THE POST-DEPOSITIONAL CYCLING OF Cd, Cu, Mo AND Zn IN SEVERAL HYDROGRAPHICALLY DISTINCT B.C. FJORDS

by

J JAY MCNEE

B.Sc., The University of British Columbia

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
(Department of Earth and Ocean Sciences)

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

March 1997

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Department of Earth and Ocean Sciences
The University of British Columbia
Vancouver, Canada

Date Apr. 1 1997
Abstract

Sediment cores from six inlets representing markedly different hydrographic regimes along the British Columbia coast were collected to acquire high-resolution distributions of both solid-phase and interstitial metals in addition to an extensive suite of ancillary data. A technique for small-volume trace metal extraction (<1 mL) was developed to remove the metals Cd, Cu, Mo and Zn from the salt-water matrix prior to analysis. The cycling of these metals was studied in detail within the context of the hydrographies of the environment presented by the various inlets. By observing and comparing the behaviour of each metal under different depositional conditions, the relative influence of hydrography on each element was characterized.

The solid-phase inventories of the four elements broadly fall into one of two categories: those deplete in terrestrial detritus (Cd and Mo) and those enriched in lithogenic material (Cu and Zn). The distribution of the former two are influenced most markedly by post-depositional diagenesis while the latter two respond more to detrital inputs.

Cadmium is introduced to many deposits in association with biogenic material; its release and efflux to bottom waters is attenuated by lower redox potential. Where sulphate reduction nears the sediment-water interface, the efflux is minimized as liberated Cd is converted to authigenic sulphides. Consequently, enhanced accumulation occurs under conditions of high primary productivity, low sedimentation rate and restricted estuarine circulation. Molybdenum is introduced most commonly in association with Mn-oxides, or, under sub-oxic regimes, by diffusion across the sediment-water interface followed by precipitation as an authigenic sulphide. In oxic core-tops, there exists a strong association between Mo and Mn-oxides; however, high sedimentation rates or periods of dysaerobia inhibit disproportionation of Mn thereby decoupling the relationship. Whole-core accumulation of Mo occurs only under conditions of interfacial sub-oxia/anoxic. Consequently, the oceanographic factors which most markedly influence the
accumulation of Mo (like Cd) are sedimentation rate and redox potential. Elevated sedimentation rates enhance the dilution of these elements by increasing the accumulation of lithogenic material which is deplete in both metals. Lower redox potentials enhance the accumulation of authigenic sulphides.

Copper and zinc behave similarly in many coastal deposits; they are both elevated in lithogenic detritus. Both metals are associated with post-depositional release from organic matter oxidation, and display strong associations with diagenetic oxides; a preferential association with Mn oxides shifts to Fe oxides under less aerobic conditions. Both Cu and Zn display strong associations with both solid and dissolved sulphide species; however, unlike Cd or Mo, anoxia does not necessarily translate to elevated sedimentary concentrations. Lithogenic sources appear to be more important. The hydrographic factor which most influences the inventory of these elements is sedimentation rate (the primary influence on terrestrial inputs), while redox potential (fundamentally controlled by organic carbon content and bottom water oxygen) exerts the greatest post-depositional influence on cycling.

Anthropogenic inputs affect the inventory of all four metals (Mo to a lesser degree), but appear to have little influence on the degree of post-depositional cycling. Paradoxically, anthropogenic loadings of nutrients, manifested as eutrophication, exerts a greater influence on the cycling of trace metals.
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Acknowledgments

There are many individuals to whom I am indebted and deserve my most sincere thanks for their patience and support through the last several years.

I owe thanks to the many people who have shared their coveted laboratory bench- and office space over the years, in particular, Maureen Soon and Bert Mueller for their support in the lab and field, and to Bert for his many contributions to the generation of ideas. I am grateful to Ali and David at Lorax who have waited patiently for and supported the completion of this project.

I owe a great deal of thanks to Tom Pedersen and Steve Calvert for their support of this project; in particular, Tom’s guidance, patience, enthusiasm and insight in the face of missed deadlines and “part-time” jobs are admirable and enviable qualities in a supervisor. My sons Connor and Declan, despite the “all-nighters”, have always welcomed their father home (and have found creative ways to recycle drafts). I thank Shelagh’s and my parents for their support and for not asking the question, “So how is the thesis coming along?”, too frequently.

Most of all, I must thank my soul-mate Shelagh, who has patiently taken in the slack through missed dead-lines, tuition payments, work and life with a science geek.
Chapter One - Introduction

1.1 The Problem

Interest in trace metal cycling in the marine environment has a broad foundation. Trace metals have been studied not only to further fundamental knowledge, but also to investigate their utility as tracers in the study of oceanic and global processes (e.g. Boyle, 1988; van Geen et al, 1988; van Geen et al., 1991) and to assess the effects of anthropogenic influences on the environment (e.g. Chow et al, 1973; Bruland et al., 1974; Nriagu et al., 1979; Gobeil and Silverberg, 1989). Due to the toxic nature of many trace metals, recent research efforts have focused on the nature and behaviour of anthropogenic contributions to coastal environments (Nriagu and Pacyna, 1988). However, unlike organic compounds and radionuclides introduced to coastal waters, abatement of toxicity does not take place through either decomposition or decay: trace metals exist in perpetuity.

Human activities currently contribute significantly to the global trace-metal inventory in the biosphere (Nriagu, 1989). In places, environmental manipulation (dredging, sewage discharge, agricultural runoff, industrial and municipal waste disposal, mining waste disposal) has created trace metal 'hot-spots'. Unfortunately, the long-term impacts of such inputs remain largely unrecognized.

Trace metals enter the oceans primarily through rivers, aerosols and hydrothermal sources, their fate being incorporation and burial within the sediments (Li, 1981a; Li, 1981b; Honeyman et al., 1988). Sediments, however, are not necessarily a permanent sink. Many trace metals are known to undergo natural post-depositional remobilization through:

- remineralization of biogenic material such as organic matter, calcium carbonate and opal (e.g. Pedersen et al., 1986; Gobeil et al., 1987; Heggie et al., 1987; Gerringa, 1990; McCorkle and Klinkhammer, 1991);

- reductive dissolution of oxidized phases such as iron or manganese oxides (e.g. Berrang and Grill, 1974; Murray and Dillard, 1979; Shimmield and Price, 1986; Heggie
et al., 1987; Sato et al., 1989); or

- oxidation of reduced phases such as metal sulphides (e.g. Luther et al., 1982; Westerlund et al., 1986; Aller and Rude, 1988).

The presence of authigenic phases in addition to a spectrum of trace metal-adsorbing surfaces complicates trace metal geochemistry. As a result, post-depositional diagenesis is the aspect of trace metal cycling most poorly understood.

It is of paramount importance that a sound understanding of trace-metal geochemistry be fostered, not only to improve comprehension of natural cycles but also to enable more accurate prediction of the fate of natural and contaminant metal inputs to the oceans. The purpose of this thesis, therefore, is to address two deficiencies in our knowledge: first, the lack of understanding of aspects of specific trace metal cycles; and second, the scarcity of data applicable to understanding chemical diagenesis in coastal and fjord sediments of the northeastern Pacific.

1.2 Limits of Existing Data

The paucity of reliable data has in part arisen from an historic inability to collect and measure samples without compromising ‘trace-metal cleanliness’, particularly in the case of dissolved metals in sediment pore waters. The deficiency of quality data has been further exacerbated by an absence of suitable ancillary information required for interpretation of diagenesis. For example, it is difficult to ascertain the relative importance of natural environmental parameters (i.e. redox potential, mineralogy and bulk sedimentation rate) on the cycling of trace metals in a given sediment. While high quality data are now collected more routinely, mechanisms controlling trace metal distributions are still frequently obscured by the lack of ancillary information.

Very few data on trace metal distributions and behaviour have been previously collected from the more remote regions of the B.C. coast, although many studies have been performed on some of the more accessible inlets (i.e. Saanich Inlet, Burrard Inlet and Howe Sound). In general, interpretation of the existing data is constrained by low sampling resolution, or an absence of vital
supporting information. This is reflected by the present lack of meaningful information on the ultimate fate of trace metals, natural or contaminant, in most B.C. coastal environments.

1.3 Improving Present Understanding

Much of the trace metal work carried out to date on coastal sediments has involved observing a given sedimentary environment and identifying trace metal behaviour in the context of that specific setting (e.g. Gobeil et al., 1987; Skei, 1988). While this approach is useful, a deeper understanding of trace metal cycling lies in the study of each metal individually in a number of contrasting depositional environments (e.g. Shaw et al., 1990). In this approach, delineation of the dominant diagenetic controls on metal cycling stems from utilizing the different depositional settings of various sites as interpretative end-members. In this way, the relative importance of each diagenetic control may be more clearly isolated from the obscuring influence of the others.

The multi-basin approach is adopted in this dissertation. The thesis first characterizes the diagenetic state of the sediments in each of several hydrographically distinct inlets along the B.C. coast, in each case identifying the dominant end-member conditions. Secondly, it discusses the distribution of Cd, Cu, Mo and Zn, drawing on the data from different 'end-member' inlets to explain the prevailing controls on the cycling of each metal. This approach enables partial delineation of the intertwined controls of trace metal cycling in these and other coastal deposits. This approach represents one of the first attempts to comprehend the controls on trace metal cycling through a comparison of pore water and solid-phase metal distributions in differing hydrographic and depositional regimes.

The multi-basin approach was enabled through the development of a trace-metal extraction technique tailored to address the difficulties associated with the small volumes generated by pore water sampling techniques. Considerable effort was also invested in minimizing potential sources of contamination from sample collection through to analysis. Nonetheless, contamination with respect to zinc is a pervasive problem in pore water studies. In the work reported here, dissolved interstitial zinc profiles are considered to be reliable for Jervis and Ucluelet Inlets. At the other sites, the quality of the Zn data was considered to be inadequate.
to warrant inclusion in this thesis.

This thesis consists of four additional chapters. Background information relevant to trace metal cycling is presented in Chapter Two: first, an overview of the diagenetic process is offered, and this is followed by a brief review of the current knowledge of each metal studied. Analytical results from the six fjords or embayments studied are described and discussed in Chapter Three. Chapter Four presents an interpretation of the data from the perspectives of both collective and discrete influences on the diagenetic behaviour of the four principal metals studied. Conclusions are offered in Chapter Five. A major focus in the latter two chapters is hydrography, the objective being to determine the extent to which physical oceanographic differences among the various fjords influences the post-depositional behaviour of the metals.

It should be noted that because the focus of this thesis is post-depositional cycling of trace metals, emphasis is placed on the interpretation of dissolved species in the sediment pore waters. With the exception of authigenic phases, no attempt has been made to characterize mineralogy or major element chemistry as they generally have little influence on diagenetic interactions. Furthermore, the direct identification of authigenic phases through techniques such as x-ray diffraction, sequential extractions or thermodynamic speciation modelling are of little utility in such an approach. Techniques such as XRD are insufficiently sensitive for detection of low solid-phase concentrations. Sequential extractions are not sufficiently phase-specific and pore water compositions are too complex to adequately model. However, the distributions of trace metals and ancillary components in pore waters provide sufficiently strong evidence to deduce many of the controls on trace metal cycling. Even though this approach does not provide "direct" evidence of associations, it is the most versatile technique applicable to understanding post-depositional metal cycling.
Chapter Two - Background

2.1 Diagenetic Parameters - An Overview

The term "diagenesis" embraces all post-depositional chemical, biological and physical processes which induce changes in subaqueous sediments (Berner, 1980). Several factors influence trace metal diagenesis; four of the most important are:

- the nature, content and accumulation rate of organic matter in sediments;
- sediment and water-column redox potential;
- bulk sedimentation rate; and
- the specific chemical reactivity of the trace metal of interest.

Although each of these parameters represents a unique influence on trace metal diagenesis, their respective effects are difficult to isolate because of the intimately intertwined biogeochemical relationships associated with sedimentary systems. The following sections attempt to delineate these variables as they pertain to trace metal cycling.

2.1.1 Organic Matter

Organic matter is central to any biogeochemical considerations of sediment diagenesis, not only because it represents chemical potential energy capable of driving diagenetic reactions but also because it plays a critical role in the cycling of trace metals. Bulk organic matter is a complex mixture of components having different origins, labilities, chemical potentials and reactivities toward trace metals. Thus, the behaviour of organic matter in a given system depends on a number of variables ranging from its source to its age. The most significant variables are discussed below.

2.1.1.1 What is Organic Matter?

Organic matter can be described from different perspectives, with the two most practical descriptions being those pertaining to its biological and thermodynamic nature.

Organic matter is produced by autotrophic organisms, but cycles through all levels of the food chain (Parsons et al., 1984). For the purposes of this thesis, the ultimate source of organic
matter for the coastal ocean is assumed to be from primary productivity viz. photosynthesis, from either terrestrial or marine organisms. Although chemosynthetic autotrophs exist, they are assumed to have little influence on coastal organic matter cycles.

From a chemical perspective, the creation of organic matter by photosynthesis produces thermodynamically unstable concentrations of carbon, nitrogen, phosphorus, sulphur and oxygen. Specifically, photosynthesis produces confined centres of low redox potential (pE) in the form of high-energy chemical bonds between these elements (Stumm and Morgan, 1981). In creating localized, reduced states of matter, photosynthesis must also produce separate reservoirs of high pE. This is accomplished through the production of molecular oxygen. Thus, in converting electromagnetic energy to chemical potential energy, photosynthesis creates a thermodynamic instability (a pE disparity) between low-pE organic matter and the resulting high-pE environment. It is this chemical potential energy of sedimentary organic matter that fuels diagenesis. The success of organic matter as a fuel is therefore determined by its reactivity or biochemical potential and the suite of oxidants available to accept its electrons.

Because organic matter is a complex and variable mixture of elements, structures and oxidation states, it has a spectrum of reactivities. There are two types of lability: structural and thermodynamic. Structural lability refers to the degree to which the shape of the carbon skeleton of an organic polymer inhibits bacterial enzymatic hydrolysis. Certain carbon structures pose steric difficulties to hydrolytic enzymes; lignins, waxes and resins are all structurally resistant to microbial attack (Hedges et al., 1985; Prahl et al., 1989). The aromatic rings of lignin are difficult to cleave, whereas the hydrophobic nature of both waxes and resins interferes with hydrolysis. Thus, the presence of these compounds in bulk organic matter enhances its structural stability. Terrestrial organic matter (mostly the remains of vascular plants) has higher concentrations of these components and therefore tends to be less easily degraded than marine organic matter (mostly unicellular algae) (Fenchel and Blackburn, 1979; Hedges et al., 1985, 1988a, 1988b).

As bulk organic matter is progressively oxidized, the more labile components are preferentially removed; the residual material becomes more resistant to bacterial enzymatic
attack, acquiring higher proportions of less labile components. Abiotic polymerization of the remaining material further decreases lability by increasing aromaticity and structural complexity (Fenchel and Blackburn, 1979; Stumm and Morgan, 1981). In this regard, the process of humification typifies a path to increasing structural stability. However, the precursors of marine humics (amino acids, non-structural carbohydrates, lipids and pigments) are less aromatic and more aliphatic than those of their terrestrial counterparts, and they produce more labile humic material.

Thermodynamic lability is the ease with which electrons from organic matter are transferred to an oxidant, most commonly oxygen. The thermodynamic tendency for such a reaction to proceed is expressed by the Gibbs free energy ($\Delta G^0$) of the redox couple (Stumm and Morgan, 1981); if $\Delta G^0$ is negative, the reaction proceeds spontaneously. More negative $\Delta G^0$ values describe less impeded reactions; thus, for a given oxidant, more highly reduced organic matter will be thermodynamically more labile because the oxidant-organic matter pE difference is greater. Additionally, functional groups or portions of organic matter that are of lower pE will be more easily or preferentially oxidized with respect to the rest of the organic substrate (Mathews and van Holde, 1990). As bulk organic matter is oxidized and the more labile components are removed, the remaining material becomes, on average, less reduced and hence thermodynamically refractory. As a result, organic matter is most labile when it is first created.

It is useful to distinguish between the two basic types of organic matter found in coastal marine sediments: terrestrial and marine. They differ not only in elemental composition, but also in type and number of functional groups, as well as skeletal structure. As a result, they exhibit markedly different degrees of lability, metal complexing capacity and reactivity towards other phases.

Terrestrial plants are mostly vascular. They consist of about 75% carbohydrate, most of which is structural, such as cellulose, hemicellulose and pectin (Hamilton and Hedges, 1988), and they contain lignin (an aromatic polymer synthesized for strength) (Hedges and Mann, 1979; Curtis, 1983).
Marine organic matter does not require the structural integrity of its terrestrial counterpart. As a result, planktonic organic matter tends to be only 20 to 40% carbohydrate (less than half of which is structural) (Hamilton and Hedges, 1988), as well as being less aromatic and more aliphatic than terrestrial organic matter. Consequently, terrestrial organic matter is less labile than marine organic matter as it contains more structural material which tends to be more resistant to microbial-mediated oxidation.

Oxidants

For the oxidation of organic matter to proceed, there must be a corresponding reduction. Electrons from organic matter, liberated by oxidation, must return to oxygen or in the absence of oxygen, to a secondary oxidant. The specific electron receptor depends upon availability of the oxidant with vacant orbitals of lowest energy (Stumm and Morgan, 1981); a sequence of naturally occurring oxidants that accept electrons from organic matter is listed in Table 1. The increasing difficulty with which electrons are received by each successive oxidant (i.e. in the transfer of electrons to vacant orbitals of higher and higher energy) is reflected as a diminishing loss of Gibbs free energy (Froelich et al., 1979).

While the transfer of electrons between organic substrate and oxidant occurs spontaneously, heterotrophic bacteria are known to catalyze the transfer, dramatically increasing the rate of organic matter oxidation (Emerson et al., 1985; Rowe and Deming, 1985). The bacteria take advantage of chemical potential energy found in the organic matter - oxidant disequilibrium and use the energy released in the electron transfers to drive their own metabolism (Stumm and Morgan, 1981; Curtis, 1984). More negative \( \Delta G^0 \) values allow bacteria to utilize more energy. For this reason, bacteria preferentially utilize oxidants with the largest free energy loss (Froelich et al., 1979). Those bacteria that utilize oxygen as a terminal electron acceptor have a potentially larger energy reserve at their disposal than those using a secondary oxidant. Therefore, aerobic bacteria out-compete anaerobes where oxygen is present. When all available oxygen is consumed, a different bacterial assemblage (nitrate reducers; Table 1) dominates the redox cycle (Fenchel and Blackburn, 1979). The result is a temporal or spatial
sequence of bacterial species beginning with aerobic bacteria followed by nitrate reducers, and so on, finally ending with fermentors, sulphate reducers, and methanogens. There is little overlap between these groups as the oxidants or metabolites of one group are usually toxic to another (Froelich et al., 1979); hence, the bacterial species assemblages closely follow the redox state of the sediment column. However, recent work (Postma and Jakobsen, 1996) suggests that some overlap may occur under certain conditions of pH and oxide stability. Additionally, microenvironments may displace discrete zones of reducing species (e.g. Fe$_{2}^{+}$ or H$_{2}$S) into otherwise oxic horizons. The net effect is a “smearing” of the biogeochemical zonation created through the oxidation of organic matter.

<table>
<thead>
<tr>
<th>Oxidation Type</th>
<th>Chemical Reaction</th>
<th>$\Delta G^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxygen</strong></td>
<td>$(\text{CH}<em>2\text{O})</em>{106}(\text{NH}<em>3)</em>{16}(\text{H}_3\text{PO}_4) + 138 \text{O}_2 \rightarrow 106 \text{CO}_2 + 16 \text{H}_2\text{O}$</td>
<td>-3190 kJ/moleグルコース/glucose</td>
</tr>
<tr>
<td><strong>Denitrification</strong></td>
<td>$(\text{CH}<em>2\text{O})</em>{106}(\text{NH}<em>3)</em>{16}(\text{H}_3\text{PO}_4) + 94.4 \text{HNO}_3 \rightarrow 106 \text{CO}_2 + 55.2 \text{N}_2 + 16 \text{H}_3\text{PO}_4 + 177.2 \text{H}_2\text{O}$</td>
<td>-3030 kJ/mole</td>
</tr>
<tr>
<td><strong>Manganese Oxide Reduction</strong></td>
<td>$(\text{CH}<em>2\text{O})</em>{106}(\text{NH}<em>3)</em>{16}(\text{H}_3\text{PO}_4) + 236 \text{MnO}_2 + 472 \text{H}^+ \rightarrow 106 \text{CO}_2 + 8 \text{N}_2 + 236 \text{Mn}^{2+} + 16 \text{H}_3\text{PO}_4 + 366 \text{H}_2\text{O}$</td>
<td>-3020 kJ/mole</td>
</tr>
<tr>
<td><strong>Iron Oxide Reduction</strong></td>
<td>$(\text{CH}<em>2\text{O})</em>{106}(\text{NH}<em>3)</em>{16}(\text{H}_3\text{PO}_4) + 212 \text{Fe}_2\text{O}_3 (\text{or} \ 2 \text{FeOOH}) + 848 \text{H}^+ \rightarrow 106 \text{CO}_2 + 16 \text{NH}_3 + 16 \text{H}_3\text{PO}_4 + 530 \text{H}_2\text{O} (\text{or} \ 742 \text{H}_2\text{O})$</td>
<td>-1410 kJ/mole (or -1330 kJ/mole)</td>
</tr>
<tr>
<td><strong>Sulphate Reduction</strong></td>
<td>$(\text{CH}<em>2\text{O})</em>{106}(\text{NH}<em>3)</em>{16}(\text{H}_3\text{PO}_4) + 53 \text{SO}_4^{2-} \rightarrow 106 \text{CO}_2 + 16 \text{NH}_3 + 53 \text{S} + 16 \text{H}_3\text{PO}_4 + 106 \text{H}_2\text{O}$</td>
<td>-380 kJ/mole</td>
</tr>
<tr>
<td><strong>Methanogenesis</strong></td>
<td>$(\text{CH}<em>2\text{O})</em>{106}(\text{NH}<em>3)</em>{16}(\text{H}_3\text{PO}_4) \rightarrow 53 \text{CO}_2 + 53 \text{CH}_4 + 16 \text{NH}_3 + 16 \text{H}_3\text{PO}_4$</td>
<td>-350 kJ/mole</td>
</tr>
</tbody>
</table>

| Table 1 The most common oxidants and the free energies associated with their reduction (from Froelich et al., 1979). The formula for organic matter is hypothetical. |
The release of secondary metabolites by bacteria in conjunction with vertical zonation of bacterial assemblages allows the use of dissolved metabolite profiles as indicators of redox conditions in sediments (see Table 1). While it is difficult to measure sediment redox potential accurately, it is relatively easily inferred from the vertical distribution of oxidants and metabolites within interstitial waters (e.g. $O_2$, $NO_3^-$, $NH_4^+$, $Mn^{2+}$, $Fe^{2+}$ and $H_2S$; Froelich et al., 1979; Blackburn and Henrikson, 1983; Bender and Heggie, 1984; Bender et al., 1989; Berelson et al., 1990) despite any biogeochemical smearing. For example, $H_2S$ does not generally appear in sedimentary porewaters until oxygen is exhausted as an oxidant and the redox potential has decreased sufficiently to allow sulphate reduction to occur (Jorgensen, 1982; Howarth and Jorgensen, 1984; Luther and Tsamakis, 1989).

### 2.1.1.2 Effect of Organic Matter on Sediments and Trace Metals

Organic matter profoundly influences the sedimentary behaviour of many trace metals. Three prominent effects are: 1. control of diagenetic intensity; 2. influence on the fluxes of metals into the sediment system; and 3. providing a source of dissolved organic matter for trace metal complexation in interstitial waters.

The concentration of sedimentary organic matter is of considerable importance to the rate of diagenetic reactions; in general, higher concentrations of organic matter foster greater intensities of diagenesis. The organic carbon content of marine sediments is dependent upon two factors: the flux of organic matter to the sediments and the bulk sedimentation rate (Calvert, 1987). Oxidant availability exerts a secondary control (Calvert and Pedersen, 1992), as does sediment-particle surface area (Hedges and Keil, 1995).

The flux of organic matter to the underlying sediment is directly related to the magnitude of primary production within the euphotic zone and inversely related to water depth (Bogdanov, 1979). Because primary productivity is controlled largely by the vertical advection of nutrient-rich water into the euphotic zone, more intense upwelling results in a larger flux of organic matter leaving surface waters. Despite the relatively short residence time of organic matter traversing the
water column, depth has a significant influence on the quantity of material that reaches the sediment-water interface. A large fraction of organic matter is remineralized within the water column due to its high initial lability in concert with the presence (typically) of abundant oxygen. Thus, for a given rate of production, the flux of organic matter at the sediment-water interface decreases by one order of magnitude for every 10-fold increase in water depth (Suess, 1980).

Bulk sedimentation rate is an equally important control on the organic matter content of sediments. This is due in part to the inherent coupling of sedimentation rate and organic matter flux. But more importantly, faster burial removes labile organic matter from the sediment-water interface, the zone of highest metabolic activity where microbial biomass is greatest (Muller and Suess, 1979). Furthermore, rapid burial isolates organic matter from oxidants that are replenished diffusively from bottom water (Calvert, 1987). Recent work on the preservation of organic matter suggest that the surface area to mass ratio of a sediment plays an important role in governing the quantity of organic carbon preserved in sediments (Mayer, 1994; Keil et al., 1994; Hedges and Keil, 1995). Aside from reasons of hydrodynamic equivalence, organic matter accumulates in fine-grained deposits because there is more available surface area for sorption to occur. Furthermore, it has been suggested that adsorption to particle surfaces may aid in preservation by inhibiting enzymatic hydrolysis (Mayer, 1994).

Many metals associate strongly with organic matter; thus, the flux of organic matter from the water column can be thought of as a conveyor of trace metals to the sediments (Honeyman et al., 1988). The characteristics of the metal-organic association is complex, variable and depends both on the metal and the nature of organic matter. Interactions of organic compounds with metals (complexation) occurs through the donation of lone pairs of electrons from ligand atoms of the organic substrate to vacant orbitals on a metal cation (Nissenbaum and Swaine, 1976; Cotton and Wilkinson, 1980; Stumm and Morgan, 1981; Piotrowicz et al., 1984; Tessier et al., 1996). Ligand atoms (mostly oxygen, nitrogen, sulphur and occasionally phosphorus) typically occur in functional groups at the periphery of organic molecules. Thus, proximal functional groups on an organic molecule can allow the formation of multidentate complexes thereby increasing complex
stability (Stumm and Morgan, 1981).

The differences in organic-metal interactions between marine and terrestrial organic matter are generally unclear; however, some dissimilarities can be inferred. It is conceivable that the larger fraction of nitrogen and sulphur moieties found in marine organic matter enhance trace-metal binding (Nissenbaum and Swaine, 1976). Furthermore, the increased aromaticity and structural rigidity of terrestrial organics tends to stiffen the carbon skeleton, inhibiting multidentate complexation (Piotrowicz et al., 1984). However, actual metal-organic interaction probably depends as much or more on the individual metal as on the type of organic ligand (Section 2.1.3). Complexation is discussed in more detail in later sections.

**Organic-Metal Pathways to Sediments**

There are three important metal-organic pathways to the sediments: biogenic uptake of metals by organisms, metal adsorption to inorganic particles coated ubiquitously by organic films, and flocculation of river-borne organic matter with adsorbed metals.

The contributions of phytoplankton and zooplankton to the flux of trace metals to the sediments is very important; not only do these organisms concentrate trace-metals relative to seawater (Knauer and Martin, 1973; Martin and Knauer, 1973), but they represent an efficient mechanism for transporting trace metals rapidly through the water column to the sediments. Many trace elements are either incorporated biochemically or adsorbed to surfaces of living and dead biogenic material (Price and Morel, 1990). Adsorption is a simple surface phenomenon where metals are reversibly complexed by the ligand atoms of functional groups on the surfaces of organisms. In this respect, adsorbed metals are in equilibrium with those dissolved in the water column (Jannasch et al., 1988). Biochemical uptake differs from adsorption in that trace-metals are non-reversibly bound to either the soft tissue or hard parts of an organism; the metal is released only upon remineralization of the organic host (Boyle et al., 1976; Sclater et al., 1976). In addition, bio-incorporation is thought to be a much slower process than adsorption, taking on the order of days (cf. minutes for adsorption; Jannasch et al., 1988).

Biochemical uptake may or may not be intentional. Metals such as Zn, Cu, and Fe are
classified as micronutrients, and are required by most organisms in trace amounts. However, it has been suggested that other metals, although serving no obvious biochemical purpose, are taken up inadvertently as chemical analogues for required nutrients (e.g. Cd and Co; Boyle et al., 1976; Price and Morel, 1990). Regardless of how organisms sorb trace metals, when they die some fraction of their remains sink to the ocean floor as discrete organic detritus or encased in fecal material; the associated trace metals are delivered to bottom waters and sediments.

Sorption is not restricted to biogenic particles - there are many inorganic particles species in natural waters capable of sorbing trace metals. Hydrous metal oxides, clay minerals and other solids are known to coprecipitate or incorporate trace metals within their crystal lattices (Davis and Leckie, 1978; Balistrieri and Murray, 1981; Hunter, 1983; Davis et al., 1987; Paulson et al., 1988). However, it has been noted that regardless of particle composition, the surface-adsorbing characteristics always resembled those of organic matter rather than those expected from particle composition (Balistrieri et al., 1981; Tipping, 1981; Tipping and Cooke, 1982; Loder and Liss, 1985; Hirose, 1990). Field observations and lab experiments involving colloidal aluminum oxides and Fe and Mn oxyhydroxides (with and without the presence of dissolved organic matter (DOM)) suggest that the uniform adsorptive properties of natural particles are due to ubiquitous coatings of organic matter. The trace metals complex with adsorbed organic molecules rather than with sites on the particle surface (Laxen et al., 1984; Hunter and Liss, 1982; Hunter, 1983; Balistrieri et al., 1981; Davis, 1984; Loder and Liss, 1985; Tessier et al., 1996). The sinking of these particles delivers the scavenged metals to the sediments. The rate and degree to which a trace metal is scavenged depends on: 1) the nature of the trace metal (Section 2.1.3), and 2) the concentration of particulate matter (Hirose, 1990). Consequently, scavenging is a strong transport mechanism for trace metals in nearshore systems where particle concentrations are high as a result of high primary productivity and sediment resuspension.

The organic matter - trace metal pathway to sediments is particularly important in the estuarine environment. Rivers deliver dissolved and colloidal metals as well as organic matter to estuaries where some of the organic material and associated metals destabilize, flocculate and
settle out of the water column (Boyle et al., 1977; Kerndorff and Schnitzer, 1980; Sholkovitz and Copeland, 1981). River water - seawater mixing experiments have shown DOM to be a strong coagulating agent for some metals (e.g. Fe, Mn, Cu). Furthermore, the presence of adsorbed DOM in the estuarine environment suppresses differential flocculation that might otherwise occur with pure colloidal Fe, Mn and Al oxides (Hunter and Liss, 1982). Adsorbed DOM effectively decouples these aquatic components from their expected solubilities and adsorptive properties (Sholkovitz and Copeland, 1981; Hunter and Liss, 1982; Tipping and Cooke, 1982).

Perhaps the most important fraction of organic matter with regard to trace metal cycling in sediments is the dissolved fraction. Dissolved organic matter in interstitial waters is thought to influence trace metal speciation, toxicity and mobility (Elderfield, 1981; van den Berg and Dharmvanij, 1984; Calvert et al., 1985; Moffett et al., 1990; Bruland, 1992; Davison and Zhang, 1994). Sedimentary DOM forms in situ from aerobic and anaerobic decomposition of terrestrial and marine organic matter (Lyons et al., 1979; Orem and Hatcher, 1987). If the sediments contain terrestrial organic matter remineralized under oxic conditions, DOM is dominated by aromatic and paraffinic structures. If the source is predominantly marine or if decomposition is anaerobic, carbohydrate and paraffinic structures dominate; it has been suggested that lignin decomposes minimally under anaerobic conditions (Orem and Hatcher, 1987; Cowie and Hedges, 1995). Most DOM is produced in anaerobic sediments from the incomplete oxidation of organic matter by sulphate reducers and methanogens. With time these simple organic molecules undergo abiotic condensation and polymerization reactions (humification) in which more complex structures are formed (Krom and Sholkovitz, 1977; Orem and Hatcher, 1987). Thus, humification results in the formation of a spectrum of molecules ranging in molecular weight from a few hundred to many million amu. The corresponding size-spectrum ranges from "dissolved" through "colloidal" to "particulate" material. The size of the humic molecules is broadly proportional to age. As a result, DOM mobility in interstitial waters decreases with time (Elderfield, 1981). The metal-complexing capacity of DOM alters concurrently, reflecting changes in functional groups, structure and elemental composition (Lyons et al., 1979; Lyons and Fitzgerald,
For example, during diagenetic alterations, the N content of organic matter often decreases, while the S content increases (Francois, 1987; Kohnen et al., 1989); humification in general leads to alterations in chemical composition as well as increasing degrees of structural rigidity and aromaticity. Thus, one might expect trace metal mobility to alter dramatically with the changes that occur to DOM in the interstitial waters with time. These observations and their significance to the individual metals will be discussed below.

2.1.2 Redox State

2.1.2.1 What is Redox Potential?

Redox potential (Eh), when expressed as pE, is a convenient way of representing the oxidizing intensity or electron activity of an environment. In the same way that low pH represents an environment with a high proton activity (a tendency for species to be protonated), low pE represents a high electron activity (a tendency for species to be electron-rich). Thus, reduced, electron-rich species in an oxic, electron-poor environment tend to oxidize or lose electrons to the environment (Manahan, 1979; Stumm and Morgan, 1981). Organic matter is a source of electrons and oxidants are a sink; the redox potential is governed by the flow of electrons between these two pools. In sediments, the redox state of any given horizon is the result of a balance between the content and lability of organic matter in the sediments in concert with the quantity and type of available oxidant (Froelich et al., 1979; Jahnke et al., 1982).

Because organic matter is highly reduced, the presence of labile material results in a rapid decrease in pE by generating a larger flux of electrons to the interstitial medium. Similarly, higher concentrations of sedimentary organic matter contribute more to lowering pE by generating more electrons. Thus, in sediments replete with electron-rich organic matter, redox potential decreases with depth as deeper horizons have had more time to restore the thermodynamic equilibrium between organic matter and the sedimentary environment.

The type and quantity of available oxidant is an equally important influence on redox potential. An oxidant that can consume electrons quickly and easily (i.e. one with vacant, low
energy orbitals) will sustain high sedimentary pE (low electron activity) by 'mopping-up' electrons as quickly as organic matter releases them. Redox potential is therefore high in the presence of oxygen because oxygen has very low-energy orbitals that easily accept electrons from organic matter; the low electron activity and high electronegativity of oxygen affords it the classification of strong oxidant.

It follows that redox conditions within sediments are to a large degree governed by the presence or absence of oxygen. The concentration of oxygen within interstitial waters is controlled by the rate of diffusive replenishment from bottom water relative to the rate of oxygen consumption (Revsbech et al., 1980; Reimers et al., 1984; Westerlund et al., 1986; Reimers and Smith, 1986). The diffusive influx is controlled by the bottom water $O_2$ concentration, the molecular diffusion coefficient, and the steepness of the $O_2$ concentration gradient (Emerson et al., 1984; Jorgensen and Revsbech, 1985; Westerlund et al., 1986; Archer et al., 1988; Hall et al., 1989). Bioturbation increases the flux of dissolved species across the sediment-water interface by advectively transporting water through the benthic boundary layer. This process allows oxygen to reach depths it could not attain by diffusion alone. Conversely, bioturbation displaces reduced porewater species to more oxic horizons than attainable by diffusion (Aller, 1983). Thus, bacterial metabolites ($NH_4^+$, $Mn^{2+}$, $Fe^{2+}$, $H_2S$) produced from secondary oxidants in more reduced horizons of the sediments migrate upward by diffusion (perhaps enhanced by bioturbation) to be oxidized by more oxidized species, and ultimately by oxygen (Emerson et al., 1980; Elderfield et al., 1981; Grundmanis and Murray, 1882; Hall et al., 1984, 1989; Edenborn et al., 1985; Aller and Rude, 1988). In this sense, oxygen is often considered the ultimate electron acceptor; it is consumed by other reduced porewater species besides organic matter. Consequently, the mutually exclusive nature of oxygen and the various secondary metabolites in sediment porewaters allows relatively accurate determinations of spatial variations in sedimentary redox state (Froelich et al., 1979).
2.1.2.2 Effect of Eh on Trace Metals

There are two ways in which redox potential may effect trace metal cycling: alteration of the oxidation state of certain metals (i.e. Fe, Mn, Mo) and alteration of the oxidation state of ligand atoms (i.e. N and S) within a complexing substrate.

Metals such as Fe, Mn, Mo, U, Cr, and V are directly affected by changes in redox potential; they have multiple oxidation states dictated by the redox potential of their environment. Fe and Mn are unique in that they are both abundant in the sedimentary environment and, in their oxidized forms, exist as solids with strong sorption characteristics (Berrang and Grill, 1974; Balistrieri and Murray, 1982, 1986; Tessier et al., 1985, 1996). Thus, even though other metals may not be subject to direct changes in oxidation state, they can be indirectly affected by redox potential being scavenged by or coprecipitated with Fe and Mn-oxides. The result is often the formation of a metal-enriched, oxide-bearing sediment layer near the sediment-water interface (e.g. Lynn and Bonatti, 1965; Tessier et al., 1996). At the base of such a layer, where the redox potential is lower, Fe and Mn oxides undergo reductive dissolution and are remobilized to the interstitial waters. Some of the reduced ionic iron and manganese diffuse upwards, encounter oxygen and reprecipitate as amorphous oxides with concomitant coprecipitation of other metals. Thus, porewater profiles of Fe and Mn typically show strong metal concentration gradients spatially coincident with the base of an enriched, solid-phase layer (Calvert and Price, 1972; Grill, 1982; Klinkhammer et al., 1982; Pedersen et al., 1986).

Redox potential also affects the sedimentary environment of trace metals by altering the oxidation state of certain ligand atoms. For example, nitrogen and sulphur are common ligand atoms that have multiple oxidation states with different complexing characteristics. In oxic waters, sulphur (primarily sulphate, oxidation state +6) is a weak complexer of trace metals (Stumm and Morgan, 1981; Morel, 1983). However, in anoxic waters, sulphur (as HS-, oxidation state -2) is such a strong complexer that not only does it complex with most metals, but it also forms insoluble metal-sulphide precipitates (Emerson et al., 1983; Skei et al., 1988 and others). Similarly, in oxic waters, nitrogen exists primarily as NO$_3^-$ (+5 oxidation state) and as NH$_4^+$ (-3 oxidation state).
under more reducing conditions. The oxidation state of nitrogen is known to affect its complexing characteristics (Stumm and Morgan, 1981). Presumably, the more reduced forms of ligand atoms complex metals more effectively as they have available more electrons to donate to empty orbitals on a metal centre.

2.1.3 Metal Type

The sorption properties of a metal depend as much on the metal as on the ligand atom. For convenience, metals are commonly divided into three groups (class A, transition and class B) based on their electronic configuration and the complexation behaviour of their common oxidation states. The characteristics of each are briefly reviewed below.

2.1.3.1 Class A Metals

Class A metals have a d° electronic configuration (inert gas-like, e.g. Ca²⁺, Mg²⁺, Na⁺, K⁺, Si⁴⁺). Having empty d-orbitals, class A metals exist as small, compact, spherically symmetrical cations whose electron cloud is difficult to deform under imposed electric fields from adjacent ions (Stumm and Morgan, 1981). Such cations behave as 'hard spheres' and prefer ligand atoms with the same properties. Thus, class A cations tend to associate with small, non-polarizable ligands such as F⁻, and ligands having O as a donor atom. They do not form complexes with large polarizable ligand atoms such as S (or N), and as a result do not readily form sulphide precipitates or complexes. Rather, class A cations form insoluble complexes with OH⁻, CO₃²⁻ and PO₄³⁻ (Stumm and Morgan, 1981). Class A complex stability can be likened to simple electrostatic attraction as there are no d electrons to add crystal field stabilization energy (CFSE). Thus, complex stability increases with increasing ionic charge to radius ratio (Stumm and Morgan, 1981).

2.1.3.2 Transition Metals

Transition metal cations have between one and nine d electrons. Because their d orbitals are only partially filled, transition-metal complexation tends to involve the overlap of full ligand orbitals with partially empty d orbitals on the metal centre (Cotton and Wilkinson, 1982). Thus,
transition-metal-ligand stability generally follows the Irving-Williams order \((\text{Mn}^{2+}(\text{d}^5) < \text{Fe}^{2+}(\text{d}^6) < \text{Co}^{2+}(\text{d}^7) < \text{Ni}^{2+}(\text{d}^8) < \text{Cu}^{2+}(\text{d}^9) > \text{Zn}^{2+}(\text{d}^{10}))\) reflecting an increasing tendency to form complexes as ionic potential (valence/radius) and electronegativity increase. Specifically, CFSE increases from \(\text{d}^6\) to \(\text{d}^9\) (\(\text{d}^5\) and \(\text{d}^{10}\) have no CFSE). Transition metals are aptly named as they bridge the characteristics from class A to class B cations; low \(d\) configurations behave more like class A, high \(d\) configurations behave more like class B cations.

### 2.1.3.3 Class B

Class B cations (e.g. \(\text{Cd}^{2+}, \text{Zn}^{2+}, \text{Hg}^{2+}\)) have full \(d\)-orbitals (\(\text{d}^{10}\)) and thus have a thick electron sheath that is readily deformed under an imposed, external electric field from adjacent ions. They resemble soft spheres and prefer ligands of the same nature. Most notably, class B cations interact strongly with reduced sulphur, forming insoluble and soluble sulphide complexes.

Electrostatic attraction is not the sole mechanism to class B interactions; charge to radius ratio does not correlate with complex stability. Rather, it appears that both coulombic and covalent forces play significant roles. Complex stability is governed by intricate interactions of orbital overlap but is in general higher for cations with higher ionization potentials and ligands with lower electronegativity. Thus, class B ligand stability is: \(\text{F} < \text{O} < \text{N} < \text{Cl} < \text{Br} < \text{I} < \text{S}\), the reverse of electronegativity. However, because class B cations are large and deformable, steric hindrance often plays a role as do entropy effects; stability sequences are often irregular and difficult to predict (Stumm and Morgan, 1981).

### 2.1.4 Authigenic Phases

In sediments where organic matter accumulates relatively quickly, metabolite concentrations within the interstitial waters may increase and exceed the solubility products of certain solid phases. This often results in the formation of specific authigenic minerals which may profoundly affect the cycling and mobility of a wide range of elements (Suess, 1979).

Among the most common authigenic phases are: carbonates, phosphates, Fe-silicates (glauconites), sulphides and oxides of Fe and Mn (Calvert, 1976; Suess, 1979; Baturin and
Bezrukov, 1979; Luther et al., 1982; Anderson et al., 1987; Luther and Church, 1988). Each will be discussed in turn.

2.1.4.1 Carbonates

Carbonate minerals (of calcium, manganese, iron and others) are important authigenic constituents of marine sediments (Suess, 1979; Pedersen and Price, 1982; Morse, 1986; Anderson et al., 1987; Mucci, 1988). Seawater in the upper ocean is supersaturated with respect to calcite (and aragonite) but inorganic precipitation is inhibited by the presence of Mg$^{2+}$ (Broecker, 1974). However, relatively small physicochemical changes in sedimentary pore waters are often sufficient to increase the degree of supersaturation to the point where calcite will precipitate. Chemogenic precipitation of calcium carbonate is thought to occur in anoxic marine environments where the total carbonate concentration is high from remineralization of organic matter. Authigenic precipitation is enhanced by high pH; thus, the alkalinity generated by sulphate reduction is thought to compensate for the generation of acidity associated with remineralization of organic matter by oxygen; chemogenic precipitation is thereby intensified in reducing sediments (Hein et al., 1979; Suess, 1979; Murray et al., 1980; Anderson et al., 1987).

Precipitation of manganese carbonate is similar to that of calcium carbonate except that the concentration of dissolved manganese is more dynamic than that of Ca$^{2+}$. In oxic surface waters, the concentration of Mn$^{2+}$ is very low, typically < 1 nM (Landing and Bruland, 1987); Mn exists primarily as Mn(IV) in solid oxyhydroxides. Under reducing conditions, Mn oxides are reductively remobilized, causing the concentration of Mn$^{2+}$ to increase with depth within the sediments (Froelich et al., 1979). At some depth, the concentrations of dissolved carbonate (also increasing with depth) and dissolved manganese may be sufficient to surpass the solubility product for certain manganous carbonate phases (Pedersen and Price, 1982; Calvert and Pedersen, 1996).

Trace metals are known to adsorb and coprecipitate with carbonates (Lorens, 1981; Shen et al., 1987; Comans and Middleburg, 1987). The success with which a given trace metal sorbs to calcite depends mostly on the ionic radius of the metal; a closer radius match to that of Ca$^{2+}$
increases the likelihood of sorption (Comans and Middleburg, 1987). Trace metals are incorporated within the host calcite lattice when structural distortion is minimal (Framson and Leckie, 1978). Such incorporation is thought to involve a two stage process: rapid adsorption onto the calcite surface followed by diffusion into a hydrated calcite surface layer (taking hours to days), followed in time by a slower co-crystallization step from the disordered hydrated surface layer (lasting days to weeks) (McBride, 1980; Comans and Middleburg, 1987; Davis et al., 1987; Fuller and Davis, 1987; Mucci, 1988; Stipp et al., 1992).

It is important to note that the environments where carbonates form authigenically (anoxic waters) typically have very low trace metal concentrations resulting from sulphide precipitation. Thus, sorption onto or into diagenetic carbonates is probably not a significant sedimentary sink for trace metals (Anderson et al., 1987). However, where carbonate hard parts are formed by plankton, uptake of certain trace metals is thought to occur (e.g. Boyle, 1981; Shen et al., 1987).

2.1.4.2 Oxides of Iron and Manganese

Iron and manganese are respectively the first and second most abundant transition metals in the earth's crust. Their multiple oxidation states and corresponding solid-state associations in concert with the ability of their oxides to complex many other trace elements make them critical to considerations of trace-metal cycling.

In oxic seawater and sediments, iron and manganese exist almost exclusively in their +3 and +4 oxidation states, respectively, predominantly as solid oxides or oxyhydroxides. As redox potential decreases, both Fe and Mn reduce to the +2 oxidation state, resulting in dissolution of their solid forms (Froelich et al., 1979). Such situations typically occur where solid oxide particles sink across a redox boundary within a water column (e.g. Saanich Inlet, the Baltic Sea, Framvaren Fjord) or, more commonly, when solid oxides become buried below the oxic/anoxic redox boundary within sediments. Below this redox boundary, Mn and Fe oxides are utilized as terminal electron acceptors during the oxidation of organic matter and subsequently undergo reductive dissolution from their oxidized to reduced forms.
Iron and manganese released in this manner may exist in dissolved form for a period of time sufficient to diffuse away from the zone of release. That fraction of dissolved metal diffusing upwards toward the sediment-water interface eventually re-encounters oxygen and is oxidized, yielding amorphous oxide and oxyhydroxide precipitates. These are in turn reburied and remobilized within subsequent burial cycles. The result of continued cycling is a pronounced accumulation of both Fe and Mn within surficial, oxic sediments (Lynn and Bonatti, 1965; Froelich et al., 1979; Klinkhammer, 1980; Balzer, 1982; Sundby and Silverberg, 1985; Balistrieri and Murray, 1986).

Iron and manganese oxides and oxyhydroxides are important scavengers of trace-metals, because of their ability to reversibly adsorb and coprecipitate trace metals. Generally, adsorption and coprecipitation are thought to represent the end-members of a continuum of trace-metal - oxide-surface interactions (Farley et al., 1985). As a metal is adsorbed onto an oxide surface, a new mixed-oxide (or hydroxide) surface is formed; further mass transfer of metal from solution to the solid-phase creates additional mixed-metal oxide having a range of compositional characteristics. Because they have large surface areas with many potential sorption sites, Fe and Mn oxides are capable of sorbing significant quantities of trace metals. This results in an often-observed concomitant increase in specific trace element concentrations within oxic sediments (Balistrieri and Murray, 1982; Klinkhammer et al., 1982; Graybeal and Heath, 1984; Laxen, 1985; Balistrieri and Murray, 1986; Paulson et al., 1988; Tessier et al., 1996).

The sorption sites of an oxide are essentially oxygen-containing ligands that have characteristic binding energies for various trace metals. It has been suggested that the affinity with which a metal sorbs to a pure oxide surface is correlated with its ability to hydrolyze in solution (Balistrieri et al., 1981; Table 2); however, more often than not, real samples do not reflect this generality. This may be due in part to the tendency of mono- and divalent cations to associate with Mn-oxides while tri- and tetravalent cations tend to associate more with Fe-oxides (Balistrieri and Murray, 1984; Tessier et al., 1996). Additionally, binding sites exhibit a large spectrum of energies and trace element affinities, adsorption to those sites being analogous to solution
complexation with the addition of an electrical double layer at the oxide-solution interface (Balistrieri and Murray, 1982). Because different sediments contain different proportions of oxides, metal ions and competing phases, trace element sorption to metal oxides is not only dependent on the nature of the trace element but is strongly modified by changes in pH and ionic strength as well as the nature of competing sorbers and sorbants (Stumm and Morgan, 1981; Tessier et al., 1996).

<table>
<thead>
<tr>
<th>Mineral Phase</th>
<th>Affinity for Mineral Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Goethite (FeOOH)</td>
<td>Cu&gt;Pb&gt;Zn&gt;Cd</td>
</tr>
<tr>
<td>Pure Birnesite (MnO₂)</td>
<td>Pb&gt;Cu&gt;Zn&gt;Cd</td>
</tr>
<tr>
<td>Oxic Interfacial Sediments (MANOP Site H)</td>
<td>Pb&gt;Cu&gt;Zn&gt;Ni&gt;Cd</td>
</tr>
</tbody>
</table>

Table 2 Adsorption affinities of various oxide phases for several trace metals (compiled from Balistrieri and Murray, 1982; 1984; 1986; Paulson et al., 1988)

### 2.1.4.3 Sulphides

Reduced sulphur is ubiquitous in coastal marine sediments, and is capable of precipitating or adsorbing a wide range of trace metals (e.g. Fe, Cd, Zn, Hg, Mo, Cu and others) (Korelev, 1958; Davies-Colley et al., 1985; Jean and Bancroft, 1986; DiToro et al., 1990; Jean et al., 1990; Hyland et al., 1990; Huerta-Diaz and Morse, 1992). The most abundant authigenic sulphides are those of iron: FeS (mackinawite, greigite) and FeS₂ (pyrite, marcasite), reflecting both the abundance of iron and its reactivity towards reduced sulphur.

While FeS may be abundant in recent sediments, it is considered to be meta-stable to pyrite, the thermodynamically-favored sulphide of iron. The conversion of FeS to pyrite is thought to require on the order of years; however, where free HS⁻ is limited, FeS may persist for longer periods of time (Berner, 1981; Perry and Pedersen, 1993). FeS is known to be associated with many trace metals and as a result may play host to a significant inventory of metals in reduced sediments (Framson and Leckie, 1978; Davies-Colley et al., 1985; Hyland et al., 1990; Arakaki
Indeed, certain metals (e.g. Cd and Mo) preferentially precipitate with FeS rather than pyrite (Korelev, 1958; Huerta-Diaz and Morse, 1992). However, the precise relationship between FeS and many trace-metals remains unclear; it is not fully understood whether many metals coprecipitate with FeS or if they exist as discrete metal sulphides (e.g. Jacobs and Emerson, 1982).

Pyrite, the most common sulphide of iron, occurs in one of two forms: framboidal or microcrystalline pyrite (Luther et al., 1982; Berner, 1984; Skei, 1988). Framboidal pyrite is thought to form where FeS is oxidized through greigite in the presence of elemental sulphur derived from the oxidation of HS⁻; the process proceeds slowly, requiring years to complete. However, if elemental sulphur is present in the form of polysulphides, microcrystalline pyrite may precipitate rapidly from solution (Luther et al., 1982; Berner, 1984; Morse and Cornwell, 1987; Skei, 1988). Perry and Pedersen (1993) demonstrated that in the absence of abundant free H₂S, where FeS was undersaturated, pyrite can precipitate without the FeS precursor. Reaction occurs through a presumed interaction between polysulphide sulphur and soluble Fe-sulphur complex.

Although pyrite has been inferred to be a significant sink for many trace elements, there is little evidence suggesting a direct association between the two. In general, concentrations of trace metals are low in the interstitial water of pyrite-rich sediments leading workers to suspect that FeS₂ coprecipitates trace metals or, at the very least, adsorbs them. However, recent work (Huerta-Diaz and Morse, 1992) has suggested that pyritization is an important consumption mechanism for some trace metals, with the degree of trace-metal pyritization being metal dependent. Metals that form very insoluble sulphides (i.e. transition metals) are incorporated into pyrite to a greater degree than class B metals which form more soluble sulphides. Additionally, the degree to which trace metals are incorporated into the pyrite matrix appears to be related in part to the abundance of reactive Fe and free H₂S; trace metal pyritization is enhanced in Fe-poor, H₂S-rich sediments and diminished in Fe-rich, H₂S-poor sediments. It would seem that trace metal incorporation into pyrite is maximized through the slow pyrite precipitation mechanism where FeS is involved, rather than by direct rapid precipitation involving Fe, H₂S and polysulphide.
2.2 The Trace Elements Investigated

Several trace metals were selected for study in this project, including Cd, Cu, Mo, Zn, Mn and Fe. However, limited porewater sample volumes restricted the suite of metals analysed in some inlets. Metal selection was based on complementary diagenetic behaviour as well as ease of extraction from the saline water matrix using the procedure developed for the project (Appendix III).

A summary of the current understanding of the natural and anthropogenic cycles of each metal is given below.

2.2.1 Cadmium

Although cadmium has been studied extensively within the past decade (Lee and Kittrick, 1984; Gendron et al., 1986; Gobeil et al., 1987; Comans and van Dijk, 1988; Pedersen et al., 1989; McCorkle et al., 1991; Rosenthal et al., 1995(a), 1995(b)), it is one of the most poorly understood metals from a diagenetic perspective. One would expect the aquatic chemistry of Cd to be straightforward given that it has only one naturally-occurring oxidation state (unlike Fe and Mn) and is therefore not directly involved in redox chemistry. Moreover, cadmium does not appear to bond covalently with carbon (Astruc, 1986). Interactions of Cd with all but a few chemical species found in natural waters and sediment porewaters are best described as weak. However, it is for precisely this reason that identification of Cd interactions is ambiguous, depending on many variable parameters such as ionic strength, major ion chemistry and redox state. As a result, a comprehensive understanding of cadmium diagenesis has proven elusive.

2.2.1.1 Crustal Abundance and Sources

The mean crustal abundance of cadmium is between 0.1 and 0.2 μg g\(^{-1}\) (Simpson, 1981; Lee and Kittrick, 1984; Thornton, 1986). In general, cadmium is depleted in igneous and metamorphic rocks (usually < 0.2 μg g\(^{-1}\)) and soils (0.06 μg g\(^{-1}\); organic-rich soils may have much higher concentrations); however it does substitute into some mineral lattices (e.g. for Ca\(^{2+}\) in some feldspars and apatite) and can be found in some ferromagnesian minerals (Gong et al., 1977; Thornton, 1986). Cadmium is enriched primarily in organic-rich sediments and sedimentary
rocks (Gong et al., 1977; Baturin and Oreshkin, 1984; Gobeil et al., 1987; Pedersen et al., 1989). This likely reflects its intimate association with organic matter cycles.

**Sources**

Cadmium is introduced to the oceans naturally by both rivers and aerosols. Rivers deliver Cd weathered from terrestrial rocks \(3.25 \times 10^9 \text{ g yr}^{-1}\) (Simpson, 1981) whereas aerosol-delivered Cd comes from both volcanic activity (as inorganic particulate matter) and biogenic sources (as particulate organic matter from forested regions) as well as wind-borne soil particles (Nriagu, 1989). The natural, background atmospheric flux has been estimated at \(1.3 \times 10^9 \text{ g yr}^{-1}\) (Nriagu, 1989). Thus, while riverine delivery is large, it is not an overwhelming transport mechanism of Cd to the oceans; natural atmospheric fallout contributes substantially (-30%) to the ocean inventory.

Sources of anthropogenic cadmium include: zinc and lead smelters, waste incineration, combustion of fossil fuels, manufacture of phosphate fertilizers, dredging, sewage discharge and emissions associated with the production of plastics, pesticides and paints (Simpson, 1981; Garrett, 1985; Prause et al., 1985; Thornton, 1986; Nriagu and Pacyna, 1988; Pruell et al., 1990; Seidemann, 1991). The anthropogenic flux of Cd to the oceans now exceeds the natural flux, due largely to increases in the atmospheric component (Nriagu and Pacyna, 1988; Nriagu, 1989). While suggestions have been made that atmospheric fallout of Cd has decreased by as much as a factor of 2.5 since the late 1960's (Boutron et al., 1991), the anthropogenic component is still almost six times its natural counterparts \((7.6 \times 10^9 \text{ g yr}^{-1} \text{ vs. } 1.3 \times 10^9 \text{ g yr}^{-1}\) respectively; Nriagu, 1989). As a result, anthropogenic cadmium emissions impact the global cadmium inventory significantly.

**2.2.1.2 Metal Description**

Cadmium is a group II B element, and as such is considered a class B metal; it has a valence electronic configuration of \(4d^{10} 5s^2\). The 5s electrons are most loosely bound and are lost preferentially upon ionization, leaving the inner 4d shell full. Because Cd\(^{2+}\) has no vacant 4d orbitals, it has no crystal field stabilization energy (CFSE), and generally forms only weak
complexes (Cotton and Wilkinson, 1980). The class B behaviour of Cd comes from its full 4d orbitals; the resulting thick electron cloud is easily deformed and polarized under external electric fields imposed from adjacent ions (Cotton and Wilkinson, 1980; Stumm and Morgan, 1981). Thus, cadmium complexes most strongly with large, electron-rich, deformable, polarizable ligands, most commonly Cl\(^-\) and reduced sulphur.

While Cd has only one naturally occurring oxidation state, it is nonetheless affected by redox chemistry. Cadmium has varying affinities for specific oxidation states of certain ligand atoms, most notably sulphur with which it displays its strongest interaction. Cadmium interacts weakly with S\(^6+\) (as SO\(_4^{2-}\)) yet interacts with S\(^2-\), sorbing with FeS and forming insoluble CdS as well as several soluble complexes with bisulphide and various polysulphides (Ste-Marie et al., 1964; Kremling, 1983; Davies-Colley et al., 1985; Gobeil et al., 1987).

**Solid-Phase Associations**

The associations of Cd with most solid-phases are predictably weak. Carbonates, phosphorites (apatites), Fe and Mn oxyhydroxides, organic matter and most clay minerals rely on oxygen (a transition/class A ligand atom) as the principal ligand atom; the class B character of Cd inhibits strong interactions. Conversely, solids containing reduced sulphur (i.e. sulphides) interact strongly with cadmium.

**Carbonates**

The success with which a cation sorbs to calcite depends on how closely its ionic radius matches that of Ca\(^2+\) (Comans and Middleburg, 1987). Cadmium has an ionic radius of 0.97 Å, one of the closest of all metals to the 0.99 Å of Ca\(^2+\) (Weast, 1984). As a result, Cd\(^{2+}\) substitutes into the host calcium carbonate lattice with minimal crystal distortion, yielding one of the highest distribution coefficients amongst the trace metals that proxy for Ca\(^2+\) in calcite (Lorens, 1981). Additionally, Ca and Cd have similar electronic configurations: 4s\(^2\) versus 4d\(^{10}\) 5s\(^2\) respectively (Shen et al., 1987); both elements lose their respective two s-electrons during ionization.

Cadmium sorption to calcite is thought to involve a two stage process: rapid adsorption onto the calcite surface requiring hours to days, followed by a slower crystallization step lasting days to
The first step is suggested to involve rapid adsorption of cadmium to the calcite surface followed by diffusion into a hydrated calcite surface layer. In the slower second stage, a crystalline solid solution of Cd and Ca carbonate forms from the disordered hydrated surface layer (McBride, 1980; Comans and Middleburg, 1987; Davis et al., 1987; Fuller and Davis, 1987). However, it is also likely that during both chemogenic and biogenic carbonate precipitation, Cd is incorporated directly into the carbonate lattice as an analogue for Ca$^{2+}$ during precipitation.

Typical concentrations of Cd within biogenic calcite are as high as 0.1 to 0.8 $\mu$g g$^{-1}$ (Boyle, 1988). Because calcite concentrations in coastal sediments rarely exceed a few percent, it is doubtful that biogenic calcite could act as a significant sink for cadmium. However, in pelagic sediments dominated by calcium carbonate, it is conceivable that carbonates could host a significant fraction of cadmium, as typical Cd concentrations in ocean sediments range from 0.1 to 1.0 $\mu$g g$^{-1}$. Chemogenic calcite on the other hand may support cadmium levels as high as 3 $\mu$g g$^{-1}$ (Davis et al., 1987), suggesting that this phase could act as a sink where free Cd exists for precipitation. However, chemogenic calcite forms most commonly under anoxic conditions, an environment containing sulphide that would presumably precipitate Cd$^{2+}$ as CdS. In such an environment, sulphide will outcompete calcite for sorption of cadmium (Stumm and Morgan, 1981).

**Iron and Manganese Oxides**

Interactions of cadmium with Fe and Mn oxides are not fully understood, mainly because studies of such phenomena employ experimental conditions far removed from those encountered in natural systems (i.e. pure, isolated, solid phases; exceedingly high sorbent and sorbate concentrations; artificial seawater solutions; etc.). However, there is evidence to suggest that cadmium interacts weakly with both Fe and Mn oxides (McCorkle and Klinkhammer, 1991). The absence of a strong interaction is evinced by the effect of major ions on Cd sorption to oxide surfaces. While sulphate enhances adsorption by modifying the oxide surface characteristics, Mg$^{2+}$ has the opposite effect, competing for adsorption sites (Balistrieri and Murray, 1982; Laxen, 1985). Cadmium complexation to oxide surfaces must be weak if major ion interactions with
oxide surfaces, which are typically weak, are able to elicit an influence on Cd sorption. Millwood (1980) and Balistrieri and Murray (1983) showed that Cd desorbs from oxide surfaces when the supporting electrolyte is changed from NaNO₃ to artificial seawater. This suggests that the presence of an anion such as Cl⁻ is sufficient to outcompete the oxide surface for Cd complexation (Tessier et al., 1984). Additional evidence of a weak interaction is seen in the solid phase as the absence of a Cd-enriched surface layer coincident with the ubiquitous Mn- or Fe-oxide layer formed diagenetically; Cd escapes diffusively through oxic surface sediments to the water column unabated by oxide coprecipitation (i.e. Gendron et al., 1986; Gobeil et al., 1987). It could be that the quantity of Cd remobilized is insufficient to manifest a significant increase in oxic solid sediments; indeed, dissolved Cd has been suggested to be removed from solution in some oceanic sediments by oxide scavenging (McCorkle and Klinkhammer, 1991). However, the general observation of no relationship between Cd and diagenetic oxides is consistent with the known chemistry of Cd; sorption to oxygen-containing ligands is weak, and correlations are rarely if ever observed.

To the extent that interactions occur, cadmium is more likely to be associated with Mn oxides than with those of Fe (Oakley, 1981; Davies-Colley et al., 1984; Balistrieri and Murray, 1986). Despite this preference, Cd sorption to Fe oxides is probably more important in most sediments as Fe oxides are usually much more abundant (Balistrieri and Murray, 1986).

**Clay Minerals**

Interactions of cadmium with clay minerals are not well understood; the few experiments performed involved unnaturally high Cd concentrations (e.g. Farrah and Pickering, 1979) or involved modeling of Cd adsorption by ideal clay surfaces (pure-phase isotherm studies; Davies-Colley et al., 1984). The available data suggest that Cd-clay interactions are at best weak; Cd can be displaced from clay mineral surfaces by relatively weak complexation with organics. However, it has also been suggested that Cd adsorption to clay minerals may be enhanced slightly by the presence of adsorbed organic matter acting as a bridge between the clay surface and the Cd²⁺ ion (Chubin and Street, 1981).
It is generally thought that at the pH and ionic strength of seawater, Cd-clay adsorption-strength decreases in the order montmorillonite > illite > chlorite > kaolinite (Farrah and Pickering, 1979; Pickering, 1981). In general, clay minerals and aluminosilicates are probably insignificant sinks for Cd.

**Organic Matter**

The oceanic distribution of cadmium is influenced profoundly by the cycling of soft parts of organisms living within the ocean and sediments. Indeed, the water-column distribution of Cd results from a strong tie between Cd and the synthesis / destruction cycles of organic matter. This is best observed in the strong global correlation between dissolved Cd and phosphate (Boyle et al., 1976; Frew and Hunter, 1992) and is additionally seen as strong correlations between Cd and P within microplankton (Bruland et al., 1978). While the exact relationship between Cd and planktonic organisms is not currently understood, the strong correlation between Cd and organic matter is incontestable (Boyle and Sclater, 1976; Sick and Baptist, 1979; Flatau and Gauthier, 1985; Price and Morel, 1990).

Phytoplankton are now known to accumulate Cd relative to concentrations of the metal in seawater by factors approaching three orders of magnitude, a concentration factor intermediate to class A metals (lower) and transition metals (higher) (Fisher, 1986). It has been suggested that while Cd is not biochemically essential, it may substitute for Zn in certain metalloenzymes under conditions of Zn limitation (Price and Morel, 1990). Additionally, higher trophic levels do not bioaccumulate Cd, yet they have been observed to harbour elevated concentrations of Cd relative to their surrounding environment (Martin and Knauer, 1973; Sick and Baptist, 1979) suggesting that Cd accumulation occurs naturally through the life-cycle of most organisms.

As organic matter is remineralized within the water-column or sediments, it releases Cd; thus, organic matter is usually considered a vector for Cd transport to the sediments rather than a sink. Within the sediments, Cd-organic matter associations have only been inferred near the sediment-water interface where much of the organic-matter remains unoxidized (e.g. Gobeil et al., 1987). Below that zone, organic matter oxidation decouples the relationship and Cd associates
with other solid phases such as authigenic sulphides. Ironically, given the intimate tie between Cd distribution and organic-matter cycles, the interaction between Cd and organic matter is still considered weak. The functional groups that define the vast majority of organic matter are oxygen containing, resulting in class A and transition type ligand atom behaviour. The weak interaction between Cd and organic matter (relative to that of Cu and organic matter) has been explained along these lines (Stumm and Morgan, 1981; Elderfield, 1981). However, organic matter is known to alter significantly during diagenesis; the humification process changes not only the structure of an organic molecule but more importantly the elemental composition, increasing the sulphur content (Francois, 1987; Kohnen, 1989) and decreasing the nitrogen content. It is conceivable that the nature of the Cd-organic matter relationship may change as organic matter ages and incorporates more sulphur (hence class B character) into its structure.

Sulphides

The relationship between Cd and reduced sulphur is particularly strong in light of the behaviour of Cd with other complexing ligands. The Cd-sulphur interaction is manifest in most sulphidic waters by markedly low concentrations of dissolved Cd (Jacobs and Emerson, 1982; Jacobs et al., 1985; Jacobs et al., 1987; Dyrssen and Kremling, 1990). However, in some instances, relatively high steady-state concentrations exist (i.e. Gobeil et al., 1987). This seemingly contradictory behaviour of Cd in sulphidic systems has been ascribed to different aspects of the same elemental chemistry: the Cd-S class B interaction.

Cadmium is for the most part insoluble in sulphidic waters where it has been suggested to form one of three solid-phases: pure CdS, CdS admixed with coprecipitated FeS, or FeS admixed with coprecipitated CdS (Framson and Leckie, 1978; Morse and Arakaki, 1993). Additionally, Cd has been shown to adsorb strongly to a variety of sulphide minerals (i.e. FeS, ZnS and pyrite; Jean and Bancroft, 1986). While pyrite has often been cited as an important solid-phase sink for many trace-metals (i.e. Skei et al., 1988), it appears not to incorporate Cd to a significant degree (Huerta-Diaz and Morse, 1992). Thus, it is conceivable that remobilization of Cd at depth in certain sulphide-bearing sediments is due to ejection of Cd from the Fe-sulphide
system as iron mono-sulphide is converted to pyrite. The liberated Cd may in turn be stabilized by free bisulphide or polysulphide existing in the interstitial waters.

2.2.1.3 Cycling and Distribution

Water Column

Traditionally, cadmium speciation in oxic seawater has been considered to be dominated by chloride complexation (Comans and van Dijk, 1988). However, Bruland (1992) observed strong Cd-DOM interactions within the surface waters of the central North Pacific. While Bruland found that the concentrations of Cd and dissolved organics were exceedingly low, the ligands were specific to Cd and vastly outcompeted complexation by chloride. It seems that this type of interaction is an important influence on open-ocean surface-water Cd speciation. The primary control on Cd distribution within the water column, however, appears to be the inadvertent uptake by organisms in the surface waters of the oceans, in concert with remobilization in deeper waters. This results in the often-observed nutrient-like profile, low dissolved Cd concentrations in surface waters (~0.001 nM) ranging to higher values in deeper waters (0.5 to 1.1 nM), (Boyle et al., 1976; Bruland, 1980; Jacobs et al., 1987; Kremling and Pohl, 1989). There exists a remarkably strong phosphate-Cd correlation in open ocean waters where observations of biogeochemical metal cycles are not clouded by proximal trace-metal inputs. The relationship breaks down in coastal waters where inputs to the water column include aerosols, rivers and sediment remobilization. Surface ocean distributions are controlled by a balance between advected shelf water and aerosol inputs on the one hand, and seasonal removal on the other, primarily via biogenic uptake (Kremling and Pohl, 1989). As a result, the open ocean surface-water Cd distribution appears to have a seasonal signal.

Where a redox boundary occurs in a water column, Cd speciation changes abruptly (e.g. Framvaren Fjord; Black Sea; Baltic Sea; Saanich Inlet; Cariaco Trench), its distribution being dominated not by biological cycles but rather by sulphide chemistry, which results in a marked decrease in concentration of the dissolved fraction in the sulphidic zone (Jacobs and Emerson,
1982; Jacobs et al., 1985; Jacobs et al., 1987; Dyrssen and Kremling, 1990). As in interstitial waters, however, bisulphide or polysulphide complexes appear to play a role in stabilizing dissolved Cd within the anoxic zone of the water column (Kremling, 1983; Brugmann, 1988).

**Sediment**

The distribution of Cd in sediment solids is highly variable, depending on the source of the primary components of the material as well as the nature of Cd accumulation. In general, the single most important parameter influencing Cd content and hence distribution with sediments is the marine organic matter content. Marine organic matter not only represents a significant vector of Cd to the sediments but serves to lower the redox potential, allowing dissolved Cd to become fixed by reduced sulphur within the sediments (Gobeil et al., 1987; Pedersen et al., 1989).

Within sediment interstitial waters it has been suggested that Cd interacts weakly with dissolved organic matter (Elderfield, 1981). Strongly-binding Cd-specific ligands have not yet been observed but may exist within the myriad of dissolved organics present within porewaters. Cadmium interacts strongly with reduced sulphur in the form of bisulphide and various polysulphides. Thus, elevated porewater concentrations of Cd appear to result from two mechanisms: 1. the remineralization of organic matter and subsequent release of Cd to the interstitial waters within surficial sediments; and 2. the stabilization of remobilized Cd by bisulphide and polysulphide complexation in reducing sediments.

The release of Cd through the remineralization of organic matter has been observed frequently (Boyle and Sclater, 1976; Gobeil et al., 1987); however, the stabilization of dissolved Cd in porewaters by reduced-sulphur species is less well known. Dissolved cadmium has been observed to increase in reducing pore waters where there is excess HS\(^{-}\) or polysulphides present (Boulegue, 1983; Daskalakis and Helz, 1992). Presumably, available HS\(^{-}\) and HS\(^{x}\) compete with S\(^{2}\) for Cd complexation, the former drawing Cd into the dissolved phase, the latter to the solid phase. This balance determines the actual behaviour of Cd in any given reducing environment. Unfortunately, in reality, solubility controls are not so clear cut: some reducing systems with high HS\(^{-}\) concentrations yield vanishingly small concentrations of dissolved Cd (e.g. Jacobs et al.,
1985; Lapp and Balzer, 1993). Clearly, the relationship between Cd and reduced sulphur is not so simple. Perhaps very small concentrations of specific polysulphide or thiol species are able to complex Cd in reducing environments, but as of yet, the routine analytical methods utilized to detect reduced sulphur species are neither sensitive nor specific enough to detect such compounds.

2.2.2 Zinc

Ranked fourth of all metals for annual consumption, zinc finds its way into a myriad of industrial applications. Due largely to its chemical versatility, Zn is used in materials ranging from alloys to rubber to pigments. The ubiquitous distribution of this element in the modern world has significantly impaired our ability to study its natural cycles; indeed, most scientific tools are inherently zinc-contaminated. As a result, aqueous samples uncontaminated by Zn have been particularly difficult to collect and analyse. While many workers intend to incorporate Zn in their studies (it is easy to measure by most analytical methodologies), contamination often precludes its inclusion in the final data set. Nonetheless, there is now an increasing inventory of information in the literature.

2.2.2.1 Crustal Abundance and Sources

Zinc is a minor constituent within the earth's crust, occurring in its most concentrated form as sphalerite ((Zn, Fe)S), commonly found in association with galena (PbS). In such deposits it exists in high concentrations (3 to 10 wt.%); however sulphide deposits are relatively rare and as a result, the average concentration of Zn in the crust is much lower (65 to 80 µg g\(^{-1}\); Turekian and Wedepohl, 1961; Wedepohl, 1971; Shuman, 1980).

Zinc is introduced to the oceans naturally through both riverine and atmospheric sources. Rivers deliver a poorly quantified component of Zn weathered from continental rocks (the fluvial input of anthropogenic and natural dissolved Zn is estimated at \(-13 \times 10^9 \) g yr\(^{-1}\); Shiller and Boyle, 1985). Total inputs of natural atmospheric Zn to the world's oceans (\(-45 \times 10^9 \) g yr\(^{-1}\)) originate primarily from: wind-borne soil (\(19 \times 10^9 \) g yr\(^{-1}\)), volcanic activity (\(9.6 \times 10^9 \) g yr\(^{-1}\)) and forest fires.
Anthropogenic zinc arises from many sources, the most significant to the marine environment include domestic waste water and sewage sludge, as well as the smelting, refining and manufacturing of metals. Thus, the primary vectors to the ocean are atmospheric fallout and riverine input. The total input of anthropogenic Zn to the aquatic environment is estimated to be $226 \times 10^9$ g yr$^{-1}$; of this, atmospheric fallout contributes roughly 20 to 30% (Nriagu and Pacyna, 1988). Thus, although anthropogenic introduction of Zn to the atmosphere has been suggested to have fallen off in recent years by a factor as much as 2.5 (Boutron et al., 1991), anthropogenic sources still greatly exceed natural inputs of Zn to the ocean.

2.2.2.2 Metal Description

Zinc, like Cd and Hg, is a group IIB element and is similarly labeled a class B metal. Having a valence electronic configuration of $3d^{10} 4s^2$, Zn preferentially loses its 4s electrons upon ionization and as a result occurs only as Zn$^0$ or Zn$^{2+}$ in natural systems. The lack of vacant 3d orbitals results in an absence of CFSE, and as a consequence, Zn generally forms weaker complexes than its transition metal neighbors; its stereochemistry is determined by electrostatic forces, size and covalent bonding forces (Cotton and Wilkinson, 1980). The class B behaviour of Zn arises from the full 3d orbitals, creating a deformable electron cloud around the nucleus; under external electric fields from adjacent ions, the electron cloud deforms relatively easily. However, Zn is the smallest of the group IIB elements (ionic radius 0.69 Å, cf. 0.92 Å and 0.93 Å for Cd$^{2+}$ and Hg$^{2+}$ respectively) and thus exhibits the least class B character of the three metals; its small, relatively compact size allows it to form complexes with some fluoride- and oxygen-containing ligands (Stumm and Morgan, 1981). Indeed, Zn interacts significantly with many different solid and dissolved phases, behaving at times more like a transition element than a class B metal.

Redox Speciation

Zinc experiences no changes in redox state under natural conditions, but like most metals
is affected by changes in the oxidation state of adjacent ligand atoms. A chalcophilic element, Zn is particularly sensitive to the reduction of sulphur from sulphate to sulphide, with which it forms insoluble precipitates.

**Solid-Phase Associations**

While clays, hydrous oxides and organics appear to be the most important solids for Zn adsorption (Pickering, 1980), sulphides play a critical role in reducing environments. Additionally, biogenic silica appears to be an important phase particularly with respect to the oceanic cycling and distribution of zinc.

**Clay Minerals**

Zinc (primarily Zn$^{2+}$ and Zn(OH)$^+$) is adsorbed strongly by clay minerals through coulombic surface adsorption as well as irreversible sorption into the octahedral layer (Shuman, 1980). Zinc adsorption to clays is dependent on pH, as well as the nature of competing ions and ligands (Farrah and Pickering, 1977). However, zinc-clay interactions do seem to be clay mineral specific; the reaction order for Zn adsorption to various clay minerals is generally thought to be vermiculite $>$ montmorillonite $>$ kaolinite (Shuman, 1980). Interestingly, the amount of Zn sorbed to clays increases in the presence of dissolved Si; the clay surface is thought to adsorb silicic acid (as an amorphous gel) which enhances Zn sorption (Hem, 1972; Willey, 1977; Pickering, 1980). This behaviour is consistent with the association observed between Zn and the siliceous hard-parts of organisms in ocean waters (Bruland et al., 1978; Bruland and Franks, 1983; Bruland, 1989).

**Carbonates**

While the ionic radius of Zn$^{2+}$ (0.69 Å) does not closely match that of Ca$^{2+}$, it is nonetheless incorporated into carbonate minerals at concentrations greatly elevated relative to seawater (Comans and Middleburg, 1987). Both calcite and aragonite are sinks for zinc; during carbonate precipitation, they preferentially acquire Zn:Ca ratios greater than those found in seawater. Indeed, carbonate precipitation may be an important mechanism in governing oceanic Zn budgets. Unlike Cd$^{2+}$, which substitutes for Ca$^{2+}$ due to its similar ionic size, zinc is likely incorporated into calcite and aragonite due to the relative insolubility of ZnCO$_3$ at seawater pH
(Weast, 1986). Additionally, adsorption of Zn to carbonates can be an important mechanism of uptake in sediments as significant fractions of Zn have been observed to associate with the carbonate component in some contaminated deposits (e.g. Hickey and Kittrick, 1984).

**Organic Matter**

Zinc has an unusual affinity for the oxygen-containing functional groups abundant in organic matter, given its class B designation. It is likely the small, compact nature of the zinc ion (relative to the other class B metals) that allows it to behave like a transition metal in the absence of CFSE.

Francois (1988) observed Zn additions to Saanich Inlet sediments via planktonic materials, presumably associated with the organic fraction rather than the siliceous portion. Additionally, work such as that of Westerlund et al., (1986) suggests that Zn in surficial sediments is remobilized by oxidation (presumably of organic matter) rather than reductive dissolution of an oxide phase. Zinc has also been observed to associate with the high molecular weight humic acid fraction of marine sediments (Calvert et al., 1985; Luther et al., 1986). Furthermore, organisms are known to accumulate Zn in their systems to concentrations greater than ambient levels (Knauer and Martin, 1973; Martin and Knauer, 1973); that Zn is a micronutrient central to many enzymes suggests that the metal is capable of interacting significantly with organic matter.

**Silicates**

Zinc has been observed to correlate very strongly with dissolved silicon in the water column of both marine and lacustrine systems. Although the exact relationship has never been completely elucidated, it is most often assumed that Zn is incorporated into the hard-parts of siliceous organisms and subsequently released upon remineralization (Broecker and Peng, 1982; Balistrieri et al., 1992; Reynolds and Hamilton-Taylor, 1992). Zinc forms various insoluble silicates (i.e. Zn$_2$SiO$_4$). Presumably, through the processes of taking up Si to form hard-parts and using Zn as a micronutrient, an organism creates an environment in which the solubility product of zinc silicate is exceeded (Willey, 1977). As a result, Zn is incorporated within biogenic shells.
Sulphides

Solubilities of trace metals in anoxic systems are rarely controlled by the solubility of a single solid phase (Jacobs et al., 1985), and as a result, workers have considered the interactions of competing sorbents. However, sphalerite is considered to be the dominant zinc sulphide species ($K_{sp} = 1.58 \times 10^{-11}$) and is often assumed to control its solubility in reducing environments (Hayashi et al., 1990; Morse and Arakaki, 1993). Sulphide precipitation is often invoked to explain sedimentary zinc enrichments under anoxic conditions as well as Zn depletions in anoxic porewaters and water columns (Skei, 1983; Brügmann, 1988).

Zinc has been observed to adsorb to FeS, pyrite, and pyrrhotite as well as a host of other sulphide minerals in anoxic sediments at typical seawater pH (Jean and Bancroft, 1986; Morse and Arakaki, 1993). With respect to long-term incorporation or coprecipitation of Zn into sulphide minerals, ZnS is a more likely host phase than pyrite (Morse and Arakaki, 1993), although significant associations with pyrite have been observed (Huerta-Díaz and Morse, 1992).

Iron and Manganese Oxides

Perhaps the strongest Zn-sorbing solid phases in oxic sediments are the Fe and Mn oxides (Hickey and Kittrick, 1984). Hydrous oxides complex Zn more strongly than clay minerals (Balistrieri and Murray, 1984) and have been observed to enhance Zn sorption from river water by forming oxide coatings on the surfaces of suspended particles (Grieve and Fletcher, 1977; Johnson, 1986). Additionally, Zn sorbs to oxic sediments enriched in either of the hydrous oxides (Balistrieri and Murray, 1983; Tessier et al., 1985 and 1996; see also Table 2). However, dissolved and solid correlations between Zn and Mn are typically much stronger than those for Fe suggesting that binding to Mn oxides is stronger than complexation by Fe oxide phases (Feely et al, 1983; Graybeal and Heath, 1984; Balistrieri and Murray, 1986; Paulson et al., 1988). Such preferential sorption is confirmed by experiments which show that changes in major ion composition more easily displace Zn from Fe oxides than from Mn oxide phases (Balistrieri and Murray, 1982; Tessier et al., 1985 and 1996).
2.2.2.3 Cycling and Distribution

Water Column

Typical concentrations of dissolved Zn in the water column range from 0.1 to 10 nM (Bruland, 1989). While the details are poorly understood, the distribution of dissolved Zn in the water column is thought to be controlled by the cycling of siliceous hard parts of planktonic organisms. Despite the fact that the oceans everywhere are undersaturated with respect to opal (and Zn-silicate), siliceous organisms have the ability to precipitate silica within their systems, depleting surface waters of both Si and Zn. Because of the ocean-wide undersaturation, siliceous planktonic remains undergo dissolution within the water column but at a lower rate relative to the more labile organic matter in soft parts. The resulting profiles of dissolved Si and Zn correlate very strongly classifying Zn as nutrient-like in character, with a deeper regenerative maximum than that seen for phosphate. The residual inventory of dissolved Zn in surface waters is predominantly associated with dissolved organic matter (Bruland, 1989).

Where Zn profiles cross a redox boundary within a water column (e.g. Cariaco Trench, Saanich Inlet, Framvaren Fjord), the dissolved concentration typically drops to very low values as the metal is drawn out of solution by precipitation as ZnS or by coprecipitation with FeS (e.g. Jacobs et al., 1987).

Sediment

Like any other trace element, the distribution of zinc within coastal sediments is source specific: elevated levels of the metal can arise from certain lithogenic, biogenic, hydrogenous and anthropogenic sources. However, the natural cycles are most strongly dominated by inputs of Zn-bearing marine organic matter (Reynolds and Hamilton-Taylor, 1992). Additionally, high fluxes of organic matter to the sediments favour reducing conditions, which encourage preservation of zinc in authigenic sulphide minerals. Furthermore, the sorption of zinc to Fe and Mn oxides leads to diagenetic cycling of the metal within the oxic and sub-oxic zones of most sediments. Zinc-rich surface layers are often observed associated with diagenetic surficial Mn enrichments (Balistrieri and Murray, 1986).
Porewater

Very few reliable dissolved Zn measurements have been reported for marine porewaters; much of its post-depositional chemistry is based on extrapolation from its general oceanic behaviour. Within surficial sediments, a sub-surface maximum is often observed from the remineralization of organic matter or possibly from dissolution of the silicate matrix of siliceous organisms (Willey, 1977; Bruland, 1989). Zinc is also remobilized at the base of oxic surface layers as Mn oxides undergo reductive dissolution (Balistrieri and Murray, 1984; 1984). Zinc that diffuses away from such maxima may be adsorbed or reprecipitated by Mn and Fe oxides within the oxic zone above the peak or precipitated as a sulphide within the reducing horizons below. Generally, dissolved zinc concentrations remain low within reducing sediments due to the insolubility of metal sulphides. However, dissolved Zn has been observed to increase at depth in some reducing deposits presumably due to complexation by dissolved organic matter, bisulphide or polysulphides (Boulègue, 1983).

2.2.3 Molybdenum

Interest in molybdenum has grown over the years on several levels. Not only is Mo an important metal used industrially in alloys, catalysts and pigments, but it is also an important bio-element required in several enzymes (i.e. nitrate reductase, nitrogenase, xanthene oxidase and aldehyde oxidase). More recently, it has seen use as a paleo-tracer of anoxic water masses (e.g. Emerson and Huested, 1991; Legeleux et al., 1994).

While the generalities of Mo cycling are known (i.e. that it is highly soluble in oxic water yet insoluble under anoxic conditions), specific details of its observed behaviour remain based as much on speculation as on fact.

2.2.3.1 Crustal Abundance and Sources

The highest concentrations of Mo in the lithosphere occur chiefly as molybdenite (MoS₂) but also in some cases as molybdates (such as PbMoO₄). However, these deposits are relatively rare, and the majority of Mo in the lithosphere occurs as isomorphic substitutions for
more abundant elements (Sutulov, 1979) or as microinclusions of MoS₂ within minerals such as feldspar or biotite. As a result, the average crustal abundance of Mo is low, typically 0.5 to 1.5 μg g⁻¹; however, the concentration in average shale is higher (~2.6 μg g⁻¹) probably due to an indirect association with organic matter cycles (discussed below).

**Natural Sources**

Molybdenum enters the marine environment naturally from the continents in association with windblown particles (soil and some biogenic particles) or in eroded continental soil and rock introduced to the rivers (Nriagu and Pacyna, 1988). The dissolved riverine component is presumably derived from solubilization of these components, with dissolved Mo concentrations typically averaging 5 nM in river water (Martin and Meybeck, 1979). Within the oceans, hydrothermal sources are generally presumed to be unimportant - the concentration of Mo in hydrothermal waters differs little from that of seawater (Emerson and Huested, 1991).

**Anthropogenic Sources**

The primary anthropogenic vector of Mo to the oceans is river water; aerosol contributions, which result mainly from the combustion of coal and oil, are relatively small by comparison. River inputs arise from the use of Mo as an alloy in the steel industry as well as its use in catalysts and pigments; additionally, domestic waste-water and sewage sludge can account for large inputs to aquatic systems (Nriagu and Pacyna, 1988). The median value for anthropogenic Mo contributions to the oceans is estimated at ~11 x 10⁹ g yr⁻¹. However, the oceanic inventory is so large (~1.4 x 10¹⁶ g) that such inputs are rarely observable.

**2.2.3.2 Metal Description**

Molybdenum is a 2nd row, group VIB transition metal and has the electronic configuration 4d⁵ 5s¹; its chemistry often resembles that of Cr and W. With a maximum valence of +6, Mo often has a high charge to radius ratio (Mo⁶⁺ = 0.42Å), and as a result hydrolyses easily, characteristically forming an oxyanion in natural oxic waters (Cotton and Wilkinson, 1980; Stumm and Morgan, 1981).
Redox Speciation

Molybdenum exists primarily as MoO$_4^{2-}$ in oxic seawater and to a lesser degree as HMoO$_4^-$. However, like Fe and Mn, Mo is known to undergo changes in oxidation state under different redox conditions. Molybdenum may occupy many oxidation states ranging from 0 to +6; however, thermodynamic data suggest it should have oxidation states of VI in oxic seawater and IV in anoxic environments (Stumm and Morgan, 1981). These states are reflected by the dominance of molybdate in oxic systems as well as the presence of authigenic Mo-sulphide minerals in anoxic sediments.

Solid-Phase Associations

Organic Matter

Molybdenum seems to accumulate preferentially in organic-rich sediments more than most other elements (Contreras et al., 1978; Brumsack and Gieskes, 1983; Calvert et al., 1985; Malcolm, 1985; Francois, 1988; Legeleux et al., 1994; Crusius et al., 1996). However, the Mo-organic association may be indirect and due more to sulphide precipitation in the reducing conditions often associated with organic-rich sediments. While minor amounts of dissolved organic complexation and removal have been observed in estuarine systems (Khan and van den Berg, 1989), and dissolved organic carbon (DOC) is often held responsible for dissolved Mo concentrations in anoxic porewaters (e.g. Elderfield, 1981; Brumsack and Gieskes, 1983; Malcolm, 1985), in all likelihood the Mo-particulate organic matter affinity is probably weaker than that of Mo with other solids such as oxides or sulphides.

Iron and Manganese Oxides

Molybdenum in oxic environments sorbs preferentially to Mn oxides (Berrang and Grill, 1974; Shimmield and Price, 1986). This is unexpected as Mo exists as an oxyanion (MoO$_4^{2-}$) and should not be subject to coulombic interactions. This suggests that sorption of Mo to metal oxides is as much due to surface coordination and metal oxide structure as to coulombic attraction (e.g. Murray and Brewer, 1977). The observation that MoO$_4^{2-}$ appears to be associated with Mn$^{4+}$ rather than total Mn (Shimmield and Price, 1986) is consistent with this idea. When the
redox potential lowers to levels where Mn reduction occurs, Mo (VI) has been suggested to reduce concurrently to Mo (IV). As Mo\(^{4+}\) has no significant affinity for Mn\(^{4+}\), it is released to solution. Furthermore, as both Mn\(^{4+}\) and Mo\(^{6+}\) reduce at the same redox potential, it is conceivable that Mn\(^{2+}\) (reductively released from the oxide surface) outcompetes Mo\(^{4+}\) for complexation to the remaining oxide (Mn\(^{2+}\) has a very strong affinity for Mn-oxide surface sites: Murray et al., 1984).

**Sulphides**

Elevated concentrations of Mo have been associated with anoxic sediments, particularly when such deposits are overlain by anoxic or minimally oxygenated bottom waters (e.g. Saanich Inlet, Framvaren Fjord, Cariaco Trench and the Black Sea) (Francois, 1988).

Under conditions of low redox potential, molybdenum is believed to be reduced to Mo (IV) and then coprecipitated with FeS (Bertine, 1972) rather than precipitating directly as MoS\(_2\) or MoS\(_3\). Korelev (1958) has intimated that Mo has an inability to precipitate directly as a sulphide in seawater, presumably due to the formation of soluble thiomolybdates at a slightly alkaline pH. Rather, during conversion of FeS to pyrite, Mo is thought to be ejected from the monosulphide (Korelev, 1958), and may form crystals or crystallites of MoS\(_2\) or MoS\(_3\). This is consistent with observations of microinclusions of Mo sulphides in sulphide minerals such as pyrite and chalcopyrite (Sutulov, 1979).

As FeS ages to a more crystalline polymorph or to pyrite, Mo is suspected to be ejected from the lattice (due to the large difference in ionic radius between Mo\(^{6+}\) and Fe\(^{2+}\): Bertine, 1972; Contreras et al., 1978; Lyons et al., 1980) either as MoS\(_3\) which may slowly dissolve (Bertine, 1972) or as dissolved Mo which may slowly precipitate as MoS\(_2\) or MoS\(_3\) (Bertine, 1972; Bertine and Turekian, 1973). As a result, the dissolved Mo content is often observed to increase in reducing porewaters. Perhaps where DOM exists, it can stabilize dissolved Mo released from the conversion of FeS to pyrite; a positive correlation has been observed between absorbance at 280 nm and dissolved Mo (Malcolm, 1985). Further, thiooxymolybdates (Mo\(_2\)O\(_6\)S\(_2^2-\) and MoO\(_2\)S\(_2^2-\)) and molybdenum polysulphides (MoS\(_4^{2-}\)) are thought to be stable in dissolved-sulphide
containing porewaters (Bertine, 1972; Lyons et al., 1980). Nonetheless, pyrite is seen to host substantial concentrations of Mo (Jean and Bancroft, 1986; Hyland et al., 1990; Huerta-Diaz and Morse, 1992).

Clays

It has been suggested that certain clay minerals may adsorb a small fraction of Mo within sediments (Bertine, 1972). However, when compared to competing solids such as Mn-oxides and FeS, clay minerals adsorb inconsequential quantities of the metal. To the extent that clay minerals adsorb Mo, kaolinite, montmorillonite and illite are the most likely phases to sorb small fractions of Mo$^{2+}$.

2.2.3.3 Cycling and Distribution

Water Column

The distribution of Mo in the oceans maintains a remarkably uniform ratio to salinity. It is perhaps surprising that Mo, while biologically required, does not exhibit the typical nutrient-like distribution in the water column. It has been suggested that this paradoxical behaviour is due to the large inventory in seawater relative to the minute biological requirement (Collier, 1985; Malcolm, 1985). Indeed, Mo is the most abundant transition element in seawater.

The molybdenum content in anoxic water bodies (Saanich Inlet, Cariaco Trench and others) changes markedly across the oxic-anoxic interface (Jacobs et al., 1987; Emerson and Huested, 1991). Mo (VI) is reduced to Mo(IV) which coprecipitates with FeS. This results in a sharp concentration decrease below the boundary, and contributes to enrichments in the underlying sediments.

Sediments and Porewaters

In most coastal and hemipelagic sediments, Mo contents are high in the surficial, oxic zone, reflecting adsorption onto Mn oxides (Shimmield and Price, 1986). Progressive burial and reductive dissolution of the oxide releases Mo to solution which can diffuse upward to be readsorbed in the Mn precipitation zone, or downward to be fixed by sulphides. Thus, the
chemical principles and transformations that govern the distribution of Mo in the water columns of stratified basins apply in general to the sediments.

The sedimentary Mo content in permanently anoxic basins can reach very high levels (e.g. \( \sim 100 \, \mu g \, g^{-1} \) in Saanich Inlet; Francois, 1988). This is significantly higher than seen in the particulate matter suspended in the deep waters in such basins (Francois, 1988). This contrast is probably due to the nature of Mo accumulation in such deposits. The primary mode of accumulation occurs at the sediment-water interface via sulphide precipitation or coprecipitation with FeS rather than in the water column. This may arise from longer reaction times required to first reduce Mo and then form Mo-S interactions compared to the simple sulphide precipitation for other metals; there is possibly insufficient time in the periodically oxic bottom waters of Saanich Inlet for Mo sulphides to form and accumulate in the surface sediments.

2.2.4 Copper

Copper is one of the most intensely studied trace elements, a result largely of its diverse chemical behaviour. While industry accounts for the wide range of uses and emissions of Cu to the environment, it is the biochemistry of the metal that has inspired much recent research. For example, copper is a micronutrient, a required constituent in many metallo-enzymes, but at high concentrations the element is toxic due to competitive inhibition of other enzyme-required metals (e.g. Brand et al., 1986). Consequently, the last 15 years have seen substantial research invested in the cycling of this trace element.

2.2.4.1 Crustal Abundance and Sources

Cu\(^{2+}\) is capable of limited substitution for Na\(^{+}\), Fe\(^{2+}\) and Mg\(^{2+}\) in many mineral lattices, but it occurs mostly as sulphide inclusions within igneous rocks; upon weathering, it is oxidatively released from its sulphide matrix. As a result, Cu is generally depleted in lithogenic material, averaging 60 to 120 \( \mu g \, g^{-1} \) for the most common igneous rocks; ultra-mafic rocks contain much more Cu than the felsic end of the series (Krauskopf, 1979; Cox, 1979). Quartz and K-feldspar, two important minerals often found in coastal sediments, are noticeably depleted in Cu, hosting
levels in the 1 to 5 \( \mu g \ g^{-1} \) range (Cox, 1979). Copper is also known to occur as native metal, chlorides, carbonates and oxides (Cotton and Wilkinson, 1980).

Copper is introduced naturally to the oceans through riverine and aerosol inputs. Atmospheric fallout of biogenic particles, wind-blown dusts and seasalt sprays account for approximately half of the aerosol component; the remainder is anthropogenic (Nriagu and Pacyna, 1988; Nriagu, 1989). River waters contribute substantial quantities of dissolved Cu to the oceans; natural concentrations of Cu in lakes and rivers have been estimated to be \( \sim 2 \ \mu g \ g^{-1} \) (Nriagu, 1979; Nriagu and Pacyna, 1988). However, dissolved Cu in river water is susceptible to many precipitation reactions in estuaries (Sholkovitz and Copland, 1981) and, as a result, the fraction of this material that escapes to the open ocean is not well constrained.

The principal source of anthropogenic Cu to the ocean is industrial and domestic waste (Nriagu and Pacyna, 1988), while mineral leaching and industrial plating provide significant point source inputs (Manahan, 1979). Atmospheric deposition of anthropogenic Cu to the oceans arises principally through mining and mineral processing. However, this component accounts for only 20% of the total anthropogenic input to the oceans (Nriagu and Pacyna, 1988); waste water is the dominant vector.

### 2.2.4.2 Metal Description

Copper is a first row transition element and has the electronic configuration \( 3d^{10} \ 4s^{1} \). As a result, the metal exists in nature in either the +1 or +2 oxidation state by losing its lone s electron followed by one of its d electrons. The third ionization energy is markedly higher than the second and as a result \( Cu^{3+} \) does not occur naturally. Because the d orbitals of Cu are not as penetrating as they are in other elements, the outer s electron is not as shielded from the nucleus. Consequently, the first two ionization energies do not differ substantially, and as a result, both electrons are typically lost with \( Cu(II) \) being the most common oxidation state for the element (Cotton and Wilkinson, 1980). The electronic configuration of \( Cu^{2+} \) is \( 3d^{9} \), thus, some complexes are stabilized by CFSE. Because \( Cu^{2+} \) has a \( d^{9} \) configuration, it is first in the Irving-Williams order.
(Stumm and Morgan, 1981) and therefore preferentially complexes with ligands containing oxygen ligand atoms, particularly in the form of organic matter and metal oxides.

**Solid-Phase Associations**

Copper associates relatively strongly with many naturally-occurring solid phases: it forms soluble complexes and insoluble sulphides with reduced sulphur, and is also known to associate to varying degrees with Fe and Mn oxyhydroxides as well as with clay minerals and carbonates. However, the well recognized affiliation of Cu with organic matter in natural sediments is arguably the most important. These associations are described below.

**Sulphides**

Copper is highly reactive in the presence of reduced sulphur, forming insoluble sulphides such as CuS (covellite is one of the least soluble sulphides; Morse and Arakaki, 1993) or Fe(Cu)S₂ (chalcopyrite).

Because mackinawite is metastable to pyrite and does not persist in most sediments, the incorporation of most trace metals (including Cu) into iron mono-sulphide is considered a transient process (Morse and Arakaki, 1993) that is confined to near-surface sediments. Authigenic pyrite has been observed to host moderate amounts of Cu (relative to Cu, less Cd and more Mo are incorporated; Huerta-Diaz and Morse, 1992). The degree of incorporation of Cu into pyrite is proportional to the degree of pyritization of the sediments (Huerta-Diaz and Morse, 1992), but since it also depends on the availability of dissolved Cu, the association of copper with organic matter may enhance incorporation by releasing dissolved Cu to interstitial waters in the zone where pyrite is forming (i.e. below the zone where FeS dominates) (Huerta-Diaz and Morse, 1992). Skei et al. (1988) observed enrichments of non-leachable Cu (non acid soluble) in the sediments of anoxic Framvaren Fjord as well as concentrations of ~0.5 % Cu in framboidal pyrite forming in the water column, suggesting that while mono-sulphides may host substantial concentrations of Cu, pyrite can account for a large fraction of the enrichments of Cu often found in anoxic sediments.

**Oxides**
The transition metal character of Cu allows it to interact strongly with oxygen-containing ligands. Consequently, Cu complexes strongly with metal oxides, particularly those of Fe and Mn (Stumm and Morgan, 1981). Sorption experiments have displayed strong interactions between Cu and both Fe and Mn oxides. Balistrieri and Murray (1983) demonstrated that Cu was strongly adsorbed to goethite in seawater at pH >5 while Hem et al. (1989) showed that Cu associated with Mn-oxides as a mixed oxide such as Cu$_2$Mn$_3$O$_8$ admixed with βMnOOH.

Manganese oxides have been observed to scavenge Cu in the water column (Feely et al., 1983). Additionally, Sawlan and Murray (1983) observed Cu remobilization at the base of the Mn-enriched layer in hemipelagic sediments. However, while Cu adsorption to oxides is viewed as an important scavenging mechanism (Tessier et al., 1996), many authors have indicated it is not as strong an interaction as that between copper and organic matter (Tessier et al., 1985; Paulson et al., 1988).

The interaction of Cu with Mn oxides appears to occur on two levels. Many workers have observed interactions where the oxygen of the oxide have acted as the ligand atom. However, Hem et al. (1989) noted changes in the amount of sorbed Cu as the oxidation state of the Mn changed, suggesting that Mn had a direct role to play in Cu complexation. Some fraction of Cu may behave in a similar fashion to Mo with regard to Mn-oxide sorption.

**Clays**

More than most other trace metals, Cu has been observed to associate with clay minerals. This association has been described in many cases as indirect; organic matter that ubiquitously coats all marine particles (i.e. Davis, 1984) also associates strongly with Cu (Goodman et al., 1984). However, Cu is known to adsorb into the interlayer sites of montmorillonite during diagenesis (Goodman et al., 1984; Pedersen et al., 1986). Pedersen et al., (1986) suggested that in slowly accumulation pelagic sediments, authigenic nontronite could host substantial inventories of Cu, in some cases more than oxyhydroxides. Similarly, chlorite and vermiculite have been noted to host significant concentrations of Cu (Cox, 1979).

**Organic Matter**
Whereas Cu(I) is known to form Cu-C covalent bonds, the divalent Cu(II) does not. Nonetheless, Cu$^{2+}$ interacts very strongly with organic matter (Cotton and Wilkinson, 1980). Such behaviour arises from the transition metal behaviour of Cu in concert with its propensity to complex with oxygen-containing ligands. The dominance of oxygen functional groups in bulk organic matter accounts for the strong interactions with Cu.

Sediment enrichments of Cu have been observed where high concentrations of humic substances exist; direct associations have been observed (Calvert et al., 1985). Marine plants and organisms have been suggested to contain 3.5 and 1.0 $\mu$g g$^{-1}$, respectively (Nriagu, 1979); indeed, Noriki and Tsunogai (1992) have suggested that the Cu content in planktonic matter could be as high as 20 $\mu$g g$^{-1}$. However, the concentration of Cu in organic floc at the sediment-water interface of deep sea sediments has been measured as high as 3017 $\mu$g g$^{-1}$, while the actual concentration below the sediment-water interface was much lower (Balistrieri and Murray, 1984). This suggests that particulate organic matter has a strong affinity for scavenging Cu from the water column (Fisher et al., 1986) and that it is intensely recycled at the sediment-water interface.

2.2.4.3 Cycling and Distribution

Water Column

The distribution of Cu in the water column, while nutrient-like, is not actually controlled by biogeochemical cycles as are elements such as Cd and Zn. Indeed, natural concentrations of Cu in recently upwelled seawater have been reported to be toxic to surface-dwelling phytoplankton (Brand et al., 1986). Low surface water values are induced by scavenging onto particulate material, particularly organic material, and elevated deep water concentrations result from release of dissolved Cu from within the sediments; the picture is complicated by scavenging in intermediate and deep waters (Bruland, 1980).
Sediments and Porewater

The distribution and accumulation of Cu in sediments is generally considered to be influenced by three factors. First, organic-rich sediments often host large inventories of adsorbed or scavenged Cu (Francois, 1988). Second, Cu is strongly enriched in deposits underlying anoxic water bodies where the metal is rapidly precipitated in the water column as a particulate sulphide and settles to the basin floor (Francois, 1988; Skei, 1988). Third, the distribution of Cu within surface sediments is often restructured somewhat through the post-depositional recycling associated with Fe and Mn oxides in oxic and suboxic zones (Balistrieri and Murray, 1982, 1984; Tessier et al., 1988).

Profiles of dissolved Cu in the porewaters of coastal sediments show that Cu is generally released to the interstitial waters of near-surface sediments and consumed at depth. This distribution is most often attributed to subsurface release as organic matter is remineralized immediately below the sediment-water interface (Klinkhammer, 1980; Pedersen et al., 1986). The localized release establishes concentration gradients both above and below the dissolved maximum. Upward diffusing Cu can migrate across the sediment-water interface to return to the water column or can in part be fixed by recycled Fe or Mn oxides within the surface sediments. That fraction that diffuses downward is most often precipitated by sulphides at depth.

Despite the thermodynamic insolubility of Cu(II) in the presence of dissolved sulphide, dissolved Cu is occasionally seen to exist in anoxic waters. Davies-Colley et al. (1985) have suggested that polysulphides can stabilize dissolved concentrations of Cu(I); thus is possible that such inventories are dominated by Cu(I). Additionally, they suggested that when concentrations of dissolved sulphide in porewaters were >10^{-3} M, Cu^{+} was stabilized by bisulphide completion and anoxic sediments could act as a source of dissolved Cu. Additionally, dissolved organic matter has been suggested by many investigators to stabilize significant concentrations of dissolved Cu in both oxic and anoxic porewaters (Elderfield, 1981).
Chapter Three - Results and Discussions

The diagenetic status of the sediments of each inlet discussed in this thesis is expected to reflect a range of geochemical conditions imposed primarily by hydrography. Although geochemical variability on a broad scale may be minimal within individual inlets, some variability within cores is often observed. Few sediment cores actually fit the steady-state paradigm of geochemical theory - many contain episodes of non-steady state accumulation (e.g. turbidites, changes in the type of organic material). It is critical that consideration of non-steady-state be borne in mind while interpreting interstitial water data (indeed, steady state is often a fundamental assumption central to many interpretations). Fortunately, even though the solid phase may not be in equilibrium with the surrounding environment, the associated interstitial water often reaches "meta-stability" with the solid phase within relatively short time frames. For interpretative purposes, "pseudo-equilibrium" is assumed between interstitial waters and the adjacent solid sediments. In this chapter, the data from several hydrographically distinct inlets are presented and discussed in order to establish a framework for the interpretation in Chapter Four of the controls on the behaviour of specific metals. Core collection, sample handling and analytical methods are described in Appendices I through III, and all data are listed in Appendix VI.

3.1 Ucluelet Inlet

3.1.1 Inlet Description and Core Locations

Ucluelet Inlet is located on the northwest corner of Barkley Sound, southwestern Vancouver Island, and is immediately adjacent to the Pacific Ocean (Figure 1). The inlet is small (approximately 8 km long by 0.5 to 1 km wide) and shallow, hosting mean and maximum depths of 10 m and 25 m respectively. There are few to no hydrographic data available for Ucluelet Inlet; however, given a 5 m tidal prism in concert with its shallow basin, the water column must be well mixed. Ucluelet Inlet sediments reflect tidal sorting, displaying barren rock and very coarse-grained sands and gravels near the inlet mouth where tidal currents are strongest, whilst the deposits at the head of the inlet are dominated by fine-grained mud-flats.
Figure 1 Station locations map for Ucluelet Inlet, British Columbia
Fresh water inflow to the inlet is low ($1.3 \times 10^8 \text{ m}^3 \text{ yr}^{-1}$) despite receiving the highest annual recorded rainfall in Canada ($3.3 \text{ m}$). This apparent paradox arises from the fact that Ucluelet Inlet receives fresh waters from a few small streams that drain a very small ($43 \text{ km}^2$) watershed (Pedersen and Waters, 1987). The inlet receives a correspondingly small input of lithogenous material.

The Ucluelet area is considered relatively pristine; the first significant industrial activity occurred after WW II with the establishment of more intensive logging practices. Since that time, fishing, logging and limited mining have made up the bulk of activity in the region; however, none of these have contributed substantially to the trace-metal inventories within the inlet (Pedersen and Waters, 1987).

Core locations for Ucluelet Inlet (Figure 1) were selected to match the previous locations of Pedersen et al. (1989), and to sample a representative cross-section of sedimentary facies within the basin. Three cores were collected: U-1, located mid-inlet in a shallow depression (~10 m water depth); U-2, located toward the inlet head, at the shallow site of core S3.1 (~7 m water depth) of Pedersen et al. (1989), and U-3, raised from a depth of 10 m near the inlet mouth. Unfortunately, the sediments at U-2 were determined to have been disturbed very recently based on $^{210}\text{Pb}$ profiles, while those of U-3 consisted mainly of shell hash. Consequently, only core U-1 is discussed in detail.

### 3.1.2 Stratigraphy

Core U-1 has a well-mixed surface layer on the order of 4 to 5 cm thick as reflected by excess $^{210}\text{Pb}$ data (Figure 2(a)). Below 4.5 cm, the decline in excess $^{210}\text{Pb}$ activity corresponds to a sedimentation rate of ~$0.3 \text{ cm yr}^{-1}$. This estimate agrees well with that published previously ($0.28 \text{ cm yr}^{-1})$ and is based on the assumption that the supported $^{210}\text{Pb}$ is 0.5 dpm g$^{-1}$ (Pedersen et al., 1989). Sedimentation rate was determined as described in Appendix IV using the porosity data shown in Figure 2(b) for decompacting the depth scale; these data were collected at the same site and reported by Pedersen et al. (1989).
A discontinuity at ~9 cm depth (~16 cm decompacted depth) is observable in both the $^{210}$Pb data and in profiles of organic parameters in the core (Figure 3). Above the discontinuity, the organic carbon content is elevated (3.8 to 4.5 wt.%) relative to below. Commensurate increases and decreases are seen in the $C_{org}$:N weight ratio and $\delta^{13}$C values, respectively, suggesting that the increase in organic carbon arises from increased accumulation of terrestrial organic matter. The reversal of all three parameters toward the sediment-water interface suggests that recent additions of terrestrial organic matter have decreased.

Assuming a sedimentation rate for core U-1 of 0.3 cm yr$^{-1}$, the original change in the nature of deposition would have occurred in the late 1940's. This is coincident with the onset of logging in the area that commenced during the post-war years (Pedersen and Waters, 1987). It is suggested that the inception of logging increased the input of terrestrial organic matter as indicated by higher mean $C_{org}$:N weight ratios and slightly lighter $\delta^{13}$C values above 6.5 cm depth.
3.1.3 Diagenetic Description

Ucluelet Inlet sediments contain unusually high $C_{\text{org}}$ concentrations given the rather low sedimentation rate (Figure 3). The organic matter is predominantly marine in origin as evinced by its low $C_{\text{org}}/N$ weight ratios and heavy $\delta^{13}C$ values (Figure 3(b)). It has been suggested by Pedersen et al. (1989) that the preferential accumulation of marine organic matter in Ucluelet Inlet occurs via net landward transport of fine-grained, organic-rich material on the flood tide in concert with a low input of stream-borne lithogenous material. This premise is corroborated by the occurrence of mud-flats at the head of the inlet.

The high content of labile organic matter in Ucluelet Inlet drives an oxidant demand sufficient to create sub-oxic to anoxic conditions very near the sediment-water interface, despite the presence of a shallow, well-mixed water column above. The behaviour of solid and dissolved Fe and Mn in U-1 reflects this. Solid-phase Fe displays a very slight enrichment (Figure 4(a))

Figure 3 (a) organic carbon and (b) $\delta^{13}C$ and $C_{\text{org}}/N$ weight ratio for the sediments of core U-1.
suggesting an oxide phase is scarce in the near surface deposits, and that much of the Fe in Ucluelet Inlet is detrital in origin. This is corroborated by the dissolved Fe profile which displays a distinct sub-surface maximum at ~2 cm depth followed by near quantitative removal, presumably by sulphide precipitation, towards the bottom of the core. Sulphide data from Core U-1 agree in that dissolved sulphide is not detectable until dissolved Fe is removed from solution (Figure 4(a)), reflecting the relative rates of production and consumption of Fe(II) and sulphide with changing redox potential.

![Solid-Phase Fe (wt.%) and Mn/Al weight ratio](image)

Figure 4 (a) Dissolved Fe and $\sum H_2S$ and (b) Mn/Al and dissolved Mn in core U-1, Ucluelet Inlet.

Solid-phase Mn is uniform throughout the core, while dissolved Mn displays a subsurface maximum of <2 $\mu M$ at ~5 cm depth (Figure 4). The lack of a Mn surface enrichment in concert with minimal concentrations of dissolved Mn (two orders of magnitude lower than dissolved Fe) suggests that there is little Mn-oxide available for reduction in these sediments. The contrast between the two oxides could arise from the presence of suboxic conditions at the sediment surface and the different precipitation kinetics of Fe$^{2+}$ and Mn$^{2+}$. Because dissolved Fe reacts
very quickly with molecular oxygen at pH 8 (Stumm and Morgan, 1981), upward-diffusing Fe$^{2+}$ cannot readily migrate into bottom waters. However, dissolved manganese precipitates as MnO$_2$ much more slowly where oxygen is encountered, and this may have allowed a much larger proportion of the remobilized manganese to diffuse out of the deposits and into the overlying water column.

### 3.1.4 Metal Behaviour

#### 3.1.4.1 Cadmium

Cadmium is enriched in the sediments of Ucluelet Inlet relative to other typical, coastal regimes (Simpson, 1981; Gobeil et al., 1987; Pedersen et al., 1989). In core U-1, solid-phase Cd concentrations are relatively constant at ~2.2 μg g$^{-1}$ in the upper layer and ~3.4 μg g$^{-1}$ in the lower layer (Figure 5).

![Figure 5 Solid-phase Cd in core U-1.](image)

Three fractions: lithogenic, biogenic and authigenic, typically account for the majority of Cd in coastal marine sediments. The proportion of lithogenic Cd (silicate lattice-bound) in Ucluelet
Inlet is largely unknown. Stream sediment concentrations have been measured and range from 0.1 to 0.5 μg g\(^{-1}\) (Pedersen and Waters, 1987). Marine organic matter typically contains \(~10\) μg g\(^{-1}\) Cd (Knauer and Martin, 1973; Bruland, 1978) and could potentially account for a significant fraction of the Cd in Ucluelet sediments given the abundance of organic material. However, because the concentration of Cd in the deposits is unusually high, it has been suggested that authigenic accumulation may give rise to a substantial fraction of the total (Pedersen et al., 1989).

Dissolved cadmium in core U-1 decreases in concentration from bottom water (~0.8 nM) into surficial sediments, reaching its lowest concentration (0.05 to 0.1 nM) by depths of 5 to 10 cm (Figure 6).

![Dissolved Cd concentrations and model fits in core U-1.](image)

The concave downward profiles (most pronounced in the upper few centimetres) suggests maximum consumption in near-surface sediments, presumably by precipitation as CdS or coprecipitation by FeS (i.e. Davies-Colley et al., 1985). The relative magnitude of authigenic Cd
as a source to the sediments is tested below by calculating the diffusive flux and corresponding accumulation rate. Flux calculations (Appendix V) were performed using a simple linear diffusion model (based on Fick's first law) as well as a diffusion/first-order consumption model (after Lerman, 1977). The results (Table 3) are compared to Cd accumulation rates estimated from solid-phase Cd concentrations, sedimentation rate and porosity data. The model fit to the data is shown in Figure 6.

Authigenic Cd was estimated for U-1 by normalizing solid-phase Cd to Al to account for dilution by lithogenic detritus. Aluminum is used as a element of normalization because it exists almost exclusively in association with terrestrial material. The increase in the Cd/Al weight ratio over the first 2.5 cm of U-1 (the same interval occupied by the steep concentration gradient in pore water) was assumed to be authigenic in origin (Figure 7). The proportionate increase in Cd/Al was converted to an absolute concentration (0.21 μg g⁻¹) which was in turn used to calculate the recent authigenic accumulation rate via:

\[ AR = (\omega)(1 - \phi)(\rho_g)\langle [Cd]\rangle \]  

where \( \omega \) = the bulk sedimentation rate (0.3 cm yr⁻¹); \( \phi \) = the interfacial porosity (assumed to be 0.9); \( \rho_g \) = bulk grain density (assumed 2.4 g cm⁻³); and \( [Cd] \) = the accumulated concentration of Cd in excess of the lithogenic and biogenic background.

The diffusive fluxes calculated by both models yields consistent results (Table 3; see Appendix V for a detailed description of each model). Additionally, the recent accumulation rate of Cd (based on the observed enrichment and the sedimentation rate) is close to the calculated fluxes suggesting that the assumptions are reasonable and that the observed relative enrichment in the upper 2.5 cm can be explained by diffusion from bottom water.
Table 3 Cadmium accumulation rates as derived from the linear flux model, the diffusion-consumption model and equation (1).

<table>
<thead>
<tr>
<th></th>
<th>Linear Flux Model</th>
<th>Diffusion-Consumption Model</th>
<th>Accumulation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core U-1</td>
<td>0.014 µg cm(^{-2}) yr(^{-1})</td>
<td>0.013 µg cm(^{-2}) yr(^{-1})</td>
<td>0.015 µg cm(^{-2}) yr(^{-1})</td>
</tr>
</tbody>
</table>

Assuming steady-state, the absolute magnitude of the authigenic Cd enrichment resulting from diffusion from bottom water is determined from the flux estimate of Table 3 (0.013 µg g\(^{-1}\) yr\(^{-1}\)) and equation (1) with the same values for \(\phi\) and \(\rho_g\). Approximately 0.18 µg g\(^{-1}\) of the 2.2 µg g\(^{-1}\) inventory can be accounted for by diffusive additions from bottom water. Assuming that the lithogenic contribution of Cd to the inlet sediments is small (e.g. < 0.5 µg g\(^{-1}\)) then either a large fraction of Cd in U-1 must be associated with the biogenic fraction or the steady-state assumption is incorrect. These possibilities will be examined in Chapter Four.
3.1.4.2 Copper

Solid-phase Cu in core U-1 exhibits a concentration range typical of the lithogenic background in many coastal sediments (i.e. Willey and Fitzgerald, 1980; Ridgway and Price, 1987), ranging from 20 to 30 \( \mu g \) \( g^{-1} \) throughout the core (Figure 8).

Dissolved Cu increases from bottom water values of 6 nM to a subsurface maximum (66 nM) ~1.25 cm below the sediment-water interface. Below that depth the metal is consumed by a solid phase as indicated by a precipitous decline to values of ~10 nM (Figure 8). This distribution may arise from the association of copper with organic matter and the release of Cu to porewaters upon remineralization; diffusion both upward toward the water column and downward to more strongly reducing sediments could produce the observed profile. However, it is also possible that Cu is in part remobilized through reductive dissolution of Fe oxides, as the dissolved Fe maximum overlaps to a large degree with the dissolved Cu maximum. The sink below 2 cm is almost

Figure 8  (a) Solid and dissolved Cu and (b) \( \Sigma H_2S \), dissolved Fe and Cu/Al weight ratio in core U-1, Ucluelet Inlet.
certainly sulphide precipitation as suggested by the appearance of free sulphide immediately below the zone of consumption and the commensurate decrease in dissolved Fe over the same interval (Figure 8).

That dissolved Cu never reaches undetectable concentrations at depth in core U-1 probably reflects several factors. First, Cu remobilization likely arises from both oxide dissolution and organic remineralization. Dissolved Fe persists throughout the majority of the core most likely as a result of residual quantities of reducible Fe-oxides becoming buried within the sulphate reduction zone; \( \text{H}_2\text{S} \) is not produced in sufficient quantities in the upper 9 cm to remove all of the Fe produced from oxide dissolution. Release of Cu from both Fe oxides and organic matter in concert with limited concentrations of free sulphide allows Cu to persist in solution at depth in core U-1. Second, complexation by polysulphides may occur at depth resulting in retention of measurable dissolved Cu (e.g. Shea and Helz, 1988). Third, complexation by dissolved organic matter (DOM observed within the core as a characteristic yellow colouration of the porewaters and a tendency to rapidly clog 0.45 μm filters), may protect dissolved Cu from precipitation by competing with sulphide.

Authigenic Cu in Ucluelet sediments accumulates via a mechanism different from that of authigenic Cd, in that Cu does not diffuse into the deposits directly from bottom waters. Rather, Cu diffuses out of the sediments to the water column and downward from a sub-surface maximum as discussed above, and as seen in other coastal basins (i.e. Heggie et al., 1987). Thus, authigenic Cu represents that fraction that undergoes a transition from an organic matter host to an authigenic solid such as an oxide or sulphide. Figure 8 indicates approximately equal concentration gradients upward and downward of 4.5 ng cm\(^{-4}\), suggesting that roughly half of the Cu associated with the subsurface release is returned to the water column; however, decreasing porosity with depth will minimize the downward flux relative to that above. Assuming a diffusion coefficient corrected for porosity and tortuosity of 100 cm\(^{2}\) yr\(^{-1}\) (Li and Gregory, 1974), the estimated downward flux is 0.45 \(\mu\)g cm\(^{-2}\) yr\(^{-1}\). Using this value as an accumulation rate and assuming a sedimentation rate of 0.3 cm yr\(^{-1}\), a bulk grain density of 2.4 g cm\(^{-3}\) and porosity of 0.9,
yields an authigenic concentration of ~6.3 µg g⁻¹. A similar quantity of Cu is presumably lost to the water column or to oxide precipitation through diffusion along the concentration gradient towards the sediment-water interface. Although remobilization of Cu to this degree is conceivable, the solid phase distribution between 1.5 and 2 cm depth does not reflect such a restructuring. As Cu has a profound affinity for organic material, using a diffusion coefficient for uncomplexed Cu²⁺ (i.e. Li and Gregory, 1974) undoubtedly results in an overestimate of the diffusive flux. It has been suggested by Elderfield (1981a) that complexation of Cu by dissolved organic matter ranging from 2000 to 300,000 amu (i.e. 20 to 100 Å; a fraction which readily passes through a 0.45 µm filter) may retard the diffusion of dissolved Cu by one to two orders of magnitude. Consequently, the accumulation of authigenic Cu inferred from the observed concentration gradients is almost certainly overestimated, and this can explain the disagreement between the calculated addition at depth and the measured solid-phase Cu profile.

3.1.4.3 Molybdenum

Solid phase Mo in core U-1 increases in concentration from 0.6 µg g⁻¹ at the sediment-water interface (a value lower than that typically observed in shales, ~2.6 µg g⁻¹; Turekian and Wedepohl, 1961) to values as high as 4 µg g⁻¹ at the base of the core (Figure 9). Because the concentration of Mo increases with depth, it has been suggested that it accumulates by diffusion from bottom water followed by solid-phase fixation as described by Pedersen et al. (1989). The dissolved Mo profile supports this premise indicating diffusion down a near-linear concentration gradient from a bottom water concentration of ~150 nM to a concentration of 50 nM at 5.5 cm depth. Below this level, dissolved Mo increases to the base of the core reaching concentrations >200 nM by 13 cm depth.

The dissolved Mo minimum at approximately 5 cm depth (Figure 9) implies precipitation with or adsorption to FeS (i.e. Bertine, 1972). The distribution of dissolved Fe (Figure 4) is consistent with this mechanism, indicating removal from pore water below depths of 2 cm. Because Ucluelet Inlet sediments are Mn starved and sub-oxic very near the sediment water interface, it is unlikely that Mn-oxides influence the distribution of Mo within this deposit.
The general increase in dissolved Mo between 5.5 cm and the base of the core suggests that a source exists at depths ≥11 cm, or that the metal is being returned to solution below 6 cm from an unstable solid phase. A likely contributor is the dissolution of a metastable solid, perhaps FeS as it converts to the more stable pyrite (Korelev, 1958). In the absence of abundant H₂S, Mo released in such a fashion will not rapidly reprecipitate. Indeed, dissolved Mo appears to decrease only when the concentration of H₂S becomes substantial (at 13 cm depth, ΣH₂S >300 μM; Figure 9). It is also possible that dissolved Mo at depth is stabilized by DOM in the porewaters (Malcolm, 1985) further inhibiting precipitation in the presence of low concentrations of free H₂S.

While organic matter has been implicated in Mo transport to sediments (Shaw et al., 1990), direct biogenic association is generally considered to be unimportant (Collier, 1985). Rather, the elevated concentration of dissolved Mo in seawater and anoxic conditions very near the sediment-water interface in Ucluelet Inlet suggest that diffusion from bottom waters into the
sediments followed by authigenic precipitation is the most likely mechanism that can account for the observed solid-phase Mo enrichments. This will be considered below.

The dissolved Mo concentration gradient into the sediments from bottom waters is approximately $2.4 \times 10^{-9}$ g cm$^{-4}$ in core U-1 (Figure 9). Assuming a diffusion coefficient (corrected for porosity and tortuosity) of 220 cm$^2$ yr$^{-1}$ (Li and Gregory, 1974), the Mo influx is estimated to be 0.53 $\mu$g cm$^{-2}$ yr$^{-1}$. Using this value as an accumulation rate for authigenic Mo, and assuming the previous values for $\omega$, $\phi$ and $\rho$$_{grain}$ yields an authigenic contribution of $-7.3$ $\mu$g g$^{-1}$ Mo. This value is at least twice the maximum enrichment observed in the core, suggesting that authigenic additions of Mo should indeed be significant in these deposits. As in the case for Cu, the overestimate probably results from the failure to account for complexation by dissolved organic matter, which would produce a smaller effective diffusion coefficient (Elderfield, 1981).

Assuming steady state, Mo enrichment arising from a diffusive flux into the sediments should occur in the same depth interval as the concentration gradient. The enrichment observed over the upper five cm of core U-1 ($-1.5$ $\mu$g g$^{-1}$) corresponds spatially to the Mo concentration gradient into the sediments (Figure 9). Assuming that the enrichment is due to authigenic precipitation alone, an operational diffusion coefficient can be determined by back calculation. This assumption-dependent calculation yields a revised accumulation rate of $-0.11$ $\mu$g cm$^{-2}$ yr$^{-1}$, and a diffusion coefficient, presumably corrected for organic complexation, of $-45$ cm$^2$ yr$^{-1}$.

3.1.4.4 Zinc

Solid-phase Zn in core U-1 increases in concentration with depth from $-80$ $\mu$g g$^{-1}$ at the sediment-water interface to $-100$ $\mu$g g$^{-1}$ at 13 cm depth (typical crustal values range from 65 to 80 $\mu$g g$^{-1}$; Turekian and Wedepohl, 1961). Dissolved Zn increases dramatically from a bottom water concentration of 60 nM to a maximum of 400 nM within the upper 0.5 cm horizon (Figure 10). The concave-downward decline below this maximum indicates near quantitative consumption by 6.5 cm depth. The coincidence of sulphate reduction through this zone suggests that, like Cd and Cu, Zn is consumed by sulphide precipitation.
The Zn/Al weight ratio indicates an enrichment in Zn within the upper several cm of core U-1. Assuming steady state, it is possible that this enrichment is authigenic, derived from the observed flux into the sediments from remobilization at the sediment-water interface (Figure 10). The increase indicated by the change in the Zn/Al weight ratio over the upper four cm (2.5 x 10^{-4}) corrected for Al (~7 wt.%; Appendix VI) is ~18 μg g^{-1}. Using a diffusion coefficient for Zn of 120 cm^2 yr^{-1} (Li and Gregory, 1974), the diffusion-consumption model (Figure 10) yields a downward flux estimate of ~49 nmol cm^{-2} yr^{-1} or 3.2 μg cm^{-2} yr^{-1}, while the linear flux model yields 3.1 μg cm^{-2} yr^{-1}. Assuming the same values for porosity, sedimentation rate, and bulk grain density used previously, such an influx would add ~44 μg g^{-1} of authigenic Zn to the sediments.

This estimate is approximately 2.5 times greater than the concentration increase implied by the Zn/Al weight ratio over the upper few centimetres of this core. This suggests that the enrichment can indeed be accounted for by authigenic accumulation and implies that the Zn

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**Figure 10** (a) Zn/Al weight ratio and (b) solid and dissolved Zn in core U-1, Ucluelet Inlet.
diffusion coefficient requires correction for organic complexation by at least the same factor; the effective diffusion coefficient indicated by the data is therefore $\leq 60 \text{ cm}^2 \text{ yr}^{-1}$.

### 3.2 Knight Inlet

#### 3.2.1 Inlet Description and Core Locations

Knight Inlet is situated ~300 km north of Vancouver and is connected to the Pacific Ocean through Queen Charlotte Strait (Figure 11). Because of its remoteness, the inlet can be considered to be relatively pristine.

Knight Inlet is a typical B.C. fjord: deep (mean and maximum depths of 298 and 540 m respectively), narrow (2-3 km wide), long (80 to 90 km) and separated from the ocean by a relatively shallow sill (70 m deep). A second sill (also ~70 m deep) is located one third the way up the inlet, forming an additional barrier to circulation for the inner basin. The basins are well oxygenated (typically 4 to 5 mL L$^{-1}$ through most of the water column), as they receive a relatively constant flow of oxygenated water from Queen Charlotte Strait over both sills (Pickard, 1961).

Knight Inlet receives fresh water from two principal sources: the Franklin and Klinaklini Rivers both of which enter the fjord at its head. The drainage basin for these rivers lies within the Coast Mountain Range (Coast Plutonic Complex), which is covered partially by ice-fields. As a result, Knight Inlet receives strong seasonal inputs of melt-water and fluvially-transported glacial flour from erosion of the granitic batholiths, resulting in exceptionally turbid surface waters. The Franklin and Klinaklini rivers provide 10% and 85% of the fresh-water input to the inlet, respectively. The Klinaklini River drains an estimated 6460 km$^2$ and has seasonal flow rates ranging from winter lows of 50 m$^3$ s$^{-1}$ to summer freshet highs of 680 to 1100 m$^3$ s$^{-1}$ (Farrow et al., 1983). The corresponding sediment plume moves down inlet rapidly in a well-defined surface layer ~5.5 to 6.5 m thick near the inlet head; the layer thins toward the inlet mouth as it slowly mixes with the underlying saline water. The concentration of suspended particulate matter (SPM) progressively decreases toward the inlet mouth from ~200 mg L$^{-1}$ to ~1 mg L$^{-1}$; this is reflected in Secchi-disk depths as shallow as 10 cm at the inlet head, deepening to 5 to 6 m near the mouth (Pickard, 1961).
Figure 11 Station locations map for Knight Inlet, British Columbia
Three cores were collected from Knight Inlet. Given its length and the substantial point-source input of lithogenic material, the inlet was expected to offer a broad spectrum of depositional conditions including a wide range of sedimentation rates with compositional domination by the extensive terrestrial input. Stations located near the inlet mouth (KN-1), at mid-inlet (KN-3) and near the inlet head (KN-2) were selected to represent this breadth (Figure 11).

3.2.2 Stratigraphy

The three cores collected in Knight Inlet represent distinctly different depositional environments (Table 4). Core KN-1 was intended to represent the least terrestrially dominated sediments within the fjord but was found to contain a turbidite between 1.75 and ~6.5 cm (Figure 12). The segments of the $^{210}$Pb profile on either side of this stratum show continuous declines in activity with depth suggesting that the rest of the core is undisturbed. The $^{210}$Pb data show that core KN-3 (mid-inlet) accumulated under steady-state conditions (Figure 12). Core KN-2 (inlet-head) consists of undifferentiated gray glacial flour with a hint of yellow discolouration at the sediment-water interface. The distribution of $^{210}$Pb at this site (Figure 13) indicates rapid accumulation of terrestrial detritus; indeed, the core is too short to display any appreciable decay in $^{210}$Pb activity. Sedimentation rates adjacent to this site (but closer to the inlet head) have been reported as high as 30 cm yr$^{-1}$ (Farrow et al. 1983).

<table>
<thead>
<tr>
<th>Location</th>
<th>KN-1 (mouth)</th>
<th>KN-3 (mid)</th>
<th>KN-2 (head)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Depth</td>
<td>177 m</td>
<td>345 m</td>
<td>330 m</td>
</tr>
<tr>
<td>Core Length</td>
<td>40 cm</td>
<td>68 cm</td>
<td>54 cm</td>
</tr>
<tr>
<td>Sed. Rate</td>
<td>0.2 - 0.4 cm yr$^{-1}$</td>
<td>0.7 - 1.4 cm yr$^{-1}$</td>
<td>*4 - 7 cm yr$^{-1}$</td>
</tr>
</tbody>
</table>

Table 4 Description of the three cores collected from Knight Inlet. *based on observed accumulation of Cd and Mn in the surface sediments
Figure 12 Excess $^{210}$Pb activity in cores KN-1 and KN-3, Knight Inlet. Note: the linear scale for KN-1 allows for visualization of the turbidite.

Figure 13 Total $^{210}$Pb in core KN-2, Knight Inlet.

3.2.3 Compositional and Diagenetic Description

Cores KN-1 and KN-3 contain equal quantities of organic carbon (~2 to 3 wt.%) despite
having different sedimentation rates, implying that the carbon accumulation rate is higher mid-inlet. In contrast, organic matter concentrations near the inlet head (core KN-2) are one order of magnitude lower as a result of dilution by lithogenic detritus (Figure 14). This trend is reflected in the relationship between the $C_{\text{org}}/N$ weight ratios and $\delta^{13}$C values. These parameters are strongly correlated in the inlet mouth (KN-1) and mid-inlet (KN-3) cores, where the low $C_{\text{org}}/N$ weight ratios and heavy $\delta^{13}$C values indicate that the organic matter is predominantly marine in origin (Figure 15). Higher $C_{\text{org}}/N$ weight ratios coupled with relatively light $\delta^{13}$C values in core KN-2 imply dominance of the organic fraction in the upper inlet deposits by terrestrially-derived carbon. The organic matter in cores KN-1 and KN-3 also displays a recent trend toward the sediment-water interface to greater contributions from terrestrial organic matter (increasing $C_{\text{org}}/N$ weight ratios and $%C_{\text{org}}$ values combined with decreasing $\delta^{13}$C values) probably as a result of recent logging activities.

The relatively low sedimentation rates in KN-1 and KN-3 permit diffusion of oxygen into the interfacial deposits, creating an aerobic surface zone which is marked by a Mn enrichment in the top centimetre and by low dissolved Mn and Fe concentrations in near-surface porewaters (Figure 16 and Figure 17). The maximum concentrations of dissolved Fe and Mn appear in the porewaters of both cores at 5 cm and 2 cm depth, respectively. However, the redox potential differs at greater depths. While $\Sigma H_2 S$ in KN-1 does not appear in appreciable concentrations (>20 $\mu$M) until depths >30 cm, $\Sigma H_2 S$ in KN-3 increases rapidly to 2 mM below 5 cm depth. The contrast can be attributed to a greater oxidant demand at the mid-inlet site (thus, a higher rate of sulphate reduction) in response to the relatively high rate of accumulation of organic carbon in this area.

Although core KN-2 hosts an order of magnitude less organic carbon than the other two cores (Figure 14), the much higher sedimentation rate yields a comparable $C_{\text{org}}$ burial flux. Indeed, the mean organic carbon accumulation rate in KN-2 is intermediate to averages for KN-1 and KN-3 assuming similar values for grain density and porosity, and a mean sedimentation rate of 5 cm yr$^{-1}$ at the inlet head (Table 5).
Figure 14 Organic carbon content, $C_{org}/N$ weight ratios and stable carbon isotope ratios in the Knight Inlet cores.
Figure 15 $C_{\text{org}}/N$ vs. $\delta^{13}C\,\%_{\text{PDB}}$ of organic matter in the deposits of Knight Inlet.

Figure 16 (a) Dissolved and solid Mn and (b) dissolved Fe and $\Sigma H_2S$ in core KN-1.
The relatively low $C_{\text{org}}/N$ weight ratios and moderately heavy $\delta^{13}C_{\text{org}}$ values indicate that the organic matter in KN-2 has a more terrestrial provenance than in the other Knight Inlet cores. However, the sediments at this upper inlet site still contain a significant labile marine organic matter component (Figure 14). Even though the organic carbon content of KN-2 is much lower than elsewhere in the inlet, the organic carbon accumulation rate is relatively high (twice that of...
KN-1); diagenetic activity is intense. The net effect is a poised deposit having an oxic surface layer >3 cm thick and low ΣH₂S at depth despite much sulphate reduction (as inferred from the production of ~7 meq L⁻¹ of alkalinity). It is worth noting that this apparent paradox illustrates the importance of sedimentation rate on redox potential; despite the low content and terrigenous origin of the organic carbon, diagenetic activity is very pronounced. This environment is further emphasized in the dissolved Fe and Mn data (Figure 18).

Manganese displays a pronounced surficial enrichment in the solid-phase in the upper 3 cm of KN-2. The commensurate absence of dissolved Fe in the upper seven cm indicates clearly that oxic conditions persist at the core top.

Dissolved Fe concentrations increase sharply below 6 cm indicating the onset of sub-oxic conditions. Although dissolved sulphide is not measurable until depths >15 cm, sulphate reduction almost certainly occurs as shallow as 5 or 6 cm depth as indicated by marked increases in alkalinity over the upper decimetre (Figure 19). Interestingly, however, the concentration of H₂S

Figure 18 (a) Solid and dissolved Mn and (b) solid and dissolved Fe in core KN-2.
is never high enough to completely consume dissolved Fe. While the organic carbon accumulation rate is sufficient to fuel rapid rates of sulphate reduction, the high sedimentation rate at this site buries a substantial quantity of reducible Fe oxide that acts as a continuing source of dissolved Fe within the sulphate reducing zone. Although this would appear to present a thermodynamic paradox, since available Fe oxides should be quantitatively reduced before sulphate reduction commences, it has recently been demonstrated that under certain conditions, sulphate reduction can precede Fe reduction (Postma and Jakobsen, 1996). It has also been observed in B.C. fjords that H$_2$S can be produced in reducing microenvironments even in the aerobic zone (Francois, 1988). In this case, the rapid rate of sedimentation likely buries particles (or microzones) enriched in Fe-oxide which produce the abundance of dissolved Fe present in the deep porewaters. The geochemical sequence of oxidants at depth in KN-2 is displaced from "steady-state" by the high sedimentation rate.

<table>
<thead>
<tr>
<th>Alkalinity (meq/L)</th>
<th>Dissolved Fe (µM)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
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<td>4</td>
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<td>6</td>
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</tr>
<tr>
<td>8</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 19 (a) $\Sigma$H$_2$S and alkalinity and (b) dissolved Fe and $\Sigma$H$_2$S in core KN-2.

In order to estimate the sedimentation rate at KN-2, the upward diffusive flux of dissolved Mn
above ~1.5 cm depth is assumed to support the observed surficial Mn enrichment. Using a concentration gradient of \(3.2 \times 10^{-7} \text{ mol L}^{-1} \text{ cm}^{-1}\) (calculated over the upper 0.5 cm) and a diffusion coefficient of 150 cm\(^2\) yr\(^{-1}\) yields an authigenic flux of \(~2.6 \times 10^{-3} \text{ g cm}^{-2} \text{ yr}^{-1}\). Assuming steady state, an authigenic Mn concentration of \(~800 \mu \text{g g}^{-1}\) (the increase in Mn over the same interval), and the same assumptions of porosity and bulk grain density used previously, an estimated sedimentation rate of \(~7 \text{ cm yr}^{-1}\) is computed. Because the Mn concentration gradient appears to extend across the sediment-water interface, this approach places an upper boundary on the sedimentation rate.

### 3.2.4 Trace Metal Behaviour

#### 3.2.4.1 Cadmium

Solid-phase Cd in Knight Inlet increases in concentration from a low of \(~0.1 \mu \text{g g}^{-1}\) at the inlet head to maximum values of \(~0.5 \mu \text{g g}^{-1}\) near the mouth, suggesting that lithogenic detritus is depleted in Cd and serves only to dilute other sources (Figure 20).

![Solid-Phase Cd in Knight Inlet](image)
The abundance of Cd in core KN-1 (Figure 20) mimics the stratigraphy defined previously: the average 'background' concentration of 0.3 to 0.4 μg g⁻¹ is punctuated by a turbidite hosting concentrations of ~0.1 to 0.2 μg g⁻¹ between 1.75 and 6.5 cm depth. Dissolved Cd is observed to decrease precipitously from a maximum value at the sediment-water interface of 2.1 nM to near undetectable values by 4 cm.

Solid-phase cadmium in core KN-3 is uniformly distributed at a concentration of ~0.30 μg g⁻¹ (Figure 20). Dissolved Cd decreases from ~1.6 nM at the interface to a near constant value of 0.1 nM below 5 cm depth (Figure 21). Although the decrease through the oxic layer in both cores could result in part from oxide adsorption or coprecipitation, which is implied by the very slight non-linearity of each profile in the uppermost few cm, it is more likely that most Cd consumption occurs at ~2 and ~5 cm depth where sulphate reduction commences in KN-1 and KN-3, respectively (Figure 21). The Cd distribution can also be explained if sulphate reduction occurs with or precedes Fe reduction as described by Postma and Jakobsen (1996).

Figure 21 Dissolved Cd, Fe and ΣH₂S in core KN-1 and KN-3.
Interactions of Cd with oxides are generally considered weak; thus, it is unusual that consumption by an oxide could be both rapid and quantitative. Moreover, the absence of increases in dissolved Cd commensurate with dissolved Fe in the horizons where sub-oxic conditions persist implies that other phases are responsible for its consumption. By default, it is suggested that Cd precipitates as a sulphide probably in shallow reducing microenvironments or in association with a shallow zone of sulphate reduction (cf. Francois, 1988 or Postma and Jakobsen, 1996). Free H$_2$S cannot be detected in the upper part of the core because the high concentration of dissolved Fe prevents its accumulation. Similar phenomena have recently been described by Rosenthal and Boyle (1995); in their work, near-surface uptake of Cd by the solids (prior to precipitation of FeS) was ascribed to the lower solubility of CdS relative to FeS.

In order to quantify the relative importance of the diffusive influx of Cd for KN-1 and KN-3, the Diffusion-Consumption Model (DCM) has been applied to the upper few cm (Figure 22). Using the appropriate values from Table 6, and assumptions of steady-state, the authigenic Cd content associated with the diffusive influxes are -0.23 and 0.063 µg g$^{-1}$ (or 51% and 20% of the total Cd inventory) for KN-1 and KN-3, respectively.

<table>
<thead>
<tr>
<th></th>
<th>KN-1</th>
<th>KN-3</th>
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</thead>
<tbody>
<tr>
<td>porosity</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>sedimentation rate (cm yr$^{-1}$)</td>
<td>0.3</td>
<td>1.0</td>
</tr>
<tr>
<td>bulk grain density (g cm$^{-3}$)</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>DCM (µg cm$^{-2}$ yr$^{-1}$)</td>
<td>0.038</td>
<td>0.029</td>
</tr>
<tr>
<td>LCM</td>
<td>0.036</td>
<td>0.032</td>
</tr>
<tr>
<td>Authigenic Cd (µg g$^{-1}$)</td>
<td>0.23</td>
<td>0.063</td>
</tr>
<tr>
<td>% of Total Cd</td>
<td>51%</td>
<td>20%</td>
</tr>
</tbody>
</table>

Table 6 Assumptions and parameters for estimating authigenic Cd in Knight Inlet sediments.
The distribution of solid-phase Cd in core KN-2 differs from the other two cores (Figure 20) in that concentrations are much closer to the detrital background content. Cadmium levels increase from 0.09 µg g\(^{-1}\) at the interface to ~0.11 µg g\(^{-1}\) at 8 cm depth (Figure 23). The steep dissolved Cd concentration gradient (~1.5 pmol cm\(^{-4}\)) into the sediments (from 0 to 10 cm) and the small increase in solid Cd over the same interval both imply the presence of an authigenic component (Figure 23).

Figure 22 Dissolved Cd and diffusion-consumption model results for the top 10 cm of cores KN-1 and KN-3.

Dissolved Cd decreases in concentration from a maximum of 15 nM at the sediment-water interface to undetectable values below 10 cm depth. While the shape of the profile appears similar to those of the other two cores, the maximum concentration is approximately one order of magnitude higher. The profile appears to arise from diffusion from the sediment-water interface to approximately 10 cm depth where sulphide precipitation occurs; free H\(_2\)S is detectable in the interstitial waters below this horizon (Figure 23). Why the near-surface concentrations are so high in this portion of the fjord is unknown.
The accumulation rate of the authigenic component implied by the increase in solid-phase Cd over the depth interval occupied by the concentration gradient is large given the high sedimentation rate determined for core KN-2.

Sulphate reduction commences at ~5 cm depth, and it is assumed that Cd diffuses from the interface to that horizon without being adsorbed or precipitated. The linear flux model is applied here in place of the Diffusion-Consumption Model as the latter inherently assumes consumption over the entire depth interval, which could lead to erroneously high diffusive flux estimates.

Figure 23 (a) Solid and dissolved Cd and (b) dissolved Fe and $\Sigma H_2S$ in core KN-2.

Application of the Linear Flux model over the upper 5 cm yields a flux of 0.036 $\mu$g cm$^{-2}$ yr$^{-1}$ using a diffusion coefficient of 160 cm$^2$ yr$^{-1}$ (Figure 24). Using the previous assumptions for bulk grain density and porosity in concert with an authigenic Cd concentration of ~0.020 $\mu$g g$^{-1}$ (estimated from the Cd/Al increase over the upper 10 cm of KN-2), a sedimentation rate of ~4 cm yr$^{-1}$ is calculated. This is similar to that derived from Mn enrichments ($\leq$7 cm yr$^{-1}$), which lends credence to the approach and the assumptions used therein. However, because the assumption of steady-state is probably not tenable, the computed estimates of sedimentation rate
and metal accumulation must be viewed with caution.

3.2.4.2 Copper

Solid-phase Cu in Knight Inlet sediments ranges in concentration from 40 to 120 μg g⁻¹. The average content increases towards the head of the fjord suggesting that the primary source of Cu is lithogenic detritus. The distribution at each coring site is approximately uniform with the exception of the upper few centimetres of KN-3 which are depleted relative to the sediments immediately below (Figure 25).

![Figure 24 Dissolved Cd and model fit to the data for core KN-2.](image)

The form of the dissolved Cu distribution is identical at the three sites: copper increases from the sediment-water interface to a shallow subsurface maximum within the upper 1 cm. The magnitude of the maximum increases toward the inlet head with values of 11, 18 and 240 nM for KN-1, KN-3 and KN-2, respectively (Figure 26 and Figure 27). In all cases, dissolved Cu decreases precipitously immediately below the subsurface maximum to values ranging from 2 to 5 nM throughout the remainder of each core. These distributions are likely caused by common
mechanisms. The near-surface maximum at each site probably reflects release due to organic matter remineralization (i.e. Klinkhammer et al., 1982; Pedersen et al., 1986; Shaw et al., 1990). In KN-3, the maximum overlaps to some extent with the subsurface dissolved Fe peak suggesting that oxide reduction may account for some of the dissolved Cu at this site. However, there is no such evidence in either of the other two cores, nor are there any solid-phase enrichments corresponding to the oxic zone. This implies that metal oxides play only a limited role at best in the cycling of Cu in Knight Inlet.

![Solid-Phase Cu in Knight Inlet.](image)

Figure 25 Solid-phase Cu in Knight Inlet.

The peak concentration in KN-2 is approximately one order of magnitude higher than in either KN-1 or KN-3, similar to the contrast seen for Cd. There is no obvious reason for this difference. One possibility is that additional particulate (but diagenetically labile) Cu is added to the sediments at the inlet head as a result of the flocculation of riverine dissolved Cu during estuarine mixing. The elevated Cu may be sustained in part by the absence of sulphate reduction in the surface layers. Furthermore, it is also possible that the release of dissolved Cu at 1.25 cm depth also contains a component released from dissolution of Mn-oxides which are
seen to be reduced in that zone.

Figure 26 Cu/Al weight ratio and dissolved Cu and select redox indicators from cores KN-1 and KN-3. Contamination may have affected the dissolved Cu value at 34 cm depth in core KN-1.

The decline in dissolved Cu observed below the maximum in each core is coincident with the onset of sulphate reduction, suggesting that precipitation of an insoluble sulphide is the
dominant sink at depth. Furthermore, the Cu profile below the sub-surface maximum is almost identical in form to that of Cd, suggesting that both metals are consumed through a common mechanism, presumably sulphide precipitation.

![Graph](image1)

Figure 27 Cu/Al weight ratio and dissolved Cu and $\Sigma H_2S$ in core KN-2.

### 3.2.4.3 Molybdenum

Solid-phase Mo exhibits a wide range of concentrations from $<0.08 \mu g \ g^{-1}$ (an unusually low value; discussed in more detail below) at the inlet head to 7.5 $\mu g \ g^{-1}$ at the inlet mouth (Figure 28). The spatial trend through the inlet is opposite that of Cu in that the concentration of Mo increases away from the inlet head suggesting that terrestrial detritus serves to dilute molybdenum.

**Knight Inlet - 1**

Solid-phase Mo in core KN-1 exhibits a highly variable distribution with depth. The upper decimetre hosts relatively uniform concentrations (0.4 to 0.8 $\mu g \ g^{-1}$) with the exception of an enrichment in the top 0.5 cm of the core that is similar in magnitude to that seen at the other two
sites. Below 11 cm depth, concentrations increase dramatically, reaching ~7.3 μg g⁻¹ at ~18 cm. Below this depth values vary between ~2 and ~5 μg g⁻¹ (Figure 29). The dissolved Mo content throughout the upper 11 cm matches that of seawater (~110 nM, Figure 29). Increasing concentrations between 11 and 26 cm reflect diagenetic reactivity below the turbidite.

Figure 28 Solid-phase Mo in Knight Inlet sediments. Note the differing scales on the abscissae. Concentrations in core KN-2 below 1.5 cm are lower than the analytical detection limit of 0.08 μg g⁻¹ but are plotted at that value.

The solid-phase and dissolved Mo distributions at this site can be explained by three phenomena. First, the slight enrichment of sedimentary Mo at the surface is attributed to adsorption of MoO₄²⁻ from seawater onto manganese oxides, which are clearly accumulating in the upper centimetre (Figure 29b). Using the Mo/Mn weight ratio of 2 x 10⁻³ determined by Shimmield and Price (1986) for hemipelagic Pacific deposits, the ~400 μg g⁻¹ of excess (i.e. oxide) Mn in the core-top sediments can accommodate 0.8 μg g⁻¹ of Mo; this agrees well with the observed enrichment of 0.8 μg g⁻¹ (Figure 29a), suggesting that adsorptive scavenging is indeed plausible. It is unclear, however, why Mo is not released to interstitial waters in the zone of Mn
reduction as it is in both KN-3 and KN-2 (see below). Second, the maximum in the dissolved Mo profile between 20 and 28 cm depth may be ascribed to ejection of Mo from FeS during the diagenetic conversion of iron monosulphide to pyrite (e.g. Korelev, 1958). Third, the lower values toward the base of the core probably result from precipitation of MoS₂ in the H₂S-rich zone (Figure 29b).

Knight Inlet - 3

Solid-phase Mo is enriched in the surface sediments of core KN-3, increasing from an interfacial concentration of ~0.70 to a peak of ~1.0 μg g⁻¹ at 0.75 cm. The concentration declines dramatically to <0.30 μg g⁻¹ within the next 2 cm where it remains until 25 cm depth. Below this horizon, Mo contents increase sporadically to levels ranging from 0.40 to 1.2 μg g⁻¹ (Figure 30).

Dissolved Mo increases from an interfacial concentration of ~200 nM to a subsurface maximum of 570 nM at 0.75 cm depth. A first-order decline marks the profile below the maximum; concentrations are undetectable (<6 nM) at the base of the core (Figure 30).
As at the other sites, Mo appears to be affiliated with authigenic Mn-oxides in the surface deposits. Dissolved profiles for both elements suggest consumption near the interface followed by rapid release coincident with Mn reduction. Precipitation of Mo sulphide or coprecipitation with FeS is indicated by near quantitative consumption in the reducing sediments at depth.

Figure 30 (a) solid and dissolved Mo and (b) solid and dissolved Mn in core KN-3.

Knight Inlet - 2

Solid-phase Mo is enriched in the oxic surface sediments of core KN-2 and decreases to undetectable levels (0.08 µg g⁻¹) within the upper decimetre (Figure 31). The surface enrichment most likely arises from authigenic accumulation in association with Mn⁴⁺, as illustrated by the correlation between solid Mo and Mn (Figure 32). If the Mo/Mn ratio of Shimmield and Price (1986) represents an "oxide saturation ratio", then the Mn surface enrichment of 1700 µg g⁻¹ in KN-2 should host 3.4 µg g⁻¹ of authigenic Mo. The observed Mo enrichment is 0.36 µg g⁻¹, one order of magnitude less. Furthermore, the slope of the Mo vs. Mn regression for the surface...
sediments is $\sim 2 \times 10^{-4}$, ten times lower than expected (Figure 32). These observations suggest that the Mn within the surficial sediments may not have disproportionated fully to $\text{MnO}_2$. If the sedimentation rate of core KN-2 is too high to allow disproportionation to occur, Mn will be buried and reduced before sufficient quantities of $\text{Mn}^{4+}$ accumulate; this could account for the limited association of Mo with Mn at this site.

![Figure 31](image)

Figure 31 (a) Solid and dissolved Mo and (b) solid and dissolved Mn in core KN-2.

Molybdenum is undetectable in the core below 1.5 cm depth, suggesting that the element is a scarce constituent in the lithogenic material entering Knight Inlet. It is unusual that solid-phase Mo should be so low given a typical crustal abundance of 0.5 to 1.5 $\mu$g g$^{-1}$. The results are not an artifact of incomplete digestion during the microwave procedure because a suite of rock standards of similar bulk composition to the sediments was run and indicated complete Mo recovery (Table 7). Furthermore, residual precipitates were not noted during the digestions; thus, there is no reason to suspect the data. It appears that the deposits at this site are dominated by detrital mineral phases depleted in solid-phase Mo. Regardless of the reason for the low Mo
values, the concentration of detrital Mo has no bearing on the interpretation of Mo cycling in these sediments. These observations further imply that the vast majority of sedimentary Mo occurring elsewhere in the fjord arises from authigenic sources.

<table>
<thead>
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<th>Sample ID</th>
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<td>JA-2</td>
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<tr>
<td>JG-1a</td>
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</table>

Table 7 Reported and measured Mo contents in granitic reference materials determined by microwave digestion and graphite furnace atomic absorption spectroscopy.

Figure 32 Mo vs. Mn in the surface sediments of core KN-2, Knight Inlet.

Dissolved Mo in core KN-2 decreases in concentration from 400 nM at the sediment-water interface to a subsurface minimum of 240 nM at 2.5 cm depth. Below this level, values increase to a maximum of ~900 nM at 5.5 cm before declining to near undetectable values over the next 15 cm. From 20 cm to the bottom of the core, dissolved Mo remains below 30 to 40 nM.

The elevated dissolved Mo at the sediment-water interface is approximately three to four times higher than concentrations typically found in seawater. It is possible that localized dysaerobia (perhaps produced by a very recent non-steady-state event) could result in the release of dissolved Mo, Mn and perhaps other metals to the interstitial solution. Further,
dysaerobia could reduce the oxidation state of the Mn sufficiently to inhibit Mo sorption while leaving the Mn-oxide enrichment intact (Shimmield and Price, 1986).

The maximum at 5.5 cm represents the zone of maximum Mo release at the time of sampling. The decrease in dissolved Mo below 5.5 cm most likely arises through precipitation of dissolved Mo with FeS (Section 3.1.2.3.2). The presence of free $\text{H}_2\text{S}$ in concert with a suspected absence of DOM near the base of the core (i.e. ease in filtration of porewaters) is sufficient to inhibit the accumulation of dissolved Mo that might be released from the conversion of FeS to pyrite.

3.3 Indian Arm

3.3.1 Inlet Description and Core Location

Indian Arm is a long narrow fjord ~21 km long by 1 km wide contiguous to Vancouver Harbour, but separated from it by a sill ~30 m deep (Figure 33). Circulation is influenced by semi-diurnal tides, but the deep nature of the inner basin (218 m maximum depth) in concert with a substantial fresh water inflow from the Indian and Buntzen rivers results in reasonably strong stratification (Pickard, 1961). As a result, inlet bottom waters remain isolated for much of the year and over time tend to fluctuate between oxic and dysaerobic conditions.

Like many of the other local inlets, the geology of the Indian Arm drainage basin is dominated by the Coast Plutonic Complex. The fjord receives the majority of lithogenic material from the Indian River, and the waters are moderately turbid; secchi depths frequently range from 4 to 7 metres throughout the inlet (Pickard, 1961).

Indian Arm hosts relatively pristine waters and sediments despite its proximity to Vancouver Harbour and Port Moody Arm where the sediments are moderately to highly contaminated with trace metals (Pedersen and Waters, 1987; Johnson, 1991). There is no significant urban development in the drainage basin or on the shores of the inlet, nor is there any industrial activity beyond Port Moody. One core (IA-1) was collected in Indian Arm from the centre of the deep basin, immediately south of Croker Island (Figure 33). Previous unpublished geochemical studies have shown that cores across this basin exhibit a consistent geochemical stratigraphy (Pedersen, pers. comm.).
Figure 33 Station location map for Indian Arm, British Columbia
3.3.2 Stratigraphy

The distribution of 210Pb in core IA-1 indicates that the rate of sedimentation in the deep basin has been approximately constant for at least 40 years. A mixed surface layer ~2 cm thick is clearly defined by the profile (Figure 34). The sediments at station IA-1 have been studied previously (Pedersen and Waters, 1987) and as a result, proxy porosity data were available to aid in the estimates of decompaction and sedimentation rate. The estimates of uncorrected and compaction-corrected sedimentation rate at IA-1 are 0.25 cm yr⁻¹ and 0.37 cm yr⁻¹ respectively.

Core IA-1 displays some variation in the distributions of major elements with depth, as illustrated by the Si/Al weight ratio and organic carbon profiles (Figure 35). Most of the variation occurs in the upper 10 cm, implying that the nature of sedimentation, or the provenance of the lithogenic fraction, has changed progressively during the last 30 to 40 years. While the upper few cm of the deposits are depleted in both Si and Al, the Si/Al weight ratio increases towards the sediment-water interface (Figure 35) indicating a gradual change in the composition of the deposits with time.

3.3.3 Diagenetic Description

Organic carbon in IA-1 is abundant (3.5 to 4.5 wt.%). The low Corg/N weight ratio (~12) and relatively heavy δ¹³C values (~23.5 ‰) indicate that the organic component is dominated by material of marine origin (Figure 36). The higher organic carbon content in the upper decimetre implies that there has been a recent increase in organic matter input to the deep sediments in the basin. A commensurate increase in δ¹³Corg values suggests that the higher near-surface Corg content represents an enhanced input of marine organic detritus. This premise is supported by an increase in the Si/Al weight ratio, coincident with the increase in Corg, which could be interpreted to reflect an increase in opal content. Because the enrichments commence within the last several decades, it is possible that they reflect the onset of cultural eutrophication resulting from progressive increases in nutrient fluxes to the inlet waters.
Despite relatively high rates of deposition of organic matter, the seasonal incursion of oxygenated bottom-waters creates an oxic layer extending several cm below the sediment-water interface. The presence of a Mn-rich surface layer supports this premise (Figure 37). However,
Mn remobilization was occurring at and immediately below the sediment-water interface at the time of sampling and H$_2$S was observed in all porewater samples (Figure 37) suggesting that the solid and dissolved phases were not in steady-state. Indian Arm bottom waters are known to become dysaerobic as a result of intermittent bottom water circulation (Burling, 1982). Thus, the non-steady-state conditions indicated by the dissolved and solid-phase Mn profiles probably reflect ongoing hydrographic variation in the fjord.

Figure 36 Organic carbon content and $C_{org}/N$ ratio and $\delta^{13}C_{\%o}$ (PDB) in core IA-1.

3.3.4 Trace Metal Behaviour

3.3.4.1 Cadmium

Solid-phase Cd in IA-1 is approximately uniform in concentration, ranging from 0.4 to 0.6 $\mu$g g$^{-1}$. However, the Cd/AI weight ratio indicates relative enrichments in the upper 3 cm as well as at the base of the core (Figure 38). Dissolved Cd decreases in concentration from 0.8 nM at 0.25 cm depth to 0.05 nM by 2 cm and remains generally low in the porewaters throughout the remainder of the core (Figure 38). The presence of free sulphide immediately below the sediment-water interface in concert with the rapid increase in alkalinity with depth suggests that sulphate reduction.
is occurring at very shallow depths (Figure 37). Thus, it is highly probable that dissolved Cd is consumed by sulphide precipitation in the near-surface sediments.

![Graph showing solid and dissolved Mn; and ΣH₂S and alkalinity in core IA-1, Indian Arm.]

Figure 37 Solid and dissolved Mn; and ΣH₂S and alkalinity in core IA-1, Indian Arm.

The accumulation of authigenic Cd in the Indian Arm deposit is estimated as done previously. The DCM yields a Cd flux of 0.014 μg cm⁻² yr⁻¹ (Figure 39). Using a value for porosity of 0.8, a sedimentation rate of ~0.3 cm yr⁻¹, a bulk grain density of 2.4 g cm⁻³ and the above flux as an accumulation rate results in an accumulated concentration of ~0.097 μg g⁻¹. This value accounts for approximately 22% of the total inventory but assumes that Cd accumulates in such a fashion year-round. It is not clear whether dissolved Cd is in steady-state with regard to the solid phase. It may be that authigenic accumulation at this rate only occurs when bottom waters are sufficiently dysaerobic, thereby shallowing the zone of sulphate reduction and shortening the diffusional path-length.

96
Figure 38  Solid and dissolved Cd vs. depth and Cd/Al weight ratio in core IA-1; the points in parentheses are suspected to represent contamination.

Figure 39  Dissolved Cd data and diffusion consumption model fit for core IA-1.
3.3.4.2 Copper

Copper in core IA-1 is twice as abundant as in typical lithogenic detritus (i.e. 120 to 150 μg g⁻¹ versus 40 to 50 μg g⁻¹; Figure 40). The elevated Cu/Al weight ratio in the upper 2 cm corresponds to similar enrichments in Cd and Zn suggesting a common source.

Dissolved Cu decreases linearly with depth from a maximum concentration of 37 nM at the sediment-water interface to a minimum of 10 to 15 nM between 3 and 9 cm depth (Figure 40). Concentrations increase between 9 and 18 cm, reaching in excess of 30 nM at 14 cm depth, suggesting remobilization within this zone. Lower concentrations prevail in the bottom half of the core.

The peak in dissolved Cu at or immediately below the sediment-water interface is thought to arise from release of biogenic Cu followed by sulphide precipitation at ~3 cm depth. H₂S does occur in interstitial waters throughout the core (Figure 40). The peak between 7 and 20 cm is of unknown origin and may in some way be related to the non-steady-state nature of the deposits.

![Graphs showing Cu/Al and dissolved Cu as well as solid-phase Cu and free sulphide in core IA-1, Indian Arm. Data in parentheses are suspected of contamination.](image-url)
3.3.4.3 Molybdenum

The Mo distribution in core IA-1 is similar to that in many other oxic cores: concentrations are high in surface deposits (≤ 7.6 μg g⁻¹) and decline quickly with depth to 2 μg g⁻¹ (Figure 41). Dissolved Mo displays a sharp subsurface maximum, increasing from an interfacial concentration of 200 nM to 400 nM at 0.75 cm before decreasing with depth to values <50 nM. Below 20 cm, the concentration gradually increases to 180 nM by the base of the core (Figure 41).

The enrichment in solid-phase Mo in the upper 2 cm coincides with high Mn concentrations in the same interval. However, the Mo/Mn weight ratio in these surface deposits is inordinately low (~0.5 x 10⁻³) particularly when compared to other regimes, including many of the deposits of this study (i.e. Mo/Mn weight ratio in hydrogenous Mn oxides of ~ 2 x 10⁻³; Shimmield and Price, 1986).

Shimmield and Price (1986) have suggested that Mo tends to associate with Mn⁴⁺, regardless of Mn oxide mineralogy. Manganese oxides in surficial sediments are often

![Figure 41 Mo/Al weight ratio and dissolved Mo in IA-1, Indian Arm.](image-url)
dominated by hausmannite (Mn$^{2.5+}$, as Mn$_3$O$_4$), the most easily precipitated oxide. Over time, Mn$_3$O$_4$ undergoes disproportionation, increasing the effective oxidation state of some of the Mn, creating Mn$^{4+}$ as MnO$_2$ (Hem and Lind, 1983). The affinity of Mo for Mn oxides increases under these conditions. The lack of a well developed Mo-Mn relationship in Indian Arm sediments suggests that much of the Mn exists in a relatively low oxidation state. It is possible that seasonal dysaerobic conditions in bottom waters inhibit, or reverse, disproportionation of Mn in the surface sediments that has accumulated under previously oxic conditions; eutrophication would serve to enhance the decoupling between Mo and Mn. The Mn oxides in IA-1 do not appear to have acquired the capacity to bind substantial quantities of Mo. The elevated values of dissolved Mo within the interfacial horizon (200 nM, approximately twice the value typically found in seawater) are in support of this premise, suggesting that Mo is actively released from Mn oxides within the interfacial sediments (Figure 41). Much of this Mo is presumably lost to the water column, while some is reprecipitated deeper in the sediments as a sulphide. The data at greater depths (> 20 cm) imply that Mo is remobilized at depth, presumably as a result of conversion of FeS to pyrite.

3.4 Jervis Inlet

3.4.1 Inlet Description

Jervis Inlet, located ~100 km to the north of Vancouver (Figure 42), is the deepest fjord on the B.C. coast; mean and maximum depths are ~495 and 730 m respectively. The inlet receives minimal fresh water at its head (mean annual discharge 180 m$^3$ s$^{-1}$); thus, circulation is weakly estuarine and depends as much on tides and wind as on density differences (Pickard, 1961). A relatively deep outer sill (~300 m) provides only limited restriction to estuarine circulation.

The absence of large glaciers in the local water shed means that fresh water input to the inlet responds more to coastal rainfall patterns (which peak in the winter months) than to the spring freshet. The absence of ice fields in concert with limited river flow constrains the quantity of lithogenous material introduced to the inlet. However, extensive logging throughout the region has recently enhanced the inputs of terrestrial organic matter and lithogenic detritus to greater degrees than in the past (Jones, unpublished data).
Figure 42 Station locations in Jervis Inlet, British Columbia
3.4.2 Stratigraphy

Three cores collected from Jervis Inlet, JV-3, JV-7 and JV-9, were raised from the inlet mouth, mid-inlet and inlet head respectively (Figure 42; Table 8).

<table>
<thead>
<tr>
<th>Location</th>
<th>JV-3</th>
<th>JV-7</th>
<th>JV-9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>Hotham Sound</td>
<td>Princess Royal</td>
<td>Queens Reach</td>
</tr>
<tr>
<td>Water Depth</td>
<td>712 m</td>
<td>556 m</td>
<td>355 m</td>
</tr>
<tr>
<td>Core Length</td>
<td>43 cm</td>
<td>66 cm</td>
<td>60 cm</td>
</tr>
<tr>
<td>Sed. Rate</td>
<td>0.24 - 0.48 cm yr⁻¹</td>
<td>0.29 - 0.58 cm yr⁻¹</td>
<td>0.30 - 0.60 cm yr⁻¹</td>
</tr>
</tbody>
</table>

Table 8 Description of the three cores collected from Jervis Inlet. The range for sedimentation rate in each case represents uncorrected to maximum compaction-corrected.

The $^{210}$Pb profiles for all three cores are remarkably consistent (Figure 43) and suggest that the sediments at all three sites have accumulated under steady-state conditions during the period represented by at least the upper 20 cm. Over this interval, $^{210}$Pb decreases from the sediment-water interface in a uniform, exponential fashion without any obvious discontinuities. The calculated sedimentation rates for all three cores fall within a narrow range, reflecting similar particle settling fluxes throughout the inlet (Table 8).

3.4.3 Diagenetic Description

The organic carbon content in all cores of Jervis Inlet is relatively high, decreasing from a maximum at the sediment-water interface (between 3.5 and 4.5 wt.%) to lower values (3.0 to 4.0 wt.%) at depth (Figure 44). The $C_{org}/N$ weight ratios and $\delta^{13}C$ data suggest that the organic material is derived primarily from marine sources, particularly in core JV-3 at the inlet mouth. However, the progressive depletion in $\delta^{13}C$ and increase in $C_{org}/N$ weight ratio toward the
surface in all three cores suggests that the relative input of terrestrial organic matter to the inlet has increased in the past several decades. This likely reflects the effect of logging in the watershed within the last century.

Figure 43 Excess $^{210}$Pb in all three cores of Jervis Inlet. Circles = JV-3, squares = JV-7 and crosses = JV-9.

Solid and dissolved Fe and Mn profiles (Figure 45) indicate that core JV-3 hosts oxic interfacial sediments. A solid Mn enrichment in concert with low dissolved Mn and Fe concentrations to 2 and 8 cm respectively suggest that Mn reduction does not commence until 2 to 3 cm depth while Fe reduction begins at ~10 cm. Anoxia does not develop until depths > 9 cm as suggested by dissolved Fe and $\Sigma H_2S$; $\Sigma H_2S$ first appears at ~9 cm (Figure 45). Thus, the upper 2 to 3 cm of core JV-3 are oxic and sub-oxia persists to a depth of ~8 cm. Deeper sediments are anoxic.
Figure 44 Organic carbon, $C_{\text{org}}/N$ weight ratio and $\delta^{13}C$ of the organic matter in the cores of Jervis Inlet. Circles = JV-3, squares = JV-7 and crosses = JV-9.
In JV-7, dissolved and solid-phase Mn and Fe indicate an aerobic zone at the core top that is significantly thinner than that in JV-3 (Figure 46); Fe reduction commences at much shallower depths in JV-7 (~4 cm) compared to JV-3 (~8 cm). The interfacial sediments of core JV-9 are also oxic. Solid-phase and dissolved Mn profiles indicate that the aerobic layer is only a veneer 1 to 2 cm thick at this site (Figure 47). The suboxic zone is sandwiched between this veneer and the fully anoxic conditions that prevail below ~6 to 10 cm depth. The sediments of JV-9 are as reducing as those of core JV-7, yet contain less organic carbon with a proportionately larger terrestrial component. Differences in C$_{org}$ lability cannot account for the redox disparity; indeed, the more strongly reducing subsurface deposits at both the JV-9 and JV-7 sites contain less marine organic matter than the sediments at JV-3. This suggests that diminished bottom water oxygen towards the inlet head influences the redox state of these sediments, as proposed by Grill (1978). If so, the distribution of trace metals should reflect such an "oxygenation gradient".
Figure 46 Solid and dissolved Fe and Mn and $\Sigma H_2S$ in core JV-7, Jervis Inlet.

Figure 47 Solid and dissolved Fe and Mn and $\Sigma H_2S$ in core JV-9.
3.4.4 Trace Metal Behaviour

3.4.4.1 Cadmium

Sedimentary Cd contents in Jervis Inlet are elevated five to fifteen-fold over the typical detrital background concentration of 0.1 µg g\(^{-1}\). The solid-phase profiles are typically characterized by subsurface maxima between 2 and 4 cm depth, and near-constant concentrations at greater depths although Cd in core JV-7 increases marginally below 30 cm (Figure 48).

![Solid-Phase Cd in the three cores of Jervis Inlet. Circles = JV-3, squares = JV-7 and crosses = JV-9.](image)

Figure 48 Solid-phase Cd in the three cores of Jervis Inlet. Circles = JV-3, squares = JV-7 and crosses = JV-9.

Core JV-3 hosts a dissolved Cd maximum of 2.8 nM in the 0 to 1 cm horizon, more than twice the bottom water concentration of 1.2 nM. Below 0.75 cm, dissolved Cd decreases progressively to values of ~0.1 nM at depth with the exception of a secondary maximum of 1.5 nM centred at ~5 cm. The elevated concentration of dissolved Cd within the near-surface deposits most likely reflects release from oxidizing marine organic matter. Cadmium from that zone diffuses both upward to the overlying waters and downward, deeper into the sediments. The origin of the dissolved peak at ~5 cm depth is unclear. This secondary maximum occurs at a slightly shallower depth than the dissolved Fe peak, and corresponds more closely to the depth of
maximum Mn reduction (~4 cm; Figure 49). However, the correspondence between low dissolved Fe and an elevated Cd/Al weight ratio in the upper 6 cm suggests that Fe-oxides may also play a role in governing the distribution of Cd in this core. If either scenario is true, it implies uptake of Cd onto oxides in the upper few cm at this site.

Sulphide precipitation undoubtedly accounts for the diminishing dissolved Cd concentrations below 7 cm. Because sulphide reduction can occur simultaneously with Fe reduction and because Cd is more insoluble than Fe in the presence of sulphide, dissolved Cd may be removed from solution while Fe is released (Rosenthal et al., 1995). This may explain the contrast between the Fe and Cd profiles below 7 cm.

Figure 49 (a) Dissolved Cd and Mn and (b) Cd/Al weight ratio, \( \Sigma H_2S \) and dissolved Fe in core JV-3.

Dissolved Cd distributions in cores JV-7 and JV-9 are identical to that of core JV-3 with two exceptions. First, the maximum concentration observed in near-surface porewaters decreases toward the inlet head (i.e. Cd in JV-3 > JV-7 > JV-9) and second, there are no secondary maxima
in either JV-7 or JV-9; subsurface remobilization is followed immediately by rapid precipitation (Figure 50). This suggests that the distribution of dissolved Cd in these two cores is influenced by oxidative release from organic matter in the near surface sediments followed by near-quantitative consumption via sulphide precipitation at depth (Figure 50). \( \text{H}_2\text{S} \) production in core JV-7 occurs below \(-4.5\) cm, a depth coincident with the point of consumption of dissolved Cd; similar observations hold for core JV-9.

![Figure 50 Dissolved Cd and \( \Sigma \text{H}_2\text{S} \) in cores JV-7 and JV-9, Jervis Inlet.](image)

### 3.4.4.2 Copper

Solid-phase Cu throughout all three Jervis Inlet cores ranges between 60 and 80 \( \mu \text{g g}^{-1} \) with the exception of core JV-7, where the upper 4 cm host concentrations as high as 160 \( \mu \text{g g}^{-1} \) (Figure 51). The absence of a surficial enrichment of solid-phase Cu in the oxic zone in the other two cores suggests that only a small fraction of the total metal is associated with authigenic oxides. The dissolved Cu profile in core JV-3 differs from those at the other two Jervis Inlet sites, increasing from a concentration of 15 nM at the sediment-water interface to a subsurface maximum of \(~70 \)
nM centred between 5 and 8 cm depth. Below 8 cm, the concentration of the element decreases precipitously (Figure 52). In contrast, dissolved Cu in both JV-7 and JV-9 increases from core top concentrations of 2 and 8 nM respectively to between 15 and 18 nM immediately below the interface. In both cores, Cu decreases with depth to values less than 3 nM; however, where Cu in JV-7 diminishes to 3 nM by ~20 cm depth, the corresponding decrease in JV-9 occurs by 2.5 cm depth as a result of the lower redox potential. The decrease in dissolved Cu at depth in all three cores most likely reflects sulphide precipitation as it is coincident with depletion of dissolved Fe and increasing H$_2$S concentrations. Dissolved Cu increases marginally at the base of all three cores (Figure 52, Figure 53 and Figure 54), despite the presence of free H$_2$S. The increases may reflect complexation by DOM, bisulphide or polysulphide species, none of which were measured directly.

![Solid-Phase Cu](image)

Figure 51 Solid-phase Cu in the cores of Jervis Inlet.
Figure 52 (a) Dissolved Cu, $\Sigma H_2S$ and dissolved Fe and (b) solid and dissolved Mn in core JV-3, Jervis Inlet.

Figure 53 Dissolved Cu and $\Sigma H_2S$ in cores JV-7 and JV-9, Jervis Inlet.
The subsurface maximum in dissolved Cu in JV-3 does not correspond well with the dissolved Fe maximum but seems more strongly associated with dissolved Mn (Figure 52). In core JV-7, the solid-phase Cu enrichment in the upper 4 cm corresponds closely to the zone of diminished dissolved Fe (Figure 59) suggesting that it may be associated with authigenic Fe-oxides. The lack of evidence for an oxide association of Cu in JV-9 is likely an indirect result of diminished bottom water oxygen concentrations toward the inlet head. It seems likely that the oxide associations of Cu are influenced by the effect of bottom water oxygen concentrations as inferred by Grill (1978). In the fully oxic surface sediments of JV-3, Cu appears to associate with Mn-oxides. It is conceivable that as the redox potential of the surface sediments decreases (because of lower bottom water oxygen values), the dominant oxide association shifts to Fe, until finally, at the inlet head, where bottom water conditions foster dysaerobic conditions near the sediment-water interface, Cu/metal-oxide interactions disappear entirely.

Figure 54 Solid-phase and dissolved Cu in core JV-7, Jervis Inlet.
3.4.4.3 Molybdenum

Jervis Inlet - 7

Solid-phase Mo is strongly enriched in the near-surface sediments of all three Jervis Inlet cores relative to the underlying deposits (Figure 55). In particular, the upper centimetre of cores JV-3 and JV-7 host concentrations of ~24 and 30 µg g\(^{-1}\) respectively. The strong correlations between Mo and Mn in all three cores (Figure 56) suggests that sequestration of Mo by Mn oxides is the likely enrichment mechanism. The values of the Mo/Mn ratio as determined from the slopes of the regressions in Figure 56 decrease from 7 \(\times\) 10\(^{-3}\) at JV-3 to 0.7 \(\times\) 10\(^{-3}\) at JV-9. Diminishing bottom water oxygen concentrations up-inlet, as suggested by Grill (1978), may influence the relationship as discussed further in Chapter 4.

Dissolved Mo in both JV-7 and JV-9 (data for JV-3 are not available) is seen to increase from core-top concentration of ~50 nM to ~150 nM within 1 to 2 cm of the sediment-water interface. Commensurate increases in dissolved Mn in both cores confirm that the core-top distribution of Mo is influenced by the cycling of authigenic oxides (Figure 57 and Figure 58).

![Solid-Phase Mo in Jervis Inlet](image)

*Figure 55* Solid-phase Mo in Jervis Inlet.
Figure 56 Solid-phase Mo vs. solid-phase Mn in the upper several centimetres of the three Jervis Inlet cores.

Figure 57 Solid and dissolved Mo and; solid and dissolved Mn in core JV-7, Jervis Inlet.

Dissolved Mo concentrations are elevated at depth in core JV-7 despite the presence of free H₂S and evidence of FeS formation below 6 cm (Figure 46 and Figure 57). It is possible that
DOM complexation of Mo inhibits sulphide precipitation, although the presence of DOM was not noted during core processing. In core JV-9, dissolved Mo decreases to values ranging from 50 to 100 nM before defining a broad maximum between 10 and 35 cm depth where values of 150 nM are reached. Dissolved Mo exists at substantial concentrations in the anoxic portions of core JV-9 as in JV-7, suggesting that consumption is inhibited. However, unlike the case in JV-7, the dissolved Mo content diminishes toward the base of the core.

Figure 58 Solid and dissolved Mo and; solid and dissolved Mn in core JV-9, Jervis Inlet.

3.4.4.4 Zinc

Jervis Inlet - 3

Solid-phase Zn distributions in all three cores share one similarity in that a 10 to 20 cm thick layer of Zn-enriched sediments overlies lower and relatively uniform concentrations at depth (Figure 59). The close correspondence between Zn and Pb (Figure 59) suggests that much of the Zn may be anthropogenic as Pb is a notorious contaminant of recent Jervis Inlet and other
sediments (MacDonald et al., 1991). Zinc in core JV-7 is anomalous in that the concentration profile displays an additional enrichment that spans the upper 2 cm of the core. The enrichment corresponds to diminished dissolved Fe suggesting that it could be associated with diagenetic Fe oxides; however, the close correspondence of Pb suggests that it may also be anthropogenic.

Figure 59 Solid-phase Zn and Pb in the three cores of Jervis Inlet.

Dissolved Zn profiles show a progressive variation up the inlet. In JV-3, the Zn distribution suggests release from two phases within the upper decimetre of the deposit. Subsurface maxima of 38 and 25 nM occur at 3.5 and 9 cm depth respectively. The thick oxic zone at this site apparently allows Zn contributions from organic matter remineralization and Fe oxide reduction to be observed in the porewaters. In contrast, only one zone of Zn remobilization is seen in JV-7, centred at 7 cm depth where a concentration in excess of 700 nM is attained (Figure 60). It is possible that the shallowing of the redoxcline toward the inlet head has caused the overlap of the two distinct zones of Zn release seen in JV-3. At the inlet head (JV-9), the lower maximum dissolved Zn content in pore waters can be attributed to a shallow redoxcline, commensurate with reduction of sulphate and production of H₂S which precipitates zinc from solution. Below the zone
of Fe reduction at the other sites, dissolved Zn is presumably similarly consumed via sulphide precipitation (Figure 61).

Figure 60 Dissolved Zn and dissolved Fe in core JV-3 and JV-7, Jervis Inlet.

Figure 61 Dissolved Zn and Fe in core JV-9, Jervis Inlet.
3.5 Saanich Inlet

3.5.1 Inlet Description and Core Locations

Saanich Inlet is an intermittently anoxic fjord located on the southeast corner of Vancouver Island (Figure 62). Approximately 25 km long and 7 km wide at its widest, the inlet connects to the Strait of Georgia through Satellite Channel. The main basin is deep (~230 m) and defined at its northern end by a moderately shallow sill (~75 m) which constrains deep-water renewal. The small drainage basin of Saanich Inlet sits in the rain-shadow of Vancouver Island. Consequently, the run-off (and associated lithogenic detrital input) received by the inlet directly via Goldstream River at its head is minimal (typically 0.9 m$^3$s$^{-1}$). Most of the fresh water entering Saanich Inlet is derived from the Cowichan River via Satellite Channel (Figure 62). The Cowichan flow follows the seasonal precipitation pattern (90 m$^3$s$^{-1}$ in December; 5 to 10 m$^3$s$^{-1}$ in August) and enters Saanich Inlet at very shallow depths. Because the majority of fresh water enters the inlet through Satellite Channel, estuarine circulation is relatively weak, diminishing towards the inlet head and is insufficient to flush waters below the sill depth; anoxia thus develops annually, in particular in the spring following the spring bloom (Francois, 1987). The deep water in Saanich Inlet is replaced in the late summer, when cold saline water wells up off the continental shelf and penetrates through Juan de Fuca Strait to Satellite Channel (Emerson et al., 1983; Francois, 1987). The extent of such renewal varies from year to year (Thompson, 1981).

Two cores were collected in Saanich Inlet, one in the central deep basin (SN-3) and a second in Squally Reach (SN-0.8) (Figure 62). In general, the sediments consist of highly anoxic, laminated, diatom-rich facies. Previous studies suggest that sedimentation rates are about 3 and 7 cm yr$^{-1}$ for sites SN-0.8 and SN-3 respectively (Matsumoto and Wong, 1977).

3.5.3 Diagenetic Description

Organic carbon concentrations in both SN-3 and SN-0.8 are relatively high in the upper decimetre (~4.5 to 5.5 wt.%), progressively decreasing towards the base of the core to approximately two-thirds of the values at the interface (Figure 63). The correlation between $\delta^{13}\text{C}$ and the $C_{\text{org}}/N$ weight ratio indicates slight variation in the provenance of organic carbon; both
Figure 62 Station locations map for Saanich Inlet, British Columbia
indicate that the organic component is dominated by material of marine origin (Figure 64).

Figure 63 Organic carbon in the cores of Saanich Inlet.

Figure 64 $\delta^{13}C$ (PDB) and $C_{org}/N$ weight ratio in the Saanich Inlet cores.
The high content of labile marine organic matter coupled with seasonal anoxia fosters reducing conditions throughout both cores. This is illustrated by high alkalinity and free sulphide within shallow interstitial waters (Figure 65), and by methane degassing upon core retrieval.

3.5.4 Trace Metal Behaviour

3.5.4.1 Cadmium

Sedimentary Cd in Saanich Inlet is enriched relative to most inlets observed within this and other studies. Contents in the surface sediments of cores SN-0.8 and SN-3 are 4 and 2 µg g⁻¹, respectively; concentrations increase with depth to values approximately twice as high by the base of each core (Figure 66). Dissolved Cd in both cores increases from an interfacial concentration of ~0.1 nM to a subsurface maximum between 0.6 and 0.8 nM at 1.25 cm depth before decreasing precipitously to values ≤0.1 nM where it remains to a depth of 25 cm. Below this horizon, concentrations increase progressively, reaching ~0.6 to 0.7 nM at the base of each core (Figure 66).
The similarity of the dissolved Cd profiles at the two coring sites reflects the influence of three major controls. First, the shallow subsurface release can be attributed to the remineralization of planktonic remains very near the sediment-water interface. Second, precipitation of CdS consumes dissolved Cd throughout the core. Third, the increase in dissolved Cd seen in the lower horizons of each core most likely occurs as a result of polysulphide or bisulphide complexation. Despite the qualitative observation that dissolved organic matter was abundant in all porewater samples from both cores, Cd concentrations were very low in the intermediate-depth pore water samples. Thus, organic complexation appears to play only a small role in the mobility of dissolved Cd; the majority of the apparent remobilization at depth must arise from complexation with reduced, soluble sulphur species, as discussed in Chapter 4.

3.5.4.2 Copper

Solid-phase Cu in cores SN-0.8 and SN-3 ranges from 40 to 80 \( \mu g \text{ g}^{-1} \), concentrations
typical of many coastal sediments. Dissolved Cu in both cores increases from an interfacial concentration of ~4 nM to two poorly-defined subsurface maxima located at 0.25 and ~5 cm below the sediment-water interface in core SN-0.8 and 1.25 and ~12 cm in core SN-3 (Figure 67). Below the deeper maxima, Cu decreases to values between ~4 and 6 nM where it remains before increasing towards the base of the core (Figure 67).

The release of dissolved Cu associated with the shallower of the subsurface peaks may reflect organic matter remineralization in the near-surface sediments. Dissolved Cu, like Cd, never reaches high concentrations in the porewaters due to the ubiquitous presence of free dissolved sulphide; Cu released from the organic matrix is precipitated as a sulphide resulting in a diminished transient concentration relative to more oxic sediments elsewhere. However, because the dissolved Cu content does not fall below 3 nM anywhere in either core despite high concentrations of free sulphide, it is likely stabilized in solution by dissolved organic matter or polysulphides. These possibilities will be evaluated in Chapter 4.

![Figure 67](image)

**Figure 67** Solid and dissolved Cu and $\Sigma H_2 S$ in the Saanich Inlet cores.
3.6 Vancouver Harbour

3.6.1 Inlet Description and Core Locations

Vancouver Harbour is located at the southern end of the Strait of Georgia within Burrard Inlet (Figure 68). The inner harbour is approximately 8.5 km long by about 3.5 km wide at its widest point. Average and maximum depths are ~25 m and ~66 m respectively. Vancouver Harbour is separated from the Strait of Georgia by the First Narrows sill (15 m deep) and receives minimal direct inflow of fresh water from either Indian Arm or the Seymour River. As a result, the circulation in the harbour is best described as weakly estuarine (Thomson, 1981). Tidal currents are significant within some reaches of the harbour, particularly near the First and Second Narrows, and as a result, bottom waters are perennially well oxygenated.

The majority of the sediment load into Vancouver Harbour comes from the high-relief mountains immediately to the north; deeply incised rivers deliver eroded material from this source. In addition to this natural input, the harbour sediments are in places heavily loaded with anthropogenic metals introduced via past and present industrial and shipping activities and discharge from storm and domestic sewers (Goyette and Boyd, 1989).

A large fraction of the Vancouver Harbour sediments is tidally scoured and sorted and as a result, the sediments are relatively coarse-grained. Core VH-1 was collected from the southern side of the basin in an effort to recover unwinnowed sediments representative of the recent depositional history of the harbour. The core was raised from 12 m of water, immediately outside of Coal Harbour (Figure 68), an area known to accumulate fine-grained sediments preferentially.

3.6.2 Stratigraphy

The $^{210}$Pb distribution in core VH-1 indicates that the deposits accumulated under steady state conditions for at least the interval represented by the upper decimetre of the core (Figure 69). The sedimentation rate implied by these data ranges from ~0.25 cm yr$^{-1}$ to 0.5 cm yr$^{-1}$ for uncorrected and maximally corrected rates respectively, suggesting that uninterrupted deposition occurred for at least the last 20 to 40 years at this site.
Figure 68  Station location map for Vancouver Harbour, British Columbia
3.6.3 Diagenetic Description

The sediments of core VH-1 contain ~3 wt.% organic carbon. However, compared to the other inlets studied, the bulk organic matter contains a proportionately larger fraction of terrestrially-derived material. This is best seen in the relatively light and high $\delta^{13}C$ values and $C_{org}/N$ weight ratios, respectively (Figure 70). Periodic oscillations in the organic carbon content with depth are mirrored by fluctuations in the $C_{org}/N$ weight ratio and $\delta^{13}C$ values indicating that periods of enhanced accumulations of organic carbon resulted from increased input of terrestrially-derived material. That the $^{210}$Pb data are continuous suggests that these changes represent compositional variations in the deposited organic matter rather than rapid, non-steady-state events such as dredging, prop wash or storm-wave disturbances.

Despite the high proportion of terrestrial material, the bulk organic matter in core VH-1 is sufficiently labile to fuel diagenesis and foster dysaerobia in the near-surface sediments. Dissolved and solid-phase Fe and Mn best display this. The data indicate the presence of a thin,
oxic veneer at the sediment-water interface; the upper centimetre not only hosts minimal concentrations of the dissolved metals but also displays a small diagenetic enrichment in solid Mn (Figure 71). Reduction of Mn and Fe oxide phases occurs at 1.25 and 3.5 cm depth respectively; the decrease in dissolved Fe below this depth implies that conditions are sufficiently reducing to produce FeS. Free sulphide does not occur at concentrations greater than a few µM until the dissolved Fe supply is exhausted below ~24 cm; even then \( \Sigma H_2S \) levels do not exceed 10 µM.

Figure 70  Organic carbon, \( C_{org}/N \) weight ratio and \( \delta^{13}C \) (PDB) in core VH-1, Vancouver Harbour.

3.6.4 Trace Metal Behaviour

3.6.4.1 Cadmium

Solid-phase Cd in core VH-1 is enriched relative to typical detritally-dominated sediments or shales; concentrations increase from 0.5 µg g\(^{-1}\) at the interface to a maximum of 1.5 µg g\(^{-1}\) at approximately 10 cm (Figure 72). Below this horizon, the Cd content decreases linearly to ~0.5
Figure 71  Dissolved and solid Fe and Mn in core VH-1, Vancouver Harbour.

Figure 72  Solid and dissolved Cd; and Cd/Al weight ratio and dissolved Fe in core VH-1, Vancouver Harbour. The point in parentheses is suspected of contamination.
μg g⁻¹ at the base of the core. The similarity between the Cd and Cd/Al weight ratio suggests that the Cd distribution is not an artifact of dilution by other phases.

Dissolved Cd increases from a bottom water value of 0.5 nM to an interfacial maximum of 2.7 nM in the 0.25 cm horizon. Below this depth, dissolved Cd decreases rapidly to values <0.1 nM by 2 cm; concentrations remain very low throughout the remainder of the core. There are no indications of remobilization with depth (Figure 72).

The distribution of solid Cd mimics sulphur (and as seen below, solid Mo) suggesting that some of the enrichment may be authigenic (Figure 73). That the distribution is similar to Mo suggests that both metals may be accumulating by a common mechanism, such as diffusion into the sediments followed by sulphide fixation as observed in Ucluelet Inlet by Pedersen et al. (1989). If authigenesis is important, then the historical increase and then decrease in Cd towards the sediment-water interface implies that conditions within Vancouver Harbour must have changed recently to cause a recent decline in the rate of authigenic accumulation of the metal.

![Graphs showing Cd vs S, Cd and S vs depth in core VH-1, Vancouver Harbour.](image)

Figure 73  Cd vs S and Cd and S vs depth in core VH-1, Vancouver Harbour.
In an attempt to determine whether downward diffusion and precipitation could account for the observed enrichment of solid-phase Cd at very shallow depths, the diffusion-consumption model was applied to the near-interface dissolved Cd distribution. Using assumptions of 0.8, 2.4 g cm\(^{-3}\), 0.25 cm yr\(^{-1}\) for porosity, bulk grain density and sedimentation rate, respectively and a flux of 0.048 \(\mu g\) cm\(^{-2}\) yr\(^{-1}\) or 430 x 10\(^{-12}\) mol cm\(^{-2}\) yr\(^{-1}\) as determined from the model fit shown in Figure 74, authigenic accumulation can account for about 0.4 \(\mu g\) g\(^{-1}\) of Cd. This value represents the majority of the Cd inventory at the sediment interface and suggests that the present-day accumulation of the metal can be accounted for almost exclusively by authigenic processes.

![Figure 74](image_url)  
**Figure 74** Diffusion-Consumption Model fit to the dissolved Cd data of core VH-1, Vancouver Harbour.

Because authigenic accumulation can account for a large fraction of the Cd in the near-surface sediments of core VH-1 and since the \(^{210}\)Pb data show that the core has accumulated under steady state conditions for at least the last two decades, it is possible that recent historical authigenic enrichments account for much of the maximum Cd content observed at 10 cm.

Several factors could have produced the observed maximum:

1) The sedimentation rate may have decreased in the past and then increased once again
to the interface. The $^{210}$Pb data imply that the sedimentation rate has been constant over at least the upper decimetre, ruling out this possibility.

2) Dilution by another phase may have diminished at 10 cm. This is not indicated by the data, since the $^{210}$Pb profile shows no change in sedimentation rate and the relatively invariant profile of the K/Al weight ratio (and others) suggests that changes in mineralogy can also be ruled out as a cause (Figure 75).

3) An additional source of Cd may have been involved. This could occur if bottom water Cd concentrations or the marine organic matter flux increased or if anthropogenic contributions increased and then decreased. There is no evidence for increased marine organic matter deposition at the 10 cm depth horizon (Figure 70); however, Pb and Zn profiles indicate that anthropogenic inputs to the harbour may have been relatively high during the period represented by the 8 to 12 cm depth interval.

4) An increase and subsequent decrease in the accumulation of organic matter could have
moved the zone of sulphate reduction temporarily closer to the sediment-water interface. This would have shortened the diffusional path-length, created a steeper concentration gradient and, thereby, increased the efficiency of authigenic accumulation.

It is suspected that the latter two possibilities (changing anthropogenic accumulation history and a variable redoxcline) provide the most likely explanations for the buried Cd concentration maximum. This conclusion is supported by two observations: 1) Cd, Mo, Pb and Zn share a similar distribution with a maximum at 10 cm depth; and 2) solid-phase Mo in particular shares a common distribution with Cd; authigenic Mo accumulation is known to respond to shallowing redoxclines (see below). The organic carbon distribution supports this by displaying elevated concentrations at 10 cm depth.

3.6.4.2 Copper

Solid-phase Cu in core VH-1 generally decreases from an enriched interfacial value of 280 \( \mu g \, g^{-1} \) to \(-50 \, \mu g \, g^{-1} \) by 13 cm depth. The Cu/Al weight ratio (Figure 76) similarly declines, which demonstrates that the decrease toward the base of the core in not due to dilution by a non-copper-bearing phase. The clear increase in the Cu content above 13 cm probably reflects a progressively greater anthropogenic contribution from industrial activity in the inner harbour. That Cu does not decrease towards the sediment-water interface like the other metals may mean that the primary source of anthropogenic Cu has not yet abated (Figure 76). It is possible that Cu-based anti-fouling paint arising from the abundance of recreational boat moorage in Coal Harbour may account for the disparate accumulation of Cu.

The Cu content below \(-13 \, cm \) appears to be associated with a biogenic component as witnessed by the strong correlation between Cu and organic carbon at depth (Figure 77). The correlation presumably breaks down in the upper 13 cm due to the addition of "excess" (i.e. anthropogenic) Cu. The relationship does not result from textural or mineralogical controls as implied by uniform Si/Al and Ti/Al weight ratios and the absence of a similar relationship between Zn and organic carbon (Figure 77 and Figure 78).
Dissolved Cu increases from a core-top value of 25 nM to a subsurface maximum of 90 nM at 0.25 cm depth, and then decreases precipitously to 20 nM by 1.75 cm where it remains for the remainder of the core (Figure 76). The near-interface release likely results from remineralization of organic matter, rather than dissolution of oxyhydroxides since the dissolved Fe content is minimal.
in the upper 2 cm (Figure 76).

Flux calculations demonstrate that very little of the observed solid-phase Cu enrichment is authigenic. Assuming a concentration gradient into the sediments of 70 nM over ~1 cm (Figure 76) and a Cu diffusion coefficient of 100 cm$^2$ yr$^{-1}$ (ignoring complexation) yields a diffusive flux of 0.38 µg cm$^{-2}$ yr$^{-1}$. Using this value as an accumulation rate and assuming sedimentation rate, bulk grain density and porosity used previously yields an accumulated concentration of ~3 µg g$^{-1}$. This value is two orders of magnitude smaller than the maximum concentration of Cu in this core. Clearly, downward diffusion of dissolved Cu from bottom waters or interfacial sediments followed by precipitation at shallow depths cannot account for a significant fraction of the solid-phase copper inventory in the Coal Harbour deposits.

3.6.4.3 Molybdenum

The distribution of solid-phase Mo in core VH-1 is almost identical to those of Cd and S. Concentrations are near-uniform at 0.5 µg g$^{-1}$ to 6 cm depth, increase to a maximum of 1.8 µg g$^{-1}$
at 13 cm, and decrease with depth to 0.5 μg g\(^{-1}\) at the base of the core (Figure 79). Dissolved Mo increases into the sediments from 75 nM in core-top water to a subsurface maximum at 1.25 cm, before decreasing to 40 nM by 2 to 4 cm depth. Below this horizon, the dissolved Mo content increases to a second maximum of 120 nM before decreasing to ~40 nM at the base of the core.

The slight elevation in solid-phase Mo and Mn contents in the upper 5 mm alludes to an association between Mo and Mn-oxides. This observation is supported by an initial increase in dissolved Mo across the sediment-water interface which is very similar to the distribution of Mn in shallow pore waters. Thus, dissolution of Mn-oxides can account for the observed release of Mo just below the sediment-water interface. The decrease in dissolved Mo below 1.25 cm probably results from coprecipitation with FeS, while the deeper maximum may arise from the thermodynamically favoured conversion of meta-stable FeS to pyrite. Consumption of Mo below that zone probably reflects precipitation with free sulphide deeper in the core.

---

![Figure 79](image)

**Figure 79** Solid and dissolved Mo and Mn in core VH-1, Vancouver Harbour.

The strong correlation among Mo, Cd and S suggests that the two metals accumulated
through a common mechanism, presumably diffusion to the sediments from bottom water followed by sulphide precipitation. At present, the interfacial sediments are oxic and host a small enrichment of solid-phase MnO₂. However, elevated values of Cd, Mo and S in the past allude to periods of authigenic accumulation which must have resulted from different depositional conditions. Other conditions being equal, a historically higher organic carbon accumulation rate would for example have had the effect of increasing solid Mo and Cd contents by shallowing the redoxcline and enhancing authigenic accumulation. The consequences of these and other observations are the focus of the next chapter.
Chapter Four - Interpretation of Metal Behaviour

The distributions of metals discussed thus far clearly respond to a broad range of environmental controls. The contrasts observed among the various sites are exploited in this chapter in order to determine which environmental variable (or variables) exert primary control on metal accumulation, given specific depositional settings. Although hydrographic differences among the fjords establish the basic context for this comparison, other factors, in particular rates of detrital sedimentation and accumulation of labile organic matter, will receive special attention. Each metal will be discussed individually.

4.1 Cadmium

4.1.1 Sedimentary Distribution

The range in concentration of Cd observed in the fjord sediments spans two orders of magnitude. The lowest concentrations (0.1 µg g⁻¹) were measured in core KN-2 (Knight Inlet) and are typical of the detrital background. Higher levels, ranging from 0.3 to 8 µg g⁻¹, were observed in the other deposits (Table 9). There is no common solid-phase distribution in the suite of cores; rather, each profile reflects the influence of several controls on the accumulation of the metal.

In contrast to the variability seen in the solid-phase profiles, the dissolved Cd distributions show a high degree of consistency regardless of location. The profiles are typically defined by three overlapping zones: the sediment-water interface and interfacial sediments, a mid-depth zone (typically between 5 and 25 cm depth depending on the core) and a deeper zone (generally greater than ~20 cm depth).

The interfacial zone in almost every deposit studied is characterized by steep concentration gradients which result from localized release, diffusion and precipitation of Cd on mm to cm depth scales at or immediately below the sediment-water interface. The profiles frequently indicate diffusion into the surface sediments from bottom water (KN-1, KN-2, KN-3, U-1) or release to interfacial or near-surface sediments via rapid remineralization of a (presumed) biogenic solid
phase. The resulting concentration maxima range from 0.3 to 15 nM and seem to depend primarily on the proximity of sulphate reduction to the sediment-water interface and indirectly on the quantity of labile Cd-containing organic material deposited at a given site.

<table>
<thead>
<tr>
<th>Inlet and Core</th>
<th>Cd (μg g⁻¹)</th>
<th>Inlet and Core</th>
<th>Cd (μg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rock Type</strong></td>
<td></td>
<td><strong>Sediment Type</strong></td>
<td></td>
</tr>
<tr>
<td>Basalt</td>
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<td>Shales</td>
<td>0.3</td>
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<tr>
<td>Granite</td>
<td>0.13</td>
<td>Clays</td>
<td>0.4</td>
</tr>
<tr>
<td><strong>Ucluelet Inlet</strong></td>
<td></td>
<td><strong>Indian Arm</strong></td>
<td></td>
</tr>
<tr>
<td>U-1</td>
<td>2 - 3.5</td>
<td>IA-1</td>
<td>0.34 - 0.57</td>
</tr>
<tr>
<td><strong>Knight Inlet</strong></td>
<td></td>
<td><strong>Jervis Inlet</strong></td>
<td></td>
</tr>
<tr>
<td>KN-1</td>
<td>0.2 - 0.5</td>
<td>JV-3</td>
<td>0.5 - 0.9</td>
</tr>
<tr>
<td>KN-2</td>
<td>0.09 - 0.12</td>
<td>JV-7</td>
<td>0.8 - 1.4</td>
</tr>
<tr>
<td>KN-3</td>
<td>0.25 - 0.40</td>
<td>JV-9</td>
<td>0.4 - 0.7</td>
</tr>
<tr>
<td><strong>Saanich Inlet</strong></td>
<td></td>
<td><strong>Vancouver Harbour</strong></td>
<td></td>
</tr>
<tr>
<td>SN-0.8</td>
<td>4.0 - 8.0</td>
<td>VH-1</td>
<td>0.5 - 1.5</td>
</tr>
<tr>
<td>SN-3</td>
<td>1.5 - 3.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9 Summary of Cd concentrations in the sediments of six B.C. inlets, and in average rocks and sediments (from Turekian and Wedepohl, 1961).

In general, precipitation of Cd below the zone of biogenic release occurs very rapidly, typically in the zone where Fe oxyhydroxide is reduced. This observation is consistent with the insolubility ascribed to Cd in the presence of low concentrations of sulphide (Davies-Colley et al., 1985; Daskalakis and Helz, 1992; Rosenthal et al., 1995), and with the work of Postma and Jakobsen (1996). Consequently, the redox conditions of the interfacial sediments play a critical role in governing the amount and distribution of dissolved Cd in that zone. The precise location of the onset of sulphate reduction in part determines the quantity of biogenic Cd lost to the water column through diffusion, relative to the amount retained within the sediments through the
formation of authigenic sulphides. Where sulphate reduction occurs very near the sediment-water interface or near the zone of maximum biogenic release, Cd that would normally be released to the porewaters to diffuse upward and out of the sediments is retained within the deposit. This influence is most readily seen as a correlation between the maximum concentration of dissolved Cd associated with the interfacial sediments and the depth of the onset of sub-oxia as determined by the rapid increase in the concentration of dissolved Fe (Figure 80).

![Graph](image)

**Figure 80** The maximum concentration of dissolved Cd in the near-interface porewaters vs. the depth of onset of sub-oxia as determined by the onset of Fe reduction for the cores of Jervis, Knight (except KN-2), Saanich and Ucluelet Inlets.

The strong correlation \( r = 0.946 \) suggests that as the redox potential of the interfacial sediments decreases, so does the concentration of dissolved Cd, and, by extrapolation, the efflux of Cd from the sediments to the overlying bottom waters. Thus, estimates of the return of dissolved Cd to the water column from remobilization within interfacial sediments (e.g. the value of 80% estimated by Gobeil et al., 1986) are site specific. This is supported by the work of Lapp and Balzer (1993) who observed higher effluxes of Cu, Cd and Ni with increasingly oxic sediments in Kiel Bight. The relationship in Figure 80 suggests that the range of effluxes calculated for this suite of B.C. coastal sediments increases by at least a factor of five from the highly anoxic sediments of Saanich Inlet (SN-0.8) to the fully oxic deposits of Jervis Inlet (JV-3). Interestingly, the intercept on
the ordinate in Figure 80 (−0.5 nM Cd) suggests that even in completely anoxic deposits such as those of Saanich Inlet, the release of biogenic Cd results in a measurable sub-surface maximum and a corresponding flux toward the sediment-water interface. However, under anoxic water cover (Saanich Inlet), dissolved Cd released to bottom waters would precipitate rapidly and accumulate near the interface (i.e. Jacobs and Emerson, 1982).

Dissolved Cd in the intermediate-depth zone of all cores studied was nearly completely consumed, almost certainly as a result of sulphide precipitation. In many instances (e.g. cores U-1, KN-1, KN-2, KN-3, JV-3 and JV-7), pore water Cd contents remained below the detection limit to the base of the core. In each of these deposits (except KN-3), $\Sigma H_2S$ was < 120 µM. However, where elevated concentrations of free sulphide prevailed at depth, Cd was remobilized to varying degrees. To a first approximation, the degree of such remobilization was related to the concentration of total free sulphide (Figure 81). It has been suggested through observation (Gobeil et al., 1986) and thermodynamic calculation (Boulegue, 1983; Davies-Colley et al., 1984; Davies-Colley et al., 1985) that dissolved Cd may be stabilized by various species of reduced sulphur. The most commonly invoked species are bisulphide (HS$^-$) and polysulphides (typically HS$_4^-$ and HS$_5^-$). However, because polysulphides are produced through the partial oxidation of sulphide to elemental sulphur followed by reaction with bisulphide (Giggenbach, 1972; Luther et al., 1985), they do not necessarily exist in concentrations proportional to the total sulphide concentration. Luther et al. (1985) found that while total sulphide in anoxic porewaters increases in concentration with depth, the proportion of polysulphides actually decreases. Thus, the increase in dissolved Cd with depth in the Saanich Inlet cores (i.e. the cores with the greatest concentrations of remobilized Cd at depth and the highest concentrations of free sulphide) may suggest that bisulphide is more important to Cd complexation than polysulphides. This is in part supported by the work of Jacobs et al. (1985) in Framvaren Fjord which suggests that class B metals (in particular dissolved Cd) increase in concentration in sulphide-rich zones because of their sulphide-stoichiometry. The concentrations of metals that complex with only one bisulphide ion (e.g. Zn) do not increase with increasing quantities of free sulphide, but, those that complex
with multiple bisulphide ions (such as Cd) solublize to a greater degree. However, the imperfect correlation of Figure 81 also suggests that bisulphide alone is not responsible for the behaviour of dissolved Cd in highly anoxic porewaters; polysulphide and/or organic complexation cannot be ruled out entirely.

Figure 81  Dissolved Cd in the deepest horizons of each core plotted against the total free sulphide

Dissolved organic matter has often been suggested to stabilize significant concentrations of some dissolved metals in anoxic porewaters because of its strong "generic" complexing ability (Elderfield, 1981; Bruland, 1989, 1992). While Cd has been observed to associate with some highly metal-specific ligands in open ocean surface waters (Bruland, 1992) and to substitute for Zn as a micronutrient within phytoplankton (Price and Morel, 1990), similar associations have never been seen in pore waters. Qualitative field observations made in this study suggest that Cd remobilization at depth does not arise from complexation by organics. The presence of DOM in the porewaters of several inlets was indicated by the tendency for 0.45 μm filters to clog rapidly, by a characteristic yellow colouration of filtrates and by the formation of precipitates upon the addition of acid. These properties of pore waters are best explained by the presence of DOM. That such material occurred throughout Ucluelet and Saanich Inlet deposits in zones where dissolved Cd
was undetectable is taken as indirect evidence of the absence of a significant interaction between Cd and DOM. The association with reduced sulphur is, by default, more important. These observations are consistent with the Class B character of Cd (Stumm and Morgan, 1981; Gaillard et al., 1986) and the observations of Elderfield (1981) and Comans and van Dijk (1988) which indicated that Cd is not affiliated with DOM in estuarine waters or pore waters.

The enhanced mobility of Cd at depth does not have any impact on the overlying water column. This is because zones of elevated free sulphide are typically far removed from the sediment-water interface (usually > 20 cm). Dissolved Cd concentrations are minimal until very high free sulphide concentrations are attained (i.e. mM range); thus, concentration gradients in the “middle zone” support trivial diffusive fluxes. In addition, remobilization is marginal in the cores with several hundred micromolar levels of $\Sigma H_2 S$, with Cd concentrations remaining $\leq 0.2$ nM. When compared to the near-interface zone, the concentration gradients (hence, the upward fluxes) associated with sulphide complexation at depth are lower by an order of magnitude or more. Furthermore, Cd that diffuses from this source into shallower horizons precipitates well before reaching the sediment-water interface.

Allusions to an association of Cd with diagenetic oxides have been made in some studies (Gobeil et al., 1986; Westerlund et al., 1986; Cowan et al., 1991; McCorkle and Klinkhammer, 1991), but observations of direct associations are rare. With the exception of core JV-3, none of the deposits studied here supports the notion of an association between Cd and an oxide phase - no addition of Cd to porewaters was observed commensurate with the release of dissolved Fe or Mn. However, core JV-3, in the deep basin of Jervis Inlet, was the most oxic core studied; dissolved Fe did not appear in pore water until depths of ~7 cm. Dissolved Cd (Figure 49) was released (1.5 nM maximum) between the zones of Mn- and Fe-oxide reduction, well below the zone of biogenic release (~5 cm depth). These data suggest that an association of Cd with an oxide phase does exist but can be seen in pore water data only when sulphate reduction is displaced to deeper depths. In the majority of coastal sediments, and in the other deposits studied here, release of Cd from hydrous oxides is not observed. Previous studies in which oxide
associations were reported (Gobeil et al., 1987; McCorkle and Klinkhammer, 1991) focused on sediments with relatively thick oxic zones. Thus, intense diagenesis in coastal sediments which establishes reducing conditions near the sediment-water interface may preclude the build-up of dissolved Cd in the majority of coastal deposits. Because the transition from sub-oxic to anoxic conditions (Fe reduction to sulphate reduction) occurs over very small vertical distances in deposits that underlie productive surface waters (e.g. Shaw et al., 1990), and because Cd is very insoluble in the presence of low concentrations of free sulphide (Davies-Colley et al., 1985; Rosenthal and Boyle, 1995), any dissolved Cd released from the oxide fraction should be removed from solution by sulphide precipitation as quickly as it was released. Such a zone would be so localized as to be beyond the sampling resolution of this study. Only in a core such as JV-3, where the ‘biogeochemical rubber band’ is stretched over greater distances, is Cd release from oxide phases displaced sufficiently from sulphate reduction so as to result in a measurable concentration in the porewaters.

4.1.2 Sedimentary Accumulation

The distribution and inventory of Cd in any given core reflects contributions from several sources and controls. The Cd content appears to respond most sensitively to three influences: sedimentation rate; the flux or content of marine organic matter; and the redox state of the water column and interfacial sediments. Each is discussed in turn.

Sedimentation Rate

Because detritally-derived material is depleted in Cd when compared to metals such as Cu or Zn (Table 9; Turekian and Wedepohl, 1961; Gong et al., 1977), contributions from other sources are more important to the total inventory in sediments. The authigenic component is not only comparatively large, but is very sensitive to several depositional parameters, in particular, sedimentation rate. At sites where authigenic accumulation of Cd by sulphide precipitation is important (i.e. Ucluelet Inlet, Vancouver Harbour, Knight Inlet and Indian Arm), the sedimentation rate is inversely related to the Cd concentration (Figure 82).

Lower sedimentation rates in coastal sediments reflect diminished inputs of terrigenous
material, depleted in Cd. The relation is not linear but instead asymptotically approaches the terrestrial detrital concentration of ≤0.1 μg g⁻¹ at high sedimentation rates. This trend reflects a fundamental difference anticipated between coastal and open-ocean sediments. The sedimentation rate in oceanic sediments is in part a function of primary productivity in the surface waters, hence, the flux of organic matter to the sediments (Muller and Seuss, 1979). Consequently, higher sedimentation rates typically lead to more strongly reducing sediments (i.e. Suess, 1980); in oceanic deposits, then, higher sedimentation rates will result in higher authigenic accumulations. In coastal settings, sedimentation rate is related primarily to the input of terrestrial detritus (Farrow et al., 1983; Bornhold et al., 1994). Accordingly, a decrease in sedimentation rate in a coastal regime does not necessarily correspond to a decrease in the accumulation rate of organic matter - it may simply reflect a lower input of lithogenic material. Thus, the net effects of increasing sedimentation rate in the coastal ocean are to: dilute authigenic Cd with detrital aluminosilicates, diminish oxidant replenishment to porewaters (lowering Eh, offsetting dilution to some extent) and dilute organic matter (lessening diagenetic intensity). Collectively, these effects may account for much of the form of Figure 82. These influences are illustrated in the data from Knight Inlet which show marked changes in Cd with sedimentation rate (Table 10); the concentration of Cd in core KN-2 represents a near purely-detrital end-member.

![Figure 82 Relationship between authigenic Cd vs. sedimentation rate. Data from Ucluelet Inlet, Knight Inlet, Indian Arm and Vancouver Harbour.](image-url)
Table 10 Total Cd and sedimentation rate for the three Knight Inlet cores.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sedimentation Rate</th>
<th>Total Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>KN-1 (mouth)</td>
<td>0.3 cm yr⁻¹</td>
<td>0.45 μg g⁻¹</td>
</tr>
<tr>
<td>KN-3 (mid-inlet)</td>
<td>1 cm yr⁻¹</td>
<td>0.30 μg g⁻¹</td>
</tr>
<tr>
<td>KN-2 (head)</td>
<td>4 cm yr⁻¹</td>
<td>0.10 μg g⁻¹</td>
</tr>
</tbody>
</table>

**Marine Organic Matter**

There is little doubt that organic matter influences the cycles of Cd in the water column and in interfacial porewaters; phytoplankton, for reasons not fully understood, take up Cd from surface waters (Boyle, 1976; Price and Morel, 1990; and others). At face value, therefore, it is not surprising to find that organic-rich sediments are also enriched in Cd. Figure 83 displays the relationship between total Cd and total organic carbon for all cores of this study and shows that deposits containing elevated concentrations of organic matter also host elevated concentrations of Cd. Cadmium to organic carbon weight ratios have been estimated at ~$100 \times 10^{-6}$ for fresh planktonic material (Collier and Edmond, 1984); however, Cd is known to be released rapidly upon remineralization of the organic matrix. That the Cd/Al ratio in sediment traps has been observed to decrease by factors of three to four through several hundred metres of water column (Gendron et al., 1986) supports this notion. Thus, although Cd is associated with biogenic material and is delivered to the seafloor with this phase, the relationship seen in Figure 83 likely reflects the combined effect of elevated biogenic Cd accumulation in concert with increased authigenic accumulation associated with the more strongly reducing sediment. As the delivery of organic carbon to the sediments increases, so does biogenic Cd. At the same time, increasing the organic carbon accumulation rate shallows the zone of sulphate reduction, thereby enhancing the efficiency of authigenic accumulation of the metal.

Another factor that confounds the linearity of the relationship shown in Figure 83 can be
seen in the weak correlation between total Cd and \( C_{\text{org}}/N \) and \( \delta^{13}\text{C} \) from all inlet sediments (except the contaminated deposits of Vancouver Harbour) (Figure 84). The data suggest that the fraction of marine organic matter and not just the absolute concentration of bulk organic matter is important. This relationship arises for two reasons: first, marine organic matter is known to have a greater affinity for Cd than its terrestrial counterpart (Fisher, 1986; Price and Morel, 1990; Bruland, 1992); and second, marine organic matter is more labile, creating sediments of lower redox potential (Hedges et al., 1988), further enhancing the potential for authigenic accumulation. The contention that marine biogenic material contributes directly or indirectly to the Cd inventory is supported by evidence from deposits of Jervis Inlet which host recent additions of terrestrial organic carbon without commensurate increases in total Cd (compare Figures 44 and 48).

![Solid-Phase Cd (µg g⁻¹) vs. Organic Carbon (wt.%)](image)

Figure 83 Total Cd in all cores studied (except VH-1) vs. total organic carbon.

**Redox Conditions of Water Column and Sediments**

Perhaps the most important factor contributing to accumulation of Cd in recent sediments is the redox potential of the water column. The highest concentrations of Cd in this study were found in Saanich Inlet sediments (up to 8 µg g⁻¹; Table 9). Equally high concentrations occur in similar environments elsewhere (i.e. 10 to 20 µg g⁻¹ in Framvaren Fjord (Skei, 1988); 1 to 7 µg g⁻¹ in Baltic Sea sediments (Brügman, 1988)). In anoxic environments, not only do the sediments retain all of
the biogenic Cd released during remineralization, but dissolved Cd from the water column precipitates as sulphide phases and accumulates in the surface deposits. To some degree, this relationship is reflected in the weak correlation between Cd and total S (salt-free) in the deposits of this study (Figure 85) which display an exponential increase in Cd with increasing sulphur content. Sulphur enrichments here are assumed to represent accumulation of authigenic sulphide phases.

![Figure 84](image)

**Figure 84** Solid-phase Cd in all cores (except VH-1) vs. Corg/N weight ratio and \( \delta^{13}C \) (‰ PDB).

![Figure 85](image)

**Figure 85** Solid-phase Cd vs. total sulphur in all cores of the study

Within Saanich Inlet, higher Cd values occur at the more strongly reducing of the two stations (SN-0.8). Dilution of authigenic Cd by sediments from the Cowichan River (outside the inlet) cannot account for the difference between the deposits as Cu is also enriched (see below) in
SN-0.8 relative to SN-3; while the detrital material from this source is deplete in Cd it is comparatively enriched in Cu. If terrestrial dilution were responsible for the metal distribution, Cd and Cu would not be enriched in the same core. Since the nature and quantity of organic matter at the two Saanich Inlet sites are similar, it is logical to assume that hydrologic differences account for the differing solid-phase Cd concentrations. Specifically, the water column at SN-0.8 is less frequently re-oxygenated than SN-3; it is possible that the average water column oxygen content influences the precipitation and, hence, accumulation of sulphide-associated Cd.

4.2 Copper

4.2.1 Sedimentary Distribution

Solid-phase Cu ranges in concentration from 20 to 300 µg g⁻¹ across the spectrum of depositional environments investigated in this study (Table 11). Typical Cu values in terrigenous detritus range from 60 to 120 µg g⁻¹ (Turekian and Wedepohl, 1961), and contrast with some of the elevated values observed in this work, suggesting that additional, non-lithogenic processes contribute to the Cu inventory in some deposits.

The distribution of dissolved Cu in porewaters is more complex than for many other metals - there appears to be several overlapping processes contributing to the observed variation: biogenic release, cycling associated with metal oxides, sulphide precipitation, sulphide complexation and organic complexation. These influences will be discussed in turn.

Biogenic Release

In near-surface sediments, the distribution of dissolved Cu is characterized by steep concentration gradients originating at or immediately below the sediment-water interface. Dissolved Cu concentrations typically diminish rapidly above and below this zone. This source is assumed to be biogenic as the zone of maximum release is very shallow, as has been seen in other studies (Gaillard et al., 1986; Pedersen et al., 1986; Shaw et al., 1990; Lapp and Balzer, 1993). Copper is known to cycle with organic matter (Fischer et al., 1986; Heggie et al., 1987). Because it displays similar interstitial profiles to other metals (i.e. Cd and Zn) also known to associate with organic matter (Gobeil et al., 1987; Francois et al., 1988; Shaw et al., 1990), the
source of Cu in the near-surface sediments is assumed to arise from remineralization of this material. Furthermore, the maximum dissolved concentration in many cases does not correspond to the dissolution behaviour of other solid phases, specifically, Mn or Fe oxides. This is particularly evident in cores such as JV-7 or VH-1 (Figures 57 and 82, respectively) where Fe and Mn reduction is displaced by several cm from the shallow zone of Cu release. The absence of commensurate releases of Mo in the near-surface sediments (an element known to associate strongly with oxides but not with organic matter) supports this premise.

<table>
<thead>
<tr>
<th>Inlet-Core Cu (µg g⁻¹)</th>
<th>Inlet-Core Cu (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rock Type</strong></td>
<td><strong>Sediment Type</strong></td>
</tr>
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<td>45</td>
</tr>
<tr>
<td>Granitic</td>
<td>Clays*</td>
</tr>
<tr>
<td>10 - 30</td>
<td>250*</td>
</tr>
<tr>
<td><strong>Ucluelet Inlet</strong></td>
<td><strong>Indian Arm</strong></td>
</tr>
<tr>
<td>U-1</td>
<td>IA-1</td>
</tr>
<tr>
<td>20 - 30</td>
<td>90 - 150</td>
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<td><strong>Knight Inlet</strong></td>
<td><strong>Jervis Inlet</strong></td>
</tr>
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<td>JV-3</td>
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<td>SN-3</td>
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<tr>
<td>20 - 60</td>
<td></td>
</tr>
</tbody>
</table>

Table 11 Solid-phase Cu concentrations in several rock types and in the inlets of this study., elevated metal concentrations in deep sea clays likely result from diagenetic oxide or nontronite enrichments (from Wedepohl, 1971; Pedersen et al., 1986).

The magnitude of the dissolved Cu maximum ranges from 11 to 250 nM and appears to be influenced in part by the redox conditions of the interfacial sediments (Figure 86). Elderfield et al. (1981) and Shaw (1990) noted an absence of biogenic Cu remobilization in highly anoxic conditions.
near-surface pore waters, as seen here in Saanich Inlet, while the data of Lapp and Balzer (1993) indicate elevated dissolved Cu maxima in the surface horizons of more oxic deposits. However, unlike Cd, the overall relation between redox potential and dissolved Cu in this study is weak (Figure 86). It is possible that complexation by organic matter degrades the relationship. The most reducing sediments (Ucluelet and Saanich Inlets) qualitatively host the most dissolved organic matter. That these deposits also contain high concentrations of dissolved Cu despite the presence of free sulphide is taken as partial evidence of the importance of organic complexation. Dissolved organic matter may outcompete sulphide for complexation of Cu in interstitial waters; indeed, dissolved Cu is observed in the anoxic porewaters of many of the inlets studied here, as discussed below. If sulphide precipitation is retarded by organic complexation, the relationship between the onset of suboxia and dissolved Cu will become decoupled. The relationship may be further weakened by the influence of oxide scavenging in the zone where maximal biogenic release occurs. Because Cu consumption is not limited to sulphide precipitation, the onset of anoxia cannot represent the sole influence on Cu consumption within interfacial sediments.

Figure 86 Maximum dissolved Cu in porewaters plotted against the onset of suboxia and the average organic carbon content

The behaviour of Cu in the sea is strongly tied to the cycling of organic matter (Davis, 1984; Canabiss and Schuman, 1988; Coale and Bruland, 1988; 1990; Gerringa et al., 1991); thus, it is conceivable that the quantity of dissolved Cu released to the interstitial waters is related to the quantity and type of organic matter observed in the sediments (Gerringa, 1990; Dai et al., 1995; Shine and Wallace, 1995). However, this is not evident in the B.C. inlets data which, if anything,
display a very poor negative correlation between Cu and organic carbon (Figure 86). The chalcophilic nature of Cu naturally precludes the visible manifestation of such an association for as the organic matter content of a deposit increases, the redox potential typically decreases. Under such conditions, Cu would be expected to precipitate as a sulphide, thereby minimizing the magnitude of the dissolved Cu maximum. The implication of this is that the amount of Cu released from the biogenic phase is likely unrelated to the magnitude of its maximum concentration or to the steepness of its concentration gradient. Not only does much of the dissolved biogenic Cu precipitate as an authigenic sulphide (therefore, contributing only transiently to the dissolved inventory), but strong complexation of pore water Cu by dissolved organic matter dramatically lowers the effective diffusion coefficient by as much as two orders of magnitude (Elderfield, 1981).

**Associations with Metal Oxides**

Copper is known to associate with oxides of Fe and Mn (Balistrieri and Murray, 1982; 1984; Hem et al., 1989). However, the proximity of release of biogenic Cu with the near-interface cycling of Mn and Fe in many coastal sediments often precludes delineation of the relative importance of these controls on Cu cycling. In some B.C. inlet deposits, affiliations of Cu with oxyhydroxides do not appear to be of consequence (e.g. JV-9, KN-1) - in these cases there are no concurrent solid-phase enrichments of Cu with either Mn or Fe. However, at a number of other sites, strong relationships exist between Cu and one of either Mn oxides (cores JV-3, KN-2 and KN-3) or Fe oxides (cores JV-7 and U-1). Why Cu associates more strongly with either oxide in a given deposit is not clear; however, there are several possible explanations.

Because Cu exists naturally as either a mono or divalent cation, it should have a natural tendency to associate more strongly with Mn-oxides than with those of Fe (Balistrieri and Murray, 1984). However, the association of Cu with Mn may be complicated by ambient redox potential. Dymond (1984) has suggested that highly oxidized Mn has a greater affinity for Cu than less oxidized forms. The data of Hem et al. (1989), which considered Cu associations with Mn oxides and the dependence on the Mn oxidation state, are in agreement with the importance of the Mn
oxidation state. In the present study, Cu in the two most oxic deposits (at KN-2 and JV-3) displays a preference for Mn-oxides (Figures 27 and 52). If Cu (like Mo) has an affinity for highly oxidized Mn, a stronger relative association with Fe-oxides may arise where fully oxic conditions do not exist. By extension, the absence of an association of Cu with Mn in Ucluelet Inlet (Figures 4 and 8) may arise from sub-oxic conditions at the sediment-water interface with the resulting conditions of Mn-starvation. This occurs where interfacial redox conditions lie between Mn and Fe reduction. In such cases an association in sediments between Mn-oxide and Cu is not possible.

The influence of interfacial redox conditions is best illustrated in the suite of cores from Jervis Inlet, which differ primarily in their near-surface redox potential. It seems likely that the oxide associations of Cu are influenced by the effect of diminishing bottom water oxygen concentrations toward the inlet head. In the fully oxic surface sediments of JV-3, Cu appears to associate with Mn-oxides (Figure 52). As the redox potential of the surface sediments decreases toward JV-7, the dominant oxide association shifts to Fe (Figure 54). Finally, at the inlet head (core JV-9), where lower bottom water oxygen concentrations foster dysaerobia near the sediment-water interface, Cu/metal-oxide interactions disappear entirely. This trend is also illustrated in Figure 87 where the decoupling of Cu from oxide remobilization occurs up-inlet. The frequent observation of Cu release coincident with Fe more so than with Mn may merely reflect the greater tendency for coastal sediments to host sub-oxic conditions near the sediment-water interface rather than a preferential association of Cu with Fe over Mn.

**Sulphide Precipitation**

Sulphide precipitation of dissolved Cu in most cores is expressed as a rapid decrease in concentration with depth either below the zone of biogenic release (e.g. VH-1, IA-1, JV-7, JV-9, KN-1) or following release from a metal oxide (e.g. JV-3, U-1). Concurrent consumption of dissolved Cu and Fe in the presence of free sulphide confirms the influence of sulphide. However, as discussed previously, the zones of precipitation for Cu and Fe do not fully overlap. Like Cd, Cu precipitation occurs at marginally shallower depths than Fe precipitation (e.g. core JV-3; Figure 52). Precipitation of Cu prior to that of Fe is evident in the sediments of the Guatemala
Basin (Pedersen et al., 1986), the Eastern Equatorial Pacific (Klinkhammer, 1980), and in the water columns of Framvaren Fjord and the Cariaco Trench (Jacobs et al., 1985; 1987). Such behaviour likely arises in part from the differing solubilities of CuS and FeS; CuS is very insoluble (pK CuS = 36.1 vs. CdS = 27.0 and FeS = 18.1; Stumm and Morgan, 1981). Because Fe does not precipitate as readily as Cu or Cd, the maximum in dissolved Fe appears to be displaced to
deeper depths than the less soluble metals. However, as suggested by Postma and Jakobsen (1996), it is possible that sulphate reduction may precede that of Fe in many deposits, and thus account for such seemingly paradoxical distributions.

**Associations of Dissolved Copper**

In the anoxic deposits of this study, Cu does not precipitate quantitatively with sulphide. Even in SN-0.8, the most reduced sediments investigated, dissolved Cu increases with depth below an initial zone of precipitation. Copper is rarely precipitated quantitatively by sulphide; only sites JV-9 and KN-1 host zones of near quantitative consumption.

Relationships between Cu and reduced sulphur have been studied previously by Dyrssen (1985), Jacobs et al. (1985), Dyrssen (1988), Shea and Helz (1988) and Dyrssen and Kremling (1990). The findings suggest that Cu is capable of forming soluble complexes with various polysulphide species. Other studies (Elderfield, 1981; Calvert, et al., 1985; Gerringa and Cambon, 1991) have focused on Cu interactions with DOM and have inferred strong interactions in pore waters. In this context, two notable differences between the porewaters of Saanich Inlet and those of the other inlets studied may explain why Cu is not quantitatively consumed under strongly reducing conditions. Saanich Inlet porewaters contain high concentrations of free sulphide (as bisulphide and/or polysulphides) and qualitative observations of abundant DOM. Complexation by either or both of these components is likely responsible for elevated dissolved Cu levels in the anoxic porewaters of many coastal sediments. Near-quantitative consumption of Cu in cores JV-9 and KN-1, both of which have low concentrations of free sulphide and dissolved organic matter, support this hypothesis.

It is suspected that bisulphide or polysulphide complexation of Cu, although invoked frequently (Davies-Colley et al., 1985; Shea and Helz, 1988), is less important in controlling the copper content of pore waters than complexation by organic matter. This suspicion is in part supported by observations of dissolved Cu profiles from anoxic water columns such as the Cariaco Trench, Framvaren Fjord and the Baltic Sea. Such waters are DOM-poor relative to typical coastal pore waters and display near-quantitative consumption of copper in the presence
of elevated free sulphide concentrations (Jacobs et al., 1985; Jacobs et al., 1987; Dyrssen and Kremling, 1990; and others). The greater importance of Cu complexation by DOM over that of sulphide is illustrated by comparing the behaviour of Cu with that of Cd in Saanich Inlet. Cadmium is known to interact minimally with DOM (Elderfield, 1981); the increase in Cd solubility seen in anoxic cores is generally ascribed to bisulphide or polysulphide complexation (Davies-Colley et al., 1985). Dissolved Cd in SN-0.8 displays a concentration minimum from 2 to 25 cm depth before increasing with depth to the base of the deposit (Figure 88). By comparison, dissolved Cu does not display the same minimum, but sustains elevated concentrations or increases with depth through the entire zone. Assuming that sulphide complexation of Cd and Cu are roughly equal (if anything, Cd should be complexed more strongly by reduced sulphur than Cu as it has more class B character), the increasing solubility of Cu from 2 to 25 cm must arise from complexation by ligands other than sulphides. Presumably, these are organic in origin.

Figure 88 Dissolved Cu and Cd from core SN-0.8 in Saanich Inlet.
4.2.2 Sedimentary Accumulation

The concentration of sedimentary Cu in a coastal deposit is controlled by lithogenic inputs. This is illustrated in this study as a universal correlation between non-sulphur-associated Cu (Cu/S) and non-sulphur-associated Fe (Fe/S) (Figure 89). The only deviation from this relationship arises in the deposits of Vancouver Harbour and Indian Arm where anthropogensis is a factor. The influence of lithogenic Cu is further exemplified in the suite of cores from Knight Inlet which display increasing Cu and Cu/Al weight ratios toward the inlet head, the principal source of lithogenic detritus (Table 12).

Figure 89 Cu/S vs. Fe/S in all cores of the study and an expanded view of the data cluster near the origin as well as Cu/Al and Fe/Al weight ratios. The S data were corrected for dilution by seasalt.

Because lithogenic Cu is predominantly lattice-bound within aluminosilicates, it is non-reactive, at least over the short term. However, a component of Cu subject to diagenetic recycling
does arise from biogenic and perhaps authigenic sources. Consequently, the quantity and type of organic matter as well as the redox conditions of the water column or sediments plays an interdependent roles in the early diagenesis of this element.

<table>
<thead>
<tr>
<th>Location</th>
<th>Site</th>
<th>Solid-phase Cu</th>
<th>Cu/Al weight ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Mouth</td>
<td>KN-1</td>
<td>35 (µg g⁻¹)</td>
<td>0.6 x 10⁻³</td>
</tr>
<tr>
<td>Mid-Inlet</td>
<td>KN-3</td>
<td>60 (µg g⁻¹)</td>
<td>0.9 x 10⁻³</td>
</tr>
<tr>
<td>Inlet Head</td>
<td>KN-2</td>
<td>95 (µg g⁻¹)</td>
<td>1.1 x 10⁻³</td>
</tr>
</tbody>
</table>

Table 12 The progressive enrichment of solid-phase Cu towards the head of Knight Inlet.

A negative correlation exists between Cu/Al and δ¹³C when all deposits are considered simultaneously (Figure 90). Rather than reflecting an association between Cu and terrestrial organic matter, this trend is viewed as additional evidence for the strong dependence of Cu on the presence of lithogenic detritus as no correlation exists between the Cu/Al weight ratio and organic carbon (Figure 90).

![Figure 90 Cu/Al vs. δ¹³C (%PDB) and organic carbon in all cores of the study.](image)

While authigenic Cu accumulates preferentially under anoxic water columns (Skei, 1988; Francois, 1988), the enrichments associated with such deposits are not as pronounced as for elements with a lower crustal abundance (such as Cd and Mo) because the lithogenic background for Cu is comparatively high (Table 11).
The influence of anoxia is best seen in the two most anoxic deposits of this study (Saanich and Ucluelet Inlets) which, coincidentally, have the lowest inputs of lithogenic detritus and the lowest concentrations of solid-phase Cu. Evidence for enhanced authigenic accumulation of Cu with anoxia is seen within Saanich Inlet as a trend of increasing Cu concentrations with increasingly reducing conditions (i.e. sediments at SN-0.8 contain more Cu than those at SN-3) (Table 11). The headward enrichment of Cu does not arise from proximity to a source of Cu-containing minerals, but rather reflects greater authigenic accumulations as the sediments are markedly more reducing toward the inlet head and the primary source of lithogenic detritus is through the inlet mouth from the Cowichan River.

Solid-phase Cu is influenced by anthropogenesis more than most other metals. The sediments of Vancouver Harbour and Indian Arm (VH-1 and IA-1) contain the highest concentrations of Cu seen in the study (up to 470 μg g⁻¹). The most likely source of enrichment is recent anthropogenic accumulation (perhaps from Cu-based antifouling paints used on the many pleasure boats moored in the area) as these sediments are not well suited to accumulate Cu authigenically. Furthermore, the Cu/Al weight ratios for these cores are the highest of the study (Cu/Al = 4.5 x 10⁻³ for Vancouver Harbour and ≈ 2.0 x 10⁻³ for Indian Arm) suggesting that there are substantial enrichments of Cu beyond the detrital background of KN-2 (e.g. exclusively lithogenic = 1.1 x 10⁻³).

4.3 Molybdenum

4.3.1 Sedimentary Distributions

Molybdenum in most crustal material ranges in concentration from 0.2 to 1.5 μg g⁻¹, and solid-phase Mo concentrations within many coastal deposits fall within this range (Table 13). However, certain sediments host concentrations of the metal that are elevated by an order of magnitude or more.

The distributions of solid-phase Mo with depth in the B.C. inlet deposits studied here display one of two profiles. First, in several cores (most evident in Jervis and Knight Inlets), Mo is enriched in the interfacial sediments relative to the sediments at depth due to an association with Mn-
oxides. Second, whole-core enrichments of Mo occur in those deposits where the oxic/anoxic redox boundary intersects the sediment-water interface (Ucluelet and Saanich Inlets).

<table>
<thead>
<tr>
<th>Inlet-Core</th>
<th>Mo (μg g⁻¹)</th>
<th>Inlet-Core</th>
<th>Mo (μg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rock Type</strong></td>
<td></td>
<td><strong>Sediment Type</strong></td>
<td></td>
</tr>
<tr>
<td>Basaltic</td>
<td>1.5</td>
<td>Shales</td>
<td>2.6</td>
</tr>
<tr>
<td>Granitic</td>
<td>1.0 - 1.3</td>
<td>Clays*</td>
<td>27*</td>
</tr>
<tr>
<td><strong>Ucluelet Inlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-1</td>
<td>1 - 4</td>
<td>IA-1</td>
<td>2.0 - 7.6</td>
</tr>
<tr>
<td><strong>Indian Arm</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Knight Inlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KN-1</td>
<td>0.35 - 7.3</td>
<td>JV-3</td>
<td>1 - 24**</td>
</tr>
<tr>
<td>KN-2</td>
<td>~0 - 0.4</td>
<td>JV-7</td>
<td>0.7 - 30**</td>
</tr>
<tr>
<td>KN-3</td>
<td>0.01 - 1.1</td>
<td>JV-9</td>
<td>0.2 - 7**</td>
</tr>
<tr>
<td><strong>Saanich Inlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SN-0.8</td>
<td>33 - 84</td>
<td>VH-1</td>
<td>0.5 - 1.5</td>
</tr>
</tbody>
</table>

Table 13 Range of concentrations of solid Mo in different rock and sediment types and in the various deposits of this study. *Deep sea clays, elevated metal concentrations likely result from diagenetic oxide enrichments (from Wedepohl, 1971). **Associated with diagenetic enrichments of Mn-oxides.

**Association with Oxides**

The enrichment of Mo associated with Mn-oxides results in concentrations well in excess of the detrital background (Berrang and Grill, 1974; Shimmield and Price, 1986). In many of the deposits of this study, dissolved Mo appears to diffuse upward from a shallow subsurface maximum across the sediment-water interface into bottom waters (cores IA-1, VH-1, JV-7, KN-3). This suggests that an input of oxide-associated Mo must arise from co-precipitation within the deep water column rather than through diffusion of dissolved Mo into oxic sediments from bottom waters, and that much of the surficial solid-phase enrichment of Mo is sustained by diffusion.
upward from deeper horizons where Mn reduction occurs. Similar behaviour has been observed previously by Berrang and Grill (1974), Lyons et al. (1980), Brumsack and Gieskes (1983) and Shaw et al. (1990).

It has been suggested that Mo preferentially associates with Mn in the $\text{+IV}$ oxidation state (Shimmield and Price, 1986); the data from the B.C. inlets support this notion in several ways. First, dissolved Mo in the sub-oxic zones of several deposits (e.g. JV-9, VH-1, KN-3) increases in concentration with depth prior to the maximum remobilization of dissolved Mn suggesting that a subtle lowering in oxidation state releases much of the Mo to porewaters, rather than quantitative reduction to $\text{Mn}^{2+}$. Second, the deposits where sediments are sub-oxic or where sedimentation rates are high (i.e. where disproportionation of hausmannite ($\text{Mn}_3\text{O}_4$) to $\text{MnO}_2$ cannot occur because of rapid burial into reducing sediments) have Mo:Mn weight ratios substantially lower than where oxic core-tops and low sedimentation rates prevail (Table 14). Since high sedimentation rates result in rapid (i.e. near the sediment-water interface) decreases in redox potential, Mn undergoes reduction before disproportionation to $\text{Mn}^{4+}$ can occur and Mo cannot sorb strongly to the sites available on Mn oxides.

<table>
<thead>
<tr>
<th>Core</th>
<th>Mo:Mn weight ratio</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemipelagic Sediments and Mn-nodules</td>
<td>2 x 10^{-3}</td>
<td>(Shimmield and Price, 1986)</td>
</tr>
<tr>
<td>JV-3</td>
<td>7 x 10^{-3}</td>
<td>oxic, low $\omega$</td>
</tr>
<tr>
<td>JV-7</td>
<td>2 x 10^{-3}</td>
<td>oxic, low $\omega$</td>
</tr>
<tr>
<td>JV-9</td>
<td>0.7 x 10^{-3}</td>
<td>sub-oxic</td>
</tr>
<tr>
<td>IA-1</td>
<td>0.5 x 10^{-3}</td>
<td>sub-oxic</td>
</tr>
<tr>
<td>KN-1</td>
<td>2 x 10^{-3}</td>
<td>oxic, low $\omega$</td>
</tr>
<tr>
<td>KN-2</td>
<td>0.2 x 10^{-3}</td>
<td>oxic, high $\omega$</td>
</tr>
<tr>
<td>KN-3</td>
<td>0.7 x 10^{-3}</td>
<td>sub-oxic</td>
</tr>
<tr>
<td>VH-1</td>
<td>$-1 \times 10^{-3}$</td>
<td>sub-oxic</td>
</tr>
</tbody>
</table>

Table 14 Mo to Mn weight ratios in surface sediments of deposits that host diagenetic enrichments of Mn. $\omega$ = sedimentation rate.
The effect of variations in the oxidation state of Mn on Mo sorption is supported by the data from Indian Arm and Knight Inlet. The surface deposits at sites IA-1 and KN-2 are strongly enriched in Mn (>1 wt.% as diagenetic Mn-oxide) yet they host only small enrichments of Mo. The association of Mo with Mn in these deposits is decoupled more than in any other of the study basins, with both cores having the lowest Mo:Mn weight ratio (Table 14). As discussed previously, it is suspected that the near-surface sediments of IA-1 are in thermodynamic disequilibrium as a result of periodic water column sub-oxia. Sub-oxia will have minimized the Mn(IV) content of the oxide fraction without substantially lowering total oxide concentration. Consequently, Mo cannot sorb to the Mn-enriched surface sediments of IA-1 and is seen to diffuse along a steep concentration gradient into bottom waters. The same arguments hold true for KN-2, except that disproportionation is inhibited here by an elevated sedimentation rate; thus, there is insufficient time for disproportionation to occur.

Strong but variable correlations between Mo and Mn from Jervis Inlet sediments are also in agreement with this supposition (Figure 56). The values of the Mo:Mn ratio as determined from the slopes of the regressions in Figure 56 and Table 14 decrease from $7 \times 10^{-3}$ at JV-3 to $0.7 \times 10^{-3}$ at JV-9 suggesting that mean bottom water oxygen concentrations (which effect the Mn oxidation state; Grill (1978)) influence the relationship.

**Association with FeS and Pyrite**

Molybdenum associated with Mn-oxides is not preserved upon burial. In most of the B.C. inlet deposits, Mo is released to porewaters upon the reductive dissolution of Mn with much of the inventory being lost through diffusion to bottom waters. Elevated solid-phase Mo occurs only in sediments where suboxic or anoxic conditions intersect the sediment-water interface (e.g. Ucluelet and Saanich Inlets; Table 15). This is consistent with observations of Malcolm (1985), Emerson and Huested (1991) and others which indicate that Mo preferentially accumulates in anoxic environments. The data from Ucluelet Inlet reflect the most likely enrichment mechanism: dissolved Mo diffuses down a concentration gradient into the surface sediments (Figure 9) to precipitate as a sulphide (presumably with FeS).
While dissolved Mo was not determined in Saanich Inlet porewaters, the work of Francois (1988) suggests that because elevated Mo was not observed within sediment traps deployed within the anoxic bottom waters, sedimentary Mo must be enriched through a mechanism similar to that occurring in Ucluelet Inlet. This observation is consistent with the known geochemistry of Mo. Because the mechanism of Mo precipitation by H₂S is slower than coprecipitation with FeS (Korelev, 1958; Bertine, 1972), dissolved Mo should preferentially precipitate at the sediment-water interface where the majority of the FeS forms. There is insufficient Fe in the water column to impact the Mo inventory (<0.8 μmol L⁻¹ Fe(κ) in the anoxic water column of Saanich Inlet; Jacobs and Emerson, 1982). However, the difference between H₂S and alkalinity in Saanich Inlet sediments (1 mM H₂S and 5 meq L⁻¹ alkalinity in the near surface sediments) in concert with the loss of 3 mM sulphate (Figure 65) within the first several mm in core SN-3 suggests that up to 3 mM of Fe is consumed by sulphide precipitation over that interval. If Mo is coprecipitated with FeS in the same zone, the 3 mM of dissolved Fe is sufficient to quantitatively precipitate the
dissolved Mo (assuming a Mo-FeS stoichiometry similar to that found in IA-1 and U-1 (cores with minimal influence from Mn oxides) of ~1 nM Mo consumed for every ~1 μM Fe precipitated). The precipitation of 3 mM Fe as FeS could conceivably coprecipitate as much as 3,000 nM of Mo.

**Dissolved Mo in Anoxic Environments**

Data from several of the B.C. inlet cores (KN-1, KN-2, U-1, U-2, VH-1, JV-9 and possibly IA-1) indicate release of Mo to anoxic interstitial waters. It has been suggested previously that Mo is rejected from the crystal lattice upon thermodynamic conversion of FeS to pyrite (Korelev, 1958; Bertine, 1972; Bertine and Turekian, 1973; Contreras et al., 1978; Lyons et al., 1980). The magnitude of the Mo concentration in porewaters appears to be dependent upon the extent of coprecipitation of the metal with FeS above the zone of release and precipitation by H₂S below. Sediments with high free sulphide (KN-3) or high alkalinity (evidence of sulphate reduction: i.e. KN-2) at depth yield low concentrations of dissolved Mo. Conversely, sediments containing low free sulphide and low alkalinity (e.g. KN-1, JV-7 and IA-1) host elevated dissolved Mo at depth (Table 16). The quantity of dissolved Mo at depth in a deposit can be explained to a first approximation by the amount of sulphate that has been reduced.

<table>
<thead>
<tr>
<th>Core</th>
<th>dissolved Mo at depth (nM)</th>
<th>free ΣH₂S (μM)</th>
<th>alkalinity (meq L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-1</td>
<td>117</td>
<td>26</td>
<td>-</td>
</tr>
<tr>
<td>KN-1</td>
<td>120</td>
<td>23</td>
<td>4.4</td>
</tr>
<tr>
<td>KN-2</td>
<td>20</td>
<td>2</td>
<td>8.9</td>
</tr>
<tr>
<td>KN-3</td>
<td>10</td>
<td>1800</td>
<td>18</td>
</tr>
<tr>
<td>JV-7</td>
<td>145</td>
<td>58</td>
<td>3.3</td>
</tr>
<tr>
<td>JV-9</td>
<td>12</td>
<td>226</td>
<td>4.4</td>
</tr>
<tr>
<td>VH-1</td>
<td>30</td>
<td>10</td>
<td>3.7</td>
</tr>
<tr>
<td>IA-1</td>
<td>175</td>
<td>1.75</td>
<td>4.1</td>
</tr>
</tbody>
</table>

Table 16: The concentration of dissolved Mo, ΣH₂S, and alkalinity in the anoxic sections of several B.C. inlet cores.
Figure 91 Hypothetical distribution of dissolved Mo in porewaters. The dotted lines represent alternate scenarios where there is ample free sulphide to precipitate dissolved Mo (left line) and insufficient free sulphide for precipitation (right line).

The precise distribution of dissolved Mo with depth (Figure 91) depends on a balance of the factors described above. In sediments such as JV-7 (low dissolved Fe and low alkalinity), dissolved Mo is not consumed substantially after its release from Mn-oxides. The absence of abundant free sulphide at the base of the core (<60 µM at 55 cm depth) limits the precipitation of Mo in the deep horizons. Conversely, the same zones in a deposit such as at KN-3 (where sulphate reduction and Fe precipitation are dominant) consume dissolved Mo. In such deposits (those having higher dissolved Fe and alkalinity at depth), FeS precipitation in concert with abundant H₂S reduce the dissolved Mo concentration to extremely low values in porewaters; there is sufficient free H₂S to precipitate dissolved Mo rapidly and quantitatively. Intermediate to these cases are deposits such as those of KN-1, KN-2, VH-1 and JV-9 where there is sufficient H₂S to consume Mo at depth but not within the shallower zone where it is released from the pyrite matrix. In such cases, dissolved Mo displays a broad mid-depth maximum well within the anoxic zone of the sediments arising from release from the conversion of FeS to pyrite. Similar profiles have been observed in Loch Etive (Malcolm; 1985) and the Gulf of California (Brumsack and Gieskes, 1983). In those environments, low concentrations of dissolved Mo in near surface
horizons were suggested to result from precipitation with Mn-oxides, while the broad mid-depth maxima were attributed to complexation by dissolved organic matter. At depth, dissolved Mo was assumed to be consumed by a sulphide phase. It is possible that the mid-depth maxima observed in the sediments of this study arise in part from organic complexation. If this is true, the data suggest that interactions between Mo and sulphide are stronger than between Mo and dissolved organic matter as dissolved Mo in all cores except JV-3 eventually decreases with increasing free sulphide concentrations.

4.3.2 Sedimentary Accumulation

Several factors influence the degree of accumulation of Mo in a given deposit. First, as suggested by Turekian and Wedepohl (1961), Seralathan et al. (1986), Francois (1988) and others, because lithogenic detritus is depleted in Mo, low sedimentation rates are conducive to accumulation of authigenic phases of the metal. Furthermore, a slow sedimentation rate combined with a thick oxic layer enhances the formation of a diagenetic Mn$^{4+}$-enriched oxide layer. Molybdenum accumulates strongly in such deposits; however, this enrichment is restricted to oxic sediments only and is not preserved upon burial. Depth-independent enrichments of solid-phase Mo occur under conditions of sub-oxia (e.g. Ucluelet Inlet) or anoxia (e.g. Saanich Inlet). This requires either an anoxic water column or at the very least anoxic sediments at or very close to the sediment-water interface. In such cases, authigenic accumulation is enhanced by low sedimentation rates; not only do low sedimentation rates result in minimal lithogenic dilution, but the accumulated metal concentration resulting from a given diffusive flux is maximized. Authigenic accumulation is also enhanced by more strongly reducing conditions at the sediment-water interface, as proposed by Francois (1988). Consequently, any process that shallows the redoxcline (e.g. increasing the organic matter flux or the fostering of bottom water anoxia) results in shorter diffusional path lengths between bottom water and the zone of precipitation, steeper concentration gradients, and hence larger diffusive influxes.

Ironically, as observed in Indian Arm, alternating periods of water column dysaerobia and reoxygenation result in lower solid-phase Mo within a deposit. In this case, the redox potential at
the sediment-water interface is on average too high to allow for uptake by diffusion and subsequent coprecipitation with FeS. Furthermore, Mn is prevented from undergoing disproportionation, and a substantial fraction of Mo associated with Mn oxides is released to bottom waters even though Mn-oxides are not quantitatively reduced.

4.4 Zinc

4.4.1 Sedimentary Distribution

While typical sedimentary detrital Zn concentrations range from 50 to 150 µg g⁻¹, solid-phase Zn within the deposits studied here range from 80 to 400 µg g⁻¹, reflecting both natural and anthropogenic enrichment mechanisms (Table 17).

<table>
<thead>
<tr>
<th>Inlet-Core</th>
<th>Zn (µg g⁻¹)</th>
<th>Inlet-Core</th>
<th>Zn (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rock Types</strong></td>
<td></td>
<td><strong>Sediment Types</strong></td>
<td></td>
</tr>
<tr>
<td>Basaltic</td>
<td>105</td>
<td>Shales</td>
<td>95</td>
</tr>
<tr>
<td>Granitic</td>
<td>35 - 60</td>
<td>Clays*</td>
<td>165*</td>
</tr>
<tr>
<td><strong>Ucluelet Inlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U-1</td>
<td>80 - 100</td>
<td>IA-1</td>
<td>150 - 240</td>
</tr>
<tr>
<td><strong>Knight Inlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KN-1</td>
<td>80 - 100</td>
<td>JV-3</td>
<td>140 - 200</td>
</tr>
<tr>
<td>KN-2</td>
<td>150 - 190</td>
<td>JV-7</td>
<td>140 - 230</td>
</tr>
<tr>
<td>KN-3</td>
<td>130 - 150</td>
<td>JV-9</td>
<td>120 - 140</td>
</tr>
<tr>
<td><strong>Saanich Inlet</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SN-0.8</td>
<td>100 - 250</td>
<td>VH-1</td>
<td>200 - 400</td>
</tr>
<tr>
<td>SN-3</td>
<td>90 - 150</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 17 Range of concentrations of solid Zn in different rock and sediment types and in the various deposits of this study. *Deep sea clays, elevated metal concentrations likely result from diagenetic oxide enrichments (from Turekian and Wedepohl, 1961)
Dissolved Zn ranges in concentration from ~5 to 800 nM within the porewaters observed in this study. The general distribution is in many ways similar to Cu, displaying intense diagenetic cycling; both solid-phase and dissolved Zn display interactions with organic matter, metal oxides and sulphides.

Biogenic Cycling

Information on dissolved Zn in porewaters is scant. While there is ample evidence in many water columns of associations with organism hard-parts (Bruland et al., 1978; Bruland, 1980; Reynolds and Hamilton-Taylor, 1992) and with dissolved organic matter (Bruland, 1989), direct references to biogenic remineralization in the near surface sediments are uncommon or indirect (van den Berg, 1985; Francois, 1988; Gerringa, 1990).

Francois (1988) concluded that the majority of Zn contributed to Saanich Inlet sediments was delivered in association with planktonic remains. The data of this study are in agreement and display evidence of subsurface release, particularly in core SN-3. However, the data from most of the other deposits of the study are equivocal. The dissolved Zn distributions of some deposits (e.g. JV-3 and JV-9) indicate release of Zn from the solid-phase to the near-surface porewaters; however, the zone of release also corresponds closely to the zone of Mn reduction. As a result, it is not possible to isolate a direct biogenic association. The data from Ucluelet Inlet support the notion of biogenic release in the near surface sediments: site U-1 is Mn-starved yet it displays the same subsurface release observed in other cores. Furthermore, the pronounced shallow remobilization of Zn is displaced from the zone of Fe reduction suggesting that release from organic degradation is solely responsible for the maximum concentration. Thus, it is likely that release of dissolved Zn from biogenic sources occurs in most deposits but is obscured by the commensurate reduction and release of Mn. The inferred zone of biogenic release is generally deeper than observed for biogenic remobilization of either Cd or Cu and may result from the known association of Zn with biogenic hard-parts rather than the more labile soft tissue for Cd and Cu (Boyle et al., 1976; Boyle et al., 1977; Willey, 1977; Bruland et al., 1978).
Association with Metal Oxides

Zinc is known to associate strongly with oxides of both Fe and Mn in oxic sediments (van der Weijden, 1976; Benjamin and Leckie, 1981; Balistrieri and Murray, 1982; Helz et al., 1985; Tessier et al., 1985; Westerlund et al., 1986; Tessier et al., 1996). A very strong association with Fe-oxides is seen in many of the deposits of this study for both solid and dissolved Zn; cores JV-3 and JV-7 display unequivocal evidence of a direct Fe-oxide association. While a similar association may exist between Zn and Mn-oxides (van der Weijden, 1976; Hem et al., 1987), it is difficult to distinguish this from Zn associated with organic remineralization as the zones where Zn is diagenetically released overlap in most cores.

In some deposits, the relationship between dissolved Fe and dissolved Zn appears not to exist despite zinc enrichments in the solid phase (e.g. JV-9 and U-1). This behaviour appears only in those cores where sulphate reduction commences near the sediment-water interface. It is suspected that in these cases, the insolubility of ZnS in the presence of trace quantities of free sulphide and the onset of sulphate reduction prior to that of Fe mask the concurrent release of Zn from Fe-oxide dissolution (Boulegue, 1983; Jacobs et al., 1985; Postma and Jakobsen, 1996).

Association with Sulphides

Zinc precipitates as a sulphide in anoxic water columns and sediments (Boulegue, 1983; Jacobs et al., 1985; Morse and Arakaki, 1993). The data of this study indicate that Zn consumption in several deposits (JV-3, JV-7, U-1) corresponds very closely to that of dissolved Fe precipitation and suggest that coprecipitation with FeS may be important. This inference is indirectly supported by the work of Jean and Bancroft (1986) who demonstrated that the interaction between a trace metal and FeS is in part proportional to the insolubility of its metal sulphide; metals such as Zn, which are very insoluble in the presence of free sulphide, should interact strongly with FeS.

Despite its insolubility in anoxic sediments, dissolved Zn is observed to increase in concentration within the anoxic horizons of several deposits. Remobilization occurs at the base of cores JV-3 and JV-7, but not in cores U-1 or JV-9. Complexation of dissolved Zn by polysulphide
and/or bisulphide, as suggested by Boulègue (1983), can be ruled out in this study as a cause of this behaviour because remobilization is most pronounced in the cores with minimal free sulphide (IA-1, JV-3, JV-7); furthermore, the most anoxic cores (SN-03, SN-0.8 and U-1) do not have elevated dissolved Zn at depth (Figure 92). Rather, an inverse relationship between dissolved Zn and $\Sigma H_2S$ suggests that sulphide precipitation is a significant sink for Zn in highly anoxic sediments. These observations are consistent with those of Jacobs et al., (1985) who suggest that because of the 1:1 stoichiometry of the Zn and $H_2S$ reaction, Zn is not remobilized in porewaters that host elevated $\Sigma H_2S$ (unlike Cd). Table 16 supports the importance of a sulphide sink – despite high concentrations of Zn in lithogenic material (i.e. similar to that of Cu), some of the strongest sedimentary Zn enrichments occur in Saanich Inlet where lithogenic inputs are low.

![Graph](image.png)

Figure 92 Dissolved Zn at the base of each core vs. total free sulphide at depth.

The release of Zn at depth observed in many cores of this study may arise from the conversion of FeS to pyrite. Such a phenomenon has not been suggested previously but is evident in the data of Huerta-Diaz and Morse (1992) who observed a progressive decrease in Zn associated with Fe-monosulphide without a commensurate increase in pyrite-associated Zn as a function of age in sulphide-rich deposits. They concluded that Zn is less efficiently transferred to pyrite than many other metals.

Despite evidence of sulphide precipitation throughout the anoxic regions of all sedimentary
sections considered within this study, Zn ranged in concentration from 20 to 50 nM at the base of most cores regardless of free sulphide concentration. This fraction is presumably stabilized by organic complexation, given that polysulphide or bisulphide complexation appear not to be important. However, even organic matter cannot stabilize dissolved Zn in the presence of abundant free sulphide, as evinced by cores where abundant DOM and \( \Sigma H_2S \) coexist (e.g. U-1); these sediments do not host elevated dissolved Zn values at depth.

4.4.2 Sedimentary Accumulation

The distribution of solid-phase Zn is controlled to a large extent by the same processes that influence Cu, as suggested by the correlation from all deposits between Zn and Cu (Figure 93). The terrestrial sources of both Zn and Cu are more important to the absolute concentration than authigenic additions.

![Figure 93 The correlation between solid Zn and Cu in all of the cores of the study.](image)

The presence of anoxia in bottom waters and near-interface sediments enhances the accumulation of Zn but not to the same extent relative to Cd and Mo. Of the authigenic phases that host Zn, the strongest influence on the solid phase distribution arises from diagenetic enrichments associated with Fe-oxides; the highest concentrations seen in the study were observed in oxic, near-surface sediments where Fe was enriched. However, as with Mo, these enrichments do not survive burial; the highest values of authigenic Zn preserved in the
sedimentary record occur under anoxic bottom waters.

Outside the purely natural realm, and irrespective of authigenic Zn distributions, the greatest influence on accumulation aside from lithogenic detritus is contributions from anthropogenic sources. The sediments of Vancouver Harbour and Indian Arm (VH-1, VH-2 and IA-1) contain the highest Zn contents observed in the study (up to 400 µg g⁻¹).
Chapter Five - Conclusions

In chemistry, boundaries between contiguous phases or materials are sites of elevated chemical interaction and thus are places where reactions occur. The environment of the coastal ocean is, by analogy, similar. The proximity to and interaction of land and seafloor with physical ocean processes fosters extremes in primary productivity and biogeochemical gradients; consequently, trace metal recycling is most intense within this zone. The geochemical manifestations of such cycling are most evident in the sediments which display profound diagenetic intensities compared to open-ocean deposits. The principal effect is the vertical compression of oxidant utilization within pore waters and the dominant role of sulphate reduction on the behaviour and cycling of several trace metals. With characteristically high rates of sedimentation and organic matter accumulation, and proportionately lower influxes of oxidants, coastal sediments typically display evidence of sulphate reduction within a few millimetres to centimetres of the sediment-water interface. Consequently, thermodynamic stability of authigenic phases may change profoundly over very short vertical distances, resulting in steep chemical gradients. The resulting restructuring of elemental distributions plays a major role in the cycling and ultimate fate of many trace elements.

The study of the suite of cores collected from the contrasting environments described in this thesis has allowed the delineation of several key controls on the cycling of several trace metals, in particular, the hydrographic factors that influence them. Conclusions follow that place primary influences on the post-depositional metal cycling into the hydrographic framework of the B.C. coastal oceans.

5.1 Cadmium

Cadmium is scarce in terrestrial detritus; its distribution in marine sediments is strongly influenced by accumulation from other sources and post-depositional diagenesis. Two of the most important sources are marine organic matter and the diffusion-derived metal from Cd-enriched bottom waters, which may be indirectly related to organic remineralization.
The frequently invoked association of Cd with marine organic material is confirmed by this study. Upon degradation of the biogenic matrix, Cd is released to the near-surface pore waters (typically within a few mm of the sediment-water interface). The resulting dissolved maximum, hence the concentration gradient and the flux away from the zone of release, is dependent on the ambient redox potential of pore waters. More negative potentials result in lower Cd effluxes to bottom water, since more of the Cd released from organic remineralization is precipitated as sulphides \textit{in situ}. Because of the high levels of diagenetic reactivity found in most coastal deposits, reducing conditions prevail very near the sediment-water interface. Thus, coastal sediments should be a larger sink for Cd than pelagic deposits, not only because the accumulation of biogenic Cd is greater, but because the proximity of sulphate reduction inhibits diffusive loss of Cd. Cadmium also associates with authigenic metal-oxides; however, because release of Cd from dissolving oxides typically occurs deeper than biogenic release, the oxide-metal relationship is obscured by the proximity of sulphate reduction and concurrent sulphide precipitation. Cadmium release from oxide dissolution is detectable only in the most oxic of deposits, as was seen in core JV-3 of Jervis Inlet.

While dissolved Cd precipitates rapidly in the presence of very low concentrations of free sulphide, it is frequently remobilized in highly anoxic, deep pore waters where the activity of polysulphides and/or bisulphide allow complexation to occur. Complexation of Cd by DOM is comparatively unimportant as evinced by undetectable concentrations of Cd in anoxic horizons despite the almost certain presence of elevated levels of DOM.

The sediments most likely to host elevated solid-phase Cd contents contain abundant, labile marine organic matter. Accumulation of such material delivers biogenic Cd to the sea floor in addition to fostering reducing conditions in the near-surface sediments. Water column anoxia (induced by restricted circulation and exacerbated by elevated primary productivity) enhances precipitation of dissolved Cd in the water column while at the same time inhibits the release of biogenic Cd from the interfacial sediments to overlying bottom water by fostering the immediate precipitation of CdS. Finally, although a high sedimentation rate fosters the rapid onset of anoxia,
low sedimentation rates in productive coastal settings can paradoxically enhance the accumulation of sedimentary Cd. Low sedimentation rates occur where terrestrial detrital inputs are low. Because terrestrial material is essentially devoid of Cd and labile organic material, the net effect of minimizing sedimentation rate is to minimize dilution of authigenic Cd which accumulates in the deposits provided that the supply of labile (i.e. marine) organic matter remains relatively high. The best example of this effect occurs in Ucluelet Inlet which has among the lowest sedimentation rates observed, yet hosts some of the highest solid-phase Cd concentrations. Where sedimentation rate is not dominated by lithogenic contributions (in the open ocean), elevated sedimentation rates have the reverse effect on Cd accumulation as sedimentation rate is largely determined by the level of primary productivity. Elevated sedimentation rates in the open ocean deliver more organic matter (and Cd) to the sediments while fostering a shallower onset of sulphate reduction. One would expect further enhancement in Cd accumulation where such deposits intersect the oxygen minimum.

Coastal environments where accumulation of authigenic Cd is low are characterized by conditions opposite to those outlined above; factors that foster oxic conditions over a broad depth range below the sediment-water interface minimize the accumulation of Cd. This occurs in part because of the minimal proportion of biogenic Cd retained by the deposit; there is insufficient sulphate reduction in the vicinity of the zone of biogenic release to minimize the return of Cd to bottom waters. Thus, Cd accumulation will be minimal in inlets in which the flux of marine organic carbon to the sediments is small or where the organic material is largely terrestrially in origin. Furthermore, high accumulation rates of organic-poor, Cd-deplete terrestrial detritus-dilute both authigenic and biogenic Cd. Consequently, the depositional parameters to which Cd responds most sensitively are sedimentation rate and redox potential.

5.2 Copper

The early diagenetic cycles of Cu are dominated by associations with organic matter, metal oxides and sulphides. The strong association of Cu with organic detritus is reflected through the ubiquitous release of dissolved Cu in the near-surface horizons of almost all of the deposits.
Copper released in such a fashion diffuses upward into the overlying waters and downward into the reducing horizons below. However, the magnitude of these fluxes is difficult to discern as unquantified Cu-organic complexation serves to decrease the effective diffusion coefficient.

A strong association was observed between Cu and Fe oxyhydroxides in those deposits hosting oxic interfacial sediments. While Cu sorption to Mn oxides may be a favoured interaction, the majority of interfacial deposits within this study are not sufficiently oxic for the higher oxidation states of Mn to dominate. By default, Cu-Fe-oxide interactions prevail in B.C. coastal sediments.

Precipitation of Cu by free sulphide in anoxic facies is common to all deposits of the study; however, Cu is not quantitatively consumed due to competitive complexation by organic matter or dissolved reduced sulphur.

Copper is enriched relative to Cd in terrestrial detritus; its abundance in a deposit is strongly influenced by the proximity of that deposit to lithogenic sources. Other sources are less important. Even though Cu is associated to a significant degree with organic matter, biogenic components in sediments are not proportionately large. The strong organic-Cu association does not appear as sediment enrichments because: a) there is a large detrital background such that biogenic and authigenic enrichments are minimal; and b) a fraction of the biogenic Cu is lost to the overlying water column upon early diagenetic remineralization.

Anoxic sediments and water columns increase the accumulation of Cu but not to the same extent as for elements such as Cd and Mo. This occurs in part because there is insufficient Cu in the water-column to elicit an effect over the high detrital background found in coastal regimes. Furthermore, it is unlikely that sufficiently steep concentration gradients could be sustained either through the release of Cu from organic matter or through diffusion from elevated bottom-water concentrations to add sufficient quantities of Cu even at sites where sedimentation rates are low. Dissolved Cu increases in concentration towards the base of most cores through complexation with DOM.

5.3 Molybdenum

The low crustal abundance of Mo implies that lithogenic detritus is not an important source
of this metal to coastal deposits; rather, post-depositional recycling and accumulation of authigenic minerals have a marked influence on the distribution and accumulation of the element. Unlike the other metals studied, Mo has no obvious biogenic associations; the early diagenetic cycle of Mo is dominated by strong interactions with Mn oxides, FeS, and to some degree, dissolved organic matter.

Molybdenum enters oxic deposits of this study via settling of Mo-enriched particles (presumably Mn-oxides) as most oxic cores host Mo-enriched core tops yet release Mo to the overlying bottom waters. The efflux of dissolved Mo out of the sediments to the overlying water column precludes diffusive additions from bottom water via in situ precipitation.

A very strong association between Mn-oxides and Mo exists in the surfacial sediments where conditions are sufficiently oxic; however, the degree of interaction is dependent upon the presence of highly oxidized Mn that accumulates through disproportionation of the initial amorphous precipitate, as demonstrated in Jervis and Knight Inlets. Those cores with low sedimentation rates and oxic core tops hosted the highest Mo:Mn weight ratios. Consequently, episodes of periodic dysaerobia or high sedimentation rate, which limit the degree of disproportionation, decouple the relationship as was seen in cores IA-1, JV-7, JV-9 and KN-2. In this regard, elevated solid-phase concentrations associated with Mn enrichments are not preserved upon burial; as the Mn is reduced, Mo is released to pore waters. The liberated metal diffuses upward into bottom waters or is captured by Mn oxide reprecipitation in the surface deposits; and downward into reducing sediments below where it undergoes rapid precipitation presumably with FeS. Below this zone of consumption is another zone of release where Mo is rejected from the crystal lattice upon thermodynamic conversion of FeS to pyrite. The fate of dissolved Mo in deep, anoxic sediments depends on the balance between DOM and sulphide precipitation. Dissolved Mo remains elevated where free sulphide concentrations are low (< a few hundred μM), as observed in Indian Arm sediments. The amount of sulphate reduction (sulphide precipitation) governs the quantity of dissolved Mo occurring in anoxic porewaters at depth.
Molybdenum accumulation is enhanced in sediments underlying an anoxic water column or where sub-oxia intersects the sediment-water interface; accumulation occurs by diffusion of Mo from bottom water followed by sulphide precipitation presumably with FeS.

Of the elements studied, Mo is perhaps the most sensitive to the ambient redox environment. Because elevated Mo concentrations occur mainly in the absence of an aerobic surface layer, where sulphate reduction adds free sulphide to pore (and/or bottom) waters, it may be used as a paleo redox indicator of sub-oxia or anoxia (Crusius et al., 1996).

Molybdenum is influenced by anthropogenesis; however, the increase is small compared to natural enrichments associated with either Mn-oxides or anoxic sediments. Ironically, the anthropogenic nutrient loading introduced to Indian Arm has served to decrease the accumulation of Mo in the sediments with Mn-oxides through the process of seasonal eutrophically-driven dysaerobia. Elevated anthropogenic nutrient additions increase primary productivity, which in turn increases the oxygen demand of bottom waters. The resulting periods of dysaerobia "short-circuit" the disproportionation of Mn which limits the accumulation of Mo in surface sediments.

5.4 Zinc

The early diagenetic cycles of Zn are dominated by release from biogenic material, recycling with Fe (and possibly Mn) oxides and sulphide precipitation. However, because the detrital aluminosilicate fraction is relatively rich in Zn (like Cu), the solid-phase manifestations of all but oxide associations are obscured.

Dissolved Zn is released in association with the remineralization of biogenic debris; however, the manifestation in pore waters is offset to slightly deeper depths than for Cu or Cd, most likely due to the association of Zn with siliceous hard-parts. Strong associations are seen between Zn and Fe both within solid (oxides and sulphides) and dissolved phases (Fe²⁺ and Mn²⁺). While Mn-oxides are suspected to play a role in the cycling of Zn, the interaction is difficult to delineate as release from oxide reduction overlaps with biogenic release in most cores. The influence of sulphide precipitation is very important in all deposits studied as it ultimately controls
the distribution of dissolved Zn at depth; unlike the other metals studied, Zn does not undergo remobilization at depth even where DOM is elevated. Where free sulphide is elevated, dissolved Zn levels are low.

5.5 Influence of Hydrography

Ultimately, the distribution of trace metals represents the sum of all physicochemical processes to which those elements are subjected from the time they are introduced to the ocean until their eventual burial within the sediments. However, the dominant processes that control the distribution of an element at a given site are a function of the hydrographic features of the specific water column and the secondary parameters that are controlled by hydrography. Such features and parameters include: degree of estuarine stratification and circulation, primary productivity and organic matter accumulation rate, lithogenic detrital input and bulk sedimentation rate, and redox states. Following is an overview of the influence of several of the primary factors on the distribution, diagenetic recycling and solid associations of the metals studied.

5.5.1 The Influence of Sedimentation Rate

In the coastal ocean, sedimentation rate is influenced by the quantity of lithogenic detritus arriving at the sediment-water interface; in some cases (e.g. Ucluelet Inlet), material is reworked and transported laterally. High loadings of lithogenic material result in the accumulation of metals abundant in lithogenic minerals. In this study, Cu and Zn are sufficiently elevated in detritral aluminosilicates that biogenic and to some degree authigenic phases are poorly represented. However, rates of primary production are high in the coastal oceans; thus, even where sedimentation rates are elevated by terrestrial loading, the labile organic-carbon accumulation rate is usually sufficient to foster enhanced diagenetic intensities. As a result, low sedimentation rates can foster elevated accumulations of the metals Cd and Mo which are deplete in lithogenic material by allowing authigenic solid-phases to accumulate undiluted as seen in Ucluelet Inlet.

In pelagic sediments or areas away from the influence of a source of terrestrial detritus, the sedimentation rate responds more to primary productivity. In such sediments, elevated rates of deposition typically result in larger biogenic and authigenic fractions of metals. Thus, the effects of
sedimentation rate on metal cycling within a given marine deposit are both direct and indirect. The direct effect results in increased inputs of either lithogenic metals (Cu and Zn) in the near-shore deposit or biogenic and authigenic metals (Cd, Cu, Mo and Zn) in the oceanic environment. The most important indirect effect of sedimentation rate is the influence on oxidant replenishment. High sedimentation rates seen at the heads of fjords such as Knight Inlet aid in the lowering of redox potential by limiting the amount of oxygen that diffuses into surficial sediments from bottom water. Thus, a deposit such as KN-2 may host very low concentrations of organic carbon, yet have highly reducing sediments at depth.

5.5.3 The Influence of Primary Productivity

The influence of primary productivity is reflected in this study indirectly by the accumulation rate of labile organic carbon. Elevated primary production has a multitude of influences. First, increased production enhances the flux of “biogenic” elements (Cd, Cu, Zn) to the sea floor; however, sediments with elevated organic carbon contents do not necessarily host greater fractions of directly-deposited biogenic metals. A more important effect is the associated increase in oxidant demand, which fosters more strongly reducing sediments. In extreme cases, a settling flux of organic carbon may generate an anoxic water column. The resulting sulphidic environment fosters the accumulation of authigenic minerals either by shortening the over which ions must diffuse, hence increasing the concentration gradient and resulting influx to surface sediments as seen in Ucluelet Inlet, or in the extreme case by causing direct precipitation of metal within the resulting anoxic water column.

Thus, all other things being equal, deposits underlying waters of higher primary productivity are enriched in all of the elements studied but for different reasons. Elevated production results in greater biogenic delivery of Cd, Cu and Zn. At the same time, the shallowing of the redoxcline shortens diffusive path lengths, thereby enhancing bottom water influxes for Cd and Mo. A shallow redoxcline also minimizes the diffusive loss to bottom waters of biogenic Cd, and to a lesser degree Cu and Zn, from the remineralization of organic matter. As primary productivity rises, interfacial Mo concentrations initially decrease as Mo associated with Mn(IV) is no longer
retained. However, at higher levels of primary productivity (lower sediment redox potential), Mo accumulation increases as the redox boundary approaches and intersects the sediment-water interface, thereby allowing authigenic sulphides to form; these concentrations are preserved upon burial.

5.5.2 The Influence of Restricted Circulation

Restricted circulation implies less frequent reoxygenation of bottom waters. All things being equal, sediments are more reducing where less oxygen is available to replenish that consumed in the pore waters (e.g. Jervis Inlet). In extreme cases (e.g. Saanich Inlet), the water column is anoxic. In either case, authigenic accumulation of several metals is enhanced by the shortening of diffusional path-lengths from bottom water to the zone of sulphide precipitation; in the extreme case, metals may precipitate directly in the water column and accumulate in the underlying deposit.

With the exception of contributions from biogenic sources, the arguments used to explain the consequences of elevated primary productivity apply to the case of restricted circulation. The end result is a more rapid onset of anoxia in pore waters. However, whereas elevated primary productivity diminishes the oxygen concentrations by elevating oxygen consumption, restricted circulation limits the resupply of oxygen.

Thus, all things being equal, the accumulation of all metals (except Mo) would be enhanced under conditions of restricted circulation through larger diffusive influxes arising from shorter diffusional path-lengths or water column precipitation and minimal loss of biogenic metal. Molybdenum represents a special case whereby restricted circulation, where it creates alternating cycles of aerobic and dysaerobic conditions (e.g. Indian Arm), may minimize the accumulation of Mo if conditions are not sufficiently oxic to allow for disproportionation of Mn, and yet are too oxic to allow a shallowing of the redoxcline. However, under conditions of persistent dysaerobia or anoxia, Mo is the most strongly enriched of the metals studied.

Worthy of note is the observation that heavily contaminated sediments (e.g. Vancouver Harbour) did not show any indications of enhanced metal remobilization when compared to
uncontaminated sites. Once introduced to the sedimentary environment, trace metals behave in accordance with the “rules of diagenesis” regardless of their source. In this regard, contaminant metals, if labile, will behave as those introduced from any other labile source; they are subject to precipitation by authigenic phases or complexation by dissolved species. Presumably, their concentrations in porewaters are limited by the same mechanisms that limit natural metal solubility.

5.6 Epilogue

This thesis has explored the relationships between the cycling of several trace metals in near-shore sediments within the framework of differing hydrographies. Each metal was seen to respond similarly to certain parameters but uniquely to others. Although controls on single-element distributions are difficult to delineate completely, the multi-element, multi-basin approach used in this study has shed new light on post-depositional contrasts in the geochemical behaviours of metals in coastal marine sediments. Such contrasts can be fruitfully exploited to yield clues about past oceanographic processes or to permit natural and anthropogenic inputs to be distinguished. For example, a horizon in an oceanic deposit containing elevated Cd but minimal Mo might be concluded to have accumulated under conditions of higher primary productivity rather than under conditions of restricted circulation. Similarly, high Cd or Mo concentrations in concert with low Cu or Zn contents in near-shore deposits may reflect natural augmentation of sediments deprived of significant lithogenic input, rather than anthropogenic contamination. However, as demonstrated by this work, continued progress in understanding the interrelationships between metals and depositional parameters must be based on the firm foundation provided by a full complement of ancillary data.
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Appendix I - Core Collection, Sampling and Description
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Cores were collected and subsampled under trace-metal-clean, inert atmosphere conditions in order to avoid contamination or oxidation artifacts during the pore water extraction process.

Ship-board core collection involved the use of a light-weight stainless-steel gravity corer loaded with a clean butyrate core barrel (8 cm i.d.) (Pedersen et al., 1985). In all cases, the corer was inserted slowly into the sediments to avoid disturbing the sediment-water interface. The single exception was Ucluelet Inlet where cores were collected by scuba divers who inserted butyrate core-barrels into the soft inlet sediments, sealing them in situ.

All cores were processed immediately after detailed logging (within 2 hours) by extrusion directly from the core-barrel into a nitrogen-filled glove-bag. Extrusion entailed the insertion of a PVC o-ring-fitted piston into the bottom of the core barrel. A scissors jack and sectioned PVC rod were used to push the piston through the barrel, thereby extruding sediment from the barrel top into the N2-filled glove bag. Oxygen levels within the glove bags were monitored in most cases using Gas-Pack disposable anaerobic indicators (sensitive to concentrations ≥ 0.5% oxygen). Initially, supernatant water was syringed out of the core barrel using either clean Tygon tubing or an acid-washed pipette tip and polypropylene syringe. For most cores, a sub-sample of supernatant water was collected as representing overlying bottom waters. The remaining supernatant water was carefully removed to expose the surficial sediments, at which point core sectioning began. Sub-samples 0.5 cm thick were collected near the core-top where concentration gradients were expected to be more pronounced and where porosity was highest; resolution was decreased progressively with depth in the core such that 2 to 4 cm thick intervals were collected toward the core bottom. Extruded slices were cut and manipulated with acid-washed, plastic utensils, placed in acid washed, 250 mL high density polyethylene (HDPE) centrifuge tubes and sealed under nitrogen (see Appendix II for acid washing process). The sealed samples were centrifuged at approximately 1200 gravities for 20 minutes before being transferred to a secondary, nitrogen-filled glove-bag for filtration of the supernatant-porewater.
The centrifuge supernatant was transferred under nitrogen to 30 mL, acid-washed polypropylene (PP) syringe barrels and plungers fitted with acid-washed, silicon o-rings were used to express the samples through acid-washed, disposable 0.45 μm Syrif® mixed-cellulose ester membrane filters; the first few drops were discarded. Trace-metal subsamples (for Cu, Cd, Fe, Mn, Mo and Zn) were collected in 30 mL, acid-cleaned high density polyethylene (HDPE) or polypropylene bottles and preserved by acidifying to approximately 0.2% v/v nitric acid with Seastar™ ultrapure nitric acid. Three additional filtered aliquots were collected at each horizon for: alkalinity (collected in preweighed HDPE bottles and stored refrigerated), total sulphide (collected in preweighed 30 mL HDPE sample bottles and preserved with 50 μL of 1 M Zn acetate), and the nutrient salts nitrate, ammonium and phosphate. Ammonium and phosphate were measured immediately in the field (within a few hours of collection), and the remaining sample was stored frozen for subsequent analyses of nitrate and sulphate.

The solid sample was immediately frozen under nitrogen to be freeze-dried and analysed at a later date.
Appendix II - Acid Washing
Appendix II - Acid Washing

All plastics were scrupulously cleaned in a multiple-stage acid wash to minimize contamination of trace metals associated with their surfaces. Handling was kept to a minimum by washing, drying and storing plastics in the same container. Virgin polyethylene and polypropylene plastic bottles were first rinsed with reagent grade chloroform or acetone to remove residual organics, and then placed in a 4L plastic container and soaked in hot (60°C) 20% v/v, reagent grade nitric acid overnight. The acid was removed and the bottles were rinse twice with distilled, deionized water (DDW). The 4L container was refilled with 0.1% v/v ultra-pure Seastar nitric acid and allowed to sit at room temperature overnight. Again, the container and bottles were drained of acid and rinsed once with DDW before being filled with a final bath of 0.1% v/v ultra-pure nitric acid. The plastics sat in this final solution overnight before being rinsed once with DDW and dried in a drying oven. Plastic pipette tips and graphite furnace atomic-absorption spectrophotometry sample cups were acid washed in the same manner except chloroform was not utilized as the first step. Filters were acid washed by expressing through them ~5 mL of 0.1% v/v ultra-pure Seastar nitric acid, followed by 20 to 30 mL of DDW.
Appendix III - Analytical Methods
Appendix III - Analytical Methods

Sediments

Frozen samples were freeze dried in a Edwards 4K Modulyo freeze dryer directly in 250 mL centrifuge bottles. The samples were placed on heated racks within the freeze dryer with lids ajar. Drying times varied with sample size, ranging from three to ten days. Once dry, the sediments were ground to 200 mesh in a Herzog HSM-100 tungsten-carbide mill and stored in sealed plastic vials.

X-Ray Fluorescence (XRF)

The measurement of major and minor elements by XRF involves the bombardment of a prepared sample by characteristic x-rays with subsequent detection of the fluorescent x-rays. For this project, a Philips PW 1400 x-ray fluorescence spectrometer, equipped with a Rh-target x-ray tube was used. Table 18 lists instrument parameters used for both major and minor elements.

Sample preparation for major elements (Na, K, Ti, Si, P, Mn, Al, Ca, Fe and Mg) involved preparation of fused-glass discs after Norrish and Hutton (1969). Sediment samples of 0.4000 g were mixed with 3.6000 g of Spectroflux 105 (47.0% Li₂B₄O₇; 36.6% Li₂CO₃; 16.3% La₂O₃) in a platinum/gold crucible and fused in a muffle furnace at 1000°C for 20 minutes. The samples were reweighed and made up to 4.000 grams with Spectroflux 100 (100% Li₂B₄O₇) so that the sample to La ratio would remain constant (lanthanum is a heavy absorber making inter-sample matrix differences insignificant). The samples were remelted over a Bunsen burner and poured onto heated aluminum molds, where a brass plunger compressed the molten glass into a disc. The glass discs were cooled, trimmed to size and stored for analysis.

Minor elements analysed by XRF included Mn, Mo, I, Br, Cu, Zn, Zr, Sr, Cr, Ba, Rb, Ni, V, Y and Pb. They were run as pressed-powder pellets backed by boric acid, formed in a stainless-steel die under ~10 tons hydraulic pressure. Ucluelet Inlet pellets were made with 4 grams of sediment and 0.5 grams of Hoechst XRF wax C, while all other samples were prepared by adding a few drops of PVA to 4.000 grams of sample.
<table>
<thead>
<tr>
<th>Element (peak)</th>
<th>Tube kW</th>
<th>Tube mA</th>
<th>Crystal</th>
<th>Counter</th>
<th>Peak $2\theta$ $^\circ$</th>
<th>Background $2\theta$ $^\circ$</th>
<th>Collimator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe ($K\alpha$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
<td>F</td>
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<td>20</td>
<td>LiF(200)</td>
<td>F</td>
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<td>C</td>
</tr>
<tr>
<td>Ti ($K\alpha$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
<td>F</td>
<td>86.35</td>
<td>+3.00/-1.00</td>
<td>C</td>
</tr>
<tr>
<td>Ca ($K\alpha$)</td>
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<td>10</td>
<td>LiF(200)</td>
<td>F</td>
<td>113.34</td>
<td>+1.40</td>
<td>F</td>
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<tr>
<td>K ($K\alpha$)</td>
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<td>40</td>
<td>LiF(200)</td>
<td>F</td>
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<td>+2.00</td>
<td>C</td>
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<tr>
<td>Si ($K\alpha$)</td>
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<td>40</td>
<td>TLAP</td>
<td>F</td>
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<td>+2.30/-1.20</td>
<td>C</td>
</tr>
<tr>
<td>Al ($K\alpha$)</td>
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<td>40</td>
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<td>Mg ($K\alpha$)</td>
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<td>F</td>
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<td>-1.20</td>
<td>C</td>
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<td>60</td>
<td>Ge</td>
<td>F</td>
<td>141.12</td>
<td>-1.50</td>
<td>C</td>
</tr>
<tr>
<td>Ba ($L\beta$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
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<td>+1.20</td>
<td>F</td>
</tr>
<tr>
<td>Co ($K\alpha$)</td>
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<td>40</td>
<td>LiF(220)</td>
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<td>+0.54/-0.54</td>
<td>F</td>
</tr>
<tr>
<td>Cr ($K\alpha$)</td>
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<td>LiF(200)</td>
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<td>+1.00</td>
<td>C</td>
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<tr>
<td>Cu ($K\alpha$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
<td>F/S</td>
<td>45.00</td>
<td>-0.62</td>
<td>F</td>
</tr>
<tr>
<td>Ni ($K\alpha$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
<td>F/S</td>
<td>48.66</td>
<td>+1.20/-0.60</td>
<td>F</td>
</tr>
<tr>
<td>Pb ($L\beta$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
<td>F/S</td>
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<td>+0.50/-0.50</td>
<td>F</td>
</tr>
<tr>
<td>Rb ($K\alpha$)</td>
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<td>40</td>
<td>LiF(200)</td>
<td>S</td>
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<td>+0.40/-0.90</td>
<td>F</td>
</tr>
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<td>40</td>
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<td>S</td>
<td>25.20</td>
<td>+0.60/-0.60</td>
<td>F</td>
</tr>
<tr>
<td>Y ($K\alpha$)</td>
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<td>40</td>
<td>LiF(200)</td>
<td>F</td>
<td>77.41</td>
<td>+4.00/-2.60</td>
<td>C</td>
</tr>
<tr>
<td>Zn ($K\alpha$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
<td>S</td>
<td>23.83</td>
<td>+0.60/-0.60</td>
<td>F</td>
</tr>
<tr>
<td>Zr ($K\alpha$)</td>
<td>60</td>
<td>40</td>
<td>LiF(200)</td>
<td>S</td>
<td>22.56</td>
<td>+0.74/-0.74</td>
<td>F</td>
</tr>
<tr>
<td>Mo ($K\alpha$)</td>
<td>60</td>
<td>40</td>
<td>LiF(220)</td>
<td>S</td>
<td>28.91</td>
<td>+0.70/-0.70</td>
<td>F</td>
</tr>
<tr>
<td>Na ($K\alpha$)</td>
<td>30</td>
<td>60</td>
<td>TLAP</td>
<td>F</td>
<td>55.25</td>
<td>+3.40/-0.70</td>
<td>C</td>
</tr>
<tr>
<td>I ($K\alpha$)</td>
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<td>40</td>
<td>LiF(200)</td>
<td>F/S</td>
<td>12.38</td>
<td>+0.60/-0.60</td>
<td>F</td>
</tr>
<tr>
<td>Br ($K\alpha$)</td>
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<td>40</td>
<td>LiF(200)</td>
<td>F/S</td>
<td>29.94</td>
<td>+1.10/-1.10</td>
<td>F</td>
</tr>
</tbody>
</table>

Table 18 XRF instrument parameters. Counter F = flow, S = scintillation; Collimator C = coarse, F = fine.

Because minor elements exist at concentrations too low to utilize a heavy absorber for matrix correction, mass absorption corrections were made by the Compton-scattering method. The Rh Kα Compton peak for each sample was used to normalize each element of atomic number > 27 for mass-absorption of the matrix. For those elements with atomic number < 27
which have fluorescent lines strongly absorbed by Fe, matrix correction was accomplished by normalizing the peak to an adjacent background wavelength.

International rock standards prepared by the same techniques were utilized to calibrate the instrument; the accuracy can be estimated from the results presented in Table 19. Precision was estimated by analysing multiple disks made from the same sample. Relative standard deviations are shown in Table 20.

<table>
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<tr>
<th></th>
<th>AGV</th>
<th>GSP</th>
<th>NIMS</th>
<th>W2</th>
<th>AGV</th>
<th>GSP</th>
<th>NIMS</th>
<th>W2</th>
</tr>
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<tbody>
<tr>
<td>Fe (%)</td>
<td>4.73</td>
<td>3.00</td>
<td>0.98</td>
<td>7.52</td>
<td>4.68 ± 0.04</td>
<td>3.03 ± 0.01</td>
<td>1.02 ± 0.05</td>
<td>7.59 ± 0.01</td>
</tr>
<tr>
<td>Mn</td>
<td>728</td>
<td>326</td>
<td>80</td>
<td>1300</td>
<td>796 ± 17</td>
<td>309 ± 9</td>
<td>83.5 ± 3.7</td>
<td>1242 ± 14</td>
</tr>
<tr>
<td>Ti (%)</td>
<td>0.055</td>
<td>0.390</td>
<td>0.024</td>
<td>0.636</td>
<td>0.642 ± 0.025</td>
<td>0.392 ± 0.003</td>
<td>-</td>
<td>0.629 ± 0.003</td>
</tr>
<tr>
<td>Ca (%)</td>
<td>3.53</td>
<td>1.48</td>
<td>0.486</td>
<td>7.77</td>
<td>3.51 ± 0.05</td>
<td>1.44 ± 0.01</td>
<td>0.496 ± 0.008</td>
<td>7.90 ± 0.03</td>
</tr>
<tr>
<td>K (%)</td>
<td>1.86</td>
<td>3.52</td>
<td>9.81</td>
<td>0.403</td>
<td>1.90 ± 0.05</td>
<td>3.43 ± 0.01</td>
<td>9.80 ± 0.34</td>
<td>0.395 ± 0.006</td>
</tr>
<tr>
<td>Si (%)</td>
<td>27.48</td>
<td>31.39</td>
<td>29.74</td>
<td>24.51</td>
<td>28.32 ± 0.36</td>
<td>31.61 ± 0.20</td>
<td>30.80 ± 1.23</td>
<td>24.58 ± 0.09</td>
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<tr>
<td>Al (%)</td>
<td>9.06</td>
<td>7.99</td>
<td>9.17</td>
<td>8.12</td>
<td>9.29 ± 0.25</td>
<td>8.03 ± 0.04</td>
<td>9.51 ± 0.38</td>
<td>8.07 ± 0.03</td>
</tr>
<tr>
<td>Mg (%)</td>
<td>0.923</td>
<td>0.579</td>
<td>0.277</td>
<td>3.84</td>
<td>0.905 ± 0.026</td>
<td>0.654 ± 0.022</td>
<td>0.285 ± 0.059</td>
<td>3.90 ± 0.02</td>
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<tr>
<td>P (%)</td>
<td>0.214</td>
<td>0.122</td>
<td>0.052</td>
<td>0.057</td>
<td>0.214 ± 0.006</td>
<td>0.123 ± 0.002</td>
<td>0.054 ± 0.003</td>
<td>0.057 ± 0.000</td>
</tr>
<tr>
<td>Ba</td>
<td>1226</td>
<td>1310</td>
<td>2400</td>
<td>182</td>
<td>1177 ± 34</td>
<td>1288 ± 45</td>
<td>2498 ± 82</td>
<td>167 ± 3</td>
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<tr>
<td>Co</td>
<td>15.3</td>
<td>6.6</td>
<td>3</td>
<td>44</td>
<td>14.9 ± 4.3</td>
<td>5.89 ± 1.65</td>
<td>6.00 ± 1.40</td>
<td>44.5 ± 3.6</td>
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<tr>
<td>Cr</td>
<td>10</td>
<td>13</td>
<td>12</td>
<td>93</td>
<td>9.04 ± 1.14</td>
<td>9.96 ± 0.88</td>
<td>17.4 ± 0.11</td>
<td>90.7 ± 0.1</td>
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<tr>
<td>Cu</td>
<td>60</td>
<td>33</td>
<td>19</td>
<td>103</td>
<td>64.8 ± 6.0</td>
<td>37.6 ± 2.7</td>
<td>20.0 ± 2.0</td>
<td>83.2 ± 8.6</td>
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<tr>
<td>Ni</td>
<td>16</td>
<td>9</td>
<td>7</td>
<td>70</td>
<td>13.9 ± 1.4</td>
<td>12.6 ± 1.9</td>
<td>6.40 ± 0.80</td>
<td>58.1 ± 4.0</td>
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<tr>
<td>Pb</td>
<td>36</td>
<td>55</td>
<td>5</td>
<td>9</td>
<td>36.3 ± 2.8</td>
<td>58.0 ± 2.6</td>
<td>3.30 ± 0.84</td>
<td>7.61 ± 0.42</td>
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<tr>
<td>Rb</td>
<td>67</td>
<td>254</td>
<td>530</td>
<td>20</td>
<td>68.5 ± 0.7</td>
<td>248 ± 4</td>
<td>518 ± 1</td>
<td>20.1 ± 1.4</td>
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<tr>
<td>Sr</td>
<td>662</td>
<td>234</td>
<td>62</td>
<td>194</td>
<td>675 ± 12</td>
<td>240 ± 4</td>
<td>63.5 ± 2</td>
<td>193 ± 6</td>
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<tr>
<td>V</td>
<td>121</td>
<td>53</td>
<td>10</td>
<td>262</td>
<td>134 ± 2</td>
<td>65.5 ± 1.1</td>
<td>28.7 ± 1.7</td>
<td>233 ± 3</td>
</tr>
<tr>
<td>Y</td>
<td>20</td>
<td>26</td>
<td>20</td>
<td>24</td>
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<td>31.1 ± 1.2</td>
<td>12.3 ± 0.6</td>
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<td>Zn</td>
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<td>104</td>
<td>10</td>
<td>77</td>
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<td>69.0 ± 5.0</td>
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<tr>
<td>Zr</td>
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<td>530</td>
<td>33</td>
<td>94</td>
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<td>490 ± 7</td>
<td>31.97 ± 0.31</td>
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<td>1.58</td>
<td>1.04</td>
<td>0.160</td>
<td>0.794</td>
<td>1.60 ± 0.07</td>
<td>0.161 ± 0.017</td>
<td>0.930 ± 0.011</td>
<td>0.729 ± 0.008</td>
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Table 19 - Accuracy of major and minor elements by XRF. Reported values from Abbey, 1980. Concentrations are in µg g⁻¹ unless otherwise stated.
<table>
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<th></th>
<th>Rep 1</th>
<th>Rep 2</th>
<th>Rep 3</th>
<th>Rep 4</th>
<th>Rep 5</th>
<th>Mean</th>
<th>2σ</th>
<th>%RSD</th>
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<td>3.37</td>
<td>3.43</td>
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<td>633</td>
<td>660</td>
<td>655</td>
<td>644</td>
<td>649</td>
<td>21</td>
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<td>Ti (%)</td>
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<td>0.501</td>
<td>0.481</td>
<td>0.490</td>
<td>0.485</td>
<td>0.489</td>
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<td>Si (%)</td>
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<td>28.8</td>
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<td>28.7</td>
<td>28.6</td>
<td>28.8</td>
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<td>Al (%)</td>
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<td>7.03</td>
<td>7.09</td>
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<td>Mg (%)</td>
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<tr>
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<td>0.138</td>
<td>0.136</td>
<td>0.134</td>
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<td>5.00</td>
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<tr>
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<td>15.7</td>
<td>15.1</td>
<td>17.1</td>
<td>14.2</td>
<td>16.9</td>
<td>15.8</td>
<td>2.44</td>
<td>15.5</td>
</tr>
<tr>
<td>Cr</td>
<td>72.7</td>
<td>75.2</td>
<td>76.3</td>
<td>69.8</td>
<td>77.7</td>
<td>74.3</td>
<td>6.25</td>
<td>8.40</td>
</tr>
<tr>
<td>Cu</td>
<td>23.7</td>
<td>25.2</td>
<td>24.4</td>
<td>22.5</td>
<td>21.8</td>
<td>23.5</td>
<td>2.76</td>
<td>11.7</td>
</tr>
<tr>
<td>Ni</td>
<td>25.4</td>
<td>28.4</td>
<td>26.2</td>
<td>24.1</td>
<td>22.3</td>
<td>25.3</td>
<td>4.57</td>
<td>18.1</td>
</tr>
<tr>
<td>Pb</td>
<td>22.0</td>
<td>23.3</td>
<td>20.3</td>
<td>22.2</td>
<td>25.7</td>
<td>22.7</td>
<td>3.98</td>
<td>17.6</td>
</tr>
<tr>
<td>Rb</td>
<td>33.3</td>
<td>32.1</td>
<td>34.7</td>
<td>33.3</td>
<td>35.3</td>
<td>33.7</td>
<td>2.54</td>
<td>7.52</td>
</tr>
<tr>
<td>Sr</td>
<td>296</td>
<td>301</td>
<td>297</td>
<td>292</td>
<td>291</td>
<td>295</td>
<td>8.07</td>
<td>2.73</td>
</tr>
<tr>
<td>V</td>
<td>108.4</td>
<td>105</td>
<td>102</td>
<td>112</td>
<td>109</td>
<td>107</td>
<td>7.72</td>
<td>7.19</td>
</tr>
<tr>
<td>Y</td>
<td>18.6</td>
<td>20.5</td>
<td>17.7</td>
<td>17.4</td>
<td>18.9</td>
<td>18.6</td>
<td>2.44</td>
<td>13.1</td>
</tr>
<tr>
<td>Zn</td>
<td>101</td>
<td>104</td>
<td>102</td>
<td>99.9</td>
<td>97.3</td>
<td>101</td>
<td>4.99</td>
<td>4.95</td>
</tr>
<tr>
<td>Zr</td>
<td>142</td>
<td>140</td>
<td>144</td>
<td>139</td>
<td>145</td>
<td>142</td>
<td>5.10</td>
<td>3.59</td>
</tr>
<tr>
<td>Na (%)</td>
<td>4.02</td>
<td>3.97</td>
<td>3.99</td>
<td>4.11</td>
<td>3.95</td>
<td>4.05</td>
<td>0.16</td>
<td>4.06</td>
</tr>
</tbody>
</table>

Table 20 - Precision of major and minor elements by XRF as relative standard deviation. Concentrations are in µg g⁻¹ unless otherwise stated.

**Seasalt Correction**

Seasalt associated with the interstitial waters contributes significant concentrations of specific elements (Na, Mg, Ca, Sr, I, K and S) to dried sediment samples; its presence also dilutes the bulk sediments. Correction of these analytical artifacts is carried out by determining the chloride content of the dried sediments and then using the law of constancy of composition to correct for the presence of seasalt.

Small sub-samples of dried sediment (~0.1 g) were accurately weighed into 1.5 mL
polypropylene centrifuge tubes. One mL of DDW was added to the sediment, creating a slurry which was agitated with a vortex stirrer for several minutes to dissolve chloride quantitatively. The slurry was allowed to sit for 30 minutes after which it was spun in a centrifuge (~1200 gravities) for 10 minutes. Using a micro-burette, subsamples of the supernatant were titrated with standardized AgNO3 and a potassium dichromate indicator to determine the amount of chloride present as seasalt.

Seasalt corrections for specific elements were applied using the formula:

$[E]_{sed} = [E]_{sed+salt} - \left( \frac{[E]_{sw}}{[CI^-]_{sw}} \times [CI^-]_{sed+salt} \right)$

where $[E]_{sed} = \text{corrected element concentration}$; $[E]_{sed+salt} = \text{concentration of element in dried sediment as measured by XRF}$; $[E]_{sw} = \text{element concentration in seawater}$; $[CI^-]_{sw} = \text{chloride concentration in seawater}$; and $[CI^-]_{sed+salt} = \text{chloride concentration in the dried sediment sample}$. Note that this approach over-corrects for sea-salt sulphur when sulphate concentrations in pore waters were lowered by sulphate reduction. Since sulphate depletions were not profound in most of the pore waters studied, the difference will be minor.

Dilution of bulk sediment by seasalt was corrected using the equation:

$[E]_{corrected} = [E]_{sed} \times \frac{100}{100 - 1.82[CI^-]_{sed+salt}}$

**Carbon-Nitrogen-Sulphur**

Total carbon, nitrogen and sulphur were measured by gas-chromatography on a Carlo-Erba CNS analyser Model NA 1500. Dried sediment samples (5 to 20 mg) were accurately weighed out on a microbalance into small tin cups. A few mg of V2O5 were added to the
samples to aid in complete oxidation of the sample to its gaseous components (N\textsubscript{2}, CO\textsubscript{2} and SO\textsubscript{2}). The sample cups were crimped shut and loaded into a sample carrousel on the instrument. Samples were sequentially dropped into a heated column (1000°C) containing Cu turnings and tungsten tri-oxide on alumina, which in the presence of oxygen converted C, N and S to their respective gaseous forms. A He carrier gas transported the sample gasses to the column for chromatographic separation. Detection was by thermal conductivity.

The instrument was calibrated using the sediment standards MESS-1, BCSS-1 and PACS-1 for carbon and sulphur; acetonilide was used as a standard for nitrogen (see Table 21 for accuracy and precision). Precision (n=5) (1 σ) was estimated at ±4%, ±9% and ±10% for C, N and S respectively.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Reported Values</th>
<th>Measured Values (n=5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% C</td>
<td>% N</td>
</tr>
<tr>
<td>MESS-1</td>
<td>2.99</td>
<td>-</td>
</tr>
<tr>
<td>BCSS-1</td>
<td>2.19</td>
<td>-</td>
</tr>
<tr>
<td>PACS-1</td>
<td>3.69</td>
<td>-</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>71.09</td>
<td>10.36</td>
</tr>
</tbody>
</table>

Table 21  Accuracy of CNS analyser based on sediment standards.

Carbonate and Organic Carbon

Carbonate carbon was determined by coulometry on a Coulometrics 5010 coulometer; organic carbon was derived by subtracting carbonate-carbon from total-carbon as measured by the Carlo-Erba CNS.

Coulometry measures carbonate carbon by converting carbonates into CO\textsubscript{2} through the addition of 10% HCl to dried sediment. Dried samples (25 to 100 mg) were accurately weighted out on a microbalance and placed in a clean glass reaction tube. The reaction tube was first
flushed with CO₂-free air for two minutes to remove residual atmospheric CO₂, placed in a
heating block on the instrument and a few mL of 10% HCl added. The heated solution was
bubbled with CO₂-free air to carry liberated CO₂ through a blue ethanolamine solution which
rapidly reacts with CO₂, forming a clear acid. The change in transmittance of the ethanolamine
was detected by a photo-detector, which responded by reducing water at a silver electrode to
generate OH⁻ ions electrolytically. The amount of current required to return the ethanolamine
solution to its original transmittance was directly proportional to the amount of carbonate-carbon
present.

The instrument was calibrated using high purity CaCO₃. Based on replicate analysis of
CaCO₃, the precision of the instrument was estimated to be ±0.8%; a CaCO₃ standard
(12.000% carbonate carbon) yielded a measured value of 12.06% ± 0.10% carbon (n=10). The
detection limit (6 σ of the blank) was estimated to be 6 μg carbonate carbon.

Stable Carbon Isotopes

Stable carbon isotopes (¹²C and ¹³C) were measured on a VG Isogas Prism mass
spectrometer. Samples were prepared by the addition of 1 mL of 10% v/v reagent grade HCl to a
few hundred mg of dried sediment in order to dissolve any calcium carbonate; the samples were
dried at 60°C. A small amount of the prepared sample was then weighed into a small tin cup,
crimped and loaded into the sample carousel of a Carlo Erba CHN elemental analyser which
converted the carbon in the sample to gaseous CO₂ that was then introduced into the mass
spectrometer. The CO₂ was ionized to CO₂⁺ in the ion source and accelerated down the flight
tube. The ions were mass-filtered by an magnetic field into precisely aligned Faraday buckets
where masses 44, 45 and 46 were detected. Sample and reference gas were alternately
analysed.

The relative counts of ¹²C to ¹³C of the sample were compared to that of a lab standard
calibrated with respect to Pee Dee Belemnite Chicago Standard and reported as δ¹³C by the
relationship:
\[
\delta^{13}C = \left( \frac{^{13}C/^{12}C_{\text{sample}}}{^{13}C/^{12}C_{\text{PDB}}} \right) \times 10^3 \text{permil}
\]

Precision of the instrument has been estimated at better than ±0.2% for \( \delta^{13}C \).

**Solid-Phase Trace Metals (Cd, Mo and Pb)**

Certain elements in coastal marine sediments (i.e. Cd, Mo and Pb) exist at concentrations near or below the detection limit of XRF. For these metals it was necessary to use an alternate analytical approach - quantitative acid digestion followed by elemental analysis with graphite furnace atomic absorption spectrophotometry (GFAAS).

Complete digestion of the solid phase was accomplished by bombarding a sediment- and acid-containing Teflon bomb with microwave radiation. Because the bomb was sealed, digestion pressure was elevated to as high as 100 psi, allowing the acid cocktail to attain higher temperatures than it could at atmospheric pressure as per traditional hot-plate digestion.

Sediment aliquots of approximately 0.25 grams were accurately weighed into 11 of 12 dry, acid-washed Teflon digestion bombs (part of a CEM 205 microwave digestion system); bomb 12 was used as a method blank. A two-stage digestion was utilized to completely digest the sediment aliquot. Step one comprised the majority of the digestion and consisted of a mixture of concentrated Seastar ultrapure acids containing: 4.0 mL HNO₃, 2.0 mL HCl and 1.5 mL HF. The acid-sediment slurry was swirled to expose all of the ground sediment to acid while allowing labile, CO₂-generating material to evolve gas when the bombs were still open to the atmosphere. The bombs were then sealed and heated for 90 min at 100 psi to facilitate rapid and quantitative digestion of the remaining refractory material. After the initial digestion step, bombs were allowed to cool to near room temperature. Step two involved the addition of 9 mL of 4% boric acid solution to complex any excess fluoride ion. The bombs were resealed, heated for 20 min at 40 psi and allowed to cool to room temperature. The digest was then apportioned to two fractions: 2.0 mL was diluted to 20 mL with DDW and stored in a 30 mL acid-washed PP or HDPE sample bottle for trace metal analysis by GFAAS, and the remainder was stored in an acid-washed 60 mL
HDPE container to be used for $^{210}$Pb analysis (see Appendix IV for $^{210}$Pb method details).

**Interstitial Waters**

**Titration Alkalinity**

Titration alkalinity was determined on interstitial water samples after the methods of Edmond (1970) and Gieskes and Rogers (1973). Alkalinity samples were measured by potentiometric titration directly in their pre-weighed 30 mL containers to ensure that any CaCO$_3$ that may have precipitated was included in the titration. Samples were first weighed to determine sample volume, then an electrode was immersed in the solution (stirred vigorously with a magnetic stirrer and Teflon coated stir-bar) and dilute HCl (~0.2 N) was used to titrate the solution past the second carbonate end-point. The EMF was recorded after each addition of acid from pH 4 to pH 2.5. The data were analysed as a Gran plot, the linear portion of which was utilized to back calculate the volume of acid required to reach the second end-point, hence allowing the calculation of sample alkalinity.

In a Gran plot, a function $F$ is defined as:

$$F = \left( V + V_o \right) 10^{\frac{E - E_o}{a}}$$

where $V$ = the volume of acid added; $V_o$ = the original sample volume; $E$ = the measured EMF; $E_o$ = an arbitrary EMF; and $a$ = the experimental Nernst slope of the electrode pair as determined with NBS standards. The function $F$ is determined for each titration point and plotted against $V$; the linear portion of this plot extrapolated to the acid-volume axis gives the titration end-point. Dividing this value by the sample volume yields titration alkalinity. Replicate analyses of bicarbonate standards (n=10) yielded a precision better than 1%.

**Total Dissolved Sulphide**

Total sulphide ($\Sigma$H$_2$S) was measured in interstitial water samples preserved with Zn-acetate by addition of a single mixed reagent (N,N-dimethyl-p-phenylenediamine sulphate and FeCl$_3$ • 6H$_2$O) to the sample. The diamine reagent reacted with reduced sulphur (catalysed by Fe) to produce a violet-coloured methylene blue complex. The complex was measured
colourimetrically at 670 nm.

Standards were prepared by dissolving known weights of Na$_2$S • 9H$_2$O in water and making serial dilutions of that primary stock. The diluted standards were preserved by the addition of 50 μL of Zn-acetate. Because porewater ΣH$_2$S concentrations often span three to four orders of magnitude, four ranges of reagents and standards were prepared, encompassing the range 1 to 5000 μM ΣH$_2$S. During the analysis, each porewater sample was treated with the diamine reagent corresponding to the expected concentration range of the sample. The colour solution was allowed to develop for 30 minutes after which it was measured at 670 nm on a Bausch and Lomb Spectronic 2000 spectrophotometer. Based on replicate analysis of standards and samples (n=5), precision was estimated at ±4%; the detection limit (6 σ of the blank) was 1 μM.

Sulphate

Porewater sulphate was measured by ion chromatography on a Dionex DX 100 ion chromatograph outfitted with a chemical suppressor and an autosampler. Analysis was performed on alkalinity samples or nutrient samples that were diluted by a factor between 50 to 100 with DDW or eluent. Sample cups and pipette tips were soaked in successive baths of DDW to dilute any contaminant anions. Standards were made by accurately weighing out reagent grade anion salts as well as by periodically running the anion standard ANI-04. Precision was estimated to be ±1% (n=6), while the detection limit (6 σ of the blank) was 1 μM.

Nitrate

Nitrate was not run on all porewater samples as an accidental freezer mishap reduced confidence in the integrity of some samples. Those samples analysed were run after the methods of Parsons et al. (1984) modified to run on an autoanalyser where nitrate was first converted to nitrite. Sample was injected into a sample stream where it was passed through a column of Cu-coated Cd granules that reduced nitrate to nitrite. Downstream from the reduction column, the addition of the reagents sulphanilamide and N-(1-naphthyl)-ethylenediamine first diazotized the nitrate and then formed a coloured azo dye complex which was measured colourimetrically at 543 nm. As a result, nitrate values actually represent contributions from both
nitrate and nitrite. Standards were made by dissolving reagent grade salts in an artificial seawater medium. Based on replicate measurements of standards and samples (n=5), precision was estimated at ±5%; the detection limit (6σ of the blank) was 1 μM.

**Phosphate**

Dissolved phosphate in 0.45 μm filtered porewaters was measured in the field within 3 to 4 hours of core collection by a method modified for small volume (0.5 mL) after Parsons et al. (1984). A mixed reagent containing molybdic acid, ascorbic acid and trivalent antimony was added to a 0.5 mL porewater sample (diluted to 1.00 mL with DDW). The resulting complex produces a blue/violet solution which was measured spectrophotometrically at 885 nm on a Bausch and Lomb Spectronic 2000 spectrophotometer. The method was calibrated using diluted standards made from reagent grade phosphate salts. Based on replicate analyses of standards and samples (n=4), precision was estimated at ±4%; the detection limit (6σ of the blank) was 2 μM.

**Ammonium**

Dissolved ammonium in filtered porewaters was measured immediately after sample collection (within 4 hours) spectrophotometrically after the method (modified for small volume) of Parsons et al. (1984). Samples and standards were treated with phenol, Na-hypochlorite and a Na-nitroprusside catalyst in an alkaline citrate medium to form a blue indophenol complex that was measured spectrophotometrically. Subsamples (0.5 mL) of 0.45 μm filtered porewater were diluted with 0.5 mL DDW. The mixed solutions and standards were allowed to incubate for 1 to 2 hours before being measured spectrophotometrically at 640 nm in a Bausch and Lomb Spectronic 2000 spectrophotometer. Based on replicate analysis of samples and standards (n=4), precision was estimated at ±4%; the detection limit (6σ of the blank) was 0.5 μM.

**Trace Metal Extraction**

Trace metal concentrations in sediment interstitial waters can span several orders of magnitude. At the low end, metal levels are often below the detection limits of even the most sensitive analytical instruments. For marine interstitial water samples, the problem is
compounded by limited sample volume and by the presence of a sea-salt matrix that grossly interferes with analysis, particularly by GFAAS. To alleviate these constraints, a trace metal extraction was performed to remove the metals of interest from the salt-water matrix. While extractions may afford the luxury of sample preconcentration, the limited volume of interstitial waters available prohibited this option.

Because concentrations of trace metals in interstitial waters can be very low (sub-part-per-billion), it was first necessary to minimize all possible sources of trace metal contamination. To this end, significant time was invested in cleaning the reagents used in the extraction process. Below is a list of reagents used in the trace metal extraction process and a brief explanation of the manner in which they were cleaned (Table 22).

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Method of Cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄OH</td>
<td>Isothermal distillation into DDW</td>
</tr>
<tr>
<td>MIBK</td>
<td>Sub-boiling distillation and nitric acid back extraction</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>Anion exchange (after Kraus and Moore, 1953)</td>
</tr>
<tr>
<td>APDC</td>
<td>Extraction with clean MIBK</td>
</tr>
</tbody>
</table>

Table 22 - Reagents used in trace-metal extraction and brief description of cleaning procedure

The extraction technique employed for 1.0 mL sub-samples of marine porewaters was modified after several methods, most notably those of Klinkhammer (unpub.) and Danielsson et al., 1982. Acidified porewater aliquots were spiked with a Co carrier and neutralized to pH 6.5. A transition/Class B-metal selective ligand, ammonium pyrrolidine dithiocarbamate (APDC), was added and allowed to precipitate with the Co and the other metals in solution. The resulting metal precipitate was centrifuged out of solution, washed with DDW and digested in ultra-pure HNO₃ before analysis by GFAAS. Method specifics are outlined below.

During the field processing, the ratio of the volume of nitric acid added (for preservation) to sample volume varied. Thus, neutralization was done by direct addition of NH₄OH rather than by
buffer. To determine the volume of base required, it became necessary to perform a micro-titration on a sacrificial aliquot of porewater containing the Co spike. A 400 μL subsample was spiked with 20 μL of CoCl₂ solution and titrated with NaOH using a microburette and a nitrazine yellow indicator (pH 6.5). The NaOH was then standardized against isothermally-distilled NH₄OH and neutralization volumes were calculated.

The following were added to acid-washed 1.5 mL PP micro-centrifuge tubes: 1.00 mL of acidified sample, 50 μL of CoCl₂ spike solution, followed by the predetermined volume of isothermally-distilled NH₄OH. The mixture was then agitated. Addition of 100 μL of clean, 2% w/v APDC followed by agitation and a 30 minute incubation preceded centrifugation at 1200 g for 20 minutes. The supernatant was then aspirated with an acid-washed pipette tip, leaving a metal-enriched pellet in the centrifuge tube. The precipitate was washed of residual salts by the addition of 1 mL of DDW, followed by agitation and centrifugation. Wash water was removed by aspiration and the precipitate was allowed to dry in a class 100 laminar flow hood. Samples were stored in dry form until analysis at which point the solid was digested in HNO₃ and bulked to volume with DDW. Digestion involved addition of 200 μL of Seastar ultrapure HNO₃ (3 M) to the centrifuge tube which was allowed to reflux by partial immersion in a water bath until all APDC had decomposed; the volume was then made to 1.00 mL by addition of DDW. Digested samples were analysed by GFAAS.

**Extraction Efficiency (E)**

To convert the measured metal values to original concentrations, it was necessary to know the extraction efficiency (E) and the level of contamination from each step. Additionally, it was necessary to determine the effects of variations in matrix, pH and Eh on E. To this end, a series of experiments were performed that involved the determination of E for several trace-metals in: different matrices (salt water vs. fresh water); different extraction pH (incomplete or over neutralization); and different redox conditions (oxic vs. anoxic porewaters). Following is a summary of the results of those experiments.

Extraction efficiency was determined by standard addition of spike to replicates of the same
sample (i.e. blank, 5, 10 and 20 ppb). E was evaluated by measuring the slope of the regression of a plot of measured metal concentration vs. concentration of added spike. This was done for several metals (Cd, Cu, Mo, Ni, Pb and Zn) and in several different matrices (fresh water, oxic water and anoxic porewater) as well as at several different pH values. The results are summarized in Table 23.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Metal</th>
<th>Cd</th>
<th>Cu</th>
<th>Mo</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDW</td>
<td></td>
<td>83%</td>
<td>90%</td>
<td>41%</td>
<td>82%</td>
</tr>
<tr>
<td>Oxic</td>
<td></td>
<td>75%</td>
<td>93%</td>
<td>40%</td>
<td>83%</td>
</tr>
<tr>
<td>Anoxic</td>
<td></td>
<td>80%</td>
<td>90%</td>
<td>45%</td>
<td>85%</td>
</tr>
<tr>
<td>5% over</td>
<td></td>
<td>79%</td>
<td>90%</td>
<td>42%</td>
<td>87%</td>
</tr>
<tr>
<td>5% under</td>
<td></td>
<td>82%</td>
<td>91%</td>
<td>40%</td>
<td>87%</td>
</tr>
</tbody>
</table>

Table 23 Results for extraction experiments of porewater with varying pH, Eh and ionic strength. 5% over and under represent neutralization volumes over and under a predetermined target pH.

Neither matrix nor variations in pH (±5% NH₄OH by volume) appeared to effect E; the maximum variation in E for any metal was limited to ±10% and was typically much less. It appears that there is no significant effect on E for any of the parameters measured and in this sense, APDC-CoCl₂ coprecipitation is an adequate method for extracting this suite of trace metals from coastal porewaters. With the possible exception of Mo, extraction efficiencies were high enough to warrant the use of this method for all metals studied; fortunately the geochemistry of Mo is such that it often exists at relatively high concentrations in ocean waters and some porewaters; the low extraction efficiency did not pose a problem.

**Trace Metal Analysis by GFAAS**

All trace metal analyses were performed on a Varian Spectra300 graphite furnace atomic absorption spectrophotometer equipped with Zeeman background correction and a PSD 96
autosampler. Samples were deposited by the autosampler into a graphite tube with a L'vov platform (Mo and Ni were analysed "off the wall" of a partition tube). Samples were first dried and then ashed before being atomized (see Table 24 for a typical method program and instrument parameters).

<table>
<thead>
<tr>
<th>Element</th>
<th>Tube Type</th>
<th>( \lambda ) (nm)</th>
<th>Slit Width (nm)</th>
<th>Dry Temp (°C)</th>
<th>Ash Temp (°C)</th>
<th>Atomization Temp (°C)</th>
<th>Detection Limit (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>L'vov</td>
<td>228.8</td>
<td>0.5 R</td>
<td>300</td>
<td>500</td>
<td>1900</td>
<td>0.4</td>
</tr>
<tr>
<td>Cu</td>
<td>L'vov</td>
<td>327.4</td>
<td>0.5 R</td>
<td>300</td>
<td>1000</td>
<td>2550</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>L'vov</td>
<td>248.3</td>
<td>0.2 R</td>
<td>300</td>
<td>1000</td>
<td>2550</td>
<td>13</td>
</tr>
<tr>
<td>Mn</td>
<td>L'vov</td>
<td>279.5</td>
<td>0.2 R</td>
<td>300</td>
<td>800</td>
<td>2500</td>
<td>18</td>
</tr>
<tr>
<td>Mo</td>
<td>partition</td>
<td>313.3</td>
<td>0.5 R</td>
<td>150</td>
<td>1000</td>
<td>2850</td>
<td>6</td>
</tr>
<tr>
<td>Zn</td>
<td>L'vov</td>
<td>213.9</td>
<td>1.0 R</td>
<td>300</td>
<td>700</td>
<td>2000</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^1\)Fe and Mn were run by direct injection.

Table 24 Settings, programs and detection limits (6 \( \sigma \) of the blank) for the graphite furnace atomic absorption spectrometer.

The instrument was calibrated using diluted NBS trace metal standards in a dilute nitric acid matrix. Dispensing of samples and standards was performed in a class 100 laminar flow hood to minimize potential contamination.
Appendix IV - Sedimentation Rate Determination
Appendix IV - Sedimentation Rate Determination

Because most coastal sea floors receive relatively large fluxes of material (sedimentation rates ranging from millimetres to centimetres per year; e.g. Smith and Walton, 1980), a $^{210}\text{Pb}$ sediment-dating technique (adopted from Flynn, 1968) was used to determine sedimentation rates in this study. The method involves spontaneously plating $^{210}\text{Po}$ (granddaughter in secular equilibrium with $^{210}\text{Pb}$) onto a Ni or Ag disk; $^{210}\text{Po}$ activity is then determined by alpha counting. The relatively short half-life of $^{210}\text{Pb}$ (22.3 years) allows the dating of sediments as old as about 150 years, represented by as much as a few metres of sediment.

$^{210}\text{Pb}$ Geochemistry and Assumptions

$^{210}\text{Pb}$ is a member of the $^{238}\text{U}$ decay series. Within this series, $^{226}\text{Ra}$ ($T_{1/2} = 1600$ yrs) exists ubiquitously in the earth's crust and decays to produce $^{222}\text{Rn}$, a gas. $^{222}\text{Rn}$ is able to enter the upper troposphere before its demise to $^{210}\text{Pb}$ via a series of several short-lived, radioactive intermediates ($T_{1/2} = 3.8$ days). $^{210}\text{Pb}$ is extremely particle reactive, and is quickly scavenged by aerosols and deposited back on the earth's surface. Some of this Pb enters the oceans and rapidly becomes incorporated into the sediments. This component is termed "excess $^{210}\text{Pb}$" ($^{210}\text{Pb}_{xs}$) because it exists in excess of the $^{210}\text{Pb}$ formed \textit{in situ} through the decay of $^{226}\text{Ra}$ already in the sediments (termed supported $^{210}\text{Pb}$). The $^{210}\text{Pb}_{xs}$ in a given sediment core (total $^{210}\text{Pb}$ - supported $^{210}\text{Pb}$) can be used to date the horizons of that core, yielding among other things, the sedimentation rate.

Method Details

$^{210}\text{Pb}$ was measured by a method of Smith and Walton (1980), modified after Flynn (1968). $^{210}\text{Po}$, in secular equilibrium with $^{210}\text{Pb}$, was released from the solid sediment matrix by microwave, acid digestion (see Appendix III for details); samples were stored at least 9 months to ensure secular equilibrium between $^{210}\text{Pb}$ and $^{210}\text{Po}$. After an aliquot of digest was removed for trace metal analysis, the remainder was transferred to a 60 mL, acid washed HDPE container for storage until plating.
The sediment digest (typically from the digestion of 0.25 to 0.5 grams of dried sediment) was transferred to a 125 mL glass beaker. To this was added ~0.2 g ascorbic acid and ~0.5 g hydroxylamine (to keep Fe reduced, thereby avoiding reductions in Po plating efficiency) and a $^{208}$Po spike. The $^{208}$Po spike (approximately 10 dpm) was added as a yield tracer, and to permit normalization of differences in plating and counting efficiency among samples. The mixture was made up to 100 mL with dilute HCl (0.5 N) and neutralized to approximately pH 1 to 2 with NH$_4$OH. A clean Ni or Ag disk in a Teflon holder and thermometer were submerged in the solution which was heated to 85°C. Spontaneous plating of Po onto the disks was allowed to proceed for 4 to 6 hours after which the disks were removed, rinsed with methanol and DDW, air-dried and finally alpha-counted for at least 24 hours on an Ortec 576A Muti-channel Analyser and alpha-counter.

Alpha-counts for $^{208}$Po and $^{210}$Po were integrated over approximately 200 channels each. $^{210}$Po activity was calculated using the integrated alpha-counts of the $^{208}$Po spike for normalization. $^{210}$Po activities were finally corrected for salt dilution and converted directly to $^{210}$Pb activities, as the two species were assumed to be in secular equilibrium.

**Calculation of Sedimentation Rates**

Once the $^{210}$Pb activities for the horizons of a core were determined, sedimentation rate was estimated using a Constant Input Concentration model (CIC model) (see Krishnnawami et al., 1971; Bruland, 1974; Matsumoto, 1975; Robbins and Edgington, 1976; Matsumoto and Wong, 1977).

The CIC model employs four basic assumptions in the interpretation of $^{210}$Pb data:

1. constant $^{210}$Pb flux to the sediments with time;
2. constant sedimentation rate with time;
3. $^{210}$Pb does not migrate after deposition;
4. $^{210}$Pb supported by $^{226}$Ra is constant with depth.
Because sediments compact under their own weight, core depth and age do not linearly correlate. Sediments must be "decompacted" to constant porosity using the following relationship from Robbins and Edgington (1975):

\[
z' = \frac{1}{(1 - \phi_o)} \left[ z(1 - \phi') + \frac{\phi(z) - \phi_o}{\beta} \right]
\]

where: \( z' = \) decompacted depth; \( \phi' = \) porosity at infinite depth; \( \phi_o = \) interfacial porosity; \( \phi(z) = \) porosity at depth \( z; \) and \( \beta = \) the slope of the ln \((\phi(z) - \phi')\) vs. depth regression, derived from the equation of Athy (1930):

\[
\phi = (\phi_o - \phi')e^{-\beta z} + \phi'
\]

A shortcoming of the data set used in this thesis is the lack of directly-measured sediment porosity values. This was in part overcome by the use of porosity data from other cores taken previously at the same locations. Thus, when interpreting sedimentation rate and accumulation rate from the assembled data, it should be kept in mind that to a first approximation, calculated sedimentation rates vary by up to a factor of 2 between uncorrected and maximally depth-corrected sediment cores (see below).

In order to convert the measured activity of \(^{210}\)Pb, it is necessary to know the supported \(^{210}\)Pb concentration by either measuring \(^{226}\)Ra in the sediment directly or by measuring \(^{210}\)Pb activity from deep within the sediments where the excess \(^{210}\)Pb has decayed away. In this study, \(^{210}\)Pb\(_{xs}\) was determined by the latter approach.

Excess \(^{210}\)Pb is related to sedimentation rate as follows:

\[
A(z') = \left( \frac{P}{\omega} \right) e^{-\lambda \frac{z'}{S_o}} + A_{sup}
\]

where: \( A(z') = \) the total activity of \(^{210}\)Pb at corrected-depth \( z' \); \( A_{sup} = \) the supported \(^{210}\)Pb activity; \( \lambda = \) decay constant for \(^{210}\)Pb (0.0311 yr\(^{-1}\)); \( S_o = \) sedimentation rate at interface (cm yr\(^{-1}\)); \( P = \) \(^{210}\)Pb flux to sediments (dpm cm\(^{-2}\) yr\(^{-1}\)); and \( \omega = \) accumulation rate at the sediment-water
interface (g cm$^2$ yr$^{-1}$). Thus, excess activity ($A(z')_{xx}$) is:

$$A(z')_{xx} = A(z') - A_{sp} = \left(\frac{P}{\omega}\right) e^{-\frac{\lambda z' S_o}{S_o}}$$

(4)

From (4), plotting ln ($A(z')_{xx}$) vs. compaction-corrected depth ($z'$) should produce a straight line whose slope is $-\frac{\lambda}{S_o}$ and intercept is ln ($\frac{P}{\omega}$), yielding, amongst other things, sedimentation rate.

**Sources of Error**

Precision for the $^{210}$Pb technique was determined by measurements of the activity of several sub-samples of a homogenized sample and is estimated at ±5%. Counts of unplated disks indicated negligible background activity.

The greatest weakness associated with these estimates of sedimentation rate is the lack of porosity data; it is not possible to correct accurately for compaction. Calculations were performed to explore the variability in estimated sedimentation rates in Ucluelet Inlet, given different estimates of supported $^{210}$Pb and porosity as a function of depth (Table 25). Porosity appears to influence sedimentation rate predictions in Ucluelet Inlet to a greater degree than variability in supported $^{210}$Pb. As a result, $^{210}$Pb data are used more for interpretation of steady-state throughout a core rather than as a determinant of absolute sedimentation rates; the absence of porosity data allows the calculation of 'first approximation' sedimentation rates only.

<table>
<thead>
<tr>
<th>supported $^{210}$Pb</th>
<th>$\phi$-corrected depth</th>
<th>no $\phi$ correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 dpm/g</td>
<td>0.56 cm yr$^{-1}$</td>
<td>0.26 cm yr$^{-1}$</td>
</tr>
<tr>
<td>0.5 dpm/g</td>
<td>0.45 cm yr$^{-1}$</td>
<td>0.21 cm yr$^{-1}$</td>
</tr>
<tr>
<td>1.0 dpm/g</td>
<td>0.34 cm yr$^{-1}$</td>
<td>0.16 cm yr$^{-1}$</td>
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</tbody>
</table>

Table 25 - Variability in calculated sedimentation rate for core U-1 given differences in supported $^{210}$Pb, with and without porosity depth-correction.

**Porosity Depth-Correction Model**

In order to constrain estimates of sedimentation rate, methods of decompaction corrections
to depth scales were investigated and are outlined below.

Using existing porosity data from Ucluelet Inlet, Port Moody and Indian Arm, an attempt was made to model typical porosity profiles to correct partially for decompaction, thus minimizing the errors associated with estimates of sedimentation rate. Porosity profiles were modelled using equation (2), the results of which were used in equation (1). The parameters that affect depth correction (interfacial porosity, porosity at depth and the degree of exponential decrease in porosity with depth) were used in all three inlets to determine the relative impact of different depth corrections on sedimentation rate. The results are summarized below and in Table 26 and Table 27.

<table>
<thead>
<tr>
<th>Inlet</th>
<th>( \beta_i )</th>
<th>( \phi_0 )</th>
<th>( \phi_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indian Arm</td>
<td>0.700</td>
<td>0.92</td>
<td>0.88</td>
</tr>
<tr>
<td>Ucluelet</td>
<td>0.265</td>
<td>0.84</td>
<td>0.65</td>
</tr>
<tr>
<td>Port Moody</td>
<td>0.050</td>
<td>0.85</td>
<td>0.62</td>
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</tbody>
</table>

Table 26 Parameters for sedimentation rate estimates from Indian Arm, Ucluelet Inlet and Port Moody.

<table>
<thead>
<tr>
<th></th>
<th>Indian Arm</th>
<th>Ucluelet Inlet</th>
<th>Port Moody</th>
</tr>
</thead>
<tbody>
<tr>
<td>No correction</td>
<td>0.25 (cm yr(^{-1}))</td>
<td>0.20 (cm yr(^{-1}))</td>
<td>0.87 (cm yr(^{-1}))</td>
</tr>
<tr>
<td>Indian Arm correction</td>
<td><strong>0.37 (cm yr(^{-1}))</strong></td>
<td>0.29 (cm yr(^{-1}))</td>
<td>1.31 (cm yr(^{-1}))</td>
</tr>
<tr>
<td>Ucluelet correction</td>
<td>0.47 (cm yr(^{-1}))</td>
<td><strong>0.36 (cm yr(^{-1}))</strong></td>
<td>1.78 (cm yr(^{-1}))</td>
</tr>
<tr>
<td>Port Moody correction</td>
<td>0.34 (cm yr(^{-1}))</td>
<td>0.26 (cm yr(^{-1}))</td>
<td><strong>1.57 (cm yr(^{-1}))</strong></td>
</tr>
</tbody>
</table>

Table 27 Estimated sedimentation rates using different correction factors from Table 26.

As inferred from Table 26 and Table 27, the size of \( \beta_i \) had minimal influence on the estimated sedimentation rate particularly when compared to the variability associated with the difference between interfacial and final porosity. It does not matter how quickly the porosity
decreases between interfacial and final values, what matters is the absolute difference between those values. Because decompaction is normalized to interfacial porosity, larger differences between $\phi_0$ and $\phi'$ translate to greater decompacted depth scales and thus higher sedimentation rates.

One way to use this information is to suggest that uncorrected depth profiles yield minimum boundaries for sedimentation rate estimates, and any decompaction will only increase those estimates. The degree to which an estimate increases then depends on the nature of the sediments themselves. As a result, sedimentation rates based on $^{210}$Pb data have been used in this thesis as first approximations only.
Appendix V - Accumulation Rate and Diffusive Flux Calculations
Appendix V - Accumulation Rate and Diffusive Flux Calculations

Diffusive flux calculations were performed on porewater data for some trace metals in certain cores where diffusion was thought to be an important transport mechanism. In such cases it is possible to assess the relative importance of this mechanism by comparing it to accumulation rates of the same metal as determined from sedimentation rate estimates. Thus, for several cores, diffusive fluxes were estimated using both a simple linear diffusive flux model and a diffusion-consumption model and the results compared with estimates of accumulation rate. Following are sample calculations for determining all three parameters. Note that the absence of real porosity data limits the accuracy of these types of calculations.

**Linear Flux Model**

The simple linear flux model is based on Fick's first law of diffusion which assumes linear concentration gradients such that:

\[ J = -D_{\text{sed}} \left( \frac{\partial C}{\partial x} \right) \]

where \( J \) = the diffusive flux of the dissolved species; \( D_{\text{sed}} \) = the \textit{in situ} sedimentary diffusion coefficient of that species corrected for porosity and tortuosity; and \( \frac{\partial C}{\partial x} \) is the concentration gradient. This model assumes that over short distances, steep concentration gradients can be approximated as linear.

**Diffusion Consumption Model**

The diffusion-consumption model (DCM) also uses Fick's principles of diffusion, and accounts for first-order consumption of the diffusing species. In order to sustain a "steady-state" concentration gradient, something must act as a source for the dissolved species and something must consume it; the equation describing this process (after Lerman, 1977 and Berner, 1980) is:

\[ D \left( \frac{\partial^2 C}{\partial x^2} \right) - kC = 0 \]  (2)
where $k$ = the first order rate constant for the consumption of the dissolved species and $C$ = the concentration of that species. The solution to equation (2) is:

$$C = \frac{C_1 \sinh[R(h - z)] + C_2 \sinh(Rz)}{\sinh(Rh)}$$

(3)

where: $C_1$ = the concentration at the sediment-water interface; $C_2$ = the concentration at the bottom boundary (depth $h$); and $R = \sqrt{\frac{k}{D}}$. The first order reaction constant ($k$), can be estimated from a "best fit" of the porewater data. This equation can then be solved for $J$, the diffusive flux:

$$J = \frac{D C_1 R_c \cosh(Rh) - D R C_2}{\sinh(Rh)}$$

(4)

The fit to the data for the value of the rate constant is sensitive only to large unrealistic estimates. Various fits to the Cd data of core KN-3 in Knight Inlet (Figure 94) display how little variance there is for the fits in the vicinity of the data. Table 28 presents the fluxes associated with each rate constant.
Figure 94 Fits for various reaction rate constants (k) and actual data for dissolved Cd in core KN-3, Knight Inlet.

<table>
<thead>
<tr>
<th>Rate const.</th>
<th>k=1</th>
<th>k=10</th>
<th>k=50</th>
<th>k=100</th>
<th>k=150</th>
<th>k=200</th>
<th>k=500</th>
<th>k=1000</th>
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<tr>
<td>Flux (pmol cm⁻² yr⁻¹)</td>
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<td>409</td>
<td>337</td>
<td>336</td>
<td>336</td>
<td>336</td>
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</table>

Table 28 Estimated fluxes of Cd in core KN-3, Knight Inlet using different reaction rate constants (k). See Figure A-1 for the profile associated with each constant.

Although the diffusion-consumption model is more rigorous than the linear diffusion model, it does not necessarily provide a more accurate approximation of the flux of a given element than the linear model. The DCM relies strongly on ancillary data such as porosity and reaction rates which in this study are not well constrained, whereas the linear diffusion model relies only on available information (i.e. diffusion coefficients and concentration gradients).

Accumulation Rate Calculations

Estimations of accumulation rates (AR) of a specific element in the solid phase can be calculated from the following relationship:
AR = (ω)(1 − φ)(ρ_g)[M]

where \( ω \) = the sedimentation rate in cm yr\(^{-1}\); \( ρ_g \) = the bulk grain density (typically ~2.4 g cm\(^{-3}\)); \( φ \) = sediment porosity; and \( M \) = the concentration of solid-phase metal within the sediment.
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<th>0.75</th>
<th>1.0</th>
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Ultralite R32: Core U-2
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*Note: The table represents the concentrations of various elements at different depths from 0.00 cm to 0.45 cm in Depth U-2.*
| Depth (ft) | 0 | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 | 22 | 24 | 26 | 28 | 30 | 32 | 34 | 36 | 38 | 40 |
| Core KN-1 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |

Knight Inlet Core KN-1
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<th>% Corg</th>
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**Note:** The table data is not interpretable due to the nature of the content.
**Knight Inlet: Core KN-1**

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Knight Hite Core KN-2
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**Jersey Inlet Core JV-3**
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*Note: The table contains chemical composition data for various depths.*
| Depth (cm) | [Sr] | [Y] | [Zr] | [p] | [K] | [Ca] | [Mg] | [Fe] | [Ni] | [Ti] | [Zn] | [Cu] | [Cd] | [Hg] | [Pb] | [Zn] | [Ni] | [Cu] | [Cd] | [Hg] | [Pb] |
|-----------|------|-----|------|-----|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 0         | 3.83 | 1.91| 1.73 | 0.089| 1.11| 2.48 | 2.10 | 0.69 | 7.43 | 0.359| 0.86 | 4.00 | 2.04 | 2.04 | 4.38 | 7.58 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 |
| 2.5        | 3.85 | 1.97 | 1.71 | 0.092| 1.15 | 2.65 | 2.04 | 4.38 | 7.58 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 | 4.38 | 7.58 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 |
| 5          | 3.90 | 1.72 | 0.20 | 0.093| 1.17 | 2.60 | 2.10 | 4.37 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 |
| 10         | 3.92 | 1.97 | 1.71 | 0.093| 1.17 | 2.60 | 2.10 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 |
| 15         | 3.97 | 1.92 | 1.71 | 0.097| 1.07 | 2.80 | 2.09 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 |
| 20         | 3.96 | 2.01 | 2.01 | 0.092| 1.9 | 2.69 | 2.09 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 |
| 25         | 2.0 | 2.0 | 2.0 | 0.092| 1.9 | 2.69 | 2.09 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 | 4.38 | 7.57 | 2.525| 0.362| 0.86 | 4.00 | 2.04 | 2.04 |

Jersey Inlet Core JY-9
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Vancouver Harbour: Core VH-1