is also observed in a core from the Panama Basin (BONATTI *et al.*, 1971). Manganese, Co and Ni are concentrated in the oxidizing surface layer, while Cr and V are enriched in the reducing deeper layer.

In anoxic regions, many minor elements are

retained in the sediments, except for Mn, as is described before. In Fig. 7, the contents of elements in Geostandards of a near shore sediment and reducing shales are compared with those of pelagic clay with respect to their concentration ratios to seawater. The elements which are concentrated in reducing sediments are S, Fe, As, Se, Mo, Ag, Cd, Sb, I, Au, Hg, Bi, U and probably Te, while those concentrated in oxidizing sediments are Mn, Fe, Co, Ni, Cu, Mo, Ce, Te, W, Tl, Pb, Bi, and probably Zn, Cd, La, Pt and Th. Iron, Mo, Bi, and probably Cd and Te are concentrated in both reducing and oxidizing sediments. Beryllium, B, Al, Si, Sc, Ti, V, Cr, Ga, Ge and Zr are evenly distributed and classified as the lithogenous elements. Alkali and alkaline-earth metals such as Li, Na, Mg, K, Rb and Cs have no fractionation between reducing and oxidizing sediments. The contents of Ca, Sr and Ba are dependent on primarily productivity in overlying water and water depth.

5. Summary and conclusions

a) Elements are supplied from land to the sea in dissolved and particulate states as the result of weathering of crustal rocks. Particulate elements are transported through the atmosphere as airborne dusts and by rivers as suspended matter. Airborne dusts and suspended matter in river water undergo desorption and adsorption of elements in contact with seawater, but principally keep their original composition during sinking through the water column and during diagenesis after deposition on the sea-floor. They generally have the chemical composition of average shale. Some elements (Be, Al, K, Ti, V, Cr, Ga, Zr, etc.) are recycled mainly with weathered aluminosilicates, and others mainly through the dissolved state in seawater. The proportion of dissolved to particulate differs with each elements.

b) Dissolved elements in seawater are taken up by phytoplankton and transported to the sea-floor as settling particles. Settling particles in surface water are composed of biogenous calcium carbonate, opal, organic matter and terrigenous aluminosilicates. Biogenous components in settling particles are regenerated during sinking through the water column and the proportion of the lithogenous fraction increases with depth. Below the oxygen minimum layer, Fe-Mn oxides are precipitated on settling particles by microbial mediation and play an important role in scavenging minor elements from seawater. The elements classified as "scavenged" are those which are readily taken up by Fe-Mn oxides. On the other hand, the elements classified as "biogenous" are those which have biogenous insoluble compounds (Si, Ca, Sr and Ba) and oxyanions (As, Se, Sb, I, etc.) which are reductively taken up by phytoplankton and less adsorbed on Fe-Mn oxides than cationic "scavenged" elements.

c) On the basis of redox potential which is regulated by the amount of organic matter supplied to the sea-floor via settling particles, marine sediments are divided into oxic deep-sea sediments, intermediate near-shore sediments and anoxic sediments. The chemical composition of oxic sediments can be simulated by a mixture of aluminosilicates with average shale composition and Fe-Mn oxides with the

composition of associated ferromanganese nodules. Hydrogenous Fe-Mn oxides occur as coatings on sedimentary components and micronodules dispersed in the sediment. The incorporation mechanism of elements into oxides is primarily the adsorption of elements on hydrolyzed oxides. However, cationic elements can be incorporated into oxides through their lattice substitution for oxide-forming metals during the oxide growth. Therefore, the distribution coefficients of cationic elements for Fe-Mn oxides, except for alkali and alkaline-earth metals, are generally larger than those of oxyanionic elements. The chemical composition of Fe-Mn oxides in the sediment and associated ferromanganese nodules is controlled by the supply rate of settling particles and hydrothermal activities. Oxic deep-sea sediments are divided into red clay, oxic diagenetic sediments and suboxic diagenetic sediments on the basis of the flux of settling particles. The contents of cationic transition elements are in the order: suboxic diagenetic sediments > oxic diagenetic sediments > red clay. It must be noted that in suboxic diagenetic sediments, a partial decoupling occurs between Fe-Mn oxides in the sediments and associated ferromanganese nodules, and that the contents of cationic transition elements in the former are higher than those in the latter. Calcium carbonates act as a diluent because the contents of minor elements in them are extremely low. In accordance with this, the contents of minor elements in deep-sea sediments are generally discussed on a carbonate-free basis.

d) In hydrothermal regions, so-called metalliferous sediments occur and have extremely high contents of Fe and Mn. Iron and manganese oxides in metalliferous sediments are of hydrothermal origin but other minor associated elements are from seawater. The contents of cationic minor elements in hydrothermal ferromanganese nodules are low on account of their inefficient lattice substitution in the rapidly forming oxides, while those of oxyanionic elements are comparable to those in nodules of other origins, because of the rapidity of their adsorption. Therefore, the contents of cationic minor elements in metalliferous sediments are low when they are normalized to non-litho-

genous Fe-Mn oxides.

e) Hydrothermal sulfides of Fe, Zn and Cu which are almost free of Ni and metalliferous sediments in which contents of Cu and Zn are much higher than that of Ni are restricted to the proximity of hydrothermal vent fields. With the distance from the mid-ocean ridges, the minor element composition of metalliferous sediments approaches gradually to that of ordinary pelagic sediments with respect to Mn-Fe oxides, because most parts of minor elements are scavenged from seawater by hydrothermal Mn-Fe oxides.

f) In mildly reducing or seasonally oxidizing near-shore sediments, neither manganese oxides nor iron sulfides are formed during early diagenesis, and the contents of cationic minor elements are much low relative to oxic deep-sea sediments. Elements transported by settling particles are released during early diagenesis from the sediments as benthic fluxes and conveyed to deep waters by advection through the oxygen minimum layer. The remains are similar to average shale in the chemical composition. Exceptions to this are Se and U. They are reduced and fixed in the sediments.

g) In anoxic environments where iron sulfides are formed by microbial reduction of sulfate, chalcophile elements are enriched in the sediments.

h) Partition coefficients of elements between aluminosilicates and river water (during weathering) and those between phytoplankton and seawater have some correlations with the mean oceanic residence times of elements. However, partitioning of elements between oxygen-dominated minerals and seawater (during reverse weathering) play a major role in controlling their mean oceanic residence times, because Mn-Fe oxides and biogenous silica as well as authigenic aluminosilicates are the major products for removal of dissolved elements in oxidizing marine environments. Anoxic sediments have high contents of elements which are enriched in shales relative to the crustal rocks (As, Se, Br, Mo, Cd, Sb, I, Hg, Bi and U). However, anoxic sediments will make little, if any, contribution to the control of the mean oceanic residence times of elements, because these sediments are restricted within

narrow limits.

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海底堆積物中の元素の分布：概観と合成

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要旨：鉄-マンガン酸化物が、微量元素の海水からのスキャベンジングおよびそれらの元素の海底堆積物への固定に、重要な役割を果たしていることを再評価した。1) 海水中の溶存態元素は、植物プランクトンによって摂取され、沈降粒子として海底に運ばれる。沈降粒子中の生物起源の成分は、水柱を降下する間に分解、再生され、深さと共に、陸起源のアルミノケイ酸塩鉱物の割合が増加する。酸素極少層以深では、鉄-マンガン酸化物が、微生物の媒介によって沈降粒子中に沈澱し、海水からの微量元素のスキャベンジングに重要な役割を果たす。2) 酸化的堆積物の化学組成は、頁岩の化学組成を持ったアルミノケイ酸塩鉱物と4つの起源の異なる鉄-マンガン団塊（水成起源、亜酸化的続成起源、酸化的続成起源および熱水起源）の化学組成を持った鉄-マンガン酸化物との混合物によって近似できる。3) マンガン酸化物も硫化鉄も存在し得ない沿岸堆積物は、頁岩の化学組成を持つ。それは、沈降粒子によって海底に運ばれてきた元素が、初期続成過程の間に再生され、堆積物から底層水中へ溶出してしまふからである。4) 硫化鉄が生成するような還元的环境では、親銅元素が堆積物中に濃縮する。5) 還元的堆積物の存在は狭い範囲に限られるので、多くの微量元素の現在の海水中の濃度および平均滞留時間は、これらの元素の鉄-マンガン酸化物への最終的編入機構によって支配されている。