THE GEOCHEMISTRY OF SEDIMENTS AND MINE TAILINGS IN THE ALICE ARM AREA.

by

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ABSTRACT

A geochemical study of the composition of natural sediments and contaminating mine tailings in Hastings and Alice Arms has been carried out. Apart from the geochemical investigation on the solid fraction, pore waters from six sediment cores have been analyzed to evaluate the diagenetic processes in the sediments of these two inlets. Differences in the mineralogy as well as in the chemical composition of the sediments were used to distinguish the natural sediments from contaminated sediments and pure tailings.

In Alice Arm, two types of tailings could be differentiated with these methods. The first tailings type originated from the Kitsault Mo-deposit, which was mined in the past two decades by the B.C. Molybdenum Corporation and AMAX/Canada. These tailings are characterized by a number of features which make them distinguishable from natural sediments. The K-feldspar content of the tailings is significantly increased, mainly at the expense of plagioclase, which is the main characteristic for the mineralogical identification of this tailings type. The enhanced K-feldspar content is the cause for increased K and Rb values in the Mo-mine tailings. Another indicator specific to these recent tailings is an increased Mo content.

The second tailings type is derived from an older mining operation in the Kitsault Valley, most likely the Dolly Varden Silver Mine. A specific indicator for these tailings is their high Ba content which is due to large amounts of barite. This mineral phase could be identified by X-ray diffraction methods in a heavy mineral fraction of the relevant sediment layers.

Both tailings types show enrichment in their Pb, Zn and S concentrations, caused by an increased amount of metal-sulphides in the ore materials. In this area, these elements can therefore serve as a general indicator for the contamination of natural sediment with either tailings type.

The interstitial water analyses indicated that the sediments in both inlets become reducing at a fairly shallow depth (10–15 cm), resulting in the mobilization of Mn, Fe and Mo from the solid phase. In the deeper parts of the cores, consumption of these metals could usually be observed which is likely due to precipitation of authigenic components. The dissolved Mo concentrations in the sediments contaminated with the modern tailings were much higher than in the natural sediments. In the pore water of the pure tailings the concentration reaches some 300 times that of the overlying water, which is the highest value ever reported for saline pore waters. These high Mo concentrations must support a flux of Mo from the sediment into the overlying water, and it is shown that such a flux could increase the inventory of naturally occuring dissolved Mo in the deep waters of Alice Arm by up to 4%.

Table of Contents

ABSTRACT
1. INTRODUCTION
1. STUDY AREA
1. Physiography
2. GEOLOGICAL SETTING
1. Regional geology
2. Geology of the Kitsault intrusives
3. Sediment supply
3. MINING HISTORY OF THE ALICE ARM AREA
1. History of the Lime Creek Molybdenum Deposit
2. PHYSICAL OCEANOGRAPHY OF ALICE AND HASTINGS ARMS 14
1. Temperature and Salinity Distribution
2. Currents
3 Internal Waves
A Recent Sedimentation 19
5 Previous Work on Alice Arm and Hastings Arm Sediments 21
3 MINERALOCY
$1 INTRODUCTION \qquad \qquad$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$
2. MINERAL IDENTIFICATION
$1. UUARIZ \dots \dots$
$2. FELDSPAR \qquad \ldots \qquad $
$2. K-Feldspar \dots 25$
$3. CLAY MINERALS \qquad \ldots \qquad $
1. Chlorite
2. Mica
3. Kaolinite
4. HALITE
5. BARITE
6. HORNBLENDE
7. SPHALERITE
8. PYRITE
9. MOLYBDENITE
3. Mineralogical Composition of Natural and Contaminated Sediments 27
4. GEOCHEMISTRY OF THE MAJOR ELEMENTS
1. INTRODUCTION
2. DISTRIBUTION OF THE ELEMENTS
1. Silicon and aluminium
2. Titanium
3 Potassium and sodium 45
A Calcium
5. Magnesium and lithogenous iron
6 Managnese and orde iron
0.112 uny une oce una oceane en one
1. F NOSPNOTUS
5. MINUR ELEMENT DISTRIBUTION

1.		Introduction	. 66
2.		DISTRIBUTION OF THE MINOR ELEMENTS	. 66
	1.	Distribution of Cobalt, Chromium, Nickel and Vanadium	. 67
	2.	Distribution of Molybdenum, Copper, Lead and Zinc	. 72
	3.	Distribution of Rubidium	. 81
	4	Distribution of Barium and Strontium	. 84
	5.	Distribution of Zirconium	. 87
6. S 2	EL	DIMENTS INFLUENCED BY THE ANYOX OPERATION	. 90
1.		MAJOR ELEMENTS	. 90
2		MINOR ELEMENTS	. 92
7. II	TI	TERSTITIAL WATER CHEMISTRY	. 95
1		INTRODUCTION	. 95
2		NUTRIENT DISTRIBUTION IN THE INTERSTITIAL WATER	. 97
	1	. Distribution of interstitial silica	. 97
	2	. Distribution of PO_4^{3-} , NO_3^- , NH_4^+ , SO_4^{2-} , H_2S and titration alkalinity	. 99
3		METAL DISTRIBUTION IN THE INTERSTITIAL WATER	113
	1	. Distribution of Mn^{2+}	115
	2	. Distribution of Fe^{2+} in interstitial water $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	118
	3	. Distribution of Mo in interstitial water	119
4		DISCUSSION	120
8. S	UN	MMARY	130
App	pei	ndix I: Sample collection and initial sample preparation	135
App	pei	ndix II: Analytical methods	136
1	•	Pore water sampling and analysis	136
2		Titration alkalinity	137
3	•	Sulphate	137
4	•	Nutrient analysis	138
5	•	H_2S determination	138
6	•	Dissolved Fe, Mn and Mo	139
7	•	X-ray diffraction analysis	139
	1	. Sample preparation	141
	2	. Operating conditions	142
8	•	X-ray fluorescence spectrometry	142
	1	. Major element sample preparation	142
	2	. Minor element sample preparation	143
	3	. XRF-analytical procedure	143
	4	. Accuracy of the measuring program	145
9	•	Correction for sea salt effects	146
1	0.	Carbon analysis	146
	1	. Total carbon	146
	2	. Carbonate carbon	147
Apj	pei	ndix III: Chemical data	149
Bib	lio	graphy	182

List of Figures

1	Study area and correlations	A
1.	Study area and core locations.	. 4 5
4. 2	Coolorial man of the Alice Arm area	. U
Э. А	Minoral claims in the Alice Arm area	. 0
4. E	Wonthly runoff for Alice Arm drainage area	. 12
Э. С	Tomporature and Salinity profiles in Alice Arm	. 10
0. 7	Comperature and Samily promes in Alice Arm and month	. 10
1.	Generalized grainsize distribution of Ance Arm sediments	. 20
ð.	Slow speed high resolution And-scale	· 44
9.	XRD-scan from contaminated sediments	. 31
10.		. 35
11.		. 30
12.	Si versus Al for core AA-8. \ldots \ldots \ldots \ldots \ldots \ldots \ldots	. 39
13.	Si versus Al for cores HA-2, AA-5 and AA-8.	. 40
14.	Vertical distribution of Ti	. 42
15.	Ti versus Al for cores HA-2, AA-5 and AA-8 \ldots \ldots \ldots	. 44
16.	Vertical distribution of Na and K	. 46
17.	Na versus K for cores HA-2, AA-5 and AA-8	. 47
18.	Distribution of total and cabonate free Ca	. 49
19.	Vertical distribution of Mg	. 51
2 0.	Vertical distribution of Fe	. 52
21.	Mg versus Fe for cores HA-2, AA-5 and AA-8	. 54
22.	Vertical distribution of Mn	. 56
23.	Vertical distribution of solid phase phosphorus	. 59
24.	Total sulphur distribution in the solid sediment	. 62
25.	Vertical distribution of C	. 64
26.	Correlation of Cr and Ni with V $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots$. 69
27.	Correlation of Ni, Cr, V and Co with Fe	. 70
28.	Correlation of Ni, Cr, V and Co with Mg	. 71
29.	Vertical distribution of Co, Cr, Ni and V	. 73
30.	Vertical distribution of Mo, Cu, Pb and Zn	. 76
31.	Correlations of K, Si, Fe and Al with Mo	. 77
32.	Relationships of Mo with Cu, Pb and Zn	. 79
33.	Relationship of Cu, Pb and Zn	. 80
34.	Correlation of Rb and K	. 82
35.	Vertical distribution of Rb	. 83
36.	Correlation of Ba and Sr	. 85
37.	Vertical distribution of Ba and Sr	. 86
38.	Vertical distribution of Zr	. 88
39.	Minor and major element distribution at station HA-6.	. 93
40.	Dissolved silica profiles	. 98
41	Biologically mediated redox processes	100
42	Distribution of dissolved constituents in core HA-2	102
43	Distribution of dissolved constituents in core HA-6	103
10. AA	Distribution of dissolved NH^+ PO^{3-} and Mo in core AA-4	104
45	Distribution of dissolved constituents in core AA .	105
	Distribution of dissolved constituents in core AA_{-5}	106
40.	Distribution of dissolved constituents in core AA_{-1}	107
21.	DISTURDED OF DISCOLOUS THE COLOUR AND A COLORADO AND A	101

.

48.	Distribution of dissolved constituents in core AA-8	•	•	•	•	•	•	•	•	•	•	•	•	108
49.	Theoretical profiles of interstitial constituents	•	•	•	•	•	•	•	•	•	•	•	•	114
50.	Pore water Mo and solid phase Mo	•	•	•	•		•	•	•	•	•	•	•	121
51.	Pore water Mo vs. solid Mo from core AA-4	•	•		•	•	•	•	•	•	•	•	•	126
52.	Eh/pH diagram for aqueous Mo species	•	•	•	•	•	•	•	•	•	•	•	•	128

•

List of Tables

1.	Stratigraphy of the Alice Arm area
2.	Feldspar peak-height ratios from Hasting and Alice Arm sediments
3.	Si/Al ratios of Hastings and Alice Arm sediments
4.	Mg/Al ratios of Hastings and Alice Arm sediments
5.	C/N ratio of cores HA-2 and AA-8
6.	Average abundances of minor elements
7.	average elemental abundances
8.	Oxidation-reduction reactions
9.	Instrument settings for the graphite furnace
10.	Analytical conditions for XRF-analysis
11.	XRF analytical precision for minor elements
12.	Accuracy of the measuring program for XRF analysis

1. INTRODUCTION

The disposal of mining wastes into coastal waters has been a practice in British Columbia since the beginning of mining activities at the turn of the century, and such materials have been discarded with little regard for their environmental impact (Waldichuk, 1978). Worldwide marine disposal of industrial and mining wastes has increased rapidly in the last few decades. However, there is still very little knowledge about the behaviour of these wastes after their deposition and therefore their effects on the marine environment are only poorly understood. In particular, effects on the geochemistry of sediments, apart from the addition of metals, organic substances and other waste products, are almost completely unknown. This thesis examines a particular case, that of the geochemical effects of a large disposal of mining waste (tailings) into a deep, restricted fjord.

Amax/Canada bought the Kitsault molybdenum mine from the B.C. Molybdenum Corporation in 1973. After carrying out extensive geological and feasibility studies in the following years, Amax made an application for a mining permit to the B.C. Ministry of Mines in 1978 to reopen the mine. They proposed a mill throughput of 12,000 metric tons of ore-grade material per day which, after recovery of the molybdenum, was to be discharged into Alice Arm via a submarine tailings outfall. The unmineralized waste rock was to be stored on land close to the open pit mine.

Marine disposal of the mine tailings was chosen for economic as well as environmental reasons. Subaquatic disposal of the milled ore residue makes the creation of on-land inpoundments unnecessary. This eliminates costly reclamation and monitoring programs for the tailings ponds, which are usually demanded by the authorities and generally continue for years after a mining operation is shut down. Also, terrestrial tailings deposits, especially of sulphidic ores, such as the one found in the Kitsault deposit, are prone to bacterially-mediated leaching of the unrecovered metals. Bacteria such as *Thiobacillus* can use the sulphides as an electron source, oxidizing them to SO_4^{2-} which then forms sulphuric acid. In an acidic environment, the metal sulphides become thermodynamically unstable and can even be chemically oxidized under atmospheric conditions. The more soluble metal oxides and the acid then become possible contaminants of ground and surface waters. Hence, submarine disposal reduces the risk of surface water contamination and, due to the apparently restricted chemical reactivity of mine tailings in marine or lacustrine waters, remobilization of metals in at least some subaquatic tailings deposits is not thought to occur in worrisome amounts (Pedersen, 1983).

Experience shows, however, that the proposed goals, such as the confinement of the tailings to a certain area and the nonreactive behaviour of the tailings in the waterbodies, can not always be met. The Island Copper Mine on Rupert Inlet (north Vancouver Island) is an example where insufficient knowledge of the physical characteristics of a fjord system can lead to unforeseen problems of confining the waste in a defined area (Waldichuk, 1978; Hay et al., 1982; Pedersen, 1984). In addition, recent investigations have shown that certain conditions may lead to a release of mobilized metals from tailings into the overlying water (Asmund, 1980; Hoff et al., 1982; Wong et al., submitted). To reduce the risk of such problems, AMAX/Canada, the Environmental Protection Service (Environment Canada) carried out a series of detailed oceanographic studies of Alice Arm prior to the resumption of mining. They and Fisheries and Oceans Canada (Institute of Ocean Sciences) maintained a monitoring program throughout the renewed operation of the mine, from April 1981 through October 1982 to provide surveillance of the receiving environment. Some studies are still continuing after the temporary shut-down of the mine. A considerable amount of research has been carried out on the sediments of Alice Arm by consultants for the mining company, the Environmental Protection Service and Fisheries and Oceans/IOS. This work mainly involved determination of the metal content of sediments from different locations and sedimentary environments, which was used to differentiate between natural sediment and mine-tailings. However, there has been little geochemical information available, and the composition of the porewaters has been totally neglected. Therefore, these

two aspects are the main focus of this thesis.

1.1 STUDY AREA

Alice Arm and Hastings Arm are the landward termini of a system of inlets on the northern British Columbia coast, stretching some 110 kilometres inland from the Pacific Ocean (Fig. 1). The Kitsault Molybdenum Mine, located at the head of Alice Arm, is approximately six kilometres south of the Kitsault town site. Close to the mouth of Hastings Arm at the shores of Granby Bay, is the site of the Anyox copper mining and smelting operation, which closed down in 1936.

1.1.1 Physiography

Like most other inlets along the North American west coast, Alice Arm and Hastings Arm are drowned, steepsided, U-shaped valleys carved out of the coastal mountains by the Pleistocene glaciers. They are typical fjords and referred to locally as *inlets*. A common feature of many inlets are shallow sills which often represent terminal moraines. However, unlike the very shallow sills in some Norwegian fjords, which are often compared with North American inlets, the sill depth is usually greater then the depth of the brackish surface water layer (Pickard, 1961). A complex of these sills is found where Alice Arm and Hastings Arm join with Observatory Inlet (Fig. 2); Hastings Arm is separated from Observatory Inlet by a sill of 51 metres depth. Two sills of 42 and 20 metres depth, 16 and 19 kilometres, respectively, from the head, restrict the entrance to Alice Arm. From the junction, Hastings Arm extends about 22.2 kilometres to the north and Alice Arm 19 kilometres to the east. The two inlets have maximum depths of 307 metres and 386 metres, respectively (Krauel, 1981; Goyette, 1982).





1.2 GEOLOGICAL SETTING

Most of the detailed areal, geologic mapping of the Alice Arm, Hastings Arm and Observatory Inlet region dates back to the first three decades of this century. Exploratory mapping by the Geological Survey of Canada began in 1893 and this was follwed by more detailed work in 1910 and 1911 by McConnell (Hanson, 1935). Hanson surveyed the Alice Arm area in 1921 and 1928-30 and in 1932 he worked in the vicinity of Hastings Arm. This work formed the basis for the geological map of the Portland Canal Area, Cassiar district, British Columbia (GSC Map 307A). More recent geological work in this area was done by Drummond (1961), Silversides (1961), Woodcock et al. (1966), Carter (1972), Woodcock and Carter (1976), Carter (1979) and Steininger (1985). However, these recent investigations are limited to the proximity of mineral deposits and the regional geology is mainly based on Hanson's work. The only noteworthy new development was the introduction of a revised stratigraphy of the area by Tipper and Richards (1976).

1.2.1 Regional geology

The study area is characterized by a series of mildly-metamorphosed late Mesozoic volcanic and sedimentary rocks, intruded by the Coast Plutonic Complex and the socalled Kitsault Intrusives of Tertiary age (Table 1). The eastern half of Alice Arm reaches into the Hazelton Formation and the Bowser Lake Group. To the north of Alice Arm and the Illiance River, the Hazelton Formation crops out, representing the oldest rocks in this area (Table 1, Fig. 3). For the Hazelton Group, no general dip can be reported because the intrusion of the Coast Plutonic Complex caused intensive faulting. The formations and the major synclines and anticlines strike northeast, parallel to the boundary with the plutonic intrusive.

South of the eastern end of Alice Arm and south of the Illiance River, the Bowser Lake Group unconformably overlies the Hazelton Formation (Carter, 1972; Steininger, 1985). The Bowser Lake Group at Kitsault has a northwest strike and dips generally 45 to 60° northeast. About six kilometres south of the Kitsault town site, the sedimentary rocks of the Bowser Lake Group are intruded by the Lime Creek intrusive (Fig. 3). This intrusion

AGE M.A.	PERIOD	EPOCH	FORMATION OR ROCKTYPE	LITHOLOGY	REFERENCE		
1.1-1.6	Quaternary	Pleistocene and older	plateau basalt, basalt flows	noselite trachyte	2,6		
47 +1.2	Tertiary	Eocene	Coast Plutonic Complex	quartz diorite, granodiorite quartz monzonite	1,5,6		
36-53	Tertiary .	Eocene Paleocene	Kitsault intrusives	granite, porphyritic diorite, quartz diorite, quartz monzonite por- phyry, aplite/alaskite	2,3,5,6		
<u> </u>	Cretaceous	early	Bowser Lake	siltstone, greywacke, sandstone, conglomerate.	1.4.6		
	Insocia	late	Group	argillite, minor limestone, greenschists	. ,		
	Julassic .	middle	Hazelton	andesite, basalt, dacite tuffs and breccias, sandstones			
		lower	Group	conglomerates, regionally metamor- phosed to green- schist facies			

 Table 1

 Stratigraphy of the Alice Arm area

References: 1, Hanson (1935); 2, Drummond (1961); 3, Carter (1976); 4, Tipper and

Richards (1976); 5, Woodcock and Carter (1976); 6, Steininger (1985)

has a well-mineralized zone, which forms the Kitsault molybdenum deposit.

The western part of the working area is occupied by the Coast Plutonic Complex. The plutons, which are intrusive into the Hazelton and Bowser Lake Formations, consist mainly of quartz diorite and granodiorite. The eastern margin of the Coast Plutonic Complex cuts through the Alice Arm and Hastings Arm area from south-east to north-west. Most of the shorelines of Hastings Arm and the western half of Alice Arm's shores are composed of these igneous rocks (Fig. 3)



Three major lithological units are found in the Alice Arm - Hastings Arm area:

- 1) the Hazelton Formation
- 2) the Bowser Lake Group
- 3) the Coast Plutonic Complex

The Kitsault intrusives are found intruding the Bowser Lake Group and the Hazelton Formation. The intrusives are of the same magmatic origin as the Coast Plutonic Complex (Griffiths and Godwin, 1983). The immediate vicinity of the intrusions is usually metamorphically altered into biotite hornfels. The intrusions occur mostly in the form of small stocks up to 800 metres in diameter (Carter, 1979). In the proximity of the Kitsault intrusives, one commonly finds remnants of Pleistocene and Recent basalts. This indicates a regeneration of the fault and fracture system through which the rocks of the intrusive complexes rose to the surface (Steininger, 1985).

1.2.2 Geology of the Kitsault intrusives

The volcanic and sedimentary rocks of the Hazelton and Bowser Lake Groups host a large number of mineral deposits at the boundary with the Coast Pacific Complex. The mineralized zones of early to mid-Tertiary age occur as small intrusions in the Cretaceous and Jurassic rocks. Griffiths and Godwin (1983) suggested calc-alkaline material, spatially related to subducted lithosphere or pre-existing continental crust as the possible source for the porphyritic copper-molybdenum deposits. Veins occur peripheral to the porphyry intrusions, and they often show heavy Pb, Zn, Ag and Au mineralization. These are nonpluton-related volcanogenic mineralizations, where the metals are derived by hydrothermal solution from the host rock (Griffiths and Godwin 1983). The molybdenum deposits associated with the Kitsault Intrusives usually occur as small oval or elongated stocks of up to 800 metres in diameter (Carter, 1976). The prevalent host rock of these deposits is quartz monzonite porphyry (Table 1), often cut by dykes of alaskites hosting better grades of molybdenite (Woodcock and Carter, 1976).

1.2.3 Sediment supply

The main fresh water inflow for both inlets is at their heads, where the Kshwan River enters Hastings Arm and the Kitsault and Illiance Rivers flow into Alice Arm. Another important tributary is Hans Creek which enters Alice Arm almost at its mouth (Fig.1).

At Hastings Arm, only the north-western shoreline and the shores adjacent to Anyox (Fig. 3) are composed of the volcanic and sedimentary rocks of the Hazelton Group. However, most of the sediment load which is carried into Hastings Arm by the Kshwan River is composed of glacial flour from the Cambria Icefield. The icefield is believed to overlay mostly rocks of the Hazelton and Bowser Lake Groups (Carter, 1972; Tipper and Richards, 1976), and is the source for both the Kshwan and the Kitsault Rivers, with their headwaters lying some five kilometres apart. The two rivers are the main tributaries to Hastings Arm and Alice Arm, respectively. Therefore both inlet sediments should show a very similar chemical and mineralogical composition resembling the Hazelton and Bowser Lake Formations. The Illiance River is fed by a smaller icefield, located south of the Cambria Icefield, which overlies also mainly rocks of the Hazelton Formation. Hans Creek, which enters Alice Arm near the mouth, is also a glacially-fed stream originating from an icefield to the south of Alice Arm (Fig. 3). This icefield overlies rocks of the Bowser Lake Group and the Coast Plutonic Complex. The sediments originating from there should hence be distinctly different from the remaining sediments in Alice Arm.

1.3 MINING HISTORY OF THE ALICE ARM AREA

The first prospectors were drawn into the Alice Arm and Hastings Arm area at the beginning of this century, lured by reports of gold discoveries at the Premier field, at the head of Portland Canal. The first larger orebody found in this area was a pyrite and chalcopyrite deposit, located a few kilometres inland from Granby Bay, which the early propectors did not value. This deposit was therefore not developed until 1914, when the Granby Consolidated Mining, Smelting and Power Company started to mine these minerals and founded the Anyox Copper Mine which was to become the largest copper mine at this time in the British Empire (Hanson, 1928; Canadian Mining Journal, 1929;

Loudon, 1973). In the meantime, the prospectors explored Alice Arm where they found silver ore and staked a number of promising claims. Around 1910, some prospectors started exploring the valleys above the Kitsault River. Hanson (1922) described the finding of the first mineral claim to be staked on the upper waters of the Kitsault River as follows:

"A prospector named Gus Pearson dreamed a dream. In his dream he found a mineral vein on a steep wooded hillside. The place was marked by a great white boulder. He staked the claim and named it the Dolly Varden, and eventually it became a big mine."

Consequently, more prospectors moved into the Kitsault valley and staked a large number of claims such as the Second Thought, Lucky Strike and Tiger to name but a few (Fig. 4). From all the numerous claims, however, the Dolly Varden mine was the only operation to recover a considerable amount of ore. From 1919 until 1921, 36,609 tons of ore concentrate, which yielded 1,304,409 ounces of silver, were shipped from the mine (Hanson, 1921, 1935). The tailings were dumped into the Kitsault River which then carried it down into Alice Arm. The early prospecting also revealed two molybdenite deposits in the proximity of Alice Arm (Fig. 4). From 1916 onwards, the Molybdenum Mining and Reduction Company, Ltd. started to develop the Tidewater property on the north shore of Alice Arm (Fig. 3,4). However, the molybdenite content of about 0.2% proved to be too small at the time to make the operation profitable. Only little attention was paid to the Lime Creek deposit (which would later become the Kitsault Molybdenum Mine) until 1929, when an English manufacturer of special steel was the first to show interest in this property (Can. Mining Journ., 1929, p 1146). However, development did not materialize because, like the already existing mining operations, this development was caught in the Great Depression. Plummeting metal prices forced even Granby to close down its Anyox operation in 1936. The smaller mines in the Kitsault valley, namely the Dolly Varden, Toric and Esperanza, continued to produce small amounts of ore until 1959.

Except for Anyox at the southern end, there were no major mining operations located on the shores of Hastings Arm or in the Kshwan River valley because most of the shoreline



is made up of the granitic rocks of the Coast Plutonic Complex in which valuable mineral deposits are very sparse. The only mine to ever operate in the upper reaches of Hastings Arm was the Saddle property which produced some three tons of ore in 1929 (Hanson, 1935). This mineral deposit is situated in the remnant Hazelton outcrops at the north-west shore of Hastings Arm (Fig. 3, 4).

1.3.1 History of the Lime Creek Molybdenum Deposit

The molybdenite deposit at Lime Creek has been known at least since 1920, when it was called "Cariboo Molybdenum". In 1930 the property was optioned by Dalhousie Mining Company, who by that time had also aquired the Tidewater deposit on the north shore of Alice Arm (Annual Rep., Minister of Mines, B.C., 1930). It took, however, until the mid 1950's, when Kennco Exploration (Western) Ltd. finally started to work on this property to develop the mine substantially. They conducted preliminary examinations until 1960 and consequently formed the British Columbia Molybdenum Ltd. to start mining the deposit in 1967. The mine was active until April 1972, with a daily mill throughput of 6000 tons. During this operation, the mill tailings were simply discharged into Lime Creek (Fig. 1) which carried them into Alice Arm. Climax Molybdenum Corporation of B.C. Ltd. (later renamed AMAX/Canada) purchased the property in 1973. They then enlarged the mill to double the daily throughput and the tailings from this operation were transported by pipeline from the mill and discharged into the inlet at a depth of fifty metres below the water surface. The tailings outfall is in the upper part of the inlet close to Roundy Creek (Fig. 1). Mining commenced in April 1981, but in October, 1982 the mine was again shut down for economic reasons.

2. PHYSICAL OCEANOGRAPHY OF ALICE AND HASTINGS ARMS

Due to the scouring action of the Pleistocene glaciers the inlets on the British Columbia coast are, like most fjords, very deep compared to the coastal shelf areas. They are mostly deeper than 300 meters, but depths greater than 600 meters are also found. During summer, the waters in the inlets usually show a strong stratification due to the warming of the upper layers and a high freshwater discharge caused by the snow melt in the coastal mountains. In winter, on the other hand, there is almost no horizontal stratification because of the low surface temperatures and the small river runoff, and the water column often becomes completely mixed.

2.1 Temperature and Salinity Distribution

The distribution of temperature and salinity in the coastal inlets of British Columbia is heavily influenced by the freshwater discharge into these waterbodies. The mean annual discharge of freshwater into Alice Arm is estimated to be between 51 m³ sec⁻¹ (Littlepage, 1978) and 35 m³ sec⁻¹ (Krauel 1981). There are no data for Hastings Arm available; however, since the drainage area and the freshwater sources are very similar for both inlets, a mean discharge of the same magnitude can be expected.

There are two peaks observable in the annual cycle of freshwater discharge (Fig. 5). The first peak occurs during May and June and is due to the snow melt in the surrounding mountains whereas the second peak in October is generated by the high autumn precipitation. This runoff pattern was observed by Pickard (1961) for the majority of the British Columbia mainland inlets which he consequently called "stored runoff inlets".

In the summer months, the high runoff results in a marked horizontal stratification of temperature and salinity in both inlets (Fig. 6). Low runoff during the winter months (December through February) drastically changes the characteristics of the water column. At this time of the year, the salinity can be constant throughout the water column only a short distance from the head of the inlet and there is no marked thermocline (Fig. 6; Littlepage 1978; Krauel 1981). This indicates that the water column has the lowest



Figure 5 Monthly runoff for Alice Arm drainage area; typical "stored runoff" profile. After Pickard (1961); Littlepage (1978) and Krauel (1981).



Figure 6 T/S profiles in Alice Arm, typical for summer and winter; location approximately station AA-6 (Fig. 1)

16

stability during winter, which therefore is the most likely time when deep water renewal, and mixing of the whole water column may, occur. Krauel (1981) states that indeed at least partial renewal of the deep water occurs every winter in both Alice and Hastings Arms.

Dissolved oxygen levels in Alice Arm are high throughout the water column. Most of the values are between 60 and 70% saturation and they have not been observed to decrease below 50% saturation (IOUBC 1951,1966; Littlepage 1978; Krauel 1981). In the deep waters of Observatory Inlet and Hastings Arm, the dissolved oxygen values are slightly lower, but anoxic conditions have never been observed. The amount of oxygen dissolved in the bottom waters of these inlets is another indication that deep water renewal occurs almost every year.

2.2 Currents

Direct current observations have been made only in Alice Arm; however, since the water bodies of both Alice and Hastings Arms show generally the same physical characteristics, the general circulation pattern in the two inlets is probably very similar. The main differences of the two inlets are their geographical orientation and a greater sill depth in Hastings Arm as noted in section 1.2.. Hastings Arm is the northward terminus of the Portland - Observatory Inlet system which stretches from the coast with no major bend for some 120 kilometers. Therefore, winds can be funneled along these valleys and finally reach Hastings Arm without any obstruction. Alice Arm, on the other hand, branches off from this inlet system almost in a right angle and is therefore much more sheltered from any such winds. Hence, wind-driven currents could be significantly different in Hastings Arm and Alice Arm. Krauel (1981) reported that for the only time of concurrent wind and current observation from April 15 to September 20, 1977 no wind-induced currents could be detected in Alice Arm. Any possible wind-driven currents had been obscured by the semi-diurnal tidal variations in the observed currents.

Removal of the tidally-induced water movements produces a residual net flow which

almost resembles the ideal estuarine circulation. The uppermost layer of water shows a net down-inlet movement of > $1.8x10^{-3}$ m sec⁻¹ and the water at mid-depth is slowly flowing up the inlet. The deep water in Alice Arm appears to have very little movement. Net movements with a mean speed of 0.015 m sec⁻¹ have been observed to be down-inlet in the summer and up-inlet in the winter (Littlepage 1978; Krauel 1981).

2.3 Internal Waves

Internal waves seem to be a common characteristic of Alice Arm (Krauel, 1981; Keeley, 1984). Krauel (1981) points out that the breaking of internal waves considerably increases the level of turbulence and hence causes locally intense vertical mixing. The turbulence in the water body can significantly influence the sedimentation by keeping small particles suspended long enough to enable them to be transported out of the inlet. Turbulence was found to be most intense in the head of Alice Arm and induces vertical mixing over the entire fjord. Keeley (1984) could show that during the times when turbulence occurs, bottom currents tend to be exceptionally strong, especially in areas of uniformly-sloping bottom.

2.4 Recent Sedimentation

Most of the natural sediment deposited in Alice Arm enters the inlet at the head through the two major tributaries, the Kitsault and Illiance rivers. Fig. 7 shows the general distribution of sediment texture in the inlet. This distribution pattern clearly reflects a natural sorting mechanism. The coarser particles are deposited near the river mouths, whereas the sediments in the deep trough are mainly made up of fine silt- and clay-sized particles. The tailings from the AMAX mining operation were injected at a water depth of approximately 50 meters and were designed to enter the inlet as a slurry with a density of 1275 kgm^{-3} . These conditions were chosen to ensure that the tailings would flow down the steep slope as a density current and settle in the deepest part of the inlet or at least below 100 meters depth (Burling *et al.* 1981). However, this simple concept is complicated by various processes such as ambient currents, upwelling, vertical turbulent diffusion, differential settling from the tailings slurry, resuspension and entrained air. Particles smaller than 8 μ m which make up some 3% of the tailings material, are especially affected by any of these processes.

Transmissometer measurements made during the initial production period of the mine revealed the existence of a plume of suspended tailings material at mid-depth which could be detected for a maximum of about 7 kilometers down-inlet from the outfall (Goyette and Hinder 1982; Harding 1983). This plume can only be explained by rapid differential settling of the material in the slurry. The remaining plume becomes less dense and hence stops sinking. This effect can be intensified by very dense deep water or, more likely, by local turbulence.

Resuspension is likely to occur in two ways. The first possibility is remobilization of particles due to turbidity currents and slumping, which are observed to happen at an increased rate during times of tailings deposition, as for example in Rupert Inlet (Hay *et al.* 1982). Secondly, bottom currents which can reach speeds up to 0.4 m sec⁻¹, especially during times of deep water renewal, might resuspend the deposited tailings material. The water renewal processes, as well as turbidity currents, can cause local upwelling of deep



Figure 7 Generalized grainsize distribution of Alice Arm sediments (from Littlepage, 1978)

water containing suspended sediment and tailings which then will tend to be kept in suspension by the turbulence due to the breaking of internal waves. In his investigations of the water column, Stukas (1983) found suspended particles in water layers well above 100 meters depth close to the mouth of the inlet. Due to its heavy metal content the suspension was linked to the mine tailings and this indicated that small amounts of tailings material was being transported past the sill.

2.5 Previous Work on Alice Arm and Hastings Arm Sediments

Dobrocky Seatech Ltd., as a contractor for AMAX/Canada, the Environmental Protection Service and Fisheries and Oceans/IOS, conducted a series of studies prior to the reopening of the mine to gain some knowledge of the existing conditions in the area. The data were to be used as background information for determining the impact of tailings disposal on the local environment. In his report to the Climax Molybdenum Corporation of B.C., Ltd, Littlepage (1978) summarised the surveys carried out by Dobrocky Seatech Ltd. from 1974 - 1977. With information on the metal content of subtidal and intertidal sediments, Littlepage could trace the tailings from the B.C. Molybdenum operation 15 and 8 km, respectively, down the inlet. He found that enhanced values of zinc, molybdenum and lead indicated contamination with material from the Lime Creek deposit, whereas higher than background values for copper, zinc and mercury near the mouth of Hastings Arm pointed to effluents from the Anyox mining and smelting operation as a source of contamination. Cadmium levels appeared to be slightly enhanced in both areas of Alice and Hastings Arm influenced by the mining activities. In addition, Goyette and Christie (1982 a,b) reported high lead, silver and iron levels for the B.C. molybdenum tailings and stated that lead and iron are also above background in the Anyox slag deposits.

Macdonald et al. (1984 and pers. comm.) measured the sedimentation rate in Alice Arm using sediment traps. In areas with little or no influence of the tailings they found the sedimentation rate to be about 0.5 to 1cm/year which corresponds to circa 0.5 gr cm² a^{-1} .

3. MINERALOGY

3.1 INTRODUCTION

In areas with high terrigenous input, the mineralogical composition of coastal sediments will closely resemble the mineralogical composition of the source rocks in the drainage area. In Alice Arm, the main input of material is at the head of the inlet through the Kitsault and the Illiance rivers. Both rivers cut through rocks of the Hazelton and Bowser Groups which consist of Mesozoic volcanic and sedimentary rocks (Hansen,1935). The molybdenum deposits in the Alice Arm area, however, occur in intrusions composed of quartz monzonite, granodiorite and quartz diorite with veins of alaskite. Thus, any major input of mine tailings into the inlet should result in a distinct change in the mineralogical composition of the sediments.

Therefore three cores from Alice Arm, representing pure tailings (AA-4), contaminated sediment overlain with pure tailings (AA-5) and a core with different degrees of contamination (AA-8), were compared to one core from the head of Hastings Arm (HA-5) which consists mainly of material from the Hazelton and Bowser Groups transported into the inlet by the Kshwan river and its tributaries.

Unoriented pressed powders, oriented mounts for clay-mineral determination and, where applicable, the heavy mineral fraction of the samples have been subjected to Xray diffraction analysis. Details of the sample preparation and the instrumental conditions are described in Appendix I and II.

3.2 MINERAL IDENTIFICATION

3.2.1 QUARTZ

Quartz is present in all samples and could readily be identified by the intense reflections at 3.34Å (101) and 4.26Å. In unoriented powder mounts the less intense quartz reflections at 2.46Å (110), 2.28Å (102), 2.24Å (111), 2.128Å (200), 1.980Å (201), 1.817Å (112) and 1.672Å (202) could also be identified.

3.2.2 FELDSPAR

Some peaks can be unequivocally identified as feldspar peaks. However, identification of the different minerals of the feldspar group in the untreated sample is not always possible.

3.2.2.1 Plagioclase

The main indicator for feldspars is the complex peak at 3.18Å. This peak is solely due to different plagioclase minerals and represents their 002, 004, 040, 220 and 202 reflections. However, the exact peak position varies with composition and structural state of the plagioclase. Hence, these reflections will not simply reinforce each other (i.e. increase the peak height) but rather result in a broadening of the 3.18Å peak. This can be observed by slowly scaning over this peak ($0.06^{\circ} 2\Theta/min$) and thereby resolving it to some extent (Fig. 8). The peak at 4.04Å represents the 201 reflection of plagioclase and since it is hardly affected by the variations in the composition of the plagioclase series, it has been used to estimate the abundance of plagioclase in the samples. The spacings of the 131 and 131 reflections can be used to determine the composition of the plagioclase (Peterson and Goldberg, 1962), assuming similar thermal history for the different feldspars. Unfortunately, the 2.82Å (200) halite reflection masked the 131 (2.84Å) peak of the oligoclase-albite group in regular scans. In samples with high plagioclase content these two peaks could be resolved with a slow scan from 27° - 33° 2 Θ . The 1 $\overline{31}$ (2.99Å) and 131 (2.84Å) reflections yielded a $\Delta 2\Theta$ of about 1.5° which indicates a composition in the albite-oligoclase range,



Figure 8 Slow speed high resolution XRD-scan for 3.18Å plagioclase peak of natural sediment from station HA-2.

with possibly some and sine (Peterson and Goldberg, 1962). The peaks at 6.38Å (020), 3.76Å (111) and 3.66Å (131) can also be attributed to albite-oligoclase and support this identification.

3.2.2.2 K-Feldspar

The peak at 3.24Å suggests the presence of K-feldspar with a composition close to orthoclase (Or100). However, the characteristic 201 reflection at 4.22Å is completely masked by the 100 quartz peak at 4.26Å. Therefore the presence of anorthoclase in most samples can be neither confirmed nor excluded. Only a few samples actually show evidence for the presence of anorthoclase, with a small peak at 4.11Å (201). The orthoclase reflections at 3.77Å (130) and 4.47Å (112) are also present in a large number of samples and it can therefore be concluded that the 3.24Å peak is mainly due to orthoclase.

3.2.3 CLAY MINERALS

Certain peaks in pressed powder samples can be readily attributed to clay minerals by XRD methods. In order to identify the presence of chlorite, mica, kaolinite and montmorillonite, however, oriented samples were prepared and treated according to the methods of Carroll (1970, details see Appendix II). The glycol solvation did not result in any change in the peak pattern and it therefore can be concluded that no montmorillonite or mixed layer minerals with montmorillonite are present.

3.2.3.1 Chlorite

The basal reflections of chlorite at 14.2Å (001), 7.05Å (002) and 4.73Å (003) were found in most samples. With heating the oriented samples to $550^{\circ}C$, most of the 7Å peak disappeared and could therefore be attributed to kaolinite.

3.2.3.2 Mica

The 10Å (002) peak is characteristic of the mica group, while the 3.3Å (006) peak, which normally has a similar intensity, is completely masked by the 101 (3.34Å) quartz reflection. Other mica peaks are detectable at 4.99Å (004) and 2.56Å (20 $\overline{2}$). None of the mica peaks is affected by glycolation or by heating.

One can further subdivide the mica group by separating minerals with high specific gravity using heavy liquids. Biotite is the only mineral with a specific gravity (D=2.7-3.3) significantly higher than that of the heavy liquid (bromoform D=2.93) used for the separation. For this reason all mica peaks in the heavy mineral fraction are thought to represent only biotite.

3.2.3.3 Kaolinite

The typical kaolinite reflections at 7.1Å (001), 4.46Å (020) and 3.56Å (002) could be found in all untreated samples. These peaks were unaffected by glycolation but dissappeared upon heating the sample to 550° C for one hour.

3.2.4 HALITE

The two most intense halite reflections at 2.82Å (200) and 1.99Å (220) were easily recognized in every sample. Since there are no major interferences with other mineral peaks, halite from the enclosed pore waters, can be conveniently used as an internal, angular standard.

3.2.5 BARITE

Barite could be recognized by its strongest reflections at 3.44Å (210) and 3.1Å (211). Usually it was only detectable in the heavy mineral fraction of the samples.

3.2.6 HORNBLENDE

The 8.40Å (110) peak was used to identify hornblende in the unoriented powder mounts.

3.2.7 SPHALERITE

In the heavy mineral fraction sphalerite was recognized by the 3.12Å (111) and the 1.91Å (200) reflections.

3.2.8 PYRITE

Only the two most intense reflections (200) and (311) corresponding to d-spacings of 2.7Å and 1.63Å, respectively, could be observed in the heavy mineral fraction.

3.2.9 MOLYBDENITE

Molybdenite could be identified visually in the tailings using a binocular microscope. It was found to be mostly closely associated with quartz, occurring at the edges of and within the quartz graines and more rarely as free graines. Probably because of the common intergrowth of these two minerals molybdenite could not be observed in the heavy mineral fraction.

3.3 Mineralogical Composition of Natural and Contaminated Sediments

The natural and the contaminated sediments in the Alice Arm area are not so much composed of different minerals but rather the abundance of the main mineralogical constituents varies significantly. The most obvious changes are visible in the content of different feldspars. However, since the most intense feldspar peaks do not represent a single feldspar but rather reflect a suite of feldspars with different compositions (Peterson and Goldberg,1962), quantitative analysis of the different minerals was not attempted. Also, the amount of feldspar present at a certain depth can vary significantly, as we can not as-
sume total homogeneity of the source rock, and therefore the comparison of exact amounts of a single feldspar would be meaningless. On the other hand, comparing the peak heights of the most intense plagioclase (3.18Å) and orthoclase (3.24Å) reflections appears to be a direct indicator of the degree of contamination of natural sediments with mine tailings.

The drainage area for both inlets consists mainly of argillites, sandstones, greywackes, quartzites and volcanic rocks (Chapt. 1). Their mineralogical composition of quartz, chlorite, mica and albitic plagioclase (Hanson, 1921,1935; Woodcock and Carter, 1976) is clearly reflected in the sediments of Hastingns Arm. Hence the dominant minerals in the sediments of Hastings Arm are quartz, feldspar, kaolinite, mica and chlorite. The feldspars present consist almost entirely of plagioclase. The spacing of the 131 and 131 peaks indicates that this plagioclase is oligoclase to albite in composition (Peterson and Goldberg, 1962). The peak height ratio of the 3.24Å orthoclase to 3.19Å plagioclase reflections is approximately 0.3 (Table 2). All kaolinite present in the samples can be regarded as being a weathering product of feldspars, as kaolinite is not a major constituent of the sedimentary rocks in the drainage area of the rivers delivering sediments into the head of Hastings Arm (Hanson, 1921,1935; Woodcock and Carter, 1976). The mineralogical composition of core HA-5 is fairly uniform (Table 2) and we can therefore conclude that there have been no major changes either in the river system or in the lithology of the drainage area during the period of deposition of these sediments.

Three cores in Alice Arm have been chosen for detailed mineralogical studies. Core AA-4 consists entirely of modern tailings and can therefore provide information about the make-up of the tailings dumped into the inlet during the most recent mining operation at the Kitsault Molybdenum mine. At station AA-5 the sediment consists of 15cm of modern tailings which overlay what appeared on visual examination during sampling to be natural sediments. Thus, this core could possibly provide clues about the differences in the mineralogy of the tailings and the natural deposits in Alice Arm. AA-8 was chosen as it is far away from the tailings outfall and could hence reveal the impact of finely dispersed tailings on the natural sedimentation. The mineralogical composition of the natural sediments in Alice Arm is generally very similar to the Hastings Arm deposits. The data of the milled overburden fits closely the described mineralogy of the mineralized zones in the Kitsault mine which are reported to consist mainly of quartz monzonite porphyry, quartzdiorite and alaskite (Drummond, 1961; Woodcock and Carter, 1976). All these rocks are composed of quartz and K-feldspar, where the K-feldspar is often found to have replaced plagioclase and mafic minerals. Minor constituents are plagioclase, biotite and sometimes hornblende. The comparison shows that the mineralogy of the mineralized zone is almost perfectly reflected in the mine tailings. At first glance the most striking difference between the pure tailings and all other samples is the presence of K-feldspar and the relative lack of chlorite and kaolinite. The only clay peak visible in scans of unoriented powder mounts from tailings material is the 10Å (002) mica reflection. Most of the remaining peaks are due to quartz and the different feldspar minerals. The main feldspar in these samples is orthoclase and only small amounts of plagioclase are present. Peak height ratios of the $\frac{3.24 \text{Å orthoclase}}{3.18 \text{Å plagioclase}}$ reflection are on the order of 1.6-4.5 compared to an average of 0.32 ± 0.05 in the Hastings Arm sediments (Table 2). The uppermost 15cm of sediment at station AA-5 yield as expected the same diffraction patterns as found for the pure tailings at AA-4. The sediments below 15 cm depth, which seemed to be natural sediments on visual examination, appear in the XRD-scan to be a mixture of tailings material and natural sediment (Fig.9). This is again best expressed in the peakheight ratios of K-feldspar (3.24Å) to plagioclase (3.18Å). The ratio indeed does drop significantly from > 4.0 in the overlaying tailings to values between 0.7 and 1.1 (Table 2) but are still twice as high as would be expected for natural sediments. At station AA-8, where visual examination would suggest an almost uniform sediment, the peak-height ratios of the two major feldspar peaks indicate again contaminated sediment in the top 20cm (Fig. 9). The ratios in this horizon are between 1.0 and 2.2 (Table 2). Below 20 cm the peak height ratios of the two major feldspar peaks dropped to 0.3-0.6. This compares very well with the ratios observed at station HA-5 (Table 2) and we therefore can assume that this part of the sediment column was deposited under close to natural conditions. At

the 50-55 cm depth interval the mineral composition again changes and the value of the peak-height ratio of the two most intense feldspar reflections is 1.0, but drops again to background values below 55 cm (Table 2).

<u>Denth</u>	HA-5	A A - A	A A . 5	A A _ 8
[cm]	IIA-5	2122-4	AA-0	
0-5	0.40	3.27	> 4.0	2.18
5-10	0.39	2.31	> 4.0	1.33
10-15	0.22	3.20	> 4.0	1.70
15-20	0.29	2.92	0.74	1.00
20-25	0.26	3.00	0.77	0.29
25-30	0.31	4.50	1.07	0.29
30-35	0.33	1.45	1.11	0.34
35-40	0.34	1.94	0.70	0.35
40-45	0.32	1.63		0.35
45-50	0.29	2.00		0.67
50-55	0.31	2.00		1.00
55-60	0.33	2.31		0.22
60-65				0.17

Table 2

 $\frac{3.24A(K-feldspar)}{2}$ peak-height ratios from Hasting and Alice Arm sediments

In a heavy mineral separation using bromoform (D=2.93) as a separating liquid, the pure tailings yield up to five weight percent heavy minerals. The same technique used with sediments from station HA-5 did not produce enough material for a heavy mineral XRD analysis. In the heavy mineral fraction of the mine tailings, biotite, sphalerite, and pyrite could be identified. Most of the mica peak in the unoriented powder mounts can be attributed to biotite because in the light mineral fraction (D<2.93) there was only a faint 10Å peak. The heavy mineral fraction recovered from the severely contaminated sediments at station AA-5 and AA-8 can serve as another indicator of tailings. The heavy minerals could be identified as being the same as in the pure tailings. Since contamination of the old sediment down to a depth of 40+cm (AA-5) by the incoming tailings plume seems very unlikely, the contamination of these sediments with mine waste can be attributed to the B.C. Moly operation (1967–1972). At that time the tailings material was simply discharged into Lime Creek which consequently transported it into the inlet. At station AA-8, heavy mineral separation gives the same results as found in core AA-4 below 15cm.



Figure 9 XRD-scan from contaminated sediments at station AA-5 and station AA-8. Both scans are virtually identical. Note the broad 3.18Å peak vs. the much sharper 3.24Å K-feldspar peak

Between 20 and 50 cm, however, no heavy minerals were separable. Below 50 cm, a larger amount of heavy minerals consisting of biotite, hornblende, barite, pyrite and some sphalerite was obtained. This sudden change in the mineralogy indicates either a major, sudden change in the natural conditions of the drainage area (i.e. change of the river path, different lithology being eroded) or human input. Due to the geological setting of the glaciated areas of the drainage basin and the relative short time span covered by a core of this rapidly accumulating sediment, the first possibility can almost definitely be ruled out. Thus, recalling the extensive mining history in the Alice Arm area, human activity seems to be the most likely reason to account for this contamination.

The best indicator for the origin of this deeper contaminating material is probably barite which was not observed in any of the samples discussed so far. Unusally high barite concentrations were found only at depths > 50 cm, and this depth increases as one approaches the head of the inlet. In samples from other cores which penetrated into this contaminated depth horizon, the barite content was up to 9 percent (calculated from the chemical composition; see Chapter 5). The only mining operation which could yield such high concentrations of barite is the Dolly Varden silver mine. Hanson (1922) described these deposits as being highly siliceous veins with an average of 70% or more quartz with calcite and barite as important gangue minerals. In some places barite is the most common mineral, whereas calcite is always dissipated throughout the vein. Calcite could not be detected with certainty because the main calcite peak at 3.03Å is masked by the $1\overline{3}1$ orthoclase reflection. The burial depth of \geq 50cm at which this contamination occures also points to the Dolly Varden mining venture as the source. R.W. Macdonald (1984, pers. comm.) reports a sedimentation rate of 0.5-1cm a^{-1} . Hence, a deposit of 50 cm sediment since the mine ceased production about sixty years ago is well within the range of the reported sedimentation rates.

In cores with sufficient penetration, natural sediment occurs below the barite containing horizon (Append. III; AA-7). The natural sediment is indicated by a peak-height ratio of the two most intense feldspar reflections of about 0.3.

4. GEOCHEMISTRY OF THE MAJOR ELEMENTS

4.1 INTRODUCTION

The distribution of the major elements in nearshore sediments which have a high detrital input, such as is characteristic of most inlets on the British Columbia coast, is governed almost exclusively by the chemical composition of the source material. Biogenous and authigenic components are usually diluted by the large terrigenous load to such an extent that they become almost insignificant. As Calvert (1976) points out, most of the major elements in this kind of sedimentary environment are fixed in the lattices of detrital minerals and therefore the relative abundances of the major minerals determines the chemical composition of the sediment. The observed changes in the mineralogical composition of the sediments in Alice and Hastings Arms should therefore be well expressed by simultaneous variations in the concentrations of the major elements. However, changes in the abundance of a single element do not allow conclusive interpretation of such variations; the varying amounts of certain elements may simply reflect the inhomogeneity of the source material. Under these circumstances, interelement ratios are more useful in illustrating relations of various elements as well as mineralogical changes within the sediment column.

The elements discussed in this chapter, with the exception of carbon were all analyzed by X-ray fluorescence spectrometry, as described in Appendix II. Elemental values listed here are all corrected for the dilution or enhancement effects of sea salt. All concentration data are tabulated in Appendix III.

4.2 DISTRIBUTION OF THE ELEMENTS

In the discussion below and in the later chapter on pore water chemistry, station HA-2 is used as the compositional endmember representing natural sediments. In the mineralogy chapter station HA-5 was chosen, because of its proximity to the head of the inlet and consequent major sediment source. Time constraints and sediment texture were the reasons that this station or a nearby location were not used for pore water collection. The major element distributions in Alice Arm sediments are discussed here within the context provided by the detailed description of the mineralogy presented previously.

4.2.1 Silicon and aluminium

Silicon and aluminium are the two most abundant elements in the sediments analyzed for this study. Quartz is the largest single mineral phase and accounts for a significant amount of the silicon present. Most aluminium is accounted for by the clay minerals, feldspars and other less abundant alumino-silicates.

These minerals also host the remaining silicon. In Hastings Arm the variations of silicon, which makes up 26 to 28 percent of the sediments, are generally about $\pm 1\%$ or less as is shown in Fig. 10. Aluminium exhibits the same small variability (Fig. 11), as can be seen in the Si/Al ratio data for HA-2, listed in Table 3. There are only very small changes observable throughout the core which indicates a source of almost uniform composition which did not change during the accumulation of the sediment. The Si/Al ratio for the sediments from all six stations examined in Hastings Arm varies between 3.2 and 3.6 which is close to the value (3.4) reported by Füchtbauer and Müller (1977) for average shales.

The pure tailings of core AA-4 (location see Fig. 1) have on average a 2% higher Si concentration than the natural sediment in Hastings Arm. In addition, the aluminium content of the tailings is considerably lower than in the uncontaminated Hastings Arm sediments (7.1 vs. 7.7%) resulting in a considerably higher Si/Al ratio (Table 3). This indicates that, compared to natural sediments, the tailings contain less aluminosilicates and more quartz. The higher quartz content of the molybdenum ore, reported by various







Figure 11 Vertical distribution of Al in Hastings and Alice Arm sediments. Note the different scales for each profile.

depth HA-2 AA-1 AA-2 AA-3 AA-4 AA-5 AA-8 AA-9 depth AA-6 AA-7 [cm][cm] * ¥ * 8 3.74 4.22 4.34 3.95 3.51 0-2.5 3.49 0-1 - -- -- -- -3.54 3.58 3.98 4.42 4.25 6.58 4.16 3.92 1-2 4.25 3.60 2.5-5 3.86 2-3 4.32 3.62 5-7.5 - -- -. . - -- -- -- -7.5-10 3.62 3.67 3.85 4.51 4.19 6.77 3.91 4.18 3-4 4.27 4.14 3.77 4-5 5.21 3.98 10-12.5 - -- -. . - -- -• • - -6.34 3.87 4.10 5-6 5.59 12.5-15 3.59 3.48 3.92 4.33 4.18 3.72 3.87 15-17.5 - -- -- -- -- -- -- -6-7 4.96 3.54 7-8 3.38 3.90 3.44 3.57 3.97 4.86 4.09 17.5-20 3.56 3.85 4.43 3.60 8-9 4.99 20-22.5 - -- -- -5.12 - -- -- -. . 3.97 3.37 3.58 3.94 9-10 5.07 22.5-25 3.50 3.50 4.01 4.523.90 3.58 10-12 4.85 4.40 25-27.5 • • - -- -- -- -- -- -3.63 12-14 4.55 27.5-30 3.51 3.43 3.98 4.04 4.34 3.523.90 3.90 30-32.5 - -- -- -- -- -3.62 - -14-16 4.59 5.50 32.5-35 3.77 4.14 3.68 3.58 3.89 16-18 4.60 4.56 3.513.18 3.59 18-20 4.77 35-37.5 - -4.14 - -- -- -- -- -3.42 37.5-40 3.54 3.51 3.99 4.12 3.64 **3.9**0 20-22 4.58 4.59 3.70 22-24 4.35 4.68 40-42.5 - -- -- -- -4.08 3.61 4.00 24-26 4.16 4.22 42.5-45 3.51 3.42 3.72 26-28 3.89 3.76 45-47.5 - -- -- -- -3.70 **28-3**0 3.39 3.91 4.01 3.90 47.5-50 3.55 4.10 3.78 30-32 50-52.5 4.44 3.49 - -- -- -4.26 3.74 32-34 4.21 3.36 52.5-55 3.58 3.31 55-57.5 3.68 34-36 4.25 3.87 - -- -4.07 3.68 36-38 4.48 4.27 57.5-60 3.48 3.70 60-62.5 38-40 4.47 4.15 62.5-65 3.64 40-42 4.42 3.93

 Table 3

 Si/Al ratios of Hastings and Alice Arm sediments

* in these columns the first three depth intervals are: 0-3, 3-6, 6-10 cm

-- is placed, where the depth interval spans over 5 cm,

except for the first three samples in the columns denoted with *

these columns continue in Appendix III

workers (Drummond, 1961; Woodcock and Carter, 1976; Steininger, 1985) is consistent with these findings (Chap. 3.3).

From Table 3 it can be seen that the heavily contaminated sediment (core AA-8, top 20 cm) is clearly distinguished from the underlying, sparsely-contaminated sediment by the Si/Al ratio which ranges from 4.3 to 3.9 in the upper zone and averages 3.6 in the underlying material; the latter is closely similar to the ratio in the natural sediments in

Hastings Arm whereas the values in the top 20 cm are similar to those in pure tailings (Fig. 10).

In contrast, the tailings from the Dolly Varden silver mine, which could be distinguished by their mineralogy deeper than 50 cm (Chap. 3), do not have distinctive Si/Al ratios but can be chemically distinguished on a plot of Si versus Al (Fig. 12), where both the old Dolly Varden and the modern Kitsault tailings occupy areas on the graph quite distinct from the uncontaminated sediment. The Dolly Varden tailings have low Si and Al values and plot along a mixing line with the uncontaminated sediment; the low Si and Al contents signify the dilution of the natural sediment by some non-silicate phases unique to the Dolly Varden tailings. In contrast, the Kitsault tailings plot along a mixing line which links sparsely contaminated sediment with the quartz rich end-member.

For comparison Si versus Al is plotted in Fig. 13 for the cores HA-2 (natural sediment), AA-4 (pure tailings), and AA-8 (contaminated sediment). As can be seen, the fields occupied by pure tailings (core AA-4) overlap with the field of the heavily contaminated sediment (AA-8). The field with the less contaminated sediment from station AA-8 plots close to the natural sediments of core HA-2; however, these two fields do not overlap. Since the chemical data show that we are really dealing only with a minor contamination in this core section, it is more likely that there are some minor compositional differences between the natural sediment in Hastings and Alice Arm. For reasons explained above, the Dolly Varden tailings plot separate from all other fields.

At the head of Alice Arm (Station AA-1), the tailings cannot be readily identified. Any contamination is overshadowed by the large sediment input from the Kitsault and Illiance rivers. In addition, seasonal changes in the river flow cause particles of different sizes to be variably deposited near the river mouths. Since the proportion of clay minerals increases with decreasing grain size, textural variations have a significant influence on the Si/Al ratios. In coarser grained sediments the quartz content is increased compared to the content of clay minerals and other alumino-silicates, and thus the Si/Al ratio is higher



Figure 12 Si versus Al for core AA-8. The lines do not represent regression lines but are mixing lines which join the natural sediment compositional field with end-members representing the two types of tailings. The symbols are explained in Fig. 13.



Figure 13 Si versus Al for cores HA-2, AA-5 and AA-8.

than in finer grained sediments. The variations seen in AA-1 reflect textural control rather than incorporation of tailings.

At stations AA-2 and AA-3 (Table 3), tailings are present throughout the depth of the cores and were visibly distinguishable in the top few cm in core AA-3. From the Si/Al ratios, it can be inferred that there is significant contamination of the sediment with guartz-rich modern tailings at stations AA-6 and AA-7 down to a depth of 50 cm and 54 cm, respectively (Table 3, Appendix III). Core AA-9, near the mouth of Alice Arm, is markedly different from the neighbouring core AA-8. The Si/Al ratios are on the average 4.0 and show no variation with depth. This would suggest that the entire sediment column at station AA-9 is contaminated with modern tailings which is very unlikely. As can be seen in Fig. 7, the sediment in this area is slightly coarser-grained, and therefore contains more quartz, than the natural sediment in the other cores. The sediment is probably influenced by local input from Hans Creek, which originates at an icefield south of the inlet. The Hans Creek watershed is underlain mainly by granitic rocks (Fig. 3) which, according to Krauskopf (1979) have an average Si/Al ratio of 4.18. This is similar to the values measured in core AA-9; it is possible that the input of granitic detritus is responsible for both the enhanced Si/Al ratio and the sudden change in the grain size in the sediments of this area, as described by Littlepage (1978; Fig. 7). Hence, any tailings material transported into these reaches of the ford is overwhelmed by the sediment deposited here by Hans Creek.

4.2.2 Titanium

Titanium occurs generally as its polymorphic oxides

anatase, rutile and brookite, and as ilmenite, but may also be a minor constituent in a number of aluminosilicates, sometimes substituting for Al in clay minerals (Deer et al. 1966; Calvert and Price, 1970). In Hastings Arm, the Ti values differ little from a value of 0.41% and the Ti/Al ratios are relatively constant (0.052 ± 0.002 ; Fig. 14).

The amount of titanium in the pure tailings is considerably lower than in natural sediments. In core AA-4 and the top 15 cm of AA-5, the average Ti content is 0.35%,



Figure 14 Vertical distribution of Ti in Hastings and Alice Arm sediments. Note the different scales for each profile on the abscissae.

and can be as low as 0.23%, compared with 0.42% in the Hastings Arm sediments. The upper 20 cm in core AA-8 contains about 0.4% Ti which corresponds well to the values found in the deeper parts of station AA-5. Although these values seem to be close to those observed in Hastings Arm, some dilution is implied if we compare the values of these contaminated sediments with the Ti content of natural sediments in Alice Arm and the sparsely contaminated layer below 20 cm in core AA-8. Here the average Ti content is 0.46% and is considered to represent the background value for Alice Arm. The tailings from the Dolly Varden mining operation, found in the deepest parts of cores AA-6, AA-7 and AA-8, do not affect the titanium content of the sediment.

In Fig. 15 Ti is plotted versus Al for the three different sediment types, natural sediments and sediments contaminated to different degrees with two types of mine tailings. The pure tailings and the sparsely contaminated sediment of core AA-8 plot in two distinctly separated areas, representing their different compositions. The values of the heavily contaminated sediment fall along a mixing line between these two fields, partially overlapping with the field of the pure tailings. As noted above, the Ti contents of the natural sediments in Hastings and Alice Arms differ significantly. Therefore, the field of the natural sediments from station HA-2 overlaps to some extent with the heavily contaminated sediment portion of core AA-8, but is still easily distinguishable from the pure tailings. Due to its lower Al content, the sediment contaminated with the Dolly Varden tailings occupies an area distinct from all the other sediment types.

At the other stations Ti behaves similarly. In core AA-1 the Ti values exhibit some variability, though no major dilution is indicated, whereas at the remaining stations Ti is lower where contamination with modern tailings occurs. The amount of Ti in core AA-9 is on average 0.41% and shows no significant variations with depth.



Figure 15 Ti versus Al for cores HA-2, AA-5 and AA-8

4.2.3 Potassium and sodium

Potassium and sodium are associated with feldspars and potassium is also found in various clay minerals. Throughout the main basin of Hastings Arm the Na and K contents of the sediments average 1.6 and 2.3%, respectively. Concentrations differ substantially from these average values only at station HA-6 and in Granby Bay, near the old mining and smelting operation at Anyox as shown in Fig. 16. This will be discussed in more detail in Chap 6.

Potassium and sodium do not exhibit the same degree of invariability in the tailings in Alice Arm, as is found in Hasting Arm sediments (Fig. 16). In pure tailings the average K content is about 4.4%, twice the amount found in Hastings Arm, whereas there is at least one third less Na in pure tailings than in Hasting Arm sediments. This can be readily explained by the differences in the mineralogical composition of the two types of sediment (Chap. 3.3). The additional K in the tailings is due to K-feldspar which replaces plagioclase in the ore. In a plot of Na versus K (Fig. 17), the pure tailings and the heavily contaminated sediment are therefore well separated from the other sediment types encountered in the two inlets. The sediments contaminated only to a small degree with the modern Mo-tailings (AA-8), or with Dolly Varden tailings, found at station AA-8 below 45 cm and at AA-7 between 70 and 100 cm, have roughly similar K and Na contents and therefore plot closely together. In core HA-2, however, although the same K values are found, the Na content of the sediment is significantly higher, as is evident in the distance between the two fields occupied by the sparsely contaminated and Dolly Varden facies and the distant natural sediments of core HA-2.

4.2.4 Calcium

Calcium occurs in plagioclase feldspar, clay minerals, and as $CaCO_3$ of mostly biogenic origin. Subtracting the calcium tied up in carbonate from the total Ca yields on average 1.3% Ca which must be incorporated in the terrigenous fraction in the Hastings Arm sediments. No significant spatial or vertical variation of carbonate-free Ca was observed in the entire inlet, including core HA-6 (Chap. 6). In Fig. 18 the vertical distribution of



Figure 16 Vertical distribution of Na and K in Hastings and Alice Arm sediments. Note the different scales for each profile!

46





total and carbonate-free Ca of core HA-2 is presented along with the Ca distribution of core AA-8, which represents all three sediment types found in Alice Arm.

Calcium appears in the tailings in nearly the same amount as in the Hastings Arm sediments. However, almost all the Ca is present as carbonate, which is disseminated throughout the ore as a trace constituent (Steininger, 1985), and some may also be due to lime added during the milling and flotation process (Burling et al., 1981). After subtracting the Ca derived from the carbonate, only traces remain which can be attributed to other minerals, such as feldspars (Fig. 18). Towards the bottom of the core the carbonate-free Ca content increases, which is probably caused by some old sediment being mixed in with the tailings, and hence indicates that the boundary of pure tailings and pre AMAX-operation sediments is close to the bottom of this core.

The situation is similar in the parts of the Alice Arm sediments contaminated with modern tailings. The carbonate-free Ca content is clearly lowered in this facies, and as soon as the influence of the modern tailings subsides, the carbonate-free Ca values rise to an average of 1% which is close to the amounts found in Hastings Arm (Fig. 18). The old tailings of the Dolly Varden operation also affect the total calcium content, but to a much lesser extent. The carbonate-free Ca on the other hand shows hardly any change (Fig. 18).





4.2.5 Magnesium and lithogenous iron

In his studies on the transport phases of transition metals, Gibbs (1977) found the largest modes of transport for Fe and Mn in the Amazon and Yukon rivers to be crystalline particles, and hydrous oxide and hydroxide coatings. In the glacially-fed rivers carrying sediments into Hastings and Alice Arms, the proportions are definitely going to be shifted towards the crystalline particles; however, the general trends in the importance of the different transport modes should still be very similar. Mafic minerals (e.g. hornblende and biotite), which are a common constituent of the volcanic rocks in the source region (see Chap. 1.3.), are probably the primary hosts of the Fe and Mg found in these inlet sediments. Some of the Fe entering the inlets in crystalline form is associated with the various clay minerals and is a minor constituent of feldspars, and magnetite can also account for a significant amount of the Fe present. There is also some other Fe-oxide present in the Hastings and Alice Arm sediments, as discussed in section 4.8.

In Hastings Arm the sediment shows generally invariant background values of about 4.4 and 1.7% for Fe and Mg, respectively. Only at station HA-6, which is influenced by the activities of the Anyox mining operation, is some greater variation observable (Chap. 6). At station HA-2 the Fe and Mg values are virtually unchanged throughout the core (Fig. 4.10). In the main part of Hastings Arm, the average Mg/Al ratio is 0.22, which is somewhat lower than 0.28, the value reported by Krauskopf (1979) for average crust. The Mg/Al ratios for some Hastings and Alice Arm cores are tabulated in Table 4, and it can be seen that the ratio remains nearly unchanged for the entire length of core HA-2.

The magnesium content of the tailings is only about half that in Hastings Arm sediments which is clearly expressed in the lower Mg/Al ratios in Table 3 and the iron values in the pure tailings obtained from station AA-4 are also significantly lower. The good correlation of Mg and Fe shown in Figure 21 confirms that most of the Mg is due to mafic minerals. This explains the difference in the Mg and Fe contents between the tailings and the natural sediments: there are fewer mafic minerals in the granodioritic and quartzdioritic intrusions hosting the ore than in the volcanoclastic and sedimentary rocks of the



Figure 19 Vertical distribution of Mg in Hastings and Alice Arm sediments. Note the different scale for each profile on the abscissae.



Figure 20 Vertical distribution of Fe in Hastings and Alice Arm sediments. Note the different scale for each profile.

depth [cm]	HA-2	AA-1	AA-4	AA-8
0-3	0.22	0.20	0.15	0.15
3-6	0.22	0.21	0.11	0.15
6-10	0.22	0.17	0.13	0.17
10-15	0.22	0.20	0.12	0.17
15-20	0.22	0.22	0.11	0.19
20-25	0.22	0.21	0.12	0.22
25-30	0.23	0.21	0.13	0.21
30-35	0.22	0.21	0.18	0.21
35-40	0.23	0.21	0.13	0.21
40-45	0.23	0.20	0.13	0.22
45-50	0.22	0.20	0.14	0.22
50-55	0.23	0.21	0.14	0.22
55-60	0.23		0.19	0.23
60-65	0.22			0.22

 Table 4

 Mg/Al ratios of Hastings and Alice Arm sediments

Hazelton and Bowser Lake Groups (Woodcock and Carter, 1976; Steininger, 1985).

Both the Mg and Fe concentrations of the heavily contaminated sediments at station AA-8 are affected by the mine tailings. The values are clearly lower than in the natural sediments. As can be seen in Fig. 19 and 20, the Mg and Fe contents in the deeper portions of the core do not seem to be affected by the minor contamination with Mo-tailings or the tailings of the Dolly Varden Mine. The Mg and Fe values increase to average values of 1.65% and 4.8%, respectively, and show no significant variation further down the core. These values are similar to those determined for the natural sediments in Hastings Arm (Fig. 19,20) as is obvious in Fig. 21. The fields of the pure tailings and the heavily contaminated sediment are well separated from the values of core HA-2 which plot in close proximity to the remaining portions of core AA-8.

At station AA-1 the Mg and Fe contents are fairly variable compared to the other cores (Fig. 19,20). This is probably caused by the highly variable grainsize of these sediments, due to the proximity of this station to the Kitsault and Illiance Rivers which are the major suppliers of sediment to Alice Arm. This is supported by the low Fe and Mg values found in the 3-6 cm interval and the high values found in the 30-35 cm section of the core, which coincide with a high and low Si/Al ratio (Table 3), respectively, indicating coarser texture



Figure 21 Mg versus Fe for cores HA-2, AA-5 and AA-8.

in the 3-6 cm interval, and a finer average grain size at 30-35 cm depth.

4.2.6 Manganese and oxide iron

Manganese is transported into the marine environment mainly in the form of hydroxide coatings and hosted in crystalline particles. A significant amount of Mn (up to 17%) is also carried in solution in the river waters (Gibbs, 1977). Manganese-bearing crystalline particles transported into the inlets are mainly clay minerals and, to a lesser extent, feldspars. Fe and Mn entering the inlets as discrete particles of hydrous oxides and hydroxides are rapidly removed from the water column by coagulation and precipitation processes and incorporated in the sediment (Boyle et al., 1977; Mayer, 1982 and Fox and Wofsy, 1983).

In the Hastings Arm sediments both iron and manganese show significant enrichment in the top few centimetres of the sediment column (Fig. 19, 20). The enrichment is due to diagenetic remobilization of Mn and Fe oxides and consequent diffusion of the dissolved metals within the sediments (Lynn and Bonatti, 1965; Calvert and Price, 1972; Duchart et al., 1973; Tsunogai and Kusakabe, 1982; Balzer, 1982). These diagenetic processes will be discussed in greater detail in Chap. 8. Below the enrichment zone, the Mn concentration in core HA-2 stays almost constant with an average value of 0.11% (Fig. 22). Throughout Hastings Arm the Mn values are fairly variable. This is particularly apparent at station HA-4 (location shown in Fig. 1), where the Mn content is double that of core HA-2. In the sediments of all the other coring locations the Mn content is close to the values observed at station HA-2, varying from 0.08 to 0.14%. These minor variations are not reflected in the distribution of other elements (Appendix III).

In the pure tailings of core AA-4 0.09 to 0.15% Mn is present, which is similar to the levels measured in most of the Hastings Arm sediments. However, in the uncontaminated and sparsely contaminated sediments in Alice Arm the Mn concentration is between 0.2 and 0.3%, and therefore it is likely that the Mn background values are different for the two inlets.

In the sediments at station AA-1 there is an average of 0.15% manganese. Although,



Figure 22 Vertical distribution of Mn in Hastings and Alice Arm sediments. Note the different scales for each profile on the abscissae.

Mn shows a rather high variability throughout the core (0.1 to 0.2%; Fig. 22), none of these changes can be definitely linked to the presence of mine tailings.

In locations further away from the main sediment input, however, differences in the Mn content are closely linked with the varying amounts of mine tailings in the sediments. At station AA-8, where 20 cm of heavily contaminated sediment overlies older, sparsely contaminated sediment, these differences are obvious (Fig. 22). The upper 20 cm, containing rather large amounts of tailings, are clearly depleted in Mn, with the values being about 0.16%. The Mn content shows a sharp increase to an average of 0.3% below the heavily contaminated sediment layers. This value is commonly observed at other locations where sediments are contaminated with Mo-tailings (Appendix III). Immediately below the tailings in this core, there are pronounced enrichments of both Mn and Fe at about 20 cm depth (Figs. 19,22) marking the boundary between contaminated and natural sediment. The enrichment is most likely due to a buried sediment surface, where the upper, oxidized layer, diagenetically enriched in Fe and Mn, was preserved by very rapid sedimentation. Increased sedimentation rates are obvious during periods of active mining and tailings discharge. Frequent occurrence of turbidity currents (Krauel, 1981; Hay et al., 1982) probably redistributes the tailings material throughout the inlet, influencing even distal locations such as station AA-8. At depths greater than 50 cm, the Mn content drops to an average of 0.26%, due to the impact of the Dolly Varden tailings.

4.2.7 Phosphorus

Phosphorus occurs mainly as phosphate in the form of different apatites, with Caapatite being the most common P-bearing mineral (Krauskopf, 1979). Clay minerals may also account for a considerable amount of phosphorus (Füchtbauer and Müller, 1977), and, in detrital sediments characteristic of moderately or poorly productive coastal regions, a small proportion may be contributed by organic matter.

The vertical distribution of P for some sediments from Hastings and Alice Arms is shown in Fig. 23. In the top 10 to 15 cm of core HA-2 and some other Hastings Arm cores not shown here (values listed in Appendix III) the phosphorus values are slightly higher compared to the deeper parts of the investigated sediment. This enrichment probably reflects a slightly higher organic matter content in the top few cm of the sediment column. A large quantity of the phosphorus incorporated into the sediment with organic matter gets rapidly utilized by microbial organisms and changes to dissolved phosphate. Therefore, in this particular environment with rather small amounts of organic matter, compared to other nearshore sediments, organic P has no great impact on the total P content of the solid phase.

In the Hastings Arm sediments the average P content is 0.11%, and shows no great variations throughout the inlet. The depth distribution of P at station HA-2 is plotted In Fig. 23, and it can be seen that, except for the rapid decrease in the top few centimeters, the amount of P does not vary much with depth.

Although there are some variations in the phosphorus content throughout core AA-4, the P values of the pure tailings (0.09-0.15%) are very close to the values observed for the natural sediments in Hastings Arm (Fig. 23). However, this similarity is likely coincidental, because P in the tailings must occur in apatites, whereas it is probably hosted in various phases (including organic matter) in the sediments of Hastings Arm.

The similar P content of tailings and natural sediment is also expressed in the profile for core AA-8 (Fig. 23). The average P content is 0.13% and no significant impact is





caused by the tailings from either the Kitsault or the Dolly Varden operation.

At station AA-1 the average P concentration in the solid phase is 0.14% which is the highest observed for all cores, but here, too, the variations are not significant.

The only core having clearly different P values is AA-5. The top 15 cm of this core, comprising pure tailing, have only half as much P as found in all other sediment (Fig. 23). Immediately below the pure tailings the P values rise sharply to an average of 0.13%. This difference is explained by the coarse grainsize of these tailings, which contain a much higher amount of quartz than any other sediment. Therefore it can be concluded that this difference is due merely to dilution of the sediment with P-free minerals.

The distribution of phosphorus in the sediments of Hastings and Alice Arms is dominated by the detrital fraction. Because there appears to be no significant difference between the P content of the rocks in the source area of the natural sediments and the ore hosting rocks, this element can not be used to differentiate between natural and contaminated sediment.

4.2.8 Sulphur

The principal hosts for sulphur in the natural sediments of the study area are organic matter and authigenic sulphides. Due to bacterial activity, the conditions within the sediment become reducing at a fairly shallow depth and, in the anoxic zone of the sediment, sulphate-reducing bacteria produce sulphide (H_2S) which then combines with dissolved metals, especially iron, to precipitate as authigenic metal sulphides (Chap. 8). This process can lead to an increase of S in the sediment column with depth.

In the Hastings Arm sediments the sulphur content is usually between 0.1 and 0.3%, but does not vary very much within single cores (see Appendix III). In core HA-2 there is a sharp increase in the solid phase S below 55 cm which may be due to authigenic sulphide precipitation (Fig. 24).

The sulphur content of the pure tailings in core AA-4 varies between 1 and 2%, which is

an order of magnitude higher than the values found for the natural sediments in Hastings Arm. Most of the sulphur in the tailings is tied up in metal sulphides which are not recovered during the processing of the ore (Chap. 3.3).

At station AA-8 the mine tailings are easily recognized by their S content. Sulphur increases significantly in both depth intervals contaminated with old and modern tailings. However, the values are never much higher than 1% and decrease to expected background levels as soon as the influence of either tailings material subsides (Fig. 24).

High sulphur values are also encountered at depth at station AA-1, in concert with high Mo concentrations in the solid phase (Appendix III). The background S value in this core appears to be about 0.3 - 0.4% (Fig. 24) and the higher values reflect contamination with Mo-bearing tailings.

Contamination with either of the two tailing types found in the sediments of Alice Arm results in S concentrations around 1%. This is caused by a significant amount of metal sulphides deposited with the tailings material which, in a natural sedimentation regime would likely be oxidized before they reach the inlet. Therefore sulphur appears to be a sensitive indicator of contamination by either kind of mine-tailings in this area. This conclusion is supported by observations made at the other coring locations such as in the vicinity of Granby Bay (Anyox), where the high sulphur content in certain depth horizons correlates readily with metal enrichments characteristic of the presence of mining wastes (see for example the elemental data for core HA-6 and other locations in Alice Arm, Appendix III).



Figure 24 Total sulphur distribution in the solid sediment of Hastings and Alice Arms. Note different scale for each profile on the abscissae.

4.2.9 Carbon

In the sediments of the study area carbon is mainly present as organic carbon of both terrigenous detrital and marine origin. Carbonate carbon is the second largest contributor and all other possible carbon sources for the sediments (e.g. graphite in igneous and sedimentary rocks) can be considered to be negligible.

The Hastings Arm sediments have an average organic carbon content of 1.2%, which decreases slowly with depth from 1.4% at the sediment surface to $\approx 1\%$ at depth exceeding ≈ 20 cm The organic and total carbon distribution in core HA-2 is shown in Fig. 25.

The pure tailings in Alice Arm have a much lower carbon content than the natural sediments in Hastings Arm. Most of the carbon can be accounted for by the carbonate present. The remaining carbon, which makes up 0.04 - 0.1%, may be due to organic matter scavenged by tailings particles from the water column during settling to the bottom (Pedersen, pers. comm.). Additives like collector oil and frothers are added during the processing of the ore (Burling *et al.*, 1981), but these are unlikely to be significant contributers of C_{org} to the tailings. As can be seen in Fig. 25, the concentrations of both C_{org} and carbonate C is nearly constant throughout the pure tailings core AA-4.

Total carbon in the heavily contaminated zones of core AA-8 is only about one half of what was found in natural sediments of Hastings Arm, and almost half of this carbon is due to carbonate (Fig. 25). The organic carbon is also only about one third of that determined for the natural sediments. However, the materials responsible for the organic carbon appear to be the same in contaminated and natural sediments, as is indicated by the same C/N ratio of about 10 for both sediment types (Table 5). The zones contaminated with the older Dolly Varden tailings exhibit a higher organic C content which is caused by a higher input of terrigenous organic matter; this suggestion is supported by higher C/N ratios which average 12.5 at depth in the core (Table 5). The average C/N ratio of undecomposed marine organic matter is 6.6 whereas it averages ≈ 14 for fresh terrestrial material (Sholkovitz, 1973).


Figure 25 Vertical distribution of C in Hastings and Alice Arm sediments. Note different scale for each profile on the abscissae.

C/N ratio of cores HA-2 and A						
depth [cm]	HA-2	AA-8				
0-3	10.0	11.7				
3-6	10.5	10.0				
6-10	10.5	11.2				
10-15	10.7	10.8				
15-20	10.1	11.5				
20-25	10.4	10.9				
25-30	10.9	11.2				
30-35	9.6	11.5				
35-40	9.6	10.7				
40-45	12.4	10.6				
45-50	10.0	12.9				
50-55	9.7	12.5				
55-60	9.6	12.0				
60-65	9.6	12.2				

Table 5C/N ratio of cores HA-2 and AA-8

At station AA-1 the total carbon content has not the same uniformity as found in the other cores. These variations are mainly due to changes in the organic carbon content (Fig. 25), whose concentrations range from 0.3 to 1.88%. The fluctuations in the concentration of organic C appear to be linked with changes in the grainsize of the sediment at station AA-1. The lowest carbon content is in the 6-10 cm interval where a high Si/Al ratio indicates a coarser grain size, whereas the highest C concentration is found in the 30-35 cm depth interval where the lowest Si/Al ratio for this core was determined (Table 5). This distribution is consistent with the known relative enrichment of C_{org} in finer-grained sediments, due to the hydrodynamic equivalence of clay-sized particles with typically finely-comminuted organic detritus (Calvert, in press).

5.1 Introduction

In order to fully describe the impact of mining wastes on the minor and trace element composition of nearshore marine sediments, analyses of a wide range of elements, having variable geochemical behaviours, are particularly useful. Only in this way, is it possible to describe the natural minor element variability against which the distribution of any contaminant can be understood. The mineralogical and the major element compositions of the sediments from Hastings and Alice Arms (Chap. 3 and 4) provide a clear distinction between natural sediments from two different sources and the mine tailings discharged into Alice Arm. The natural sediments in Hastings Arm are quite homogeneous throughout the main basin of the inlet and are very similar to the uncontaminated deposits in Alice Arm. In the latter area, any major changes in the mineralogy or major element distribution in the sediments can be attributed either to a different natural sediment source or to mining activities. The minor element distribution is likely to be affected in a similar way. In this chapter, the minor elements will be discussed in groups which show similar geochemical behaviour. The Hastings Arm sediments will again be used to establish the natural background values in comparison to the uncontaminated and contaminated sediments and the pure tailings in Alice Arm.

The minor elements were determined by X-ray fluorescence spectrometry, as described in Appendix II. All elemental concentrations are reported on a salt-free basis, and are tabulated in Appendix III.

5.2 DISTRIBUTION OF THE MINOR ELEMENTS

5.2.1 Distribution of Cobalt, Chromium, Nickel and Vanadium

The ionic radii of the transition metals cobalt, chromium, nickel, vanadium and copper are very similar to the radii of iron and magnesium; they therefore readily substitute for these two major elements in mafic minerals (Krauskopf, 1979; Salomons and Förstner, 1984) and tend to show similar distributions in detrital sediments, as discussed below. The situation for copper, however, is complicated here by the fact that it is associated to a minor extent with the molybdenum ore, which increases its abundance in the tailings. Therefore, copper will be discussed together with molybdenum in section 5.3.

The concentrations of cobalt, chromium and nickel show little variability in all cores collected in Hastings Arm and in the uncontaminated sediments in Alice Arm. Vanadium, on the other hand, shows somewhat higher values in the upper reaches of Hastings Arm (cores HA-4 and 5) relative to Station HA-2 and in the natural sediments in Alice Arm. The background values for cobalt (average, 40 ppm) and vanadium (average, 180 ppm; except in the upper reaches of Hastings Arm where concentrations average 260 ppm) are close to the values Krauskopf (1979) gives for basalts (Co 48 ppm, V 250 ppm; Table 6). This is consistent with the presence of the island arc volcaniclastics in the Hazelton and Bowser Lake Groups, which are the principal source of these sediments. Chromium and nickel, on the other hand, are only present at about one half and one third the amount, respectively, reported by Krauskopf (1979) for average basalts (Cr 200 ppm, Ni 150 ppm). In a plot of Cr versus V and Ni versus V, however, these three elements show a high degree of correlation (Fig. 26). This indicates that common mineral phases hosting chromium, nickel and vanadium are diluted to varible extents by other minerals in these sediments. In Figures 27 and 28, it is seen that chromium, nickel and vanadium correlate well with iron and magnesium and hence it can be concluded that these elements occur in mafic minerals, such as hornblende or biotite, which are the principal mafic constituent in these sediments (Chap. 3). Cobalt, however, does not correlate with iron or magnesium or with any other element, although it is well known to occur in ferromagnesian minerals (Krauskopf, 1979; Basaltic Volcanism Study Project, 1981; Salomons and Förstner, 1984), especially

olivine. Since olivine is very susceptible to weathering and the sedimentary material in Hastings and Alice Arms is mostly reworked sediment, it is likely that most of the olivine originally present has been removed and cobalt is now associated with another phase in the sediments.

Table 6

Average abundances of minor elements in the Earth's crust, granite, basalt and in natural sediments (background) and tailings from Hastings and Alice Arms. Crustal, granite and basalt values from Krauskopf (1979).

Element	Crust	Granite	Basalt	Hastings and Alice Arm sediments	Modern tailings	Dolly Varden tailings
Co	22	3	48	37	39	28
Cr	100	20	2 00	92	30	65
Ni	75	0.8	150	35	10	40
v	110	50	250	175	130	2 00
Mo	1.5	1.5	1	≤ 7	250	< 7
Cu	50	12	100	45	75	70
РЪ	12.5	20	3.5	18	24 0	135
Zn	70	50	100	130	400	300
Rb	90	150	30	83	165	85
Ba	500	700	300	1100-1550	1670	up to 5%
Sr	375	300	450	310- 500	270	up to 1000
Zr	165	180	140	110	100	190

In the pure tailings, the mafic minerals are much less abundant than in the natural sediments (Chaps. 3 and 4). As a result, chromium, nickel and vanadium are depleted in the molybdenum tailings; however, cobalt does not show any difference in concentration between the natural sediment and the tailings. At Station AA-8, where sediment heavily contaminated with modern tailings overlies an interval of sediment having minor contamination, the variations are most marked (Fig. 29). Thus, these metals are significantly depleted in the top 20 cm of the core. In the sediments with minor contamination, between 20 and 50 cm, the abundance of these four elements is at the expected background levels (Table 6) observed in Hastings Arm. Below 50 cm, where contamination with tailings from the Dolly Varden operation was detected, the cobalt, and especially, the chromium contents are lower than in the natural sediments; nickel remains at background level and vanadium appears to be slightly higher. However, this enhancement is more apparent than real because of the spectral interference of Ba on the V line used in the



Figure 26 Correlation of Cr and Ni with V Figs. 26, 27 and 28 show the minor element data for Station AA-1. This core shows the maximum degree of natural sediment variability, without any significant impact of tailings, because of its proximity to the mouths of the Kitsault and Illiance Rivers.







XRF analysis. Thus, although a correction has been applied (Appendix III), the very high Ba concentrations in the Dolly Varden deposits (see section 5.3) means that the V values are probably associated with a significant error. In addition, because nickel and vanadium are usually found in the same minerals, most likely pyroxenes and hornblende (Basaltic Volcanism Study Project, 1981), it is expected that they would show the same trends in their distribution within the sediment column.

In summary, it has been shown that, since the molybdenum ore is virtually free of mafic minerals, sediment consisting partially or wholly of molybdenum mine tailings has a much lower content of Cr, Ni and V compared with the natural background levels in this particular area.

5.2.2 Distribution of Molybdenum, Copper, Lead and Zinc

The average molybdenum content of the earth's crust is about 1.5 ppm (Table 6), mafic rocks (gabbro, basalt 0.8 - 1.4 ppm) containing less molybdenum than felsic rocks (e.g. granite about 2 ppm). As a general rule, the molybdenum content of rocks increases as their content in alkali metals and silicon increases (Uzkut, 1974). Due to the similar ionic radii of Mo⁴⁺ and Fe³⁺, up to 400 ppm molybdenum can be found in magnetite derived from igneous rocks (Oyarzum, 1979). In molybdenum ore deposits, the bulk of the molybdenum occurs as molybdenite MoS₂. In many of the porphyry deposits in British Columbia, high molybdenum contents are usually associated with high copper values; where copper ores are mined molybdenum is often recovered as a byproduct (e.g. Island Copper Mine at the northern tip of Vancouver Island). The Kitsault deposit, however, does not bear copper in mineable amounts. Griffiths and Godwin (1982) suggest a primary granitoid melt as the source for the porphyritic copper-molybdenum deposits found in the coastal orogens of North America. According to their model the magma is derived from local melting of deep-water shales and volcaniclastic debris due to increased heat flux above the western subduction zone. Griffiths and Godwin (1982) found that the volcanic material is likely the source for Cu-ore, whereas the Mo-ores are probably derived from the deep-water shales. The increased amounts of lead and zinc, occurring with these deposits are supposedly



derived from the wall rocks by hydrothermal solution. Under normal conditions, most of the lead and zinc, like most chalcophile elements, occur as tiny sulphide grains disseminated throughout the rocks, but to some extend they can also substitute for major cations in aluminosilicates, where Pb can replace K and Zn can replace Mg or Fe (Krauskopf, 1979).

The molybdenum content of the Hastings Arm sediments is below the lower limit of determination (7 ppm, equivalent to a concentration of six standard deviations of the background counting rate; Jenkins, 1980) of the X-ray fluorescence method used for the analysis. These low values are in accordance with the average values reported for the crust, granite and basalt (Table 6). The background for copper is a little bit more difficult to establish because of the activity of the Anyox Copper Mine in Granby Bay which has an especially significant influence on the copper levels in the Hastings Arm sediments (Chap. 6). However, it has been assumed that at Station HA-5 near the head of the inlet (Fig. 1) the influence of the Anyox mine is negligible due to the large riverine sediment input which would dominate over any influx from other sources. The copper values in core HA-5 are between 40 and 50 ppm. Taking these values as natural background for the sediments in this area, it can be seen that the sediment at Station HA-4, about 8 km north of the Anyox Mine site (Fig. 1), and the top 20 cm of core HA-2 which is from an area east of Larcom Island, well sheltered against any direct impact of mining effluents, still show enhanced copper values of around 70 ppm. Below 20 cm depth the sediment at Station HA-2 has background copper values which average 42 ppm and correspond well with the values determined for the sediments at the head of the inlet.

The lead and zinc values are low throughout the sediments in Hastings Arm and do not show any impact of the mining effluents in the main basin of the inlet. Lead is never above 30 ppm and the average zinc content is 130 ppm. Only in the restricted basin west of Larcom Island and inside Granby Bay, higher lead and zinc values are found as a result of the Anyox mining activities (Chap. 6).

Because the crustal abundance of Mo is very low (Table 6), and the background values

in Hastings and Alice Arms are close to this level, a minor amount of contamination of natural sediment with mine tailings can be easily detected. Very low level contamination can be identified by enhanced Mo-content in the sediments. Other elements which could indicate the presence of tailings have a crustal abundance which is too high to allow delineation of small admixtures of tailings. Copper, lead and zinc mimic the trends of molybdenum in contaminated sediments fairly well; however, one has to be careful in drawing conclusions about their petrological relations because the impact the milling and flotation process had on the elemental composition of the tailings can not be assessed.

In the pure tailings, the Mo-content varies between 187 and 377 ppm, Cu between 46 and 102, Pb - 165 to 369 ppm and Zn - 300 to 495 ppm (Table 6 and Appendix III). In the heavily contaminated sediments from the top 20 cm of core AA-8, the Mo, Cu, Pb and Zn values are significantly above the background, but, due to admixed natural sediment, are distinctly below the values recorded for pure tailings. In Figure 30 the vertical distribution of the Mo, Cu, Pb and Zn concentrations in core AA-8 show that the three distinct sediment facies described earlier can be easily recognized. The Dolly Varden tailings below \approx 50 cm depth are distinguished from the Mo-rich Kitsault tailings facies by their undetectable Mo content. In contrast, elevated Cu, Zn and Pb levels are characteristic of both facies.

Figure 31 shows the relationship between Mo, K, Si, Fe and Al in the three units of core AA-8. The facies plot clearly in distinct fields, and the position of the fields in the plots is always determined by the association of the specific element with Mo. The plots of Mo versus K and Mo versus Si, for example, indicate a close link of these two elements with the modern tailings but no association with the tailings from the Dolly Varden Mine, because the high or low K and Si values correspond with high or low Mo-contents. Iron, on the other hand, shows the opposite behaviour due to its association with mafic minerals, which are depleted in the molybdenum ore and more abundant in the Dolly Varden tailings. Finally, Al is depleted in the two tailing types, whereas the highest Al values appear in the least contaminated part of core AA-8. This can be easily explained by dilution of the



reported in ppm; note the variable scales on the abscissae



Figure 31 Correlations of K, Si, Fe and Al with Mo

natural sediment by tailings.

Fig. 32 shows the relationships of Mo with Cu, Pb and Zn in the three sediment types. It can be seen in all three plots that the field for the middle part of core AA-8, which is contaminated to a limited extent, is very close to the field of the natural sediment (core HA-2). The points for the uppermost 20 cm of Station AA-8 partially overlap with the field occupied by the pure tailings from core AA-4 indicating the dominance of modern tailings in the sediments of this zone. In contrast, the points representing the Dolly Varden tailings plot in areas well separated from the other groupings because of the absence of Mo. The Mo-Cu relationship, however, is somewhat more complicated because of the presence of a small amount of contamination from the Anyox copper-mine in the upper 20 cm of core HA-2. Thus, in the Mo/Cu plot, the contaminated interval of the HA-2 sediment occupies almost the same area as the samples at Station AA-8 contaminated with Dolly Varden tailings.

In Fig. 33, the copper, lead and zinc values of HA-2, AA-4 and AA-8 are plotted against each other. Again the fields of the pure tailing and the heavily contaminated part of AA-8 plot closely in each case as do the fields for the natural and the sparsely contaminated sediments. The Dolly Varden tailings plot in an intermediate position between the two endmembers, tailings and natural sediment. However, since there were no pure Dolly Varden tailings available for comparison, nothing can be said about the degree of contamination of the sediments in which the old tailings have been found.

The sediments of Alice Arm appear to be pervasively contaminated with mine tailings from at least two sources. Completely uncontaminated sediment can only be found below the tailings from the Dolly Varden operation in the deepest parts of core AA-7 (Appendix III). There the values of the four transition metals discussed in this section are as low as those in the natural sediments of Hastings Arm.



Figure 32 Relationships of Mo with Cu, Pb and Zn in the three sediment types of Hastings and Alice Arms.





Figure 33 Relationship of Cu, Pb and Zn in Hastings and Alice Arm sediments

5.2.3 Distribution of Rubidium

Rubidium substitutes readily for K in feldspars and micas (Horstmann, 1957 in Calvert and Batchelor, 1978; Krauskopf, 1979). Thus, these two alkali metals are normally highly correlated in sediments, as can be seen in the linear Rb vs K relationship plotted in Fig. 34, which includes data from the major tailings and seiment facies.

There is only minimal variation of the Rb content with depth in the Hastings Arm sediments as shown by the plot for core HA-2 in Fig. 35. However, due to the close relationship of K and Rb, and the high K-feldspar content of the Kitsault mine tailings, there are significant differences between the absolute Rb contents in the Hastings and Alice Arm sediments; in addition, the Rb concentrations are more variable within the Alice Arm cores (Fig. 35).

The homogenous nature of the natural sediments in Hastings Arm is reflected in Fig. 34, by the close grouping of the points for core HA-2. The values for the sediments contaminated with Dolly Varden tailings or with small amounts of modern tailings lie very close to the field for the natural sediments of HA-2. This confirms the previous finding of a relatively similar mineralogy and K-content. The heavily contaminated upper 20 cm of AA-8 and the pure tailings of AA-4 also plot close together but the fields for these sediments are well separated from the natural sediments. This is again an expression of the much higher K-feldspar content of the molybdenum tailings. The same can be observed in the other sediment cores taken throughout the inlet. In layers contaminated with modern tailings, as indicated by high Mo-values, the values for K and for Rb are also high. Where the older Dolly Varden tailings are the cause of contamination, however, the K and Rb contents are lower due to the lesser feldspar content in this type of tailings (AA-6,7 and 8, Appendix III).



Figure 34 Correlation of Rb and K in the Hastings and Alice Arm sediments.



Figure 35 Vertical distribution of Rb in Hastings and Alice Arms.

5.2.4 Distribution of Barium and Strontium

Barium, like Rb, is found predominately in K-bearing minerals. However, due to its smaller ionic radius (1.44Åfor Ba^{2+} , 1.46Åfor K⁺, both in six-fold coordination) and its higher charge, Ba^{2+} tends to enter the earlier crystallized minerals and is therefore more enriched in mafic minerals whereas, Rb^+ is more enriched in the later-crystallizing felsic minerals. Strontium can substitute for K⁺ and Ca²⁺ and has therefore an intermediate position, having similar concentrations in mafic and felsic rocks (Krauskopf, 1979). Moreover, Sr can also readily replace Ba in Ba-minerals.

Barium and Sr show the highest degree of variability of the minor elements throughout Hastings Arm. At Station HA-5, close to the head of the inlet, the sediment contains an average of 1550 ppm Ba and close to 500 ppm Sr. These values decrease slowly down the inlet, and at Station HA-2 the Ba content is about 1100 ppm and the Sr values average 310 ppm. The same can be observed in Alice Arm, as is seen from rather high Ba and Sr values in the minimally contaminated layers at Station AA-1, and lower levels down inlet at AA-7 where the uncontaminated basal sediments contain \approx 1100 ppm and 310 ppm, respectively, similar to the concentrations found at depth in core HA-2. The top 20 cm of core HA-2, which show some signs of being contaminated by the Anyox mining operation, also show increased amounts of Ba and Sr (Fig. 36).

In the pure tailings at Station AA-4, the average Ba content is 1670 ppm and the Sr values are around 300 ppm, and both elements have a rather variable vertical distribution (Fig. 36), but these variations can not be linked with the modern tailings. The pure tailings at Station AA-4, the sediment contaminated with Mo-tailings in core AA-8 and the natural sediments of Station HA-2 plot closely together and only the part of the sediment column contaminated with Dolly Varden tailings plots in a well-separated field (Fig. 37). In the sediments contaminated with molybdenum mine tailings outside the area where pure tailings were found, Ba averages 2500 ppm and Sr 310 ppm which is, at least for Ba, higher than expected. These sediments are most likely contaminated with tailings from the earlier B.C. Molybdenum operation. However, since the molybdenum ore does



Figure 36 Correlation of Ba and Sr from sediment cores HA-2 AA-4 and 8.



Figure 37 Vertical distribution of Ba and Sr in Hastings and Alice Arm sediments.

38

not contain abnormally high Ba concentrations, the high Ba in these sediments can not be accounted for by contamination from the Kitsault operation. The most likely source for the enhanced Ba levels is an abandoned pile of mine tailings at the Dolly Varden Mine, which have been left on a steep river bank next to the Kitsault river (D. Goyette, personal communication). Slow erosion of this tailings pile and consequent fluvial transport of this material with a fairly high barite content could well account for the above-background Ba and Sr concentrations. This argument is further supported by the high Ba values D. Goyette (unpublished results) found in Kitsault River sediments. The high barite concentration in the Dolly Varden ore is reflected by the extraordinary Ba concentrations (up to weight 5%) measured at depth in some cores (see for example AA-8 in Fig. 36 and Appendix III). The Dolly Varden tailings are buried to a steadily greater depth as increasing proximity to the riverine source at the head of the inlet results in a higher sedimentation rate.

5.2.5 Distribution of Zirconium

Zirconium can not readily substitute for any major or minor element in the common silicate minerals and is normally restricted to the accessory mineral zircon in nearshore sediments.

In Hastings Arm, the Zr content is higher and shows more variability in the sediments close to the head of the inlet; this is a clear reflection of the textural (grain-size) control; high zircon values are usually found in coarser-grained sediment. This effect is much more pronounced in Hastings Arm where, at Station HA-5 the average Zr content is 164 ppm and the range is 46 ppm. At Station HA-4, about 8 km from the junction of Hastings Arm and Observatory Inlet (Fig. 1), the average Zr content is 127 ppm and varies only by 20 ppm. In the remaining parts of Hastings Arm, the average Zr content is 110 ppm and there are no great variations with depth as can be seen for core HA-2 in Fig. 38.

In Alice Arm, the Zr content is similar to the lowest values found in Hastings Arm and is not affected by the presence of molybdenum tailings (Fig. 38). Slightly higher Zr



Figure 38 Vertical distribution of Zr in Hastings and Alice Arm sediments.

values are found in some layers at Station AA-1, but the average there is still about 110 ppm. At Stations AA-9 and AA-8, however, higher Zr values (around 120 to 140 ppm) are found which are probably caused by slightly coarser-grained material brought into Alice Arm via Hans Creek.

A higher Zr content is also found in the sediments contaminated with Dolly Varden tailings; the reason for this is unclear.

6. SEDIMENTS INFLUENCED BY THE ANYOX OPERATION

The Anyox Copper Mine and Smelter was in operation on the western shores of Granby Bay from 1914 until 1936 (Chap. 1.3). During this time substantial amounts of milling effluents and slag from the smelter were dumped into Granby Bay. The influence of this dumping can be detected over a wide area in Hastings Arm. In this Chapter, the differences between natural sediment and the Anyox effluents are emphasized, to allow easy recognition of Anyox materials at other locations in Hastings Arm. As experienced with the sediments in Alice Arm, the mine tailings are distinctly different from natural sediments. To establish the composition of the contaminant-endmember, samples from the slag pile on the shore of Granby Bay were collected and are compared to the sediments of the most severely affected areas.

6.1 MAJOR ELEMENTS

In the slag the Si and Al concentrations are significantly lower than in the natural sediments (Table 7). The average Al value is less than half that of the natural sediments, whereas the background values for Si in this area are about 1.5 times higher than the concentrations determined in the slag. This results in a very high Si/Al ratio for the slag (5.8) compared to the natural sediments (3.5). In some slag samples Na is almost completely absent and averages only 0.07% in the analyzed slags. The concurrent low values of K indicate that this might be caused by a rather low feldspar content, which might have been removed during the processing of the ore prior to the smelting. Iron, on the other hand, is the most abundant element in the slag, averaging over 30%; this is 7 times the Fe-content of the natural sediments in this area. The rather low Mg values indicate that most of the Fe must be originally attributed to pyrite and the amount of mafic minerals is probably comparable to the country-rock in this area. The sulphur of

the slag is surprisingly high. Despite the loss of S by oxidation and volatilization during ore smelting, the slag contains up to 3.1% sulphur.

Table 7

Element	natural sediment	HA-6 >35 cm	HA-6 upper 35 cm	ANY Granby Bay	slag
Major elen	nents in weight	t %			
Si	27	25.5	24	22	17.5
Al	7.7	7.4	7.3	6.0	3.0
Na	1.6	1.6	1.3	1.1	0.07
K	2.3	2.2	1.8	1.0	0.45
Fe	4.4	4.8	7.6	12.4	31.5
Mg	1.7	2.2	2.8	3.3	1.5
S	0.4	0.8	1.3	4.0	2.3
Minor elen	nents in ppm				
Cu	45 ppm	70	500	730	2500
Zn	130	160	500	1750	8500
РЪ	18	18	38	35	20 – 100

average elemental abundances of natural sediments and sediments contaminated with effuents from the Anyox operation.

The sediments at station ANY were entirely black upon recovery, indicating that a significant amount of slag material contributes to the sediments in Granby Bay. However, The chemical composition of the sediment demonstrates a significant contribution of natural sediments. This is also shown by a Si/Al ratio of 3.6 which is similar to the natural background in this area. The high Fe content is certainly in part attributable to the slag, but a large proportion of the Fe found in core ANY is likely carried into Granby Bay by Hidden Creek, which drains the old mining area. The sulphur values found in the sediments at station ANY are clearly higher than in the slag material and are probably due to metal sulphides which are carried from the old mine into the Bay.

At station HA-6 the influence of Anyox is clearly visible in the top 35 cm of this core (Fig. 39). The potassium and sodium contents are diluted by the K- and Na-deficient mining effluents and smelting wastes (Table 7). In core HA-6 a close relationship of these two alkaline elements can be observed (Fig. 39). Below \approx 30 cm Na increases from 1.3 to 1.6% and K from 1.8 to 2.3%, which are virtually the same as found in the main part of Hastings Arm throughout the sediment column (Table 7).

The Fe content in core HA-6 is almost twice the background for Hastings Arm sediment. The trend of the Mg distribution at station HA-6 is very similar to the iron distribution (Fig. 39), which indicates that a significant amount of Fe and Mg are derived from the same mineral phase, most likely mafic minerals. In the contaminated part of core HA-6 the average value is $\approx 1.3\%$ (Table 7, Fig.39). Below 35 cm the S content at station HA-6 decreases to an average of 0.8%.

6.2 MINOR ELEMENTS

The impact of the Anyox operation on the minor element composition of the sediments is reflected only by enrichments of Cu, Pb and Zn, and therefore only these three elements are discussed here.

In the slag, copper values usually exceed 2000 ppm, but these concentrations are diluted to an average of 730 ppm in core ANY. At station HA-6 the average Cu content of the contaminated sediment is 500 ppm; this concentration decreases rapidly below 35 cm. Copper appears to be the most mobile of the elements enriched in the effluents of the Anyox operation. Enhanced Cu values were determined at locations as far as 8 km away from Granby Bay (station HA-4, data tabulated in Appendix III), and Cu is therefore probably the most sensitive indicator for contamination with Anyox effluents.

The lead values in the slag and the heavily contaminated sediments are only marginally higher than in the natural sediments (Table 6.1). In the sediments, Pb is never above 40 ppm and only one slag sample showed a high Pb content of 100 ppm.

In the slag material, Zn is the most abundant of the three minor elements discussed here. Up to 1% Zn has been determined in the samples collected from the slag piles on the shore of Granby Bay. In core ANY, the average Zn content is 1750 ppm, about 3 times the amount of Cu found in these sediments. In the contaminated sediment of station HA-6, the average Zn values dropped to 500 ppm, the same value as found for Cu (Table 6.1), and in more distant sampling locations no significant increase in the Zn values could be



Figure 39 Minor and major element distribution at station HA-6. Major elements in weight %, minor elements in *ppm*; note different abscissa for each element

detected. It can therefore be concluded that, compared to Cu, Zn is rather immobile in this type of environment.

In summary, the most significant effects of the Anyox operation on the sediments in the proximity are increased concentrations of Fe, Zn and Cu, compared to the naturally derived sediments. These effects wane rapidly with distance, and outside the sheltered basin west of Larcom Island hardly any effect is noticeable. Copper can be traced the furthest distance. This is partially due to the low background values for Cu which makes even minute amounts above the natural values easily detectable. However, it can not be ruled out that the enhanced Cu concentrations at more distant locations are due to a higher mobility of Cu compared to the other elements involved.

7. INTERSTITIAL WATER CHEMISTRY

7.1 INTRODUCTION

As soon as a sedimentary particle settles out and becomes a part of the sediment column, it may participate in early diagenetic processes. The pH and redox potential of the sediment, and therefore also of the interstitial water changes in a predictable manner throughout the sediment column. These changes are brought about primarily by bacterial degradation of organic matter, but also by reactions of mineral matter with the pore waters. In areas with high sedimentation rates and large inputs of organic matter, such as the inlets along the North American west coast, the dissolved oxygen in the interstitial waters will be rapidly depleted by bacterial activity and the sediment column becomes anoxic at a very shallow depth. These changes in the sediment column cause alterations in the chemical forms of sedimentary constituents, establishing new equilibria between their solid and dissolved phases. The variations in the content of dissolved constituents in the interstitial waters can therefore be used as an indicator for early diagenetic reactions taking place within the sediment column.

In an effort to monitor early diagenetic remobilization in the tailings and natural sediments of Hastings and Alice Arms, interstitial water samples were taken from six cores in the two inlets, raised during September/ October 1983, one year after the Kitsault Molybdenum mine closed down. Therefore, there was enough time for early diagenetic reactions to develop in the sediment and the tailings, and this provides a excellent opportunity to study early diagenetic processes in tailings and contaminated sediment.

In order to assess for the first time the nature of early diagenesis in the mine tailings in Alice Arm, pore water was collected from four cores there (AA-1, 4, 5' and 8) and from two cores recovered from Hastings Arm (HA-2 and 6). The two sites in Hastings Arm were chosen firstly to have a representative natural sediment core (HA-2) and secondly to see whether any impact of the mining effluents from Anyox is detectable in the pore waters of the sediments in the restricted basin west of Larcom Island. Upon analysis of major and minor elements, the tailings material from station AA-5' did not prove to be processed ore material, but rather ground-up host rock. Its chemistry closely resembles that of the natural sediments in Hastings and Alice Arms and thus provides a control station with sedimentary conditions and residence time in the inlet comparable to the true mine tailings.

The pore waters were recovered on board ship immediately after collecting the cores. In order to avoid any oxidation effects, the cores were extruded into a glovebox flushed with N_2 and the pore water was extracted by centrifuging the sediment for 10 minutes. The interstitial water samples were analyzed for the metals manganese, iron and molybdenum as well as for phosphate, silicate, nitrate, ammonia, sulphate, sulphide and alkalinity. Most of the nutrients were analyzed immediately after recovering the pore water. Nitrate, H_2S , SO_4^{2-} , alkalinity and dissolved metals were analyzed subsequently in the lab in Vancouver. The methods used are described in detail in Appendix II and the complete results are tabulated in Appendix III.

7.2 NUTRIENT DISTRIBUTION IN THE INTERSTITIAL WATER

7.2.1 Distribution of interstitial silica

Biogenous silica in sediments appears to be rather labile, which is indicated by the fairly high concentrations of dissolved silica usually found in pore waters (in form of undissociated monomeric acid $Si(OH)_4$) and by the diagenetic recrystallisation of silica and chert formation. In natural sediments dissolved silica concentrations are known to increase rapidly with depth in the uppermost sediment layers, attaining constant values within some tens of centimetres (Calvert, 1983). Most of the dissolved silica in porewaters is due to solution of amorphous biogenic silica deposited in form of frail planktonic shells (Fanning and Pilson, 1974; Schink et al., 1974; Calvert, 1983). This can, to some extent, explain the discrepancy between the profiles of dissolved silica in the porewaters of the Alice and Hastings Arm cores.

The interstitial silica profiles of all pore water stations (except AA-5') are displayed in Fig. 40. At the two stations in Hastings Arm, HA-2 and HA-6 (Fig. 40), the vertical distribution of dissolved silica is similar to the theoretical profile outlined above. In respect to dissolved silica, the sediments in core HA-2 and 6 reflect natural (HA-2) or at least close to natural (HA-6) conditions. Concentrations around 1000 μ mol L⁻¹ are similar to the values commonly observed in nearshore sediments in highly productive areas (Schink *et al.*, 1974).

The low values between 200 to 400 μ mol L⁻¹ at station AA-4 indicate the absence of opaline silica in the pure tailings, but these values are still higher than the solubility level with respect to quartz (Calvert, 1983). In the heavily contaminated top 20 cm of core AA-8 the dissolved silica values approach 450 μ mol L⁻¹ and increase rapidly to levels around 1000 μ mol L⁻¹ in the sparsely contaminated sediment between 20 and 50 cm. The tailings of the Dolly Varden mine, which contaminate the sediments below 50 cm, do not seem to have a major impact on the amount of dissolved silica in the pore waters; however, any existing differences may have been balanced out by diffusion and migration processes within the sediment column. At station AA-1 the dissolved silica values are again as low



Figure 40 Dissolved silica profiles in porewaters collected from Hastings and Alice Arm sediments.

as in the pure tailings; the absence of opaline silica at this station can be attributed to the high terrigenous input by the two rivers at the head of the inlet.

7.2.2 Distribution of PO_4^{3-} , NO_3^- , NH_4^+ , SO_4^{2-} , H_2S and titration alkalinity

The processes controlling the distribution of dissolved constituents in interstitial waters are well studied. Most changes in the composition of the pore waters in natural sediments are induced by bacterial degradation of sedimentary organic matter (Stumm and Morgan, 1970; Presley and Trefry, 1980; Jorgensen, 1982a,b, 1983; and others). Associated redox reactions tend to occur in order of their thermodynamic possibility and are therefore, to some extent, predictable. The relevant reactions are listed in Table 8 and are summarized in Fig. 41. The occurence of these reactions in natural sediments, however, is not limited to well defined depth intervals within the sediment column. Overlap is common. The reduction of NO_3^- and MnO_2 , for example, happen at about the same pE levels and therefore concurrently in the sediment column (Stumm and Morgan, 1970). In addition, bioturbation (Goldhaber et al., 1977; Grundmanis and Murray, 1977; Berner and Westrich, 1985) and diffusion and advection processes tend to blur the boundaries of these redox processes within the sediment column (Pedersen, 1979). Also, many investigators have observed significant spatial and temporal variations in the vertical distribution of some constituents of interstitial water (Sholkovitz, 1973; Matisoff et al., 1975; Goldhaber et al. 1977).

In Fig. 42 to 48 the distribution of the dissolved constituents in the interstitial waters of the Hastings and Alice Arm sediments are shown. The nitrate distributions are not plotted, because NO_3^- was either detectable only in the top-most sample, or, it was found in deeper samples co-existing with NH_4^+ , which is thermodynamically unfavoured (Stumm and Morgan, 1970, p 330); in these cases contamination due to NH_4^+ oxidation has to be suspected.

The two cores in Hastings Arm exhibit significant differences in their pore water chem-


Figure 41 Biologically mediated redox processes (after Stumm and Baccini, 1978).

Aerobic respiration:

$$(CH_2O)_C(NH_3)_N(H_3PO_4)_P + (O_2)_{C+2N} = (CO_2)_C + (HNO_3)_N + (H_3PO_4)_P + (H_2O)_{C+N}$$

• •

Denitrification:

$$(CH_2O)_C(NH_3)_N(H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 1.4(H_2O)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.8(HNO_3)_C = (CO_2)_C + 0.4(N_2)_C + (NH_3)_N + (H_3PO_4)_P + 0.4(H_2O)_C + (NH_3)_N + (H_3PO_4)_P + 0.4(H_2O)_C + 0.4(H_2O_3)_C = (CO_2)_C + 0.4(H_2O_3)_C + 0.4(H_2O_3)_C + 0.4(H_2O_3)_C = (CO_2)_C + 0.4(H_2O_3)_C + 0.4(H_2O_3)$$

Manganese reduction:

$$(CH_2O)_C(NH_3)_N(H_3PO_4)_P + 2(MnO_2)_C + 4(H^+)_C = (CO_2)_C + (NH_3)_N + (H_3PO_4)_P + 2(Mn^{2+})_C + 3(H_2O)_C$$

Iron reduction:

$$(CH_2O)_C(NH_3)_N(H_3PO_4)_P + 4(FeOOH)_C + 8(H^+)_C = (CO_2)_C + 4(Fe^{2+})_C + (NH_3)_N + (H_3PO_4)_P + 7(H_2O)_C$$

Sulphate reduction:

$$(CH_2O)_C(NH_3)_N(H_3PO_4)_P + \frac{1}{2}(SO_4^{2-})_C = (CO_2)_C + (NH_3)_N + (H_3PO_4)_P + \frac{1}{2}(S^{2-})_C + (H_2O)_C + (H_2O)_C + (H_3O_4)_P + \frac{1}{2}(S^{2-})_C + (H_3O_4)_P + \frac{1}{2}(S^{2-})_C$$

Table 8 Oxidation-reduction reactions in order of decreasing free energy availability.



Figure 42 Distribution of dissolved constituents in core HA-2; all concentrations in μ mol L⁻¹.





 μ mol L⁻¹.



Figure 44 Distribution of dissolved NH_4^+ , PO_4^{3-} and Mo in core AA-4; all concentrations in μ mol L⁻¹.



Figure 45 Distribution of dissolved constituents in core AA-4 PO_4^{3-} , NH_4^+ , H_2S , Fe, Mn and Mo in μ mol L^{-1} ; Alkalinity in meq. L^{-1} ; SO_4^{2-} in mmol L^{-1} .



Figure 46 Distribution of dissolved constituents in core AA-5', PO_4^{3-} , NH_4^+ , H_2S , Fe, Mn and Mo in μ mol L^{-1} ; Alkalinity in meq. L^{-1} ; SO_4^{2-} in mmol L^{-1} .



Figure 47 Distribution of dissolved constituents in core AA-1, PO_4^{3-} , NH_4^+ , H_2S , Fe, Mn and Mo in μ mol L⁻¹; Alkalinity in meq. L⁻¹; SO_4^{2-} in mmol L⁻¹.



istry. At station HA-2 the distribution of the constituents dissolved in the interstitial water indicates that almost the entire sediment column is anoxic. However, H₂S was undetectable in the upper 20 cm of the core and increases in the deeper sediment layers to an approximate maximum value of only 78 μ mol L⁻¹ (Fig 42). It is unlikely that these low values are due to sulphide precipitation, e.g. pyrite formation, because the dissolved iron content of these pore waters is also very low and, after an initial increase, the iron concentrations are unchanged for most of the remaining core depth (see Section 8.2.2.). The low $[H_2S]$ indicates that there is hardly any sulphate reduction going on within the investigated depth, which is supported by the low ammonia and phosphate values determined for these pore waters (Fig. 42). Phosphate and ammonia both increase slightly with depth and reach maxima of 52 and 271 μ mol L⁻¹, respectively. Another indication of low metabolic activity in this core is the lack of change in the organic carbon concentration and the C/N ratio (about 10) from top to bottom (Chap. 4). Since the extent of sulphate reduction controls the pore water concentrations of NH_4^+ , PO_4^{3-} and alkalinity (Sholkovitz, 1973), a theoretical sulphate and alkalinity pore water profile can be inferred for station HA-2. Sulphate will probably decrease only to a very small extent throughout the core depth, with values reflecting the overlying water ($\approx 25.3 \text{ mmol } \text{L}^{-1}$, calculated from the salinity of the bottom water of about 32% as reported by Macdonald, 1984), whereas the alkalinity values will probably increase slightly with depth due to solution of carbonates. The question arises as to why the bacterial activity is so low in this sediment, especially when there is still a significant concentration of organic carbon present ($\approx 1\%$ by weight, see Chap. 5). It is likely that the more easily degradable organic carbon is already consumed by aerobic respiration at the sediment-water interface and the sedimentary organic matter at this station is mainly made up of biologically resistant compounds as has been shown for different sediment types (Sholkovitz, 1973; Westrich and Berner, 1984; Berner and Westrich, 1985). However, it cannot be ruled out that sulphate reduction occurs at a greater depth in the sediment column. An indication for this could be the marked increase of total sulphur in the solid sediment at the very bottom of core HA-2 (Chap. 4).

The situation is quite different at station HA-6. Higher dissolved phosphate, ammonia and H_2S concentrations (Fig. 43) indicate extensive sulphate reduction. Therefore the pore water sulphate should show a decrease with depth. The alkalinity would likely increase, due to formation of HCO_3^- by the microbial activity, the production of NH_4^+ and concurrent reduction of SO_4^{2-} (Presley and Trefry, 1980). Unfortunately, at this point the differences in the interstitial waters of the two cores, HA-2 and HA-6, cannot be explained satisfactorily with the data available.

The nutrient distribution in the pure tailings at station AA-4 indicates that, after the tailings were sitting undisturbed in the inlet for one year, some metabolic activity must have taken place. The nitrate concentration decreases rapidly with depth and is undetectable below 15 cm. The ammonia and phosphate profiles exhibit a striking similarity. In Fig. 44 the depth distribution of the concentrations of NH_4^+ , PO_4^{3-} , and Mo in interstitial water are plotted. It is evident that the increase of the NH_4^+ and PO_4^{3-} concentrations in the upper 30 cm is caused by some bacterial degradation of organic matter. However, below 30 cm depth both NH_4^+ and PO_4^{3-} concentrations decrease as dissolved Mo increases (Fig. 44). Both, ammonia and phosphate increase again with depth as the near the base of the core; Mo decreases in this interval. Since the content of organic carbon stays unchanged throughout the core (see Chap. 4) and there is nothing to indicate a change in the composition of the organic matter, this suggests that Mo, and other dissolved metals may possibly inhibit bacterial metabolism in the pure tailings. Molybdenum, for example, is known to inhibit bacterial sulphate reduction and is commonly used in laboratories to inhibit sulphate reduction (Sorensen et al., 1981; Banat and Nedwell, 1984). The dissolved Mo concentrations in core AA-4 are the highest ever reported for marine sediments, reaching a concentration some 300 times that of the overlying sea water. However, in lab experiments where inhibition is induced researchers usually add 20 mmol L^{-1} Mo as MoO_4 , but it should be noted that no lower limits for this particular inhibition have so far been established.

There is no indication of sulphate reduction in the pure tailings core. In fact, the

sulphate concentrations are slightly higher than would be expected. The sulphate concentration of the bottom water in Alice Arm is about 25.3 mmol L^{-1} , calculated relative to the reported salinity of 32‰(Macdonald et al., 1984). In the pore water of core AA-4 slightly higher sulphate values have been determined ($\approx 27 \text{ mmol } L^{-1}$), however, this cannot be considered significant due to the poor precision of the analytical technique used. Also the H₂S concentration in the pore water is very small (max. 25 µmol L^{-1} ; Fig. 45) and it is possible that these small amounts of H₂S migrated into the tailings from the sediments below (solid phase chemical data suggest that the core ended just a few cm short of penetrating older sediment buried by the modern tailing; see also Chapters 4 and 5). The rather low titration alkalinity values also indicate that there is only minor or no sulphate reduction occuring in this core. The values are quite variable and show no continuous trend throughout the core. Below 50 cm the titration alkalinity suddenly increases from about 5 to 10 meq L^{-1} , representing the influence of the buried sediment. The titration alkalinity above 50 cm may in part be due to lime added during the processing of the ore. This effect is very pronounced at station AA-5',as discussed below.

Station AA-5' was chosen for pore water sampling because the core recovered from this station in the previous year (AA-5) had 15 cm of pure tailing overlying contaminated sediment, and it was hoped to sample this transition again. On visual inspection the recovered core appeared to consist entirely of tailing; however, the chemical analysis revealed a composition of this core close to the natural sediments found in Hastings and Alice Arms. Any indications of ore material, like high K-feldspar, heavy metals (Mo, Pb, Zn) and enhanced Si or Mg values, or a lower Mn and Ni content, are absent from this material. This may be considered a lucky coincidence, as it provides us with a control station where the rate of sedimentation was probably similar to the pure tailings deposit and thus enables us to assess the impact of the ore material on diagenesis even more directly by comparing the pore water chemistry of this rapidly deposited "quasi natural sediment" to that in the pure tailings. The elemental composition of the solid phase is not discussed here, because of its similarity to the natural sediment, and the reader is referred to the appropriate Chapters 4 and 6. The chemical data are listed in Appendix III.

The profiles of the dissolved pore water constituents are displayed in Fig. 46. The high ammonia content of the pore water at station AA-5' indicates strong anaerobe activity in this sediment. In the pure tailings the ammonia content was lower by a factor of 4. The similar organic carbon content in both cores rules out contrasts in substrate concentration as a reason for the increased microbial activity in this core. The phosphate values in the pore water of this sediment appear rather low, assuming a molar ratio for ammonia and phosphate of N:P = 10:1 (Martens et al., 1978 cited in Pedersen, 1984). A similar phenomenon was described by Pedersen (1984) for tailings in Rupert inlet (N-Vancouver Island) and he suggested that phosphate precipitates as carbonate-fluor-apatite, due to high dissolved Ca in the pore waters caused by the addition of lime during the milling and flotation process. The same process could be happening here; however, this can not be verified because Ca concentrations have not been measured in the pore water. An indication that lime is present in this core is the high alkalinity, which cannot be accounted for only by sulphate reduction.

The nutrient distributions at stations AA-8 and HA-2 are very similar (compare Fig. 42 with Fig. 48). Nitrate was detectable with certainty only at the very top of the sediment column. Phosphate and ammonia again show similar distribution profiles; both increase rapidly in the first 20 cm, representing the sediment heavily contaminated with molybdenum-rich mine tailings. NH_4^+ and PO_4^{3-} do not show any further, significant increase with depth, but PO_4^{3-} shows some variability around an average value of 240 μ mol L^{-1} . The dissolved Mo content in the pore water of the heavily contaminated sediment is high, but, unlike the case for the pure tailings, no inhibition of organic matter decomposition can be detected. The sulphate reduction in core AA-8 is not very high; the sulphate concentration decreases only about 3.5 mmol L^{-1} over the length of the core (Fig. 46) and ΣH_2S concentrations in the pore water are low.

In the interstitial water of core AA-1, ammonia increases almost linearly with depth to

a maximum of 1100 μ mol L⁻¹ at the 40-45 cm depth interval (Fig. 48). The rapid increase of NH₄⁺ suggests that the sediment becomes anoxic within the first few centimetres. Below 45 cm the ammonia concentration decreases slightly (Fig. 48). The phosphate distribution does not follow NH₄⁺ as closely as in the pore waters of the Hastings Arm sediments and core AA-8, but the two nutrients share a common maximum at the 40-45 cm depth interval with the titration alkalinity (Fig. 48). At the maximum, the alkalinity is 16.5 meq L⁻¹ and drops to 11.5 meq L⁻¹ in the 45-50 cm depth interval. The cause for this is most likely a sediment layer with enhanced microbial activity and, in fact, the organic carbon content has a significant peak at the very same depth (Chap. 5). The sulphate distribution is a mirror image of the above described constituents, having a distinct minimum at this depth, which, as might be expected, appears to be accompanied by a maximum in the Σ H₂S concentration.

7.3 METAL DISTRIBUTION IN THE INTERSTITIAL WATER

The vertical distributions of dissolved Mn^{2+} and Fe^{2+} in interstitial water of coastal marine sediments have been well studied over the past two decades, and processes affecting their fate in the sediment are well understood (Table 8, Fig. 41). With this knowledge it is possible to derive theoretical distribution profiles for Mn and Fe in pore waters (e.g. Elderfield, 1976; Berner, 1980; Fig. 49). Although the behaviour of other metals, such as molybdenum, and the mechanisms involved in their diagenetic controls are still not completely resolved, some models have been suggested to help understand their cycling in the marine environment (Bertine, 1972, 1973; Pedersen, 1979). In the following sections the distribution of Mn, Fe and Mo in interstitial water will be presented and the implications of mine-tailings on their distribution is discussed.



Figure 49 Theoretical profiles of interstitial constituents.

7.3.1 Distribution of Mn²⁺

A significant amount of Mn incorporated in sediments is in the oxide form MnO_2 . As the sediment column becomes anoxic with depth, MnO_2 , acting as an electron acceptor during the bacterial decomposition of organic matter, is reduced to Mn^{2+} . This reduction occurs soon after the depletion of dissolved oxygen in the interstitial water, and therefore the maximum of dissolved Mn^{2+} is close to the oxic/anoxic boundary in the sediment column (Calvert and Price, 1972). From there dissolved Mn^{2+} diffuses upward into the overlying water, where it reoxidizes and precipitates. These precipitates commonly get incorporated in Mn-nodules which have been observed in fjords by various investigators (Calvert and Price, 1970; Grill, 1978). In deeper parts of the sediment column the dissolved Mn^{2+} concentration is controlled by saturation with respect to pore water carbonate and precipitation of authigenic minerals, most commonly as a mixed Mn-Mg-Ca carbonate, which is considered the main reason for the rapid decrease of dissolved Mn^{2+} concentrations with depth (Calvert and Price, 1970, 1972; Holdren et al., 1975; Grill, 1978; Pedersen 1982); but incorporation of Mn into pyrite framboids has also been shown to occur in significant amounts (Pedersen, 1979).

The vertical distribution of dissolved Mn^{2+} in core HA-2 (Fig. 42) looks very similar to the theoretical interstitial Mn profile. However, compared to the Alice Arm sediments, there is only a rather small amount of dissolved Mn^{2+} . This is probably due to the lower content of Mn in the solid sediment, compared to the Alice Arm cores (Chap. 4). The dissolved Mn^{2+} concentration is already high at the very top of the core, indicating that the oxic/anoxic boundary must be very close to the sediment-water interface. A further small increase brings the interstitial Mn concentration to a broad maximum of 77 μ mol L^{-1} between 10 and 20 cm. Below 25 cm the average Mn content of the pore water drops to 35 μ mol L^{-1} . The low Mn concentrations in this core are probably insufficient to cause precipitation of Mn-carbonates, and therefore it appears more likely that the consumption of Mn at depth, as seen in Fig. 42, is caused by co-precipitation with metal sulphides, most likely FeS. The interstitial Mn at station HA-6 does not have a pronounced subsurface maximum, as would be expected from the theoretical profile (Fig. 43). In the upper 35 cm the average Mn^{2+} concentration is 5 μ mol L⁻¹ and it steadily increases in the deeper parts of the core, where the impact of the Anyox mining effluents subsides again, and reaches a maximum value of 23 μ mol L⁻¹.

In the interstitial water of the pure tailings dissolved Mn^{2+} shows a pronounced maximum at the very top (Fig. 45), which probably indicates that anoxic conditions already exist at shallow depth. These high initial Mn values are probably caused by dissolution of Mn-oxides that were deposited on top of the tailings, after the cessation of the mining operations. High concentrations of dissolved Mn²⁺ close to the sediment-water interface probably cause substantial amounts of Mn^{2+} to diffuse into the overlying water from where it precipitates upon oxidation to MnO_2 . This precipitate becomes incorporated into a thin layer of loose, brown, flocculent material which could be seen during core collection on top of the light grey tailings and which probably consists mainly of organic matter and Fe and Mn oxides. The recovery of this undisturbed surface layer is also a good indicator that the top of the core was not disturbed by the sampling method employed. Below the initial maximum the dissolved Mn^{2+} concentration drops sharply to an average of about 20 μ mol L^{-1} and stays at this level for most of the core, because in the deeper parts is hardly any Mn-oxide available to be remobilized from the unweathered mine-tailings. Towards the bottom of the core the influence of older sediment underneath the tailings obviously causes the Mn concentration to rise again.

Because of unforeseen problems, which arose during sample storage, the values reported here for the interstitial metal concentrations at station AA-5' might not represent the actual concentrations in this core. After returning to the lab, the metal samples, which were stored frozen in preacidified containers (see Appendix II) were all checked before analysis to ensure that their pH was about 2; however, the pore water samples of core AA-5' all had higher pH and additional acid had to be added to adjust the pH to the required level. The samples were then left sitting on a clean air laminar flow bench for one week at room temperature, to allow any precipitated metal to re-dissolve. From the profile in Fig. 46 it can be inferred that Mn was not affected by this to a great extent. except for a subsurface maximum in the 6-10 cm interval, dissolved Mn is low throughout most of the core, which is probably due to absence of remobilizable Mn-oxides in the unweathered rock debris.

In core AA-8 the dissolved Mn^{2+} increases to a small maximum of almost 500 μ mol L^{-1} at the 3-6 cm interval. With greater depth the Mn^{2+} concentration drops to 300 μ mol L^{-1} , only to increase rapidly to a second maximum of 800 μ mol L^{-1} at 20-25 cm depth (Fig. 48). This second peak is directly below the boundary separating sediment heavily contaminated with modern tailings from sediment with minor contamination (Chap. 4,5). Thus, this enhanced interstitial Mn^{2+} concentration could be due to dissolution of MnO_2 associated with the old sediment surface which existed before B.C. Molybdenum went into operation. This is supported by enhanced Mn content in the solid sediment of the same depth interval (Chap. 4). Therefore, there existed a large pool of reducible Mn-oxides which were dissolved as the sediment column became anoxic. With increasing depth the Mn²⁺ concentrations decrease rapidly to about 400 μ mol L⁻¹, likely due to carbonate precipitation.

The manganese distribution in the pore waters of core AA-1 (Fig. 47) does not seem to be complicated by the influence of any tailings material. The pore water concentrations of dissolved Mn^{2+} have a maximum at the top of the sediment column, indicating rapid depletion of dissolved oxygen and the establishment of anoxic conditions in the first few centimetres of the core. With depth the manganese concentrations rapidly decrease and settle down at an average of 105 μ mol L⁻¹.

7.3.2 Distribution of Fe^{2+} in interstitial water

The most soluble iron species in interstitial water is Fe^{2+} . Most of the iron in solution is probably contributed by bacterially-mediated reduction of iron oxides and hydroxides. This causes the concentration of dissolved Fe^{2+} in the pore waters to increase to a maximum level which often exceeds the solubility product with respect to sulphide. Therefore FeS will precipitate in the deeper parts of the sediment column and in this way limit the concentration of interstitial Fe^{2+} . In an ideal case, these constraints generate the vertical distribution seen in Fig. 49.

The dissolved iron levels in core HA-2 are not very high (Fig. 42). The interstitial iron concentration increases to a maximum of 43 μ mol l^{-1} within the upper 15 cm of the core. Below the maximum the concentrations are only insignificantly reduced to an average value of 32 μ mol L⁻¹. In the last sample the dissolved Fe²⁺ drops to 4 μ mol L⁻¹; this could be a sampling artifact, but precipitation of FeS is also possible.

The vertical distribution of dissolved interstitial iron in core HA-6 is very similar to the theoretical profile displayed in Fig. 49. The iron concentrations are about four times higher than at station HA-2 (Fig. 42, 43). This difference probably reflects the higher content of labile Fe in the solid sediment at station HA-6 (Chap. 4,6) which was probably contributed by the Anyox mining and smelting operation.

In the interstitial water of the pure tailings (AA-4) the dissolved Fe content is also very low (Fig. 45), but still about twice as high as at station HA-2. A small maximum is evident in the 3-6 cm interval, where the Fe²⁺ concentration reaches 74 μ mol L⁻¹. Below this horizon, the values drop to an average of 45 μ mol L⁻¹, until, from 25 cm on downwards the interstitial Fe²⁺ increases steadily with increasing depth and attains a maximum value of 250 μ mol L⁻¹ in the very bottom of the core (Fig. 45). This increase of dissolved Fe with depth points again to the influence of the older sediment which underlies the base of the tailings near the bottom of the core.

Due to the difficulties encountered during the storage of the samples from station AA-

5' (see above), the distribution of dissolved iron does not correspond to what would be expected from the nutrient and sulphide distribution (Fig. 47). The iron profile does not display a subsurface maximum as seen in the other cores. However, the almost constant values around 200 μ mol l⁻¹ throughout the core could also be caused by a limited availability of reducible Fe in this unweathered rock debris.

The vertical distribution of dissolved Fe^{2+} in the interstitial water of core AA-8 looks exactly like that predicted by the theoretical profile (Fig. 48, 49). In the top sample no Fe was detectable. Then the concentration rapidly increases to a maximum of 260 μ mol L^{-1} at the 10-15 cm interval. From there it steadily decreases with increasing depth.

The situation is similar at station AA-1, except that the maximum is not as sharply defined (Fig. 47). This may be due to the difference in availability of labile Fe (iron oxides and hydroxides) at this station, close to the main sediment input at the head of the inlet.

7.3.3 Distribution of Mo in interstitial water

The vertical distribution of molybdenum in the interstitial waters of Hastings and Alice Arms is shown in Figs. 42 to 48. The dissolved Mo profile in the natural sediments of station HA-2 shows an initial increase from 0.11 to a maximum of 0.14 μ mol L⁻¹ at 3-6 cm depth; below this point the concentration steadily decreases with depth. This distribution looks similar to interstitial Mo profiles described by various workers for natural sediments deposited in oxygenated water (Hogarty, 1985; Malcolm, 1985; Pedersen, 1985; Seralathan and Hartmann, 1985), whereas Lyons et al. (1980) and Brumsack and Gieskes (1983), who looked at organic-rich sediments, find interstitial Mo increasing with depth. The dissolved Mo at station HA-6 (Fig. 43) behaves in a very similar fashion to that in core HA-2 (Fig. 42). At both stations the last sample shows a significant increase compared to the rest of the profile. This could be due to a sampling artifact, or it may be caused by a release of Mo, initially coprecipitated with amorphous FeS and later remobilized, as FeS crystallized to FeS₂ (Korolev, 1958; Bertine, 1972; Lyons et al., 1980); this suggestion is discussed further in section 8.3. The vertical distributions of interstitial Mo at stations AA-1 and AA-8 look similar to the profiles obtained from the natural sediment of Hastings Arm. In all these cores the interstitial Mo has a distinct subsurface maximum; however, the values for the two Alice Arm cores are about 10-30 times higher. In addition, the peaks in the pore water Mo profiles of cores AA-1 and AA-8 coincide more or less with high Mo values in the solid sediment (Fig. 50).

There is also a subsurface maximum of interstitial Mo in the pure tailings of core AA-4 (Fig. 50) which seems to be caused by diagenetic processes. A second maximum in the deeper parts of the core is obviously controlled by the Mo content of the solid sediment (Fig. 50).

At station AA-5' the distribution of dissolved Mo in the pore water reflects, like at station HA-2, the sea water value of about $0.1 \,\mu$ mol L⁻¹. In the 3-10 cm depth interval a slight subsurface enrichment has developed (Fig. 46), but in the remaining part of the core the Mo concentrations are almost constant.

The data from station AA-4 and 5' suggest, that the biological activities, and hence the diagenetic processes in the pure tailings are somewhat inhibited, but not totally suppressed. It may therefore take more time to establish natural conditions in the tailings as compared to ore-free material deposited under similar conditions; however, natural processes will sooner or later control the diagenetic reactions in the tailings.

7.4 DISCUSSION

In both natural and contaminated sediments of Hastings and Alice Arms, the vertical distributions of dissolved metals in the pore waters looks quite similar. After a rapid initial increase to a maximum, the dissolved metal values decrease again with depth. The processes governing these distributions are well known for Mn and Fe (Table 8, Fig. 41), as discussed earlier. The iron and manganese distribution in the interstitial water of the Hastings and Alice Arm can thus be used to assess the diagenetic state of the sediment column at certain depth intervals and compare this to the distribution of Mo.

120





At most locations the distribution of Mn in the pore waters can be easily explained by the processes described previously. However, at station AA-8 the interstitial Mn profile shows two peaks (Fig. 48). The upper peak can be explained by diagenetic remobilization of deposited Mn-oxides into solution and the lower peak by dissolution of Mn at an old surface enrichment. Due to the rapid sedimentation at this site, diffusion cannot keep pace with the accumulating sediment; the second maximum at the 20-25 cm interval thus represents release of Mn to solution at this depth which has not yet reached steady-state equilibrium with respect to the whole core. The approximate time it will take for this Mnprofile to reach diffusive equilibrium can be estimated by using Li and Gregory's (1974) diffusion coefficient, which is $\approx 3.8 \times 10^{-6}$ cm² sec⁻¹, corrected for *in situ* temperature ($\approx 5^{\circ}$ C) and tortuosity. Given a length scale of 25 cm, therefore, it will take about seven years after all reducible Mn is mobilized, for diffusion to eliminate the concentration gradient between the source interval and the sediment-water interface.

The concentration of Fe^{2+} , the reduced form of the next oxidant (Fe^{3+}), is low in the top few centimetres of the sediments and, due to bacterial activity, it usually rapidly increases to a maximum. But, like the case of manganese, the exact pathway of the reduction from Fe (III) to Fe (II) has not yet been determined; the most recent descriptions about the reduction process suggest only that Fe acts as an electron sink for non-photosynthetic bacteria, but it is not yet clear whether Fe-oxides are directly utilized in bacterial metabolic processes (Salomons and Förstner, 1984). Despite the fact that the processes involved in the reduction of Fe (III) are not understood in complete detail, the environmental conditions at which the reduction takes place can be determined fairly accurately. Just as the reduction of MnO_x parallels nitrate reduction, the formation of reduced Fe (II) accompanies sulphate reduction (Salomons and Förstner, 1984). Given the known controlling factors one can construct a theoretical profile of dissolved iron in interstitial water; such a profile is presented in Fig. 49.

Compared to the other pore water stations in Alice Arm, the concentrations of interstitial Fe^{2+} in the pure tailings (AA-4) are very low. This may be attributed to a limited availability of reducible Fe-oxides in the tailings, since they were never exposed to weathering and, in addition, the total Fe content of the solid tailing material is only half that of contaminated and natural sediment (Chap. 4). The increase of both, dissolved Fe^{2+} and Mn^{2+} in the pore water of the pure tailings towards the bottom of the core can not only be explained by variations in the solid phase. This increase is most likely caused by the proximity of the buried sediment, from where Fe and Mn can diffuse upward into the tailings.

The dependence of dissolved interstitial Fe on the amount of Fe in the solid sediment is clearly demonstrated in core AA-1. Although the diagenetic control is definitely significant at this station, the differences in the iron content of the solid sediment dominate the distribution of interstitial iron. In this core the highest interstitial iron concentrations were found. This is likely caused by a higher iron-oxide content in these sediments close to the river input. The principal form of iron-oxide at this location is probably magnetite, which, due to its high density (D = 4.7-5.3) settles out rapidly and becomes incorporated in the sediment.Karlin and Levi (1983) showed that the dissolution of magnetite occurs in significant amounts in marine sediments. The variations of the dissolved Fe²⁺ content in the pore water indicates that the dissolved constituents are not in a diffusive equilibrium.

At station AA-8 diagenetic processes are the most important factor influencing the distribution of Fe^{2+} in the pore water. In the top of the sediment column solution of iron-oxides causes remobilization and in deeper parts of the core precipitation of FeS is probably the controlling mechanism.

Because of its complex chemistry the geochemistry of molybdenum is rather complicated, compared to Mn and Fe. A chemistry professor at the turn of this century used to describe the chemical behaviour of Mo in his lectures as "ambidexterous, bi-sexual and bigamous". This is why processes controlling the distribution of Mo in the marine environment are not very easily described. In natural waters with a pH \geq 7, Mo usually exists as the molybdate ion MoO₄²⁻ and appears to be a conservative constituent in seawater with concentrations of 8-12 μ mol L⁻¹ (Head and Burton, 1970). In acidic environments Mo forms polymolybdates and polymolybdic acids which, due to their large size, are effectively less mobile. The chemical behaviour of Mo in such environments is similar to that of silicon (Lindqvist, 1950; Sasaki et al., 1959). At slightly acidic pH values MoO₄²⁻ can also coprecipitate with Fe (III) hydroxide, but this mechanism is not favoured at normal sea water pH, and is impossible above pH 9 (Kim and Zeitlin, 1969; Hem, 1977). Therefore, an important association of Fe-Mo as hydroxide precipitates in sea water and marine pore waters as suggested by Hogarty (1985), is not very likely.

In anoxic environments, however, coprecipitation of Mo with iron sulphides has been described as an important initial removal process of Mo from solution (Korolev, 1958; Pilipchuk and Volkov, 1968; Bertine, 1972; Pilipchuk and Volkov, 1974; Malcolm, 1985). This coprecipitation has been examined experimentally by Korolev (1958) and Bertine (1972) who showed that Mo is efficiently removed from solution at seawater pH. According to Bertine (1972), the relevant reaction is:

$$\mathrm{FeS_{amorphous} + MoO_2S_2^{2-} + H_2S + 2H^+ = FeS \cdot MoS_{3_{amorphous}} + 2H_2O}$$

As the FeS \cdot MoS₃ solid solution ages, tetragonal mackinawite (FeS) is formed and discrete MoS₃ is precipitated.

Other researchers have suggested Mo is added to the sediments via scavenging by Mnparticulates (Berrang and Grill, 1974), by Mn-oxides, especially Mn⁴⁺-oxides (Krauskopf, 1956; Pilipchuk and Volkov, 1974; Shimmield and Price, submitted) and by ferromanganese nodules (Calvert and Price, 1970; Calvert and Piper, 1984), or they have noted an association with sedimentary organic matter (Jones, 1973; Contreras, 1978; Brumsack and Gieskes, 1983; Calvert and Price, 1983; Malcolm, 1985). In addition, a significant amount may be added to the sediment by adsorption to any kind of particulates (Bertine, 1972). There is still some controversy about the importance or the possibility of some of these processes. Calvert and Price (1983) point out that oft-made positive correlations of organic matter with metals in solid sediment are possibly indirect, and a possitive correlation may be caused only by grain size effects.

The main processes governing the distribution of interstitial Mo are, therefore, similar to the control mechanisms for Fe and Mn, namely, oxide dissolution, sulphide precipitation and adsorption onto organic matter (Bertine, 1972; Calvert and Morris, 1977; Pedersen, 1985).

These mechanisms may explain the vertical distribution of interstitial Mo at stations HA-2 and 6 (Fig. 42, 43). In cores AA-1 and AA-8 the vertical distribution of pore water Mo looks very similar to the profiles from Hastings Arm, only that the concentrations are about 30 times higher. These increased amounts of dissolved Mo can not be accounted for by an increased scavenging rate of Mo from the water column, because the Mn-oxide content of the contaminated sediments appears to be smaller than that in the natural sediments. Hence, scavenging by MnO₂ from the water column would be minimal. It could be suggested that this may partially be balanced out by the increased sedimentation rate due to the dumping of tailings. A larger particulate load could hence provide increased surface area for Mo adsorption. But, because the adsorption process is rather slow (Bertine, 1972), and most of the tailings material has a fairly short residence time in the water column, due to their grainsize and the dumping methods used, this will likely have no significant effect on the amount of Mo incorporated into the sediments from the overlying water. Thus, processes within the sediment acting upon the deposited tailings material must be responsible for the increased Mo concentrations. This is clearly depicted in Fig. 50, where interstitial and solid phase Mo distribution for the three Alice Arm cores discussed here are plotted together. The direct dependency of the interstitial Mo concentration on the Mo content of the sedimented material is even more obvious if the porewater versus the solid phase data are plotted for core AA-4 (Fig. 51). The upper part of the core seems to be already affected by diagenetic processes, whereas, in the deeper parts of the core any bacterial activity which could cause the chemical environment in the sediment to change, appears to be fairly subdued. This is also indicated by the lower NH_4^+ and PO_4^{3-} concentrations in this part of the core (Fig. 44). The values for the lower part of the core





plot along a straight line which goes through the origin. This proportionality suggests that here the dissolved Mo concentrations are controlled directly by the amount of Mo in the solid phase.

The solution of Mo from the solid phase can happen in two different ways. A significant amount of MoS₂ can be oxidized during the milling of the Mo-ore, forming a coating of MoO₃ on the molybdenite grains (Castro, 1979). MoO₃ is highly soluble in water at a pH ≥ 6 and upon solution it converts into the ionic form MoO_4^{2-} . In addition, it can be seen from the Eh/pH diagram (Fig. 52) that MoS₂ is not very stable in aqueous solutions and dissolves at seawater pH even under mildly reducing conditions.

The highest dissolved Mo concentrations are found in the pure tailings of core AA-4. In the cores where tailings are mixed with natural sediments, the interstitial Mo values are about one order of magnitude lower (4 vs 30 μ mol mol L⁻¹) in samples with an equally high Mo content in the solid phase, indicating that a significant amount of soluble Mo in the discharged tailings material must have dissolved during the transport of the sediment and thus have been released to the water column. In the upper part of the tailings the Mo distribution is clearly controlled by diagenetic processes. The Mo maximum in the 3-6 cm interval in the pore water profile of core AA-4 is caused by dissolution of Mo-oxides and molybdenite and the decrease between 6 and 25 cm is likely controlled by coprecipitation with FeS. At station AA-1 and AA-8 the same mechanisms must be operating and this may be the explanation why the maxima of the solid and the pore water Mo do not match exactly (Fig. 50).



Figure 52 Eh/pH diagram for aqueous Mo species after Titley and Anthony, 1961.

The high Mo concentrations found in the pore waters of Alice Arm sediments will certainly result in diffusion from the sediment into the overlying water. The possible diffusive flux of Mo can be estimated using Fick's First Law

$$J_{z} = rac{D_{j}^{\circ}}{F} \cdot \phi \cdot rac{\mathrm{d}c}{\mathrm{d}z}$$

where $J_z =$ flux,

- D_j° in situ diffusion coefficient at 5°C for Mo, $\approx 5.542 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ (Li and Gregory, 1974) $F = \phi^{-m}$, with $m \approx 2.5$ (Ullman and Aller, 1982)
- $\phi = \text{porosity} \approx 0.7 \text{ (estimated)}$
- $\frac{\mathrm{d}c}{\mathrm{d}z}$ = concentration gradient = $4.6x10^{-3}\mu mol\,cm^{-4}$

Assuming, Mo diffuses only out of the pure tailings, and that about 7 km² of the floor of Alice Arm are covered with fresh mine tailings from the AMAX operation, then there could be a diffusive flux of $\approx 1.6x10^4$ mol a⁻¹ or 1535 kg a⁻¹ Mo from the mine tailings into the overlying water. This flux will add about 4.3% dissolved Mo per year to the inventory of $9x10^5$ mol (based on an estimated deep water volume in the inlet of about 4.3 km³ and an average Mo content of sea water of 0.1 μ mol L⁻¹) and a maximum residence time of one year for the water in the inlet (Krauel, 1981). This estimate is very probably an upper limit, and suggests that the diagenetic release of Mo to the inlet deep waters from deposited tailings is minor but may be measureable.

8. SUMMARY

In this thesis the effects of mine tailings disposal on the geochemistry of sediments in Alice Arm have been described. Geochemical evidence was used to distinguish tailings and contaminated sediment from natural sediment. Pore waters of these sediments have been analysed to evaluate the diagenetic processes which occur in the sediments of Hastings and Alice Arm.

The mining activity in this area has a long history and the earliest mining operations date back to almost the beginning of this century. In the Alice Arm sediments two major periods of tailings disposal could be distinguished in the investigated depth of the sediment column. The uppermost parts of the sediment in Alice Arm are contaminated with tailings from the recent mining operation at the Kitsault Mo deposit, and in deeper parts of the collected cores the impact of an older mining venture, most likely the Dolly Varden Silver Mine, could be determined.

The natural sediments of both Alice and Hastings Arms are very similar due to adjoining source areas which cover geologically-related terrains. This is expressed by the same mineralogical composition of the natural sediment in both inlets, with the main components being quartz, feldspar, kaolinite, micas and chlorite. The mineralogy of the tailings is not very different from the natural sediments, because the two major mineral groups, quartz and feldspars, are present in both sediment types in about equal amounts. However, the modern Mo mine tailings can be distinguished easily from the natural sediment, because chlorite and kaolinite are almost completely absent in pure tailings, and the feldspars consist mainly of oligoclase, which is of secondary importance in the natural sediment compared to plagioclase. In the tailings previously deposited by the Dolly Varden operation the most important mineralogical difference is undoubtedly the presence of barite. In most samples contaminated with the Dolly Varden tailings, the presence of barite was verified by isolating it in a heavy mineral fraction.

Small variations in the abundance of the different major and minor elements in the

natural sediments of both inlets are consistent with the mineralogical data and indicate a single, fairly homogeneous source for the sedimented material.

The most important differences between the compositions of the natural sediments and the two tailings types, as revealed by the chemical analysis, are highlighted here. The contrasts in the elemental composition result from the distinctly different sources for the two sediment types; the natural sediments are derived from formations with a great abundance of basaltic rocks and are therefore characterised by a rather large content of mafic minerals, whereas the Mo-ore is hosted by granodiorites and quartz-diortes which are intrusive into the Bowser Lake Group. The tailings therefore reflect the chemistry of a felsic rocktype. This provenance explains, why the Si content of the modern tailings is considerably higher than that in the natural sediments, while Ti, Fe and Mg, in contrast, are much less abundant in the tailings, due to their association with mafic minerals. Cr, Ni and V, which are also hosted mainly by mafic minerals, are also depleted in the modern tailings. Pb and Zn are enriched in both tailings types found in Alice Arm, and can be used to indicate contamination of natural sediments with tailings. The high concentration of Mo in the tailings, however, makes this element the best specific indicator for contamination with materials from the B.C. Molybdenum and AMAX operations.

The increased amounts of K-feldspar in the modern tailings are reflected by K and Rb concentrations higher than background; Rb is included because it can readily substitute for K in the crystal lattice, and therefore parallels variable K contents in any source material. The older tailings resulting from the Dolly Varden operation can be identified by their enhanced concentrations of Ba and Sr, which is due to the large amounts of barite associated with these tailings. Except for the enrichment in Fe, Pb and Zn and the higher barite content, the chemical composition of the Dolly Varden tailings is very similar to that of the natural sediment, which indicates that this ore body, unlike the Kitsault deposit, is hosted in rock tpyes similar to those comprising the sources for the natural sediment.

The mineralization in the study area produced generally sulphidic ores and it was shown

as a result that the S content of the sediment can serve as a rather sensitive indicator of contamination with either of the two tailings types.

The major and minor element analysis provided a sound geochemical context for the explanation of the diagenetic processes which were implied by the pore water data. The dissolved nutrient distributions in the interstitial water indicate that the sediment at the sampled locations becomes anoxic within the first few centimetres below the sediment water interface. This is clearly reflected in the distribution of dissolved Fe and Mn in these sediments, which generally show a rapid increase in their concentration within the upper 10 to 15 cm of the sediment, due to dissolution of their respective oxides. In the deeper parts of the cores consumption of the metals from solution is observed, which is almost certainly due to precipitation of authigenic components. The distribution of the interstitial nutrients and Fe and Mn concentrations allows a reasonably detailed assessment of the diagenetic environment and so provides a well established background which is used to interpret the distribution of dissolved Mo in the pore waters. In the natural sediments of Hastings Arm, the vertical distribution of Mo closely resembles interstitial Mo profiles which have been reported recently by a number of researchers. In the pure tailings, however, the dissolved Mo concentrations greatly exceed any values previously reported for saline pore waters, reaching concentrations some 300 times that in the overlying water. Such high Mo concentrations in the pure tailings must support a flux of Mo from the sediment into the overlying water column. It is shown that such a flux could add up to 3.9% to the natural dissolved Mo inventory in the deep water of the inlet. Dissolved Mo concentrations in interstitial water of Alice Arm sediment contaminated with modern tailings are also higher than reported for any natural sediment so far, but the concentrations are not high enough to cause significant diagenetic release of Mo from these sediments into the overlying water. It is speculated that the Mo is released into solution from MoO_3 , a soluble alteration product of MoS_2 which probably forms during milling of the ore.

This thesis has established the impact of tailings deposition on the sediments in Alice Arm and it has been shown that remobilization of Mo occurs which must result in the release of some dissolved Mo into the overlying water. This release, however, is not believed to have a significant effect on the dissolved Mo inventory in Alice Arm, considering the frequent water renewal in the inlet. Further research should be carried out to determine the diagenetic fate of other metals, such as Pb and Zn, enriched in the tailings, which could be potentially mobilized from this widespread anthropogenic deposit.

APPENDICES

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Appendix I: Sample collection and initial sample preparation

During two cruises to Alice Arm in September 1982 and September/October 1983, a total of 28 cores were collected in Alice Arm and the neighbouring inlets. The cores were recovered with a stainless steel gravity corer, as described by Pedersen *et al.* (1985), using an 8 cm inner diameter butyrate core barrel. With this coring device no core catcher is used which allows relatively undisturbed sampling of the sediment water interface.

Upon recovery of the cores, the supernatant water was carefully drained and the sediments were extruded immediately from the core barrel by manual insertion of a PVC piston. The sediments were subsampled in 1 to 2.5 cm thick sections, put into capped plastic containers and frozen immediately for the transport to the laboratory in Vancouver. The sediment samples used for extracting pore water were extruded into a nitrogen filled glove box to avoid oxidation of the samples. Procedures employed for the pore water recovery are described in Appendix II.

After returning to the laboratory at UBC, the samples were thawed and initially homogenized in the sample containers by stirring for a few minutes with a plastic spatula. A subsample of about twenty grams was taken and dried overnight at about 75° C, ground in 5-10 gram splits in a tungsten carbide "Herzog" disc mill for two minutes, and finally again homogenized in a shaker.
Appendix II: Analytical methods

II.1 Pore water sampling and analysis

All containers used for pore water sampling were thoroughly washed, acid cleaned and rinsed with distilled deionised water (DDW) to avoid possible sample contamination.

The cores collected for pore water sampling were clamped directly underneath a plexiglass glovebox flushed with N₂, and the sediments were extruded into the glove box through an O-ring sealed port in the base, by slowly jacking up a piston inside the core barrel. The sediment was subsampled in three to five centimetre thick intervals, in order to get enough pore water for all the projected analyses. The sediment slices were loaded into 250 ml nitrogen flushed centrifuge bottles, and centrifuged for about 10 minutes at ≈ 2000 rpm. The supernatant was carefully decanted into acid-cleaned disposable syringes (50 ml capacity) and expressed through a 24 mm diameter 0.45 μ m Millipore precleaned filters in attached Swinnex holders. The first few drops of the filtered pore water were always discarded, to avoid dilution with trapped DDW which was used for final rinses of the filters. The samples were filtered directly into acid cleaned linear polypropylene (LPE) bottles and immediately split into aliquots for the different analyses. Eight ml of pore water were placed in 30 ml LPE bottles which contained sufficient acid (Merck ultrapure HCl) to reduce the pH of the sample to about 2. Two ml of interstitial water were taken for H_2S analysis; H_2S in the pore waters was immediately precipitated as ZnS by reaction with Zn-acetate added prviously to each subsample bottle. Six to eight ml samples were reserved for subsequent nutrient analyses and the remainder was stored in pre-weighed sample bottles to be used for sulphate and alkalinity determination.

II.2 Titration alkalinity

The alkalinity of the pore waters was determined by direct titration of the sample with a strong acid, as described by Edmond (1970) and Gieskes and Rogers (1973). The titrations were done in the original sample containers to ensure that any $CaCO_3$ which might have precipitated during storage was included in the analysis. The titration was carried out with a 2 ml Gilmont micrometer burette, titrating 0.1 N HCl into the sample while constantly measuring the pH (in mV) with a electrode submerged into the sample. For the pH measurement a Corning 130 pH meter, calibrated against BDH buffer solutions, was used. The samples were stirred throughout the titration with a magnetic stirrer. The bicarbonate end point of the titration was determined by extrapolating the linear portion of a Gran function, as described by Gieskes and Rogers (1973), who report an accuracy of this method of 0.5%. At least 12 measurements were recorded in the 3.5-2.5 pH range where the Gran plot is linear. Alkalinity was subsequently calculated using a computer program written by T. Webb.

II.3 Sulphate

The sulphate content of the pore waters was measured by an indirect titration technique as described by Howarth (1977). This method involves removal of interfering metal ions by collecting sulphate precipitated as $BaSO_4$ in an acidic EDTA solution on a filter and redissolving it in excess EDTA at high pH. The excess EDTA is then titrated with MgCl₂. The specified eriochrome black-T dye changes colour from purple-blue to red-pink as soon as free Mg²⁺ ions are available. However, because the colour change at the endpoint of this titration is not very pronounced, determination of the endpoint is rather subjective. This limits the precision of this titration and for future analyses the use of a different method is suggested.

II.4 Nutrient analysis

Interstitial silicate, phosphate and ammonia were measured on board ship, employing the methods described in Strickland and Parsons (1972) scaled down to fit the small sample size of pore waters. All three nutrients were determined by colourimetric techniques using a Bausch and Lomb Spectronix 21 spectrophotometer and 1 cm optical glass cells. Although Strickland and Parsons (1972) recommend the usage of 10 cm cells, 1 cm cells were found to be sufficient for pore water analysis, as we are dealing with much higher nutrient concentrations than in seawater. In fact, the samples usually had to be diluted up to 50 times in order to stay in the measuring range of the spectrophotometer. The colour complexes were developed in 6 ml disposable plastic test-tubes by adding the reagents directly to the (diluted) pore water samples.

Replicate analyses of sea water with the down-scaled methods gave an overall precision of $\pm 2.5\%$ for silicate, $\pm 3\%$ for phosphate and $\pm 5.6\%$ for ammonia.

II.5 H₂S determination

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Hydrogen sulphide was determined using the method described by Cline (1969). This method is principally based on the reaction of H_2S with N,N-dimethyl-phenylenediamine sulphate which, in acidic medium with FeCl₂ as catalyst form methylene blue which can be measured colourimetrically. The diamine solutions were standardized by measuring a known amount of Na₂S dissolved in oxygen free water. The colourimetric measurements were made on a Bausch and Lomb Spectronix 2000 spectrophotometer and, if necessary, the samples were diluted after colour development to stay below 0.4 absorbance, because aqueous methylene blue solutions do not conform strictly to Beer's Law at higher concentrations (Cline 1969). Replicate analysis of a standard gave an overall precision of $\pm 3\%$ (n=12, 1 σ).

II.6 Dissolved Fe, Mn and Mo

Interstitial Fe, Mn and Mo were determined by flameless atomic absorption spectrophotometry, using a Perkin Elmer 560 model spetrophotometer with a HGA 400 programmable graphite furnace assembly.

All samples were analyzed by injecting pure or diluted interstitial solutions directly into the graphite furnace. Dilution was required for all Fe and Mn analyses and the samples from the pure tailings core also had to be diluted for the Mo analysis. The dilution was done by transferring the needed amounts of sample and acidified artificial sea water (pH=2) with calibrated Eppendorf pipettes into acid cleaned plastic test-tubes and mixing these solutions with a vortex generator. All standards used for calibration were also prepared in acidified artificial sea water. The calibration for Mo turned out to be very difficult, which is probably partially due to Mo-carbides formed in the graphite tubes during atomization, causing a memory effect. A number of different possibilities have been tried, and the best results were obtained using aged pyrolytically coated graphite tubes with the instrument settings listed in Table 10

The precision of the analyses was $1.6\% 1\sigma$ for Fe (n=10), $3.4\% 1\sigma$ for Mn (n=9) and $2.5\% 1\sigma$ for Mo. The heating program for the graphite furnace was designed to dry the sample in the first three or four steps. Then the temperature was raised slowly to allow residual sea salt to burn off before the actual atomization of the analysed element began.

II.7 X-ray diffraction analysis

Element: Fe Matrix: SEAWATER

Tube Type: _____ PYROLYTICALLY COATED

Sample Aliquot: <u>10 uL</u>

Keyboard Entries

STEP	1	2	3	4	5	6	7	6
TEMP (°C)	100	110	120	250	1000	1200	2700	
RAMP TIME* (s)	10	515	30	20	20	20	0	
HOLD TIME (s)	10	10	15	15	30	_30	_5	
REC								
READ	1							
BASELINE						44		
MINI FLOW	1	{						
m]/min								
STOP FLOW	Ī	[

Wavelength 248.3 nm, Purge gas Argon slit 0.2nm

HGA-400 KEYBOARD ENTRIES

Element: MO Matrix: SEA WATER

Tube Type: PYROLYTICALLY COATED

Sample Aliquot: 25 uL/ 10 uL for samples 12 umol L⁻¹

Keyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	100	130	250	1400	2800			
RAMP TIME* (s)	10	20	30	30	0			
HOLD TIME (s)	10	30	15	30_	5			
REC								
READ								
BASELINE				54				
MINI FLOW]					
ml/min								
STOP FLOW			1					

Wavelength 313.3 nm, Purge gas Argon slit: 0.2nm, norm

HGA-400 KEYBOARD ENTRIES

Element: Mn Matrix: SEA WATER

Tube Type: <u>PYROLYTICALLY</u> COATED Sample Aliquot: <u>25 ML</u>

Keyboard Entries

STEP	1	2	3	4	5	6	7	8
TEMP (°C)	100	110	150	1000	1200	2700		
RAMP TIME" (s)	3	15	25	30	15	0		
HOLD TIME (s)	10	15	50	5	40	5		
REC								
READ								
BASELINE		_			64			
MINI FLOW			}					
ml/min								
STOP FLOW			T					

Wavelength 279.5 nm, purge gas Argon slit: 0.2 nm, alt.

Table 9 Instrument settings for the graphite furnace

II.7.1 Sample preparation

From the selected cores about six-gram samples were taken for X-ray diffraction analysis. About one-gram samples were used to prepare unoriented powder mounts for examination of the gross mineral distributions. The sediment samples were packed into a standard Philips aluminium sample holder and compressed with a piston and a mechanical press. A few samples had to be backed with some instant coffee to prevent them from collapsing into the sample holder.

The same sample was usually used to prepare oriented mounts for clay-mineral analysis. The powder was dispersed in a small amount of distilled water. After allowing five minutes for settling, a fraction of the supernatant liquid, now enriched in suspended clay, was pipetted onto a glass disc which fitted into the sample holders. The suspension was allowed to evaporate in a clean air laminar flow cabinet. This procedure yields a strongly-oriented sample that will give strong basal reflections of clay minerals. Generally two oriented mounts per sample were prepared. One disc was subjected to glycolation over night while the second disc was used to obtain a scan of the untreated mount. Afterwards this sample was heated to 550°C to drive off interlayer water molecules and to desroy the lattice of kaolinite (Carroll, 1970).

To separate the heavy minerals, five grams of dried ground sample were placed in a separating funnel and bromoform $(HCBr_3, \text{spec. gravity 2.93})$ added. The mixture was shaken vigorously for a few minutes, to ensure total dispersion of the powder, and then allowed to settle over night. Since the heavy mineral fraction usually was not enough to fill an aluminium ring, it was mounted in the sample holder with some instant coffee powder for backing.

II.7.2 Operating conditions

The determinations were all made with an automated Philips PW 1710 Powder Diffractometer using CuK α X-radiation a curved graphite crystal (002) monochromator; automatically adjusting divergence slit (goniometer controlled), and 0.1° scatter and 1° receiving slits. The unoriented powder and the heavy mineral samples were scanned from 4°2 θ to 60°2 θ and the oriented mounts from 4°2 θ to 30°2 θ . During the scan, the sample is rapidly rotated to guarantee an equal irradiation of the whole sample surface and hence increase the reproducibility of a scan.

II.8 X-ray fluorescence spectrometry

II.8.1 Major element sample preparation

For the major element determination 36 mm diameter glass discs were perpared by fusion, using 0.4 g of sample and 3.6 g of ultra-pure Spectroflux 105 (Johnson-Matthey Chemicals Ltd.) consisting of $Li_2B_4O_7$, La_2O_3 and Li_2CO_3 . Before weighing, the flux was dried in a furnace at 500° C for one hour to remove adsorbed water. The weighed flux and sample were placed into a platinum crucible and fused in a muffle furnace at 1100° C for 20 minutes. After cooling the fused samples, the weight loss resulting from the removal of interlayer water, oxidation of organic matter and volatilization of some elements, was made up with Spectroflux 100 which contains only $Li_2B_4O_7$ and thus does not alter the sample/La ratio. La is needed as a heavy absorber in the glass discs to increase the total mass absorption of the glass and thereby minimize matrix absorption effects between different samples.

After adding flux 100, the glass was refused on a Meker burner and poured into an Al-mould on a hotplate set at 400° C. The molten sample was then flattened with a brass plunger, and the resulting glass disc was later directly presented to the X-ray beam. This method is based on the work of Norrish and Hutton (1969). Calibration of the analyses was provided by a large number of international rock standards.

II.8.2 Minor element sample preparation

4.0 g of the dried and ground sample (Appendix I) were used to prepare pressed powder discs of 36 mm diameter for the minor element analysis. The sediment powder was poured into an Al-tube sitting inside a stainless steel cylinder, and compressed manually with a PVC plunger. After removing the plunger and the Al-tube, boric acid was added to produce a stable backing for the powder disc. A WC-disc and a stainless steel plunger were inserted into the steel cylinder and 10 tons of pressure were applied with a hydraulic press for about 1 minute to produce a stable disc for the XRF-analysis. Mass absorbtion corrections were applied following Reynolds (1963, 1967), using the amplitude of the Rh K α Compton scattering peak as an indicator of the relative variations in mass absorption between samples and standards. Calibration of the analyses was provided by a large number of international rock standards.

II.8.3 XRF-analytical procedure

The major and minor elements were analysed with an automated Philips PW 1400 X-ray fluorescence spectrometer. A peripheral Digital PDT 11 computer was used for calculating the elemental concentrations from the X-ray counts. The XRF-instrument settings are summarized in Table 11

Analytical precision of the XRF-analysis was determined for the minor elements by making six pressed powder discs per depth interval from core AA-8 (total 10 depth intervals). The 2σ relative standard deviation for the minor elements are listed in Table 12

ELEN	1ENT	FLT	COL	DET	XTL	ORD	UPL	LWL	KV	MA	ANGLE	+OFFS	-OFFS
CP CB MC TI	КА Ка Ка	ND ND ND ND	F F C	S F F	1 5 1 1	1 1 1	80 80 80 75	20 20 20 25	60 60 60 60	40 40 40	18.415 80.000 66.000 85.350	.00 .00 .00 3.00	.00 .00 .00 1.00
SI TI1	KA	ND ND		FF	4. 1	1	8 0 75	20 25	60 60	40 40	32.230 85.310	2.30 3.00	1.20 1.00
FE	KA	ND	С	F	1	1	85	15	60	40	57.670	.00	1.60
MN1	KA	ND	С	F	1	1	75	15	50	20	63.140	.00	.86
AL Mg CA K P NA CL	КА КА КА КА КА КА	ND ND ND ND ND ND ND			4 1 1 3 4 2	1 1 1 1 1	80 80 80 80 80 80 80	20 20 20 20 20 20 20	50 50 50 30 30 50	40 60 10 40 60 60	37.875 45.210 113.335 136.755 141.120 55.250 65.820	1.00 .00 1.40 2.00 .00 3.40 2.00	.00 1.20 .00 .00 1.50 1.70 .00
52	KA	ND	С	F.	3	1	80	20	60	40	110.820	1.00	.00
BA MO ZR Y	LA KA KA	ND ND ND ND	יד. ה- ה ה-	רי מ) איר	1 5 1 1	1 1 1	80 75 80 80	20 25 20 20	00 80 80 80	40 40 40 40	87.185 28.910 22.555 23.830	1.20 .70 .74 .E0	.00 .70 .74 .50
er Re Pe 2n Cu	KA Ka Ka Ka	ND ND ND ND YE	F F F F F	S FS FS FS	1 1 1 1	1 1 1 1	75 80 75 80 80	25 20 25 20 20	00 00 00 00 00	40 40 40 40	25.200 26.660 25.290 41.780 45.000	.50 .40 .50 .72 .00	.50 .50 .00 .52
NI CD MN CR	КА Ка Ка	ND ND ND ND	F F C C	F 5 F 5	1 5 1	1 1 1	80 80 75 20	20 20 15 20	60 60 60 60	40 40 40 40	48.655 77.900 53.210 55.520	1.20 .54 1.50 1.00	.E0 .54 .00

Table 10 Analytical conditions for XRF-analysis of major and minor elements

Element	estimated total precision $(2\sigma \text{ relative standard deviation}, \%)$
Ba	. 6.0
Co	16.5
Cr	7.0
Cu	7.4
Mn	4.7
Mo	$16.0/2.0^*$
Ni	11.0
Pb	10.4
Rb	2.4
Sr	0.8
v	5.7
Ŷ	4.0
Zn	2.2
Zr	8.7

Table 11XRF analytical precision for minor elements

* precision for Mo values > 10ppm $(n = 6 \cdot 4)/$

values < 40 ppm $(n = 6 \cdot 5)$

II.8.4 Accuracy of the measuring program

The accuracy of the measuring program was checked by running several standards as unknowns and comparing the determined concentrations with the values recommended by Abbey (1983). The results for 5 standards are listed in Table 13

 Table 12

 Accuracy of the measuring program for XRF analysis

	<u></u>									
Element	AGV-1 analy.	recom.	G -2 analy.	recom.	GSP -1 analy.	recom.	BCR-1 analy.	recom.	GA analy.	recom.
Ba	1148	12 00	1801	1900	1273	13 00	608	680	899	850
Co	10	16	9	5	6	7.8	35	36	3	5
Cr	7	10	2	8	8	12	7	15	8	12
Cu	63	59	10	10	27	33	14	16	19	16
Mn	710	728	243	265	279	326	1084	13 50	731	700
Ni	13	15	4	3.5	6	9	14	10	6	7
Pb	33	33	32	3 0	46	54	17	14	29	3 0
Rb	69	67	165	17 0	245	2 50	50	47	169	175
Sr	669	66 0	480	48 0	236	24 0	341	33 0	303	31 0
v	114	125	44	36	53	54	315	42 0	39	4 0
Y	22	19	11	11	25	2 9	36	40	19	21
Zn	84	86	84	84	97	105	129	125	66	80
Zr	235	23 0	311	3 00	483	500	190	185	140	150

II.9 Correction for sea salt effects

In samples from the marine environment the concentrations of some elements are significantly altered by the presence of residual sea salt in the samples. In order to get the true elemental distribution in the sediments all analyses in this thesis were corrected for the dilution or enhancement effects of sea salt. For the sea salt correction it was assumed that the interstitial water salinity was 35% and that all chlorine in the sediments occured in sea salts. The salt corrections were done with the UBC computer using a computer program written by B. Cousens. First all elements whose concentrations are affected directly by the sea salt are corrected using the following equations (from Pedersen, 1979):

$$(wt. \% Na)_{sed} = (wt. \% Na)_{sed+salt} - 0.556 (wt. \% Cl)$$
$$(wt. \% Mg)_{sed} = (wt. \% Mg)_{sed+salt} - 0.067 (wt. \% Cl)$$
$$(wt. \% Ca)_{sed} = (wt. \% Ca)_{sed+salt} - 0.021 (wt. \% Cl)$$
$$(wt. \% K)_{sed} = (wt. \% K)_{sed+salt} - 0.020 (wt. \% Cl)$$
$$(ppm S)_{sed} = (ppm S)_{sed+salt} - 16.6 (wt. \% Cl)$$
$$(ppm Sr)_{sed} = (ppm Sr)_{sed+salt} - 4.13 (wt. \% Cl)$$

Second, the elemental concentrations of all elements were corrected for the dilution effect of sea salt using the equation:

(Element concentration)_{salt-free} = (Raw concentration) $\cdot \frac{100}{100 - 1.82(\text{wt.\%Cl})}$

II.10 Carbon analysis

II.10.1 Total carbon

Total carbon was analysed by gas chromatography using a Carlo Erba CHN Analyzer. About 10-15 mg of sample were weighed into small tin cups which were then loaded into a sample changer in the instrument. The peaks were integrated by an HP-3390 A integrator, which expressed the measured C as a peak area. Each run was calibrated by running a minimum of seven standards with 23 samples. Acetanilide (CH₃CONHC₆H₅) was used as a standard. Analytical precision for this technique was $\pm 2.4\%$ ($2\sigma n = 7$). The mean of the standards was used to determine a constant with the following equation:

$$K_C = \frac{weight_C \text{ of standard}}{area_C \text{ of standard}} = constant$$

The carbon content of the samples was calculated by multiplying the measured area with the constant.

For one core the total C values were compared to total C concentrations determined with a LECO Carbon Analyzer, employing a combustion technique where the evolved CO_2 is measured gravimetrically. The values determined by the two different techniques compared very well, and the differences were always $\leq \pm 2\%$.

II.10.2 Carbonate carbon

For the carbonate C about 0.3 g samples were weighed accurately into small glass reaction bulbs. About 5 ml 10% HCl was added and the flask was heated with a small Bunsen-burner until the mixture started boiling. Evolved CO_2 was carried in a stream of N₂ through a condenser tube and a water trap (conc. H₂SO₄) into a LECO CO₂ trap where CO₂ was absorbed onto ascarite. The CO₂ was then determined gravimetrically by measuring the weight difference from before and after the sample run.

Organic carbon was subsequently calculated by subtracting the carbonate carbon values from the total carbon concentrations. Appendix III: Chemical data

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	SI	ΤÏ	AL	FE	MN	MG	CA	NA	к	P	s
0-3	28.92	0.39	7.74	4.67	0.16	1.52	2.09	1.85	2.30	0.13	0 .30
3-6	28.21	0.42	7.98	4.96	0.14	1.66	2.01	1.80	2.50	0.14	0.34
6-10	30.16	0.41	8.23	3.90	0.14	1.37	2.09	1.36	3.78	0.13	1.00
10-15	27.82	0.42	7.99	4.97	0.15	1.62	2.05	1.57	2.65	0.13	0.67
15-20	27.19	0.44	8.05	5.40	0.19	1.75	1.89	1.42	2.57	0.15	0.38
20-25	27.61	0.42	7.88	5.18	0.16	1.69	2.21	1.62	2.35	0.15	0.35
25-3 0	27.65	0.43	8.05	5.03	0.15	1.68	1.90	1.64	2.65	0.15	0.53
30-35	26 .02	0.46	8.18	5.83	0.16	1.74	1.70	1.40	2.45	0.16	0.40
35-40	27.80	0.42	7.91	5.07	0.12	1.65	2.02	1.68	2.30	0.14	0.36
40-45	27.83	0.43	8.14	5.10	0.15	1.65	1.88	1.80	2.37	0.14	0.53
45-50	27.40	0.44	8.09	5.19	0.14	1.64	1.93	1.63	2.42	0.15	0.44
50-55	26.73	0.44	8.07	5.54	0.20	1.73	2.00	1.52	2.46	0.15	0.38

Salt-corrected Major Element Concentrations: ALICE ARM STATION AA-2

	SI	TI	AL	FE	MN	MG	CA	NA	к	Ρ	s
0-5	29.27	0.37	7.36	3.55	0.12	1.15	1.86	1.35	3.76	0.11	1.15
5-10	28.69	0.38	7.44	4.16	0.12	1.37	1.68	1.45	3,26	0.12	0.80
10-15	28.68	0.38	7.31	4.25	0.12	1.37	1.65	1.56	3.17	0.12	0.78
15-20	3 0.09	0.39	7.71	4.40	0.11	1.45	1.65	1.51	3.20	0.13	0 .90
20-25	28.78	0.39	7.25	4.40	0.11	1.39	1.55	1.54	3.08	0.13	0.82
25-30	28.70	0.38	7.21	4.60	0.12	1.40	1.72	1.53	3.02	0.13	0.97

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	SI	TI	AL	FE	MN	MG	CA	NA	к	P	s
0-5	30.97	0.32	7.00	2.45	0.07	0.84	1.83	1.22	4.49	0.09	1.34
5-10	31.11	0.30	6.89	1.96	0.05	0.79	2.13	0.8 9	4.75	0.09	1.21
10-15	30.20	0.31	6.98	2.17	0.05	0.78	2.05	1.00	4.74	0.09	1.27
15-20	28.52	0.41	7.41	3.21	0.11	1.17	2.35	1.25	4.35	0.12	1.86
20-25	29.39	0.39	7.34	3.21	0.08	1.07	2.12	1.36	3.97	0.10	1.77
25-30	29.50	0.37	7.31	3.19	0.09	0.99	2.01	1.22	4.12	0.10	1,98
30-35	28.71	0.36	7.61	3.41	0.10	1.19	2.08	1.16	4.11	0.11	1.54
35-40	29.20	0.39	7.32	3.28	0.10	1.00	1.91	1.43	4.21	0.10	1.77

	SI	TI	AL	FE	MN	MG	CA	NA	к	₽	LOI	S
0-3	29.95	0.37	7.10	3.25	0.12	1.04	1.62	1.52	3.89	0.12	4.28	1.31
3-6	30.56	0.31	7.20	2.35	0.11	0.79	1.86	1.03	4.52	0.09	4.65	1.30
6-10	30.16	0.36	7.20	2.86	0.12	0.96	1.79	1.33	4.21	0.11	4.34	1.24
10-15	29.81	0.33	7.14	2.26	0.11	0.88	2.07	0.98	4.62	0.09	4.74	1.28
15-20	30.84	0.31	6.97	2.17	0.09	0.76	1.97	0. 9 9	4.63	0.09	4.34	1.24
20-25	31.04	0.31	6.86	2.33	0.11	0.80	2.00	1.03	4.63	0.10	4.43	1.41
25-3 0	30.11	0.35	6.94	2.74	0.13	0.92	2.10	1.05	4.56	0.11	4.34	1.81
30-35	28.86	0.44	6.97	3.58	0.15	1.23	2.47	1.45	4.10	0.15	4.04	1.94
35-40	29. 8 6	O.38	7.26	3.05	0.12	0.97	2.00	1.34	4.13	0.11	4.76	1.47
40-45	29.68	0.36	7.28	3.28	0.12	0.98	1.89	1.21	3.88	0.11	4.94	1.70
45-50	29.53	0.35	7.21	3.32	0.12	1.04	1.86	1.33	4.07	0.11	5.48	1.52
50-55	29.44	0.37	6.92	3.23	0.13	0.96	1.81	1.62	3.87	0.10	4.89	1.79
55-60	29.00	0.37	7.13	3.74	0.13	1.32	1.74	1.43	3.52	0.12	6.11	1.03

	SI	TI ·	AL	FE	MN	MG	CA	NA	к	P	5
0-5	34.84	0.22	5.31	1.28	0.04	0.46	1.39	0.0	4.54	0.06	0.95
5-10	35.44	0.23	5.42	1.11	0.04	0.43	1.39	0.0	4.57	0.06	0.94
10-15	33.82	0.26	5.33	2.21	0.04	0.53	1.57	0.0	4.19	0.07	2.15
15-20	26.98	0.42	7.83	4.97	0.10	1.19	1.71	0.0	2.78	0.14	0.35
20-25	26.94	0.43	8.00	4.67	0.09	1.71	1.79	0.0	2.94	0.14	0.58
25-30	27.84	0.41	7.90	3.98	0.08	1.43	1.79	0.0	3.56	0.13	0 .90
30-35	28.14	0.40	7.65	3.90	0.11	1.41	1.73	0.0	3.49	0.12	0 .90
35-40	26.54	0.41	7.77	4.92	0.12	1.72	1.64	0.0	2.69	0.13	0.64

	SI	ΤI	AL	FE	MN	MG	CA	NA	к	P	s
3-6	25.93	0.42	8.24	5.47	0.14	2.15	1.54	1.56	2.37	0.15	0.44
6-10	26.48	0.42	8.34	5.51	0.15	2.18	1.60	1.71	2.46	0.15	0.30
10-15	26.62	0.43	8.39	5.56	0.16	2.16	1.67	1.65	2.45	0.15	0.20
15-20	26.54	0.43	8.53	5.69	0.16	2.21	1.66	1.63	2.49	0.15	0.17
20-25	26.24	0.43	8.56	5.66	0.15	2.22	1.51	1.67	2.60	0.15	0.21
25-30	26.56	0.43	8.48	5.61	0.15	2.17	1.51	1.61	2.53	0.15	0.29
30-35	26.29	0.43	8.18	5.63	0.16	2.16	1.62	1.67	2.47	0.14	0.32
35-40	26.41	0.44	8.44	5.68	0.15	2.12	1.53	1.54	2.48	0.15	0.34
40-45	26.69	0.44	8.56	5.68	0.15	2.18	1.58	1.64	2.49	0.15	0.28
45-50	26.48	0.44	8.46	5.68	0.16	2.20	1.62	1.61	2.47	0.15	0.25
50-55	26.62	0.43	8.32	5.65	0.16	2.21	1.54	1.53	2.44	0.15	0.29

	SI	TI	AL	FE	MN	MG	CA	NA	к	Ρ	s
0-1	28.61	0.37	7.25	3.84	0.19	1.27	1.46	1.70	3.37	0.13	0.78
1-2	29.96	0.36	7.05	3.44	0.14	1.10	1.63	1.38	3.81	0.12	1.14
2-3	30.12	0.37	6.98	3.31	0.12	1.06	1.74	1.46	3.95	0.12	1.28
3-4	30.26	0.36	7.09	3.27	0.13	1.05	1.81	1.53	3.93	0.11	1.19
4-5	32.58	0 .30	6.25	2.47	0.11	0.76	1.65	1.45	4.19	0.09	1.08
5-6	33.53	0.28	5.99	2.10	0.10	0.67	1.57	1.36	4.30	0.08	1.12
6-7	31.86	0.29	6.42	2.55	0.11	0.75	1.65	1.43	4.31	0.09	1.20
7-8	31.67	0.29	6.51	2.51	0.11	0.77	1.76	1.29	4.44	0.10	1.26
8-9	32.65	0.28	6.54	2.22	0.10	0.70	1.70	1.17	4.46	0.09	1.25
9-10	32.51	0.29	6.41	2.15	-0.10	0.67	1.75	1.26	4.55	0.09	1.16
10-12	31.77	0.30	6.55	2.31	0.10	0.78	2.00	1.23	4.60	0.10	1.26
12-14	30.92	0.29	6.79	2.48	0.10	0.80	1.98	1.26	4.70	0.09	1.29
14-16	31.07	0.30	6.77	2.57	0.12	0.82	1.89	1.24	4.49	0.10	1.29
16-18	30.93	0.31	6.73	2.71	0.11	0.88	1.91	1.35	4.32	0.10	1.33
18-20	30.81	0.31	6.45	2.97	0.13	0.83	1.95	1.38	4.60	0.10	1.54
20-22	3 0.76	0.33	6.72	3.03	0.12	0.91	1.97	1.44	4.14	0.11	1.50
22-24	31.60	0.34	7.26	3.21	0.13	0.98	2.05	1.40	4.25	0.12	1.53
24-26	29.33	0.37	7.04	3.48	0.14	1.12	2.16	1.42	4.33	0.12	1.66
26-28	28.54	0.43	7.34	4.00	0.15	1.32	2.20	1.66	3.77	0.14	1.69
28-30	28.54	0.42	7.11	3.86	0.17	1.33	2.35	1.71	3.94	0.15	1.67
30-32	30.52	0.36	6.88	3.25	0.13	0.97	1.81	1.66	3.95	0.12	1.38
32-34	29.85	0.37	7.09	3.30	0.14	1.05	1.97	1.52	3.93	0.12	1.44
34-36	31.71	0.35	7.46	3.08	0.11	0.96	1.90	1.50	3.77	0.10	1.39
36-38	30.97	0.35	6.91	3.31	0.12	0.99	1.89	1.56	3.84	0.11	1.69
38-40	30.39	0.34	6.80	3.18	0.12	0.94	1.80	1.47	3.78	0.10	1.61
40-42	3 0. 76	0.34	6 .96	3 .30	0.13	0.95	1.81	1.38	3.96	0.11	1.61
42-44	30.14	0.34	7.16	3.31	0.14	1.01	1.81	1.38	3.96	0.11	1.47

Salt-corrected Major Element Concentrations: ALICE ARM STATION AA-6

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	SI	TI	AL	FE	MN	MG	CA	NA	ĸ	Ρ	S
44-46	30.32	0.34	6.82	3.24	0.14	0.92	1.73	1.50	3.89	0.11	1.48
46-48	29.76	0.35	7.11	3.52	0.15	1.07	1.73	1.58	3.65	0.11	1.24
48-50	30.27	0.34	6.82	3.35	0.16	1.02	1.77	1.58	3,93	0.11	1.36
50-52	31.56	0.29	6.32	2.72	0.13	0.82	1.70	1.39	4.16	0.10	1.09
52-54	28.99	0.35	7.32	3.72	0.20	1.26	1.67	1.46	3.63	0.13	0.64
54-56	27.08	0.40	7.85	5.08	0.29	1.72	1.52	1.55	3.00	0.15	0.34
56-58	26.73	0.40	7.90	4.98	0.29	1.72	1.49	1.52	2.84	0.16	0.29
58-60	27.95	0.39	7.94	4.77	0.25	1.66	1.46	1.56	3.13	0.14	0.38
60-62	26.82	0.39	7.97	4.82	0.25	1.67	1.44	1.55	2.93	0.13	0.45
62-64	27.40	0.40	8.04	4.96	0.23	1.68	1.45	1.54	3.14	0.14	0.41
64-66	26.55	0.40	8.04	5.00	0.25	1.73	1.41	1.61	2.79	0.14	0.30
66-68	26.69	0.40	7.95	5.03	0.27	1.71	1.40	1.52	2.83	0.14	0.29
68-70	26.85	0.41	8.02	4.87	0.24	1.66	1.42	1.62	3.00	0.14	0.37
70-72	26.89	0.41	8.11	4.80	0.23	1.62	1.46	1.55	2.94	0.14	0.39
72-74	26.70	0.39	7.96	4.72	0.24	1.64	1.41	1.51	2.91	0.13	0.58
74-76	26.65	0.40	7.97	4.89	0.24	1.67	1,44	1.61	2.78	0.13	0.52
76-78	26.39	0.40	7.99	5.06	0.25	1.74	1.47	1.54	2.58	0.14	0.58
78-80	26.07	0.40	7.86	5.02	0.24	1.71	1.55	1.54	2.61	0.13	0.66
80-82	25.99	0.39	7 .90	5.29	0.25	1.78	1.55	1.54	2.39	0.14	0.75

	SI	TI	AL	FE	MN	MG	CA	NA	к	P	. S
0-1	27.62	0.39	7.86	4.37	0.26	1.47	1.45	1.40	2.94	0.16	0.57
1-2	28.29	0.40	7.93	4.18	0.24	1.42	1.54	1.47	3.75	0.12	0.65
2-3	28.35	0.39	7.68	3.89	0.16	1.33	1.67	1.44	3.53	0.13	0.78
3-4	29.45	0.38	7.19	3.50	0.13	1.14	1.73	1.48	3.72	0.12	1.17
4-5	29.43	0.37	7.41	3.54	0.13	1.20	1.77	1.50	3.62	0.12	1.07
5-6	29.57	0.39	8.09	3.87	0.13	1.34	1.67	1.40	3.54	0.13	0.92
6-7	28.10	0.39	8.04	4.08	0.14	1.39	1.66	1.51	3.33	0.12	0.81
7-8	30.38	0.36	7.40	3.59	0.13	1.16	1.70	1.45	3.64	0.12	1.11
8-9	32.30	0.30	6.28	2.65	0.10	0.72	1.60	1.34	3.95	0.10	1.41
9-10	29.62	0.36	7.53	3.38	0.13	1.13	1.75	1.38	3.72	0.12	1.08
10-12	30.89	0.33	7.00	2.92	. 0. 12	0.95	1.75	1.27	4.02	0.11	1.23
12-14	29.27	0.36	7.50	3.21	0.12	1.10	1.74	1.25	3.92	0.12	1.22
14-16	32.9 9	0.29	6.01	2.25	0.09	0.62	1.77	1.17	4.26	0.11	1.47
16-18	30.91	0.33	6.77	2.58	0.11	0.81	1.98	1.21	4.16	0.11	1.32
18-20	30.06	0.34	7.25	2.65	0.11	0.87	1.88	1.22	4.16	0.10	1.13
20-22	31.05	0.33	7.31	2.90	0.12	0.88	1.80	1.50	4.02	0.11	1.33
22-24	31.02	0.34	6.63	2.98	0.13	0.88	1.87	1.45	3.82	0.11	1.42
24-26	29.81	0.37	7.07	3.40	0.13	1.05	1.95	1.40	3.71	0.12	1,43
26-28	28.88	0.39	7.68	3.64	0.14	1.25	1.80	1.40	3.64	0.12	1.02
28-30	29.01	0.39	7.43	3.72	0.15	1.24	1.95	1.36	3.64	0.12	1.25
30-32	27 .35	0.43	7.84	4.16	0.15	1.45	1.99	1.49	3.43	0.14	1.04
32-34	27.05	0.44	8.04	4.57	0.15	1.56	1.80	1.49	3.10	0.13	0 .90
34-36	28.79	0.41	7.43	3.98	0.14	1.28	1.87	1.52	3.38	0.13	1.20
36-38	29.52	0.41	6.91	3.51	0.14	1.16	2.08	1.44	3.66	0.14	1.59
38-40	29.46	0.39	7.09	3.46	0.15	1.07	1.91	1.42	3.81	0.13	1.41
40-42	29.27	O.38	7.44	3.38	0.14	1.09	1.87	1.39	3.70	0.11	1.27
42-44	29.99	0.38	6.92	3.44	0.13	1.07	1.89	1.40	3.61	0.11	1,48
44-46	29.90	0.37	7.08	3.46	0.15	1.03	1.79	1.36	3.72	0.11	1.51
46-48	29.52	0.37	7.29	3.48	0.17	1.05	1.72	1.31	3.68	0.11	1.45
48-50	29.70	0.36	7.11	3.34	0.16	1.06	1.80	1.48	3.67	0.11	1.36
50-52	30.12	0.34	6.95	3.16	0.14	1.05	1.82	1.28	3.89	0.11	1.02
52-54	28.76	0.39	7.70	3.93	0.30	1.37	1.72	1.37	3.38	0.14	0.63
54-56	26.60	0.42	7.85	4.81	0.42	1.69	1.54	1.58	2.64	0.16	0.32
56-58	26.66	0.43	7.93	4.74	0.25	1.75	1.47	1.57	2.49	0.14	0.32
58-60	26.36	0.43	8.11	4.93	0.19	1.85	1.43	1.62	2.42	0.13	0.33

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	SI	TI	AL	FE	MN	MG	CA	NA	к	₽	S
60-62	26.75	0.43	7,62	4.64	0.19	1.79	2.05	1.69	2.11	0.12	0.54
62-64	26.67	0.41	7.81	4.92	0.52	1.80	.1.47	1.63	2.20	0.14	0.16
64-66	26.42	0.41	7.94	4.98	0.35	1.81	1.30	1.54	2.39	0.14	0.16
66-68	26 .50	0.42	8.11	4.94	0.27	1.79	1.25	1.57	2.49	0.13	0.16
68-70	26.89	0.41	8.11	4.72	0.26	1.74	1.26	1.52	2.69	0.13	0.24
70-72	26.71	0.41	7.92	4.66	0.27	1.68	1.44	1.57	2.57	0.12	0.38
72-74	26.57	0.41	7.90	4.72	0.29	1,66	1.59	1.56	2.43	0.12	0.53
74-76	26.83	0.41	7.89	4.61	0.28	1.64	1,49	1.55	2.55	0.12	0.45
76-78 -	27.14	0.41	8.00	4.53	0.33	1.64	1.49	1.48	2.65	0.12	0.42
78-80	26.64	0.41	7.86	4.64	0.32	1.66	.1.55	1.54	2.58	0.13	0.42
80-82	26.34	0.41	7.85	4.84	0.30	1.70	1.62	1.47	2.40	0.13	0.42
82-84	25.81	0.41	7 .80	5,14	0.31	1.80	1.62	1.58	2.21	0.13	0.47
84-86	25.48	0.40	7.58	5.15	0.27	1.78	1.55	1.54	2.10	0.13	0.83
86-88	24.48	0.37	7.02	5.03	0.27	1.68	2.08	1.44	1.95	0.12	1.64
88-90	24.30	0.36	6.74	4.91	0.26	1.62	2.30	1.38	1.91	0.12	1.85
90-92	25.06	0.32	6.13	4.40	0.27	1.45	2.74	1.35	1.72	0.11	2.09
92-94	25.27	0.39	7.52	5.04	0.57	1.76	1.58	1.48	2.04	0.13	0.82
94-96	25.52	0.41	7.51	5.04	0.33	1.85	1.45	1.57	2.10	0.13	0 .90
96-98	24.90	0.40	7.69	5.18	0.28	1.86	1.52	1.62	2.18	0.13	0.62
98-100	25.44	0.42	7.96	5.15	0.19	1.88	1.63	1.64	2.18	0.44	0.39
105-107	25.95	0.42	7.91	5.16	0.36	1.87	1.39	1.58	2.13	0.13	0.53
110-112	25.61	0.41	7.76	5.11	0.50	1.83	1.49	1.65	2.14	0.13	0.21
115-117	26.34	0.43	8.11	5.26	0.40	1.85	1.38	1.71	2.22	0.14	0.14
120-122	26 .90	0.44	8.21	5.18	0.38	1.92	1.41	1.65	2.23	0.14	0.30
125-127	26.23	0.46	8.28	5.47	0.23	1.90	1.44	1.76	2.29	0.15	0.52
130-132	26.46	0.43	7.68	4.93	0.37	1,75	1.70	1.79	2.07	0.13	0.52
135-140	27.91	0.43	7.82	4.74	0.24	1.79	1.57	1.77	2.14	0.12	0.14
140-142	27.25	0.42	7.98	4.85	0.19	1.74	1.72	1.80	2.19	0.13	0.21

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	SI	T1	· AL	FE	MN	MG	CA	NA	к	P	LOI	5
0-2.5	30.65	0.36	7.07	3.23	0.17	1.04	1.73	1.09	3.85	0.12	5.76	1.01
2.5-5	30.17	0.38	7.26	3.40	0.14	1.12	1.82	1.15	3.93	0.12	5.75	1.05
5-7.5	29.13	0.39	7.54	3.92	0.15	1.23	1.85	1.18	3.69	0.13	5.27	1.09
7.5-10	29.30	0.42	7.49	4.06	0.17	1.34	1.93	1.30	3.60	0.13	4.75	1,18
10-12.5	28.58	0.43	7.59	3.98	0.18	1.28	1.85	1.24	3.52	0.14	5.17	1.14
12.5-15	29.64	0.42	7.65	4.14	0.21	1.30	1.78	1.17	3.42	0.12	5.19	1.19
15-17.5	29.15	0.42	7.53	3,96	0.26	1.30	1.76	1.22	3.44	0.13	6.16	0.84
17.5-20	28.03	0.48	7.85	4.98	0.41	1.67	1.45	1.21	2.23	0.15	8.13	0.12
20-22.5	28.10	0.48	7.81	4.81	0.28	1.69	1.39	1.18	2.16	0.13	8.15	0.13
22.5-25	28.17	0.47	7.87	4.72	0.28	1.68	1.38	1.18	2.22	0.13	8.46	0.17
25-27.5	28.98	0.46	8.09	4.76	0.31	1.71	1.40	1.25	2.23	0.13	7.85	0.16
27.5-30	28.27	0.47	7.79	4.73	0.35	1.66	1.40	1.34	2.15	0.14	7.83	0.18
30-32.5	28.41	0.48	7.85	4.81	0.32	1.67	1.38	1.22	2.10	0.13	8.07	0.17
32.5-35	28.46	0.46	7.95	4.67	0.32	1.62	1.35	1.23	2.21	0.13	7.28	0.18
35-37.5	28.25	0.45	7.87	4.72	0.34	1.62	1.42	1.26	2.23	0.14	7.37	0.18
37.5-40	28.63	0.45	7.86	4.85	0.37	1.65	1.46	1.33	2.34	0.14	7.52	0.23
40-42.5	28.52	0.44	7.70	4.82	0.34	1.66	1.46	1.30	2.24	O.14	7.58	0.24
42.5-45	28.53	0.45	7.90	4,99	0.35	1.70	1.49	1.45	2.08	0.14	7.80	0.34
45-47.5	28.56	0.47	7.68	5.03	0.35	1.76	1.56	1.52	2.05	0.14	7.79	0.26
47.5-50	28.62	0.47	7.73	4.93	0.33	1.65	1.57	1.50	2.01	0.13	7.35	O.28
50-52.5	27.16	0.42	7.18	5.04	0.28	1.58	1.79	1.35	1.94	0.12	7.75	0.79
52.5-55	27.24	0.43	7.28	4.96	0.28	1.62	1.83	1.45	1.90	0.12	6.92	0. 8 9
55-57.5	27.57	0.45	7.49	5.07	0.29	1.66	1.66	1.34	1.96	0.13	7.66	0.68
57.5-60	27.74	0.45	7.47	5.11	0 .30	1.71	1.65	1.34	1.94	0.13	7.66	0. 81
60-62.5	27.79	0.46	7.52	5.02	0.33	1.68	1.59	1.44	2.01	0.13	6.62	0.56
62.5-6 5	27.1B	0.45	7.46	4.89	0.30	1.62	1.53	1.41	1,94	0.12	6.61	0.58

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	SI	TI	AL	FE	MN	MG	CA	NA	к	Ρ	LOI	s
0-3	28.22	0.45	7.75	4.41	0.34	1.56	1.44	1.71	2.59	0.13	6.64	0.31
3-6	28.55	0.41	7.74	4.05	0.16	1.47	1.64	1.49	3.30	0.13	5.78	0.84
6-10	28.76	0.39	7.57	3.59	0.15	1.27	1.77	1.28	3.76	0.12	5.66	0.96
10-15	28.48	0.41	7.67	3.94	0.16	1.35	1.84	1.42	3.57	0.1 3	5.57	1.07
15-20	28.96	0.41	7.63	3.86	0.18	1.36	1.79	1.43	3.55	0.12	5.54	1.06
20-25	27.81	0.46	7.70	4.67	0.26	1.68	1.54	1.71	2.36	0.13	6.92	0.27
25-30	28.11	0.47	7.74	4.68	0.28	1.68	1.42	1.74	2.19	0.12	7.34	0.19
30-35	27.89	0.47	7.67	4.72	0.31	1.70	1.45	1.70	2.12	0.12	7.79	0.30
35-40	27.99	0.46	7.73	4.63	0.32	1.65	1.44	1.74	2.14	0.12	7.57	0.24
40-45	28.72	0.45	7.87	4.78	0.26	1.71	1.46	1.73	2.23	0.12	7.10	0.30
45-50	28.03	0.46	7.48	4.71	0.23	1.69	1.58	1.86	2.00	0.12	6.81	0.47
50-5 5	27.86	0.47	7.41	4.68	0.24	1.66	1.64	1.80	1.95	0.12	6.57	0.48
55-60	27.94	0.46	7.50	4.72	0.26	1.66	1.57	1.80	1.90	0.12	5.99	0.49
60-6 6	27.18	0.44	7.31	4.71	0.29	1.68	2.03	1.70	1.91	0.12	6.83	0. 78

	SI	TI	AL	FE	MN	MG	CA	NA	к	P	s
0-5	29.22	0.45	7.46	4.05	0.15	1.58	1.49	0.39	1.92	0.11	0.13
5-10	32.30	0.42	7.72	3.42	0.11	1.41	1.48	0.35	1.90	0.09	0.08
10-15	30.16	0.42	7.35	3.65	0.12	1.43	1.56	0.34	1.94	0.09	0.11
15-20	29.76	0.43	7.51	3.81	0.12	1.54	1.52	0.31	1.93	0.10	0.30
20-25	29.41	0.44	7.48	3.94	0.12	1.56	1.56	0.37	1.93	0.10	0.24
25-30	29.29	0.45	7.51	4.01	0:12	1.58	1.59	0.36	1.92	0.10	0.28
30-35	29.11	0.45	7.49	4.05	0.13	1.63	1.58	0.33	1.93	0.10	0.42
35-40	29.53	0.44	7.58	3.87	0.12	1.50	1.54	0.26	1.92	0.10	0.32
40-45	29.84	0.44	7.47	3.79	0.11	1.56	1.55	0.36	1.91	0.10	0.19
45-50	30.13	0.45	7.71	3.91	0.11	1.56	1.54	0.22	1.92	0.10	0.22

	Salt	-correc	ted Maj	or Elem	ent Con	centrat	ions: H	ASTINGS	ARM ST	ATION H	1A-2
	SI	TI	AL	FE	MN	MG	CA	NA	к	P	s
0-3	26.71	0.40	7.66	4.42	0.14	1.67	2.17	1.74	2.13	0.13	0.09
3-6	26.98	0.41	7.63	4.28	0.12	1.65	2.32	1.72	2.09	0.11	0.11
6-10	26.93	Q.40	7.44	4.28	0.11	1.64	2.42	1.81	2.17	0.11	0.16
10-15	27.01	0.41	7.52	4.31	0.10	1.68	2.42	1.86	2.16	0.11	0.23
15-20	27.56	0.41	7.74	4.33	0.11	1.68	2.43	1.85	2.23	0.11	0.39
20-25	27.30	0.41	7.81	4.36	0.11	1.75	2.22	1.84	2.24	0.10	0.33
25-30	27.19	0.42	7.75	4.46	0.11	1.79	2.22	1.81	2.29	0.10	0.35
30-35	27.27	0.42	7.78	4.43	0.11	1.74	2.15	1.83	2.28	0.10	0.35
35-40	27.46	0.42	7.75	4.43	0.11	1.78	2.07	1.85	2.30	0.10	0.40
40-45	27.04	0.41	7.71	4.47	0.10	1.74	2.14	1.84	2.31	0.10	0.52
45-50	27.37	0.41	7.72	4.40	0.11	1.70	2.26	1.79	2.32	0.10	0.47
50-55	27.63	0.41	7.71	4.41	0.10	1.74	2.16	1.78	2.30	0 .10	0.43
55-60	27.44	0.42	7.88	4.45	0.10	1.78	2.04	1.81	2.29	0.10	1.77
60-65	27.46	0.42	7.80	4.47	0.11	1.75	2.03	1.85	2.29	0.10	2.09
	Salt-	correct	ed Majo	or Eleme	int Conc	entrati	ons: HA	STINGS	ARM STA	TION H	A-4
	S I	TI	AL	FE	MN	MG	CA	NA	к	P	5
0-2.5	27.51	0.40	8.01	4.43	0.27	1.87	1.87	2.09	2.54	0.13	0.04
2.5-5	27 .50	0.40	7.92	4.33	0.20	1.81	1.90	1.92	2.42	0.12	0.06
5~7.5	27.79	0.39	B.02	4.31	0.20	1.78	1.89	2.24	2.44	0.12	0.23
7.5-10	27.97	0.41	8.03	4.28	0.19	1.79	1.92	2.08	2.47	0.12	0.14
10-12.5	27.79	0.40	8.29	4.48	0.20	1.97	1 .90	1.97	2.57	0.12	0.08
12.5-15	27.25	0.41	8.21	4.65	0.22	2.01	1.89	1.95	2.47	0.12	0.06
15-17.5	26.94	0.42	8.15	4.74	0.23	2.09	1.88	1.93	2.57	0.12	0.07
17.5-20	26.41	0.42	8.16	4.91	0.23	2.16	1.88	1.91	2.60	0.13	0.14
20-22.5	26.75	0.42	8.22	4.88	0.23	2.09	1.91	1.98	2.59	0.12	0.41
22.5-25	25.96	0.42	8.08	4.77	0.23	2.11	1.91	1.99	2.56	0.12	0.35
25-27.5	27.12	0.43	8.51	4.84	0.20	2.16	1.91	1.94	2.57	0.12	0.25
27.5-30	26.89	0.43	8.27	4.75	0.19	2.07	1.93	2.01	2.56	0.12	0.19
30-32.5	26.62	0.43	8.25	4.72	0.18	2.05	1.96	2.06	2.57	0.12	0.18
32.5-35	26.95	0.43	8,13	4.51	0.17	2.00	1.96	2.07	2.55	0.12	0.27
35-37.5	27.15	0.42	8.11	4.30	0.15	1.85	1.98	2.25	2.45	0.12	0.62
37.5-40	27.36	0.42	8.10	4.27	0.15	1.81	2.05	2.21	2.44	0.12	0.37
40-42.5	27.18	0.43	8.09	4.39	0.18	1.90	2.00	2.10	2.50	0.12	0 .30
42.5-45	28.10	0.41	8.15	4.24	O. 18	1.77	1.99	2.19	2.49	0.11	0.24
45-47.5	27.95	0.41	7.98	4.28	0.18	1.85	1.91	2.09	2.46	0.11	0.27
47.5-50	27.17	0.42	8.21	4.43	0.18	1.92	1.93	2.07	2.53	0.11	0.38

	3011	001180									•
	SI	TI	AL	FE	MN	MG	CA	NA	κ	Ρ	s
0-2.5	27.83	0.37	8.09	4 . 19	0.14	1.70	2.61	2.37	2.54	0.12	0.14
2.5-5	29.87	0.37	8.36	4.18	0.08	1.56	2.84	2.47	2.56	0.13	0.11
5-7.5	27.96	0.39	8.47	4.55	0.09	1.83	2.64	2.24	2.53	0.13	0.07
7.5-10	28.49	0.37	8.17	4.10	0.08	1.64	2.74	2.32	2.55	0.12	0.07
10-12.5	30.60	0.28	7.94	3.03	0.06	1.09	2.77	2.61	2.41	0.10	0.05
12.5-15	30.14	0.09	8.11	3.40	0.06	1.23	2.76	2.41	2.48	0.13	0.15
15-17.5	28.32	0.38	8.20	4.41	0.10	1.62	2.72	2.25	2.45	0.12	0.10
17.5-20	28.53	0.38	8.13	4.27	0.09	1.54	2.76	2.29	2.45	0.12	0.08
20-22.5	29.00	0.35	8.06	3.95	0.09	1.45	2.77	2.39	2.48	0.12	0.08
22.5-25	28.50	0.37	8.24	4.17	0.08	1.64	2.68	2.23	2.59	0.13	0.07

Salt-corrected Major Element Concentrations: HASTINGS ARM STATION HA-6

	SI	ΤI	AL	FE	MN	MG	CA	NA	к	P	LOI	S
0-3	24.27	0.39	7.30	7.65	0.11	2.81	1.71	1.18	1.79	0.20	14.09	1.02
3-6	24.16	0.38	7.30	7.58	0.11	2.81	1.72	1.32	1.80	0.18	12.71	1.14
6-10	23.71	0.39	7.21	7.71	0.10	2.79	1.89	1.32	1.83	0.16	12.30	1.24
10-15	23.76	0.41	7.32	7.87	0.11	2.84	1.79	1.28	1.78	0.15	11.60	1.44
15-20	23.71	0.40	7.29	8.09	0.11	2.93	2.01	1.38	1.81	0.13	11.45	1.90
20-25	23.54	0.40	7.37	7.95	0.11	2.91	1.93	1.36	1.85	0.12	10.10	1.87
25-30	23.59	0.41	7.41	7.89	0.12	2.94	1.82	1.34	1.87	0.12	9.87	1.97
30-35	24.61	0.40	7.42	6.28	0.11	2.48	1.94	1.55	2.06	0.11	9.25	1.30
35-40	25.49	0.40	7.42	5.15	0.10	2.20	2.12	1.62	2.23	0.10	9.59	0.73
40-45	25.87	0.40	7.36	4.93	0.11	2.18	2.07	1.63	2.17	0.10	11.53	0.77
45-50	25.34	0.38	7.15	4.78	0.10	2.16	2.62	1.61	2.28	0.10	12.05	0.86

	BA	CO	CR	CU	MN	NI	PB	RB	SR	ν	Y	ZN	ZR	MO
0-3	2398.	44.	58.	67.	1364,	22.	47.	73.	380.	194.	22.	155.	113.	23.
3-6	2399.	28.	65.	76.	1133.	28.	75.	85.	357.	201.	22.	179.	109.	46.
6-10	2010.	38.	43.	85.	1110.	16.	193.	144.	318.	142.	24.	298.	108.	285.
10-15	2328.	30.	62.	92 .	1285.	25.	78.	96.	338.	204.	23.	202.	109.	92.
15-20	2477.	35.	65.	92 .	1534.	32 .	73.	92 .	327.	212.	24.	216.	104	56.
20-25	3026.	37.	61.	76.	1276.	32 .	58.	77.	369.	204.	23.	173.	113.	19.
25-30	2713.	36 .	62.	91.	1186.	29.	133.	99 .	350.	193.	23.	229.	106.	103.
30-35	2576.	35.	77.	111.	1395.	45.	86.	90.	304.	234.	27.	240.	107.	81.
35-40	3010.	41.	66.	77.	1296.	34.	72.	81.	350.	210.	25.	193.	116.	77.
40-45	2497.	31.	59.	69.	1044.	27.	56.	79.	374.	202 .	22.	166.	112.	36 .
45-50	3108.	28 .	68 .	85.	1148.	28.	81.	84.	347.	215.	23.	201.	109.	59.
50-55	2618.	28 .	69 .	98 .	1716.	38 .	75.	83.	328.	220.	24.	209 .	107.	46.

Salt-corrected Trace Element Concentrations: ALICE ARM STATION AA-2

	BA	со	CR	CU	MN	NI	PB	RB	SR	v	Y	ZN	ZR	MO
0-5	1746.	35.	46.	90.	1112.	14.	199.	146.	298.	135.	23.	337.	113.	343.
5-10	2129.	36.	64.	74.	1072.	24.	144.	115.	298.	163.	19.	276.	108.	249.
10-15	2131.	37.	63.	74.	1059.	27.	141.	112.	30 9 .	172.	23.	260.	114.	262.
15-20	2223.	38.	74.	72.	1062.	25.	141.	109.	306.	170.	24.	253.	112.	26B.
20-25	2307.	42.	73.	76.	1088.	27.	150.	103.	308.	171.	22.	249.	114.	259.
25-30	2280.	35.	72.	74.	1148.	31.	208.	101.	312.	176.	23.	238.	122.	286.

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Salt-corrected Trace Element Concentrations: ALICE ARM STATION AA-3

	BA	co	CR	cu	MN	NI	PB	RB	SR	v	Y	ZN	ZR	MO
0-5	1642.	33.	24.	64.	922.	4.	346.	172.	277.	75.	19.	469.	101.	229.
5-10	1757.	29.	18.	39 .	669.	-0.	181.	172.	251.	58.	18.	249.	100.	219.
10-15	1723.	29.	22.	53.	755.	1.	190.	166.	260.	71.	19,	287.	105.	273.
15-20	1610.	31.	39.	98 .	1315.	6.	309.	176.	354.	106.	23.	362.	110.	310.
20-25	1245.	32	36.	95.	968.	11.	223.	165.	295.	93.	26.	391,	118.	535.
25-30	1184.	31.	29.	112.	1057.	7.	258.	171.	293.	97.	25.	47,1	115.	400.
30-35	1622.	35.	32.	88.	1205.	11.	285.	158.	313,	129.	19.	611.	93.	317.
35-40	1193.	28 .	35.	112.	1160.	12.	256.	175.	290.	110.	28 .	429.	119.	333.
			Salt-c	correcte	ed Trace	Elemer	nt Conce	entratio	ons: ALI	CE ARM.	STATIC)N AA-4		
	BA	со	CR	cu	MN	NI	PB	RB	SR	v	Y	ZN	ZR	MO
0-3	1716.	60.	38.	69.	1128.	12.	377.	158.	297.	117.	21.	388.	110.	238.
. 3-6	1687.	38 .	24.	55.	1008.	3.	340.	180.	256.	86.	20.	472.	102.	193.
. 6-10	1688.	46.	37.	73.	1066.	9 .	369.	167.	297.	104.	21.	418.	106.	232.
. 10-15	1798.	41.	25.	46.	846.	-0.	212.	182.	268.	83.	18.	300.	99.	207.

•	3-6	1687.	38.	24.	55.	1008.	3.	340.	180.	256.	86.	20.	472.	102.	193.
	6-10	1688.	46.	37.	73.	1066.	9.	369.	167.	297.	104.	21.	418.	106.	232.
. 1	0-15	1798.	41.	25.	46.	846.	-0.	212.	182.	268.	83.	18.	300.	99.	207.
. 1	5-20	1754.	31.	21.	48.	747.	13.	198.	161.	248.	84.	18.	287.	102.	243.
. 2	0-25	1804.	40.	22.	48.	930.	12.	223.	163.	281.	87.	16.	435.	106.	210.
. 2	5-30	1827.	42.	27.	84.	1277.	10.	223.	174.	334.	109.	15.	339.	105.	189.
3	0-35	1480.	37.	37.	87.	1396.	19.	227.	167.	392.	113.	2 0.	308.	115.	187.
3	5-40	1506.	33.	31.	79.	1072.	7.	238.	162.	286.	107.	24.	302.	115.	338.
4	0-45	1352.	34.	39.	102.	1120.	11.	239.	156.	279.	114.	24.	434,	108.	377.
4	5-50	1569.	39.	34.	87.	1172.	6.	235.	159.	289.	128.	18.	495.	98.	299.
5	0-55	1473.	49.	34.	85.	1132.	15.	231.	159.	293.	112.	24.	400.	112.	262.
5	5-60	2104.	43.	54.	71.	1073.	16.	165.	129.	302.	158.	19.	405.	104.	193.

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	BA	co	CR	cu	MN	NI	PB	RB	SR	v	¥	ZN	ZR	MO
0-5	1732.	170.	25 .	35.	652.	-0.	112.	148.	296.	31,	9.	289.	95.	108
5-10	1818.	50.	14,	29.	639.	-0.	61.	148.	296.	34.	9.	213.	88.	129.
10-15	1822.	108.	33.	45.	715.	-0.	227.	142.	298.	45.	10.	453.	123.	106
15-20	2354.	29.	76.	79.	1101.	22.	105.	102.	323.	164.	21.	235.	113.	134
20-25	2383.	31.	70.	87.	1079.	20 .	154.	115.	334.	152.	21.	259.	112.	185.
25-30	2549.	26.	50.	92.	1020.	15.	234.	140.	338.	127.	19.	306.	114.	230
30-35	3557.	25.	49.	86.	1130.	16.	177.	136.	319.	134.	21.	296.	120.	175.
35-40	6225.	27.	65.	85.	1363.	22.	102.	103.	356.	163.	22.	275.	122.	82.

Salt-corrected Trace Element Concentrations: ALICE ARM STATION AA-5

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	BA	cσ	CR	cu	MN	NI	PB	RB	SR	v	¥	ZN	ZR	MO
0-3	1132.	33.	83.	66.	1220.	34.	24.	86.	272.	229.	23.	153.	94.	<7
3-6	1259.	37.	94.	71.	1455.	39 .	18.	89.	281.	249.	25.	157.	102.	<7.
6-10	1240.	36.	93.	70.	1434.	38.	18.	88.	281.	245.	24.	155.	100.	<7.
10-15	1237.	29.	84.	73.	1540.	36 .	26 .	88.	281.	245.	24.	152.	99.	<7.
15-20	1239.	29 .	83.	69.	1520.	39.	16.	89.	273.	250.	25.	156.	98.	<7.
20-25	1239.	29.	92.	71.	1406.	43.	25.	91.	269.	251.	24.	161.	98.	<7.
25-30	1246.	3 0.	92.	66.	1427.	3 9.	25.	89.	268.	261.	24.	162.	99.	<7.
30-35	1183.	32.	89.	96.	1427.	53.	26.	89.	268.	239.	24.	159.	99 .	<7.
35-40	1167.	3 0.	83 .	66.	1397.	43.	23.	88.	269.	249.	21.	155.	100.	<7
40-45	1198.	29 .	85.	67.	13 92 .	43.	22.	86.	272.	253.	22.	147.	97	<7.
45-50	1220.	32 .	86.	69.	1494.	43.	23.	87.	276.	250.	21.	152.	99 .	<7.
50-55	1220.	31.	90 .	69.	1409.	31.	19.	89.	268.	245.	23.	159.	101.	<7

			Salt-c	correct	ed Trace	e Elemer	nt Conce	entratio	ons: ALI	CE ARM	STATION	N AA-6		
	BA	CO	CR	cu	MN	NI	РВ	RB	SR	v	Y	ZN	ZR	MO
0-1	2454.	46.	67.	72.	1970.	24.	221.	134.	302.	176.	24.	314.	109.	141.
1-2	2177.	44.	61.	75.	1312.	18.	305.	147.	298.	126.	22.	375.	110.	176.
2-3	2065.	50.	52 .	77.	1189.	14.	336.	155.	300.	128.	23.	423.	113.	185.
3-4	2132.	45.	5 3 .	71.	1285.	17.	333.	157.	304.	143.	19.	414.	108.	193.
4-5	2188.	51.	43.	55.	1041.	10.	227.	147.	291.	100.	17.	357.	99 .	140.
5-6	2156.	73.	39.	46.	923.	8.	193.	148.	286.	68 .	16.	323.	97.	133.
6-7	2215.	75.	41.	58.	1077.	8 .	235.	153.	282.	104.	18.	396.	106.	155.
78	2233.	64.	35.	56.	1074.	7.	270.	163.	271.	92 .	15.	438.	105.	155.
8-9	2244.	67.	34.	48.	962.	6.	222.	165.	270.	85.	17.	354.	107.	150.
9-10	2312.	68 .	34.	44.	940.	7.	207.	163.	273	82 .	17.	316.	101.	160.
10-12	2349.	59 .	36 .	50.	955.	7.	185.	164.	2 79 .	86.	17.	303.	102.	171.
12-14	2389.	46.	40.	48.	899.	8 .	163.	161.	26 8 .	93.	18.	294.	104.	239.
14-16	2524.	55.	37 .	56.	1030.	10.	204.	159.	281.	101.	19.	409.	105.	212.
16-18	2518.	68.	44.	67.	1112.	11.	259.	154.	293.	112.	21.	465.	107.	175.
18-20	2460.	52.	41.	75.	1227.	13.	298.	159.	322.	120.	19.	595.	109.	165.
20-22	2360.	56.	43 .	81.	1214.	13.	271.	161.	337.	115.	20.	530.	112.	149.
22-24	2289.	24.	47.	85.	1249.	12.	223.	164.	346.	118.	21.	345.	104 .	156.
24-26	2105.	30.	49.	98.	1380.	16.	239.	171.	338.	147.	22.	340.	111.	214.
26-28	2039.	42.	64.	109.	1481.	24.	270.	165.	367.	155.	28.	329.	123.	202.
28-30	2211.	26.	60 .	102.	1640.	17.	243.	164.	395.	150.	22.	322.	113.	216.
30-32	2152.	18.	51.	82.	1292.	16.	283.	156.	317.	118.	23.	344.	116.	227.
32-34	1991.	39 .	51.	89.	1322.	16.	244.	160.	309.	133.	23.	316.	109.	266.
34-36	1785.	44.	41.	79.	1035.	10.	172.	158.	255.	114.	26.	280.	113.	356.

	BA	co	CR	cu	MN	NI	P8	RB	SR	v	¥	ZN	ZR	MO
36-38	1792.	47.	53.	90.	1171.	15.	208.	153.	309 .	120.	23.	424.	115.	362.
38-40	1753.	66.	52.	97.	1180.	13.	227.	154.	302.	112.	22.	451.	114.	301.
40-42	1867.	51.	51.	90.	1273.	12.	236.	160.	291.	123.	22.	457.	108.	305.
42-44	1919.	56.	49.	88.	1397.	13.	238.	161.	299.	139.	22 .	500.	104 .	288.
44-46	1929.	55.	46.	82.	1395.	13.	214.	156.	303.	128.	23.	445.	107.	261.
46-48	2064.	56,	50.	88.	1588.	19.	186.	148.	300.	141.	24.	390.	111.	227.
48-50	2221.	62.	48.	81.	1532.	17.	200.	149.	30 9 .	135.	24.	455.	109.	262.
50-52	2596.	53.	42.	57.	1324.	13.	179.	146.	305.	119.	16.	507.	102.	207.
52-54	2803.	62.	59.	72.	2013.	20.	142.	136.	302.	172.	19.	301.	102.	147.
54-56	2897.	42.	85.	84.	2933.	34.	125.	110.	306.	228.	26.	241.	104.	99 .
56-58	3058.	37.	87.	83.	3078.	36 .	129.	112.	304.	243.	27.	251.	102.	99.
58-60	3097.	31.	77.	84.	2545.	37.	150.	t 16 .	301.	228.	24.	253.	106.	113.
60-62	3444.	33 .	82 .	84.	2494.	30 .	154	116.	298.	242.	27.	253.	106.	113.
62-64	3601.	37.	88.	86.	2512.	38.	159.	115.	296.	245.	26.	250.	104.	112.
64-66	3343.	36.	87.	86.	2570.	38 .	139.	111.	299.	243.	22.	245.	105.	99 .
66-68	3292.	37.	90.	88.	2863.	37.	146.	111.	295.	247.	26.	238.	105.	102.
68-70	3327.	33.	78 .	92.	2496.	34.	161.	119.	297.	223.	24.	249.	106.	113.
70-72	3763.	32.	88 .	89.	2386.	34.	155.	117.	302 .	238.	27.	255.	107.	119.
72-74	5702.	31.	79.	90.	2535.	32.	158.	118.	321.	239.	26.	275.	106.	117.
74-76	7661.	41.	76.	90.	2454.	37.	147.	110.	347.	254.	24.	282.	109.	88.
76-78	9609.	37.	78.	94.	2344.	36 .	147.	103.	376.	264.	27.	298.	114	58 .
78-80	11779.	29.	72.	95.	2408.	37.	157.	101.	406.	270.	26.	314.	114.	57.
80-82	16402.	44.	68.	93.	2363.	40.	177.	92.	474.	303.	26.	347.	112.	28.

	BA	CD	CR	CU	MN	NI	PB	RB	SR	v	Y	ZN	ZR	MO
A6 0-1	2496.	40.	58.	77.	2746.	22.	167.	122.	281.	188.	24.	267.	102.	120.
1-2	2330.	39.	61.	73.	2334.	25.	201.	134.	287.	175.	25.	286.	104.	152.
2-3	2173.	35.	51.	78.	1680.	14.	249.	144.	290.	165.	23.	324.	106.	182.
3-4	2177.	67.	43.	73.	1212.	15.	303.	149.	290.	129.	21.	388.	110.	164.
4-5	2139.	42.	51.	68.	1247.	14.	285.	143.	288.	139.	23.	369.	103.	162.
5-6	2405.	35.	51.	66.	1285.	16.	257.	154.	287.	156.	23.	310.	99.	154.
6-7	2683.	37.	56.	72.	1336.	16.	215.	136.	282 .	160.	23 .	324.	103.	143.
7-8	2574.	85.	43.	69.	1200.	12.	217.	136.	282.	138.	23.	381.	105.	135.
8-9	2097.	72.	29.	49.	982.	7.	226.	144.	276.	81.	17.	428.	110.	119.
9-10	2141.	40.	44.	63.	1217.	14.	226.	149.	271.	131.	24.	365.	105.	154.
10-12	2286.	51.	38.	54.	1097.	8.	237.	154.	266.	111.	17.	386.	105.	143.
12-14	2854.	46.	38.	55.	1169.	10.	207.	152.	276.	132.	21.	317.	104.	156.
14-16	2334.	96.	19.	41.	831.	-0 .	182.	146.	280.	69.	1 6 .	336.	109.	116.
16-18	2566.	65.	31.	48.	968.	З.	187.	155.	277.	99.	18.	299.	107.	167.
18-20	2407.	49.	29 .	56.	1017.	3.	180.	154.	263.	108.	20.	314.	102.	233.
20-22	2523.	49 .	32.	62.	1147.	16.	236.	143.	296.	110.	19.	445.	102.	146.
22-24	2271.	57.	32.	66.	1102.	9.	217.	147.	322.	102.	20.	429.	104 .	129.
24-26	2525.	49 .	39 .	79.	1246.	9.	19 8 .	145.	336.	132.	19.	382.	101.	124.
26-28	2376.	48.	47.	79.	1303.	12.	172.	148.	321.	155.	22.	270.	101.	150.
28-30	2347.	45.	47.	86.	1308.	15.	191.	144.	321.	150.	20.	306.	106.	160.
30-32	2264.	6 6.	57.	94.	1494.	17.	212.	146.	317.	179.	24.	301.	108.	184.
32-34	2742.	32.	61.	92.	1471.	23.	177.	129.	307.	194.	26.	288.	107.	154.
34-36	2640.	41.	56.	81.	1377.	15.	184.	134.	329.	169.	22.	303.	108.	143.

	BA	C0	CR	cu	MN	NI	РВ	RB	SR	v	¥	ZN	ZR	MO
36-38	2216.	52.	40.	98.	1424.	10.	197.	144.	363.	134.	23.	307 .	107.	161.
38-40	2173.	53.	45.	80.	1507.	10.	265.	151.	323.	135.	22.	319.	112.	213.
40-42	1982.	33.	45.	78.	1377.	15.	201.	150.	279.	133.	24.	293.	108.	301.
42-44	2066.	46.	3 9.	84.	1265.	12.	205.	143.	30 8 .	123.	25.	409.	110.	252.
44-46	1950.	38.	41.	92.	1477.	9 .	219.	149.	292 .	132.	22.	413.	106.	292.
46-48	1863.	32.	38 .	82.	1660.	9.	232.	150.	288.	140.	25.	430.	103.	278.
48-50	2054.	37.	36 .	79.	1597.	13.	217.	148.	301.	134.	24.	461.	104.	257.
50-52	2643.	55.	39 .	65.	1445.	13.	195.	142.	311.	137.	18.	535.	101.	225.
52-54	2558.	43.	58.	66.	3078.	23.	140.	125.	301.	163.	22.	299 .	99 .	142.
54-56	2311.	43.	72.	68.	4340.	37.	107.	103.	296.	192.	23.	224.	103.	74.
56-58	2681.	40.	83.	67.	2602.	38 .	83.	97.	29 2 .	203.	25.	216.	102.	58 .
58-60	3729.	33.	95 .	64.	1936.	39 .	73.	92.	302.	214.	24.	197.	105.	36.
60-62	3205.	49.	98 .	63.	1899.	45.	53.	79.	333.	195.	24.	171.	112.	22.
62-64	2654.	40.	87.	61.	5579.	42.	68.	90.	284.	205.	25.	187.	103.	29.
64-66	3185.	35.	92.	67.	3753.	39.	82.	9 0.	275.	233.	25.	197.	102.	39 .
66-68	3036.	40.	86.	59.	2668.	39.	100.	96.	276.	215.	29.	218.	103.	57.
68-70	3202.	31.	80 .	72.	2629.	34.	. 150.	107.	286.	214.	23.	228.	101.	91.
70-72	4705.	44.	78.	81.	2703.	31.	145.	104.	306 .	217.	23.	241.	104 .	83.
72-74	6449.	3Í.	76.	71.	2982.	41.	119.	96.	323.	216.	26.	248.	109.	56.
74-76	5414.	42.	78 .	75.	2840.	36.	125.	101.	307.	204.	26.	250.	106.	71.
76-78	4699.	33.	74.	77.	3300.	31.	134.	107.	303.	203.	23.	248.	107.	83.
78-80	5449.	31.	76.	74.	3277.	34.	132.	100.	317.	205.	26.	248.	107.	72.
80-82	7159.	37.	78.	73.	2949.	37.	114.	94.	341.	221.	25.	250.	110.	47.

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	BA	CO	CR	cu	MN	NI	PB	RB	SR	v	۲	ZN	ZR	MO
82-84	11310.	34.	77.	74.	3037.	39.	109.	86.	394.	247.	23.	266.	108.	11
84-86	18629.	32.	61.	79.	2415.	42.	153.	82.	481.	231.	24.	335.	1135	6
86-88	38390.	29.	18.	98.	2251.	38 .	267.	74.	779.	246.	22.	572.	123.	4
88-90	44793.	21.	4.	103.	2115.	31.	282.	71.	862.	236.	24.	624.	129.	3
90-92	54435.	24.	-0.	85.	2048.	36 .	204.	79.	533.	-148,	25.	381.	113.	2
92-94	21820.	33.	51.	77.	5620.	37.	205.	80.	535.	246.	26.	384.	114.	2
94-96	22521.	33.	56.	75.	3083.	46.	203.	81.	529.	221.	24.	388 .	117.	2
96-98	19823.	33.	57.	74.	2383.	43.	165.	85.	491.	228.	25.	327.	112.	3
98-100	9262.	42.	78.	56.	1819.	54.	77.	76.	377.	249.	26 .	210.	108.	7.
105-107	8675.	34.	82.	82.	3632.	42.	9 9.	90 .	359.	238.	25.	210.	108.	3.
110-112	12870.	36.	66.	75.	4900.	39.	126.	82.	425.	241.	24.	241.	110.	2.
115-117	4050.	29.	83.	74.	4029.	41.	54.	87.	302.	222.	24.	184.	106.	2.
120-122	1743.	31.	99.	72.	3971.	43.	40.	82.	276.	214.	25 .	164.	106.	3.
125-127	1102.	36.	104.	84.	2239.	45.	29.	86.	273.	224.	26.	166.	105.	5.
130-132	1091.	37.	94.	80.	4106.	35.	24.	77.	291.	206.	23.	153.	111.	7.
135-140	1096.	39.	104.	71.	2462.	43.	21.	75.	285.	186.	24.	149.	109.	2.
140-142	1200.	40.	96.	65.	1967.	33.	19.	82.	290.	207.	25.	150.	110.	3.

•	BA	CO	CR	CU	MN	NI	PB	RB	SR	v	¥	ZN	ZR	MO
7 0-2.5	2519.	26 .	41.	58.	1479.	4.	174.	161.	303.	109.	18.	336.	112.	146.
7 2.5-5	291 0.	44.	36.	65.	1345.	З.	185.	162.	307 .	128.	20 .	369.	116.	161.
7 5-7.5	2910.	33 .	40.	76.	1455.	15.	177,	160.	329.	151.	18.	356.	115.	156.
7.5-10	2579.	22.	43.	84.	1565.	14.	186.	16 t .	346.	145.	23 .	319.	121.	183.
10-12.5	2495.	27.	48.	88.	1776.	16.	202.	160.	324.	139.	19.	336.	122.	249.
12.5-15	2169.	23.	50.	90 .	1935.	17.	189.	155.	315.	141.	21.	358.	123.	246.
15-17.5	2480.	33.	49.	76.	2446.	14.	16 9 .	148.	327.	149.	20.	406.	115.	190.
17.5-20	2077.	32.	83.	61.	4136.	42.	65.	100.	317.	179.	25.	187.	124.	39.
20-22.5	2481.	30.	88 .	59.	2737.	45.	56.	93 .	309 .	177.	24.	181.	124.	28.
22.5-25	2675.	31.	86.	62 .	2773.	40.	61.	94.	305.	174.	25.	189.	127.	37.
25-27.5	2679.	35.	87.	55.	3042.	40.	67.	95.	312.	176.	25.	184.	126.	32.
27.5-30	2508.	40.	83.	55.	3252.	44.	58.	91.	306.	172.	24.	183.	127.	31.
30-32.5	2677.	32.	88.	61.	3184.	43.	67.	96.	307.	177.	24.	193.	128.	38.
32.5-35	2767.	30.	81.	61.	3053.	38 .	74.	98.	303.	175.	24.	195.	124.	46.
35-37.5	3224.	29.	85.	59.	3327.	42.	80.	98.	312.	181.	23.	195.	126.	49.
37.5-40	3442.	32.	79.	61.	3528.	39.	86.	97.	321.	176.	24.	205.	127.	50.
40-42.5	3748.	32.	80.	5 8 .	3347.	40.	76 .	95.	326.	173.	23.	202 .	130.	44.
42.5-45	4610.	42.	81.	61.	3381.	48.	62.	84.	342.	179.	25 .	195.	140.	11.
45-47.5	4863.	3 9.	89 .	60.	3501.	48.	51.	85.	352.	177.	25.	190.	138	<7
47.5-50	5899.	26 .	86.	60.	2925.	49 .	59 .	82 .	373.	168.	25.	200.	148.	<7
50-52.5	17130.	19.	54.	70 .	2467.	43.	136.	83.	555.	33.	25.	345.	196.	<7
52.5-55	18112.	30 .	51.	71.	23 36 .	40.	145.	79 .	575.	209 .	22 .	363.	206.	· <7
55-57.5	13905.	28.	60.	68 .	2442.	43.	128.	85 .	498.	186.	25.	303.	18,0 .	<7
57.5-60	14979.	27.	62 .	72.	2708.	42.	138.	85.	518.	201.	25.	323.	193.	<7
60-62.5	12500.	3 0.	73.	68.	3025.	43.	114.	84.	457.	198.	25.	284.	174.	<7
62.5-65	10420.	30.	69.	59.	2697.	45.	108.	87.	432.	189.	23.	242.	166.	<7

168

			Salt-d	correcte	ed Trace	e Elemer	nt Conce	entratio	ons: ALI	CE ARM,	STATIC	N 44-8'		
	BA	CD	CR	cu	MN	NI	РВ	RB	SR	v	Y	ZN	ZR	MO
0-3	1989.	46.	91.	65.	3298.	35.	133.	104.	298.	180.	25.	217.	115.	87 .
3-6	2460.	29.	72.	75.	1561.	21.	219.	135.	297.	179.	23.	318.	105.	139.
6-10	2997.	35.	60.	70.	1432.	19.	202.	151.	288.	165.	22.	337.	105.	160.
10-15	2789.	37.	63.	82.	1517.	22.	200.	147.	313.	168.	24.	317.	109.	179.
15-20	2601.	32.	67.	82.	1653.	21.	206.	144.	304 .	158.	23.	324.	109.	201.
20-25	2388.	38 .	105.	68.	2530.	43.	88.	92.	303	209 .	25.	209.	117.	54.
25-30	2725.	41.	112.	60.	2641.	48.	71.	86.	300.	206.	26.	180.	119.	36 .
30-35	2732.	46.	114.	64.	3035.	45.	65.	84.	299 .	213.	26.	179.	122.	33 .
35-40	2868.	46.	110.	62.	3178.	44.	66.	85.	300.	205.	26.	183.	118.	35.
40-45	4356.	50.	113.	64.	2569.	48.	70 .	81.	316.	221.	26.	193.	118.	30.
45-50	7601.	44.	110.	65.	2217.	51.	73.	71.	374.	207.	25.	211.	124.	<7
50-55	9006 .	41.	103.	64.	2216.	49.	81.	71.	404.	208.	26.	225.	127.	<7
55-60	10559.	42.	100.	62.	2344.	49.	92.	71.	412.	214.	25.	230.	131.	<7
60-66	14751.	35.	87.	68.	2573.	44.	126.	71.	476.	238.	24.	267.	123.	<7

	BA	со	CR	cυ	MN	NI	PB	RB	SR	v	Y	ZN	ZR	MO
0-5	1372.	22.	88.	39.	1561.	35 .	26.	70.	338.	151.	23.	109.	126.	8.
5-10	1429.	24.	94.	25.	919.	20.	21.	62.	360.	110.	20.	93.	123.	4.
10-15	1998.	23.	87.	37.	1119.	30.	33.	67.	351.	146.	22.	109.	123.	11.
15-20	2531.	29.	89.	38.	1053.	31.	36.	68.	355.	148.	22.	117.	132.	9.
20-25	3171.	23.	86.	40.	1100.	32.	41,	69.	359.	153.	23.	125.	130.	-0.
25-30	6211.	23.	86.	44.	1130.	34.	58.	68.	394.	153.	24.	147,	143.	-0 .
30-35	8469.	21.	88.	46.	1128.	24.	65.	67.	415.	122.	23.	172.	139.	-0 .
35-40	6454.	22.	8 0.	44.	1095.	33.	58.	67.	402.	151.	23.	138.	141.	-0 .
40-45	2015.	21.	94.	40.	1026.	32.	21.	67.	365.	143.	22.	105.	131.	-0 .
45-50	1115.	27.	95 .	42.	1021.	35 .	15.	69 .	354.	143.	23.	105.	129.	-0 .

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			Salt-	Salt-corrected Frace Element Concentrations: HASTINGS ARM, STATION HA-2											
	BA	CO	CR	сυ	MN	NI	PB	RB	SR	v	Y	ZN	ZR	MO	
0-3	1601.	42.	88.	63.	1370.	34.	31.	79.	318.	179.	21.	148.	113.	<7	
3-6	1791.	33.	87.	71.	1014.	32 .	34.	80.	329.	174.	22.	152.	110.	<7	
6-10	1892.	3 3.	88.	75.	1008.	32 .	31.	78.	339.	169.	24.	148.	117.	<7	
10~15	2013.	32.	83.	74.	1024.	31.	28.	79 .	339.	176.	22.	146.	117.	<7	
15-20	1281.	41.	91.	56.	962.	30 .	20.	8 0.	330.	168.	23.	132.	116.	<7	
20-25	1124.	34.	94.	42.	959,	36 .	16.	83.	317.	172.	21.	128.	110.	<7	
25-30	1113.	39 .	100.	40.	956.	38.	18.	84.	312	177.	23.	132.	108.	<7	
30-35	1137.	38.	93 .	45,	952 .	36 .	17.	84.	315.	176.	22.	134.	112.	<7	
35-40	1123.	41.	94.	41.	954.	38.	17.	85.	305.	174.	23.	132.	112.	<7	
40-45	1046.	37 .	88.	40.	910.	39.	16.	83.	306 .	173.	21.	128.	108.	<7	
45~50	1119.	38.	92 .	38.	941.	37.	15.	82.	321.	181.	21.	134.	111.	<7	
50~55	1085.	34.	97.	38.	941.	37.	20.	84.	313.	173.	22 .	128.	111.	<7	
55~60	1085.	42.	94.	42.	943.	34.	14.	86 .	308 .	178.	22.	132.	108.	<7	
60-65	1106.	40.	101.	40.	958 .	39.	20.	88.	304.	177.	23.	133.	107.	<7	
	BA	CO	CR	cυ	MN	NI	PB	RB	SR	v	۲	ZN	ZR	MO	
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0-2.5	1479.	52.	77.	56.	2792.	29.	28.	100.	307.	256.	30 .	143.	134.	-0	
2.5-5	1449.	38.	74.	53.	1948.	27.	29.	96.	408.	254.	33.	134.	136.	-0	
5-7.5	1484.	34.	73.	51.	2027.	29.	29.	94.	401.	256.	32 .	134.	135.	-0	
7.5-10	1516.	32.	70 .	53.	1980.	43.	26.	95 .	411.	256.	29 .	110.	135.	-0	
10-12.5	1617.	40.	76.	61.	2062.	35.	28.	101.	400.	264.	32.	139.	129.	-0	
12.5-15	1617.	43.	76.	64.	2137.	31.	30 .	103.	389.	261.	32.	147.	123.	-0	
15-17.5	1745.	36.	76.	66.	2435.	29.	29.	104.	382.	282.	33.	157.	122.	-0	
17.5-20	1824.	28.	81.	6 0.	2393.	31.	32.	105.	375.	297.	34.	162.	118.	-0	
20-22.5	1819.	40.	80.	72.	2250.	32.	28.	103.	383.	286.	33.	161.	125.	-0	
22.5-25	1927.	36.	77.	70.	2373.	34.	33.	104.	383.	294.	33.	165.	122.	-0	
25-27.5	1853.	38.	80.	69.	2053.	33.	32.	104.	386.	288.	32.	167.	126.	-0	
27.5-30	1749.	36.	76.	73.	1947.	31.	33.	104.	386.	277.	35.	163.	123.	-0	
30-32.5	1532.	49.	79.	75.	1848.	29.	31.	106.	394.	282.	34.	165.	128.	-0	
32.5-35	1391.	45.	71.	78.	1639.	33.	27.	99 .	398.	268.	34.	158.	133.	-0	
35-37.5	1381.	40.	72.	77.	1501.	28.	24.	93.	413.	267.	31.	149.	138.	-0	
37.5-40	1443.	42.	70.	76.	1563.	23.	24.	94.	419.	271.	31.	143.	136.	-0	
40-42.5	1441.	34,	75.	83.	1859.	29.	29.	98.	409.	271.	32.	152.	132.	-0	
42.5-45	1421.	49.	70.	74.	1865.	26.	27.	96.	410.	264.	31.	146.	138.	-0	
45-47.5	1359.	34.	68.	75.	1903.	29 .	22.	98.	403.	262.	33.	145.	134.	-0	
47.5-50	1298.	42.	69.	61.	1742.	28.	29.	102.	397.	246.	32.	142.	127.	-0	

Salt-corrected Trace Element Concentrations: HASTINGS ARM STATION HA-4

Salt-corrected	Trace Element	Concentrations	HASTINGS	ARM STATION HA-5
		00110011010110113.	1140111400	MARE JEMETON HM J

•	BA	со	CR	CU	MN	NI	PB	RB	SR	v	¥	ZN	ZR	MO
0-2.5	1620.	46.	66.	52.	1691,	24.	20.	92 .	470.	264.	32.	117.	148.	-0.
2.5-5	1528.	38.	56.	50.	1083.	19.	17.	85.	489.	222.	32.	100.	182.	-0.
5-7.5	1503.	26.	62.	51.	1215.	27.	16.	94.	459.	252.	32.	128.	157.	-0.
7.5-10	1596.	22.	59.	47.	1105.	20.	17.	90 .	477.	245.	32 .	109.	151,	-0.
10-12.5	1619.	39.	46.	31.	791.	9.	12.	77.	530.	182.	27.	62.	175.	-0.
12.5-15	1623.	18.	54.	37.	1007.	13.	17.	79.	522.	213.	31.	76.	167.	-0.
15-17.5	·1508.	25.	63.	46.	1285.	22.	17.	86.	479.	253.	32.	109.	174.	-0.
17.5-20	1514.	22.	55.	44.	1225.	19.	18.	81.	495.	243.	34.	97.	192.	-0.
20-22.5	1618.	40.	59.	39.	1115.	19.	19.	82.	500.	235.	30.	94.	171.	-0.
22.5-25	1611.	32.	63.	51.	1159.	21.	20.	88,	488	255.	32.	109.	158.	- 0 .

Salt-corrected Trace Element Concentrations: HASTINGS ARM, STATION HA-6

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	BA	са	CR	cu	MN	NI	РВ	RB	SR	v	Y	ZN	ZR	MO
	2	••	•				. 2		•••	•				
0-3	1384.	3 8 .	96.	418.	885.	36.	44.	70.	226.	235.	24,	438	92.	<7
3-6	1396.	45.	95 .	431.	875.	38.	38.	69.	219.	236.	21.	436.	92.	<7
6-10	1408.	40.	92.	438.	892.	38.	39.	66.	213.	239.	21.	462.	91.	<7
10-15	1457.	35.	96.	446.	887.	38 .	40.	70.	206.	242.	23.	469.	93.	<7
15-20	1443.	35 .	93 .	535.	882.	38.	38 .	65.	214.	241.	25.	563.	93 .	<7
20-25	1159.	40.	95.	655.	917.	40.	39 .	64.	215.	238.	20.	608.	95 .	<7
25-30	993.	41.	101.	691.	993.	44.	34.	65.	211.	261.	23.	603.	96.	<7
30-35	944.	37 .	94.	363.	93t.	40.	29.	75.	233 .	225.	21.	367.	94.	<7
35-40	1023.	32 .	93.	110.	914.	44.	23.	78.	256	224.	20.	179.	90.	<7
40-45	1031.	30 .	97.	73.	1046.	44.	21.	81.	256.	236.	24.	161.	91.	<7
45-50	976.	33.	90.	53.	932.	44.	18.	85.	276.	180.	21.	155.	89.	<7.

	•			Salt-	correcte	ad Major	Eleme	nt Conc	entrati	ons: An	yox, Gra	anby Bay	/
		SI	ΤI	AL	FE	MN	MG	CA	NA	· K	Ρ	LOI	S
	Ay0-2.5	22.71	0.47	6.21	12.02	0.14	3,38	2.04	1.45	1.01	0.17		3.73
	2.5-5						0.0	0.0	1.28	0.0			0.0
	5-7.5	22.48	0.48	6.10	12.70	0.13	3.12	2.09	1.20	1.01	0.15		3.90
	7.5-10						0.0	0.0	1.26	0.0			0.0
	10.12.5	22.49	0.49	6.08	13.03	0.14	3.22	2.13	1.23	0.98	0.14		4.56
	12.5-15						0.0	0.0	1.16	0.0			0.0
	15-17.5	22.03	0.49	6.01	13.28	0.13	3.37	2.24	1.16	0.98	0.13		4.36
	17.5-20						0.0	0.0	1.16	0.0			0.0
	20-22.5	21.26	0.49	5.85	14.17	0.13	3.15	2.29	1.16	0.96	0.14		4.85
	22.5-25						0.0	0.0	1.08	0.0			0.0
	25-27.5						0.0	0.0	1.08	0.0			0.0
	27.5-30						0.0	0.0	1.01	0.0			0.0
	30-32.5	21.64	0.46	5.90	9.52	0.14	3.54	2.75	0.93	0.93	0.12		5.10
	32.5-35						0.0	0.0	0.82	0.0			0.0
	35.37.5						0.0	0.0	0.74	0.0			0.0
	ORE	2.71	0.12	1.80	35.65		1.63	2.22		0.08	0.04		10.30
•	S'HARD	17.89	0.18	2.75	31.32	0.10	1.03	5.72	0.07	0.50	0.04		3.10
	S'LOOSE	17.17	0.37	3,43	32.10	0.09	1.85	4.33	0.09	O. 38	0.08		1.50

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	BA	со	CR	CU	MN	NI	PB	RB	SR	V	¥	ZN	ZR
Ay0-2.5	755.	62.	72.	622.	835.	35.	28.	37.	159.	191.	24.	1228.	89.
2.5-5	802.	57.	77.	634.	898.	31.	34.	37.	159.	211.	27.	1296.	93.
5-7.5	779.	55.	72.	674.	847.	35.	34.	35.	160.	203.	25.	1399.	92.
7.5-10	749.	54.	69.	672.	810.	38.	32.	38.	153.	187.	26 .	1416.	91.
10.12.5	791.	58.	69.	686.	840.	39.	31.	36.	147.	196.	28.	1475.	97.
12.5-15	795.	52.	65.	721.	801.	33.	33.	35.	145.	186.	26.	1588.	89.
15-17.5	848.	59.	70.	723.	804.	41.	31.	34.	144.	187.	23.	1587.	95.
17.5-20	952.	65.	71.	751.	852.	43.	38.	35.	141.	199.	28.	1639.	90.
20-22.5	928.	58.	61.	808.	816.	32.	38.	34.	142.	190.	29.	1875.	92.
22.5-25	918.	62.	67.	833.	947.	36.	31.	36.	138.	194.	25.	1943.	90 .
25-27.5	807.	66.	66.	838.	826.	37.	37.	32.	131.	189.	25.	2060.	89.
27.5-30	810.	62.	63.	907 .	818.	32.	34.	34.	128.	193.	27.	2119.	102.
30-32.5	909.	51.	64.	808.	896.	33.	35.	34.	125.	198.	23.	2077.	89.
32.5-35	903.	58.	62.	724.	885.	32.	32.	32.	121.	185.	28:	2232.	92.
35.37.5	866.	69.	60 .	668.	890.	29.	29 .	28.	109.	180.	25.	2278.	90.
OPE	. 73	24	180	EDER	B10	26	40	a	24	197	14	1111	40
S'HADD	879	102	89.	2024	496	13	102	9. 13	152	64	17	442J. 9577	43. 69
S'LOOSE	559.	136.	87.	2635.	475.	24.	21.	12.	165.	124.	22.	7330 .	70.

Salt-corrected Trace Element Concentrations: Anyox, Granby Bay

1

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PO	KE WAI	ER C	JN2111	UEN13	, COR	E HA-C	
depth	Fe	Mn	Мо	Si	P043.	- NH4	H2S
CM				um	ol L		
0-3	75	5	0.05	590	125	200	nd
3-6	170	10	0.08	700	190	120	nd
6-10	170	5	0.07	780	200	160	nd
10-15	150	5	0.16	790	190	170	nd
15-20	65	4	0.03	800	150	190	70
20-25	95	4	0.03	740	120	190	9 5
25-30	15	3	0.06	630	85	130	150
30-35	15	7	0.05	930	100	430	230
35-40	6	11	0.08	1100	150	430	350
40-45	3	12	0.07	1100	170	490	470
45-50	2	25	0.15	1100	140	500	450

PORE WATER CONSTITUENTS, CORE HA-6

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POR	E WAT	ER C	TITSNC	UENTS,	COR	E HA-2	
depth	Fe	Mn	Мо	Si	Р0 ₄ 3	⁻ NH ₄ ⁺	H2S
cm				umo	lL		
0-3	0.8	70	0.11	500	10	30	nd
3-6	25	70	0.14	700	10	50	nd
6-10	30	65	0.11	810	25	100	nd
10-15	40	75	0.09	970	50	110	nd
15-20	35	75	0.11	1100	45	170	nd
20-25	35	60	0.11	1200	50	170	nd
25-30	30	40	0.10	1100	40	170	nd
30-35	35	35	0.08	1100	35	200	5
35-40	35	35	0.07	1200	40	230	35
40-45	21	35	0.06	1100	30	200	25
45-50	20	35	0.05	1150	35	210	50
50-55	20	40	0.05	1200	40	210	80
55-60	5	70	0.08	1200	30	230	70
60-65				1200	25	270	60

PORE WATER CONSTITUENTS, CORE AA-8'

1

depth	Fe	Mn	Mo	Si	P04 ³⁻	NH4	H2S	Alkalinity
cm				um	ol L			meqv.
0-3	nd	360	1.1	430	20	60	nd	1.7
3-6	50	490	1.5	460	20	180	nd	3.8
6-10	160	300	1.8	500	85	270	nd	3.8
10-15	260	400	3.5	450	100	330	nd	5.0
15-20	160	650	2.7	650	100	480	nd	5.8
20-25	95	800	1.2	750	130	560	5	5.9
25-30	90	500	0.7	750	200	580	30	8.6
30-35	75	560	0.6	870	290	580	60	8.0
35-40	75	560	0.6	1000	240	560	120	10.6
40-45	60	420	0.2	1060	260	700	230	10.8
45-50	60	330	0.1	1200	220	640	430	11.3
50-55	70	340	0.08	1200	280	69 0	470	12.4
55-60	35	360	0.08	880	190	690	480	11.7
60-65	20	400	0.09	1240	200	640	450	10.1

.

PORE WATER CONSTITUENTS, CORE AA-4

depth	Fe	Mn	Mo	Si	P04 ³⁻	NH_{4}^{+}	H2S	Alkalinity
CM				um	ol L			meqv.
0-3	2.3	290	6.7	230	nd	60	nd	2.7
3-6	75	55	20.6	200	30	250	nd	6.5
6-10	50	25	15.1	210	30	410	nd	4.4
10-15	40	20	11.9	270	30	440	nd	5.9
15-20	50	20	8.8	300	50	650	nd	4.0
20-25	40	25	7.0	380	90	670	nd	6.0
25-30	85	20	17.4	370	100	480	nd	5.0
30-35	110	25	26.9	350	50	330	5	3.5
35-40	120	15	28.4	240	70	400	15	5.8
40-45	100	20	30.0	260	30	410	18	5.2
45-50	150	90	23.7	200	20	540	10	4.8
50-55	160	90	20.5	270	50	650	25	10.7
55-60	250	190	14.6	310	100	830	20	12.3

PORE	WATER	CONSTITUENTS,	CORE	AA-1	

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depth	Fe	Mn	Mo	Si	P04 ³⁻	$\operatorname{NH}_{4}^{+}$	H2S	Alkalinity
cm				umc	ol L			meqv.
0-3	0.5	750	1.3	140	nd	130	nd	2.9
3-6	216	230	2.3	170	nd	260	nd	3.4
6-10	390	75	3.3	300	25	360	nd	4.2
10-15	480	130	4.4	200	10	470	50	7.0
15-20	480	110	3.7	220	nd	700	100	7.1
20-25	400	100	2.4	240	10	550	220	8.2
25-30	250	140	2.7	320	nd	950	320	10.9
30-35	470	150	2.4	420	15	1000	480	12.9
35-40	360	140	1.9	310	40	1100	410	18.6
40-45	330	130	1.3	360	90	1100	420	16.5
45-50	300	100	1.3	300	30	1000	530	11.5
50-55	310	80	0.6	380	20	990	440	13.8

PORE WATER CONSTITUENTS, CORE AA-5'

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depth	Fe	Mn	Мо	Si	P043-	NH_{4}^{+}	H2S	Alkalinity
cm				umo	ol L			meqv.
0-3	180	35	0.12	340	50	1110	nd	- -
3-6	200	65	0.21	330	10	1180	nd	
6-10	60	20	0.26	300	5	340	nd	
10-15	230	130	0.11	320	90	1450	60	
15-20	190	15	0.09	390	50	1900	235	22.9
20-25	190	10	0.10	450	40	2300	380	29.7
25-30	150	35	0.09	320	75	2800	450	29.0
30-35	230	15	0.06	330	50	2500	528	28.2
35-40	330	15	0.08	500	90	2800	685	31.5
40-45	230	20	0.08	630	70	2700	792	35.0
45-50	180	10	0.07	380	90	3000	1167	
50-55	250	10	0.08	440	80	2900	1053	33.0

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