Investigation of the Chemical Composition and Distribution of Mining Wastes in Killarney Lake, Coeur d'Alene Area, Northern Idaho

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Authorization to Submit
Thesis

This thesis of Scott F Bender, submitted for the degree of Master of Science with a major in Geology and titled "Investigation of the Chemical Composition and Distribution of Mining Wastes in Killarney Lake, Coeur d'Alene Area, Northern Idaho," has been reviewed in final form, as indicated by the signatures and dates given below. Permission is now granted to submit final copies to the College of Graduate Studies for approval.

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Abstract

Killarney Lake, a lateral lake of the Coeur d'Alene River in northern Idaho, received mining and milling wastes from the Coeur d'Alene mining district for nearly 100 years. Mining and milling wastes were transported by the river during flood events until 1968 when tailings ponds were built. Lake bed sediments in Killarney Lake were sampled at three separate localities using a piston core sampler operated from a raft. The cores collected 3.6 m and 3.5 m of lake bottom sediments from the north and south ends of the lake, respectively, and 6.4 m of sediments from the center of the lake. Lake bed sediments were also sampled to a depth of 59 cm using a freezer box sampler. A control core and freezer box section were extracted from Bells Lake in the nearby St. Joe River drainage, an area free of commercial mining practices. Identification of the Mazama ash, which was collected at 6.1 m below lake bottom in Killarney Lake and 3.8 m below lake bottom in Bells Lake, by microprobe analysis enabled the chronology of cores from both lakes to be constrained.

The lake bottom sediments were sampled to evaluate heavy metal concentrations downstream of the mining district. Sediments were analyzed by atomic absorption spectrometry for As, Ag, Cd, Cu, Fe, Mn, Ni, Pb, and Zn. Sediments from Bells Lake showed similar chemistry to the pre-mining sediments in Killarney Lake, suggesting that Bells Lake was an adequate control. High concentrations of heavy metals are present in the top 59 cm of the Killarney Lake bed at the center and deepest portion of the lake. Up to 17.5 cm of metallic silt were collected at the north and south ends of the lake. The highest observed metal concentrations in the sediment were 376 ppm As, 37 ppm Ag, 475 ppm Cu, 146 ppm Cd, 111,000 ppm Fe, 13,440 ppm Mn, 71 ppm Ni, 37,400 ppm Pb, and 32,850 ppm Zn. In this uppermost layer, concentrations of metals are 1 to 3 orders of magnitude greater than in deeper Killarney Lake sediments or in Bells Lake. A sharp, defined contact was observed between the natural organic silt and the introduced metallic silt. Organic silt was also observed overlying the metallic silt in the freezer box sample. Sediments with heavy metal concentrations above that of background were found to occur a maximum of 22.5 cm below the lower metallic silt and organic silt contact.

Acknowledgements

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1.0 INTRODUCTION

This study investigates mining wastes in Killarney Lake, a lateral lake in the lower Coeur d'Alene River valley. The study is intended as a contribution to the evaluation of the distribution of mining wastes in the lower river valley. The presence of heavy metals in mine tailings throughout the lower Coeur d'Alene river system is a potential long-term source of heavy metal pollution of the valley's soils, surface water, groundwater, and biota.

The general purpose of this study is to determine the variation of heavy metal concentrations with depth and lithology in the bottom sediments of Killarney Lake. Specific objectives of this study are:

1) Review past studies of heavy metal pollution in the Coeur d'Alene mining district and river basin.
2) Sample lake bottom sediments in Killarney and Bells Lakes with piston core sampler and freezer box sampler.
3) Determine heavy metal concentrations in lake bottom sediments.
4) Determine the vertical distribution of heavy metals in Killarney Lake bottom sediments and compare with the composition and distribution in Bells Lake.

1.1 Geography

The Coeur d'Alene mining district is located in northern Idaho and extends from Pinehurst to Wallace along Interstate 90 (Figure 1.1). Draining much of the Bitteroot Range of Northern Idaho, the Coeur d'Alene and St. Joe Rivers originate on opposite sides of the range divide. The South Fork of the Coeur d'Alene River in part drains the mining district, joining the North Fork of the Coeur d'Alene River 3 miles above Cataldo at Enaville. The main stem of the Coeur d'Alene River flows 48.2 kilometers from the confluence to Lake Coeur d'Alene. Lake Coeur d'Alene is drained by the Spokane River. Nine lateral lakes lie along the main stem of the Coeur d'Alene River, five on the north side and four on the south side of the river. One of these, Killarney Lake, which is the focus of this study, is located 27.4 kilometers upstream of Lake Coeur d'Alene on the north side of the river (Figure 1.2). Bells Lake is used as a control in this study and is located 30.5 kilometers up the St. Joe River, which drains into the south end of Lake Coeur d'Alene (Figure 1.2).

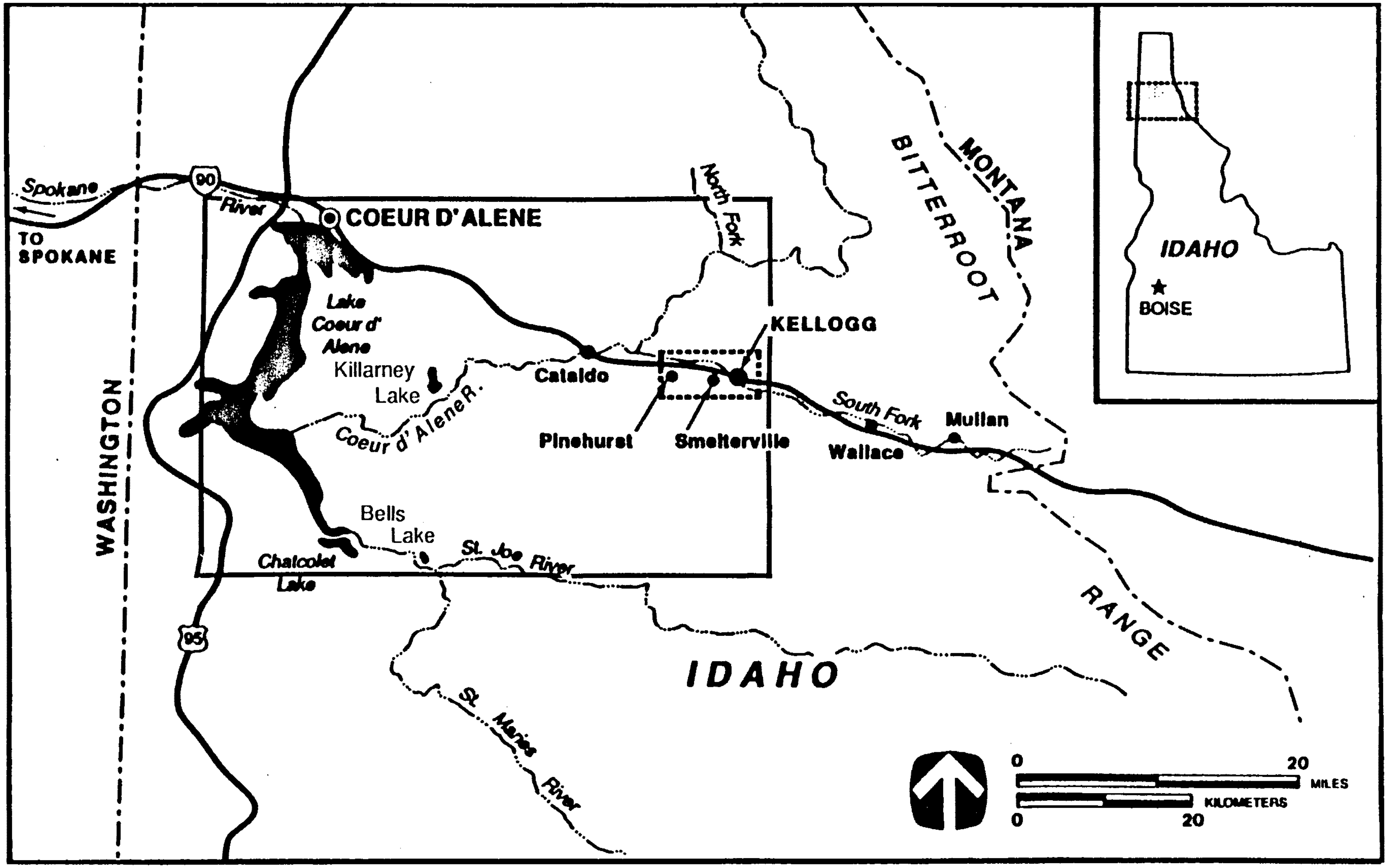

Figure 1.1. Location Map of the Coeur d'Alene Area. Dashed box represents the Superfund site. Solid box represents area enlarged in Figure 1.2

251.5 - 253.5	2	silt	5 Y, 4/1	Gray fine silt, wood fragment at 253.5.
253.5 - 258.5	5	clay	5 Y, 4/1	Gray-green clay.
258.5 - 260.5	2	organic silt	5 Y, 2.5/1	Brown organic silt.
260.5 - 263	2.5	silt, and organics, vegetation	5 Y, 3/1	Brown-green organic silt, with coarse vegetation.
263 - 265	2	organic silt	5 Y, 4/1	Brown-green organic silt.
265 - 269	3	fine sand to coarse silt	5 Y, 4/1	Two distinct layers of fine gray silt separated by a 0.25 cm gray sand.
269 - 369	100	organic silt	5 Y, 3/1	Brown-green organic silt.
369 - 372	3	clay	5 Y, 3/2	Light gray-green clay.
372 - 374	2	organic silt	5 Y, 4/2	Brown-green organic silt.
374 - 378	4	sand	5 Y, 4/1	Light gray medium "salt and pepper" sand.
378 - 381	4	organic silt	5 Y, 3/2	Brown-green organic silt.
381 - 571	190	volcanic ash	10 YR, 7/1	Light pink to gray, compact, volcanic ash. Grades from a very dry, dense ash, to a wet ash. Possible worm burrow at 487 - 501 cm filled with salt and pepper sand with micas.
571 - 582	11	organic silt	10 YR, 3/3	Black-gray organic silt.
582 - 592	10	silty clay	5 Y, 4/1	Gray-green grading to gray silty clay with organics.
592 - 629	37	organic silt	5 Y, 3/1	Black to brown-green organic silt.
629 - 631	2	sand	5 Y, 2.5/1	Gray-black fine sand.
631 - 651	20	organic silt	5 Y, 3/1	Black to brown-green organic silt.
651 - 653	2	volcanic ash	10 YR, 4/1	Gray compact volcanic ash.

Appendix A-2. Lake Bed Lithology at Site KB.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Munsell Color Chart	Description
0 - 3	3	metallic silt	2.5 YR, 5/2	Tan, yellow-brown, metallic smelling, fine silt interpreted as heavy-metal contamination.
3 - 574	571	organic silt	5 Y, 3/2	Green-brown organic silt grading to brown-green between 409 and 389 cm. Pine cone or tree knot at 197 cm. Bands of alternating dark chocolate to light chocolate brown organic silt above 164 cm (not annotated).
574 - 575	1	vegetation layer	5 Y, 5/1	Brown to black, fibrous, laminated vegetation.
575 - 609	34	organic silt	5 Y, 4/1	Soft, moist, green-brown organic silt including two 3 mm thick ash layers at 607 cm and 578.7 cm.
609 - 639	30	Mt. Mazama ash	10 YR, 4/1	Light pink to medium gray, dry, compact volcanic ash. Includes occasional worm burrows filled with salt and pepper sand.

Appendix A-3. Lake Bed Lithology at Site KC.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Munsell Color Chart	Description
0 - 19.5	19.5	metallic silt	2.5 YR, 5/2	Light and dark gray laminated fine silt with metallic smell interpreted as heavy-metal contamination.
19.5 - 28.5	9	peat/silt	7.5 YR, 3/4	Brown peat mixed with gray silt.
28.5 - 30.5	2	silt	10 YR, 5/1	Gray silt.
30.5 - 176.5	46	peat	5 YR, 2.5/1	Black peat grading into brown peat. Silty peat from 51.5 - 64.5 cm. Quartzite rock at 136 - 132 cm.
176.5 - 186.5	10	organic silt	5 Y, 3/1	Gray-brown organic silt grading into brown peat.
186.5 - 248.5	38	peat	10 YR, 4/4	Black peat. Above 226 cm, includes visible roots with mottled gray silt between 194 and 170 cm.
248.5 - 259.5	11	organic silt	10 YR, 3/2	Brown-gray silt and organics. Grades rapidly into overlying peat.
259.5 - 261.0	1.5	organic silt with silt	10 YR, 5/1	Two distinct 0.3 mm gray-brown silt layers separated by green-brown organic silt.
261.0 - 356.5	4.5	organic silt	10 YR, 3/2	Gray-brown silt increasing to approximately 40% organic material above 322.5 cm.

Appendix A-4. Lake Bed Lithology at Site KD.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Munsell Color Chart	Description
0 - 17.5	17.5	metallic silt and fine sand	5 Y, 3/2	Gray-tan coarse silt and fine sand with metallic smell. Oxidized rim.
17.5 - 118.3	100.8	peat	10 YR, 2/2	Coarse black and brown peat including silt lenses and quartzite rock at 118 - 111 cm. Top 4 cm include metallic silt.
118.3 - 127.0	8.7	fine sand to coarse silt	5 Y, 3/1	Gray fine sand to coarse silt.
127.0 - 214.0	13	organic silt	5 Y, 2.5/2	Light to medium brown organic silt increasing in organic content up the section.
214.0 - 257.3	43.3	fine sand to coarse silt	5 Y, 2.5/2	Light and dark gray laminated fine sand to coarse silt.
257.3 - 260.5	3.2	silt	2.5 Y, 3/2	Gray-brown silt including a 0.2 cm thick layer of vegetation.
260.5 - 351.5	9	fine sand to coarse silt	2.5 Y, 4/2	Light and dark gray laminated fine sand to coarse silt. 2.1 cm thick layer of volcanic ash at 334.1 cm with another distinct 0.5 cm thick layer at 288.7 cm. Some sand includes reworked ash.

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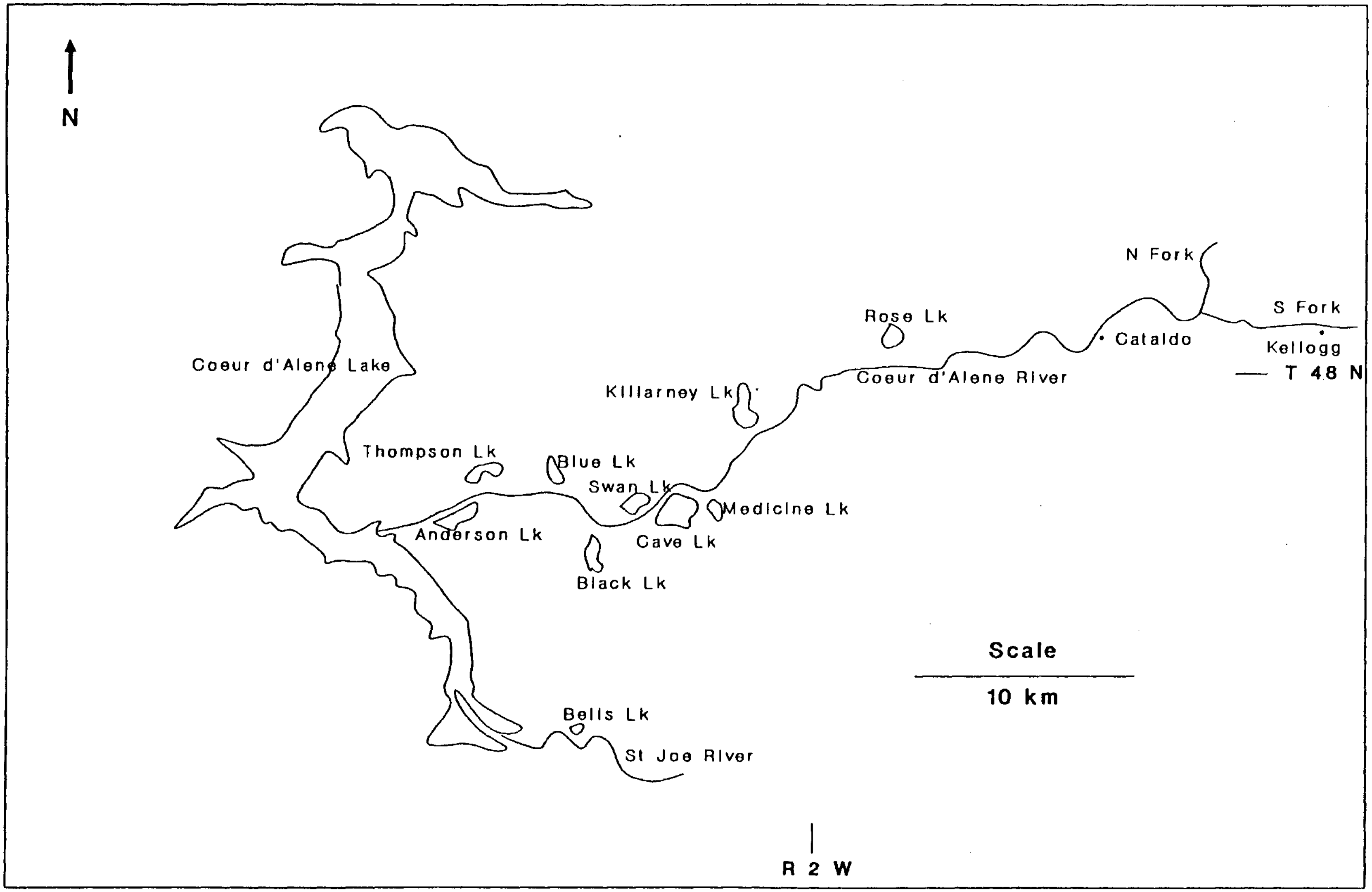


Figure 1.2. Lateral Lakes of the Coeur d'Alene River

1.2 Geology

The generalized geology of the Coeur d'Alene and St. Joe drainage basins is shown in Figure 1.3. The Coeur d'Alene and St. Joe River drainage basins are primarily underlain by the Prichard and Burke Formations of the Proterozoic Belt Supergroup. The Belt Series are slightly metamorphosed clastic rocks that are host to the veins of the Coeur d'Alene mining district. These Proterozoic metasediments have been intruded by Proterozoic and Mesozoic plutons in the Coeur d'Alene region. There are two hypothesis which explain the placement of the ore in the Coeur d'Alene mining district. Placement of the ores by hydrothermal solutions resulting from the emplacement of intrusions (Hobbs and others, 1965); or placement of base metals into the Belt geosyncline through venting from a deep source such as the mantle (Constantopoulos, 1989). The Idaho Batholith and Gem stocks crop out over a large portion of northern and central Idaho (Hobbs and others, 1965). The absence of ore bodies directly associated with these intrusions suggests that they are not related to the formation of the ores found in the Coeur d'Alene district (Constantopoulos, 1989). Age dating of ore minerals suggests that the age of some of the base-metal mineralization was approximately 825 million years before present (Constantopoulos, 1989). This date correlates to the Goat River orogeny which resulted in greenschist metamorphism of Belt sediments and structural deformation of the Coeur d'Alene district (Constantopoulos, 1989). Faults are the dominant structural features of the Coeur d'Alene mining district. Fracturing related to the faults has controlled the position of ore-bearing veins (Hobbs and others, 1965). Sulfide ores within this region include antimony, arsenic, cobalt, copper, gold, lead, silver, and zinc (Funk and others, 1973).

The region to the southwest of the study area was covered by outpourings of the Columbia River Basalt during the Miocene. Some flows reached this area and may have dammed the ancient Coeur d'Alene River in the middle Tertiary. Erosion of ridge summits in the area and deposition of gravels high above the present valleys suggests the river was dammed and diverted (Hobbs and others, 1965).

Lobes of the Cordilleran ice sheet periodically dammed the drainage of the Clark Fork River in northern Idaho, ponding huge volumes of water in the drainage and creating Glacial Lake Missoula approximately 16,000 years before present. Breaching of the ice dams led to massive flooding of the Columbia Plateau. Backwater from the floods ponded over the Coeur d'Alene region and deposited over 400 feet of unconsolidated silt in the Coeur d'Alene River valley (Norbeck, 1974).

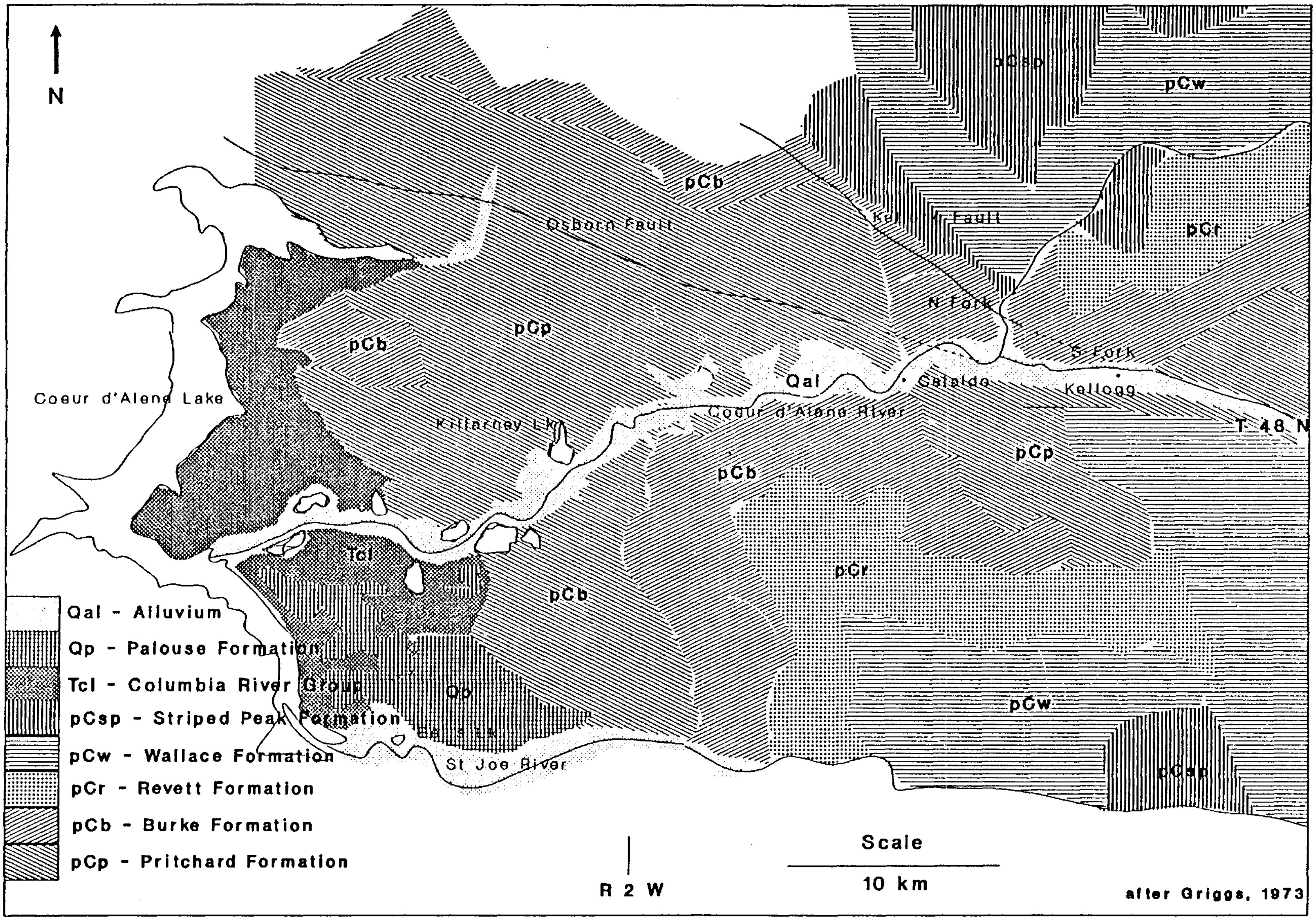


Figure 1.3. Generalized Geology of the Coeur d'Alene Region

The three major events responsible for the deposition of the natural sediments in the Coeur d'Alene River valley are as follows:

1) Glacial melt and drainage from east of the Smelterville flats area approximately 17,000 to 19,000 years before present. Medium to high-energy glacial runoff through this valley deposited silty sands and gravels as the lowest stratigraphic alluvial unit (Norbeck, 1974).

2) Ponding of waters to the west. Continental glaciation periodically dammed drainages approximately 16,000 years before present on the Clark Fork River and Columbia Plateau. Lakes and backwaters that formed from these events extended through the Spokane and Coeur d'Alene river valleys and up to the city of Wallace (Norbeck, 1974). Because drainage from the east continued, some sand and gravel lenses are also found in this unit. The lakes receded after draining of ponded waters on the Columbia Plateau.

3) Continued drainage from the east. The North and South Forks of the Coeur d'Alene River continue to drain the Bitterroot Range of Northern Idaho. Fine silt and sands are deposited in the generally low-energy environment of the study area.

1.3 Background

The Coeur d'Alene mining district has been in operation for nearly 100 years. This region has been one of the major silver, lead, and zinc producing areas in the United States. Until the establishment of tailings ponds in 1968, wastes from mining and ore-processing activities were dumped directly into the South Fork of the Coeur d'Alene River. The settling ponds have greatly reduced the amount of suspended solids discharged to the river (Mink and others, 1973). As of 1964 it was estimated that over 2200 tons per day of mine and mill slimes were being discharged to the South Fork (Keely and others, 1975). Transported by river flow and river flood events, wastes have been distributed throughout the lower Coeur d'Alene River floodplain, the nine lateral lakes, and Coeur d'Alene Lake (Figure 1.2). These sediments are contaminated with arsenic (As), antimony (Sb), cadmium (Cd), copper (Cu), lead (Pb), manganese (Mn), zinc (Zn), and other metals (Rabe and Bauer, 1977). The high residual heavy metal content of mine tailings and wastes is toxic to much of the biota in the surrounding environment. A summary of the toxicity of these metals to flora, fauna, and humans is found in Wai and Mok (1988). Because of the magnitude of this contamination, the U.S. Environmental Protection Agency established the Bunker Hill Superfund Site in 1983. The remediation program addresses a 54-square-kilometer site in the Kellogg and Smelterville Flats area (Figure 1.1). To date, this is the only major remediation project in the valley. The Superfund site addresses one area contaminated by the mining wastes, yet vast amounts of contaminated sediments are also present in the river valley downstream of this site. The sediments of the river bed and banks are an additional source of heavy metal contamination as flood waters seasonally transport and redeposit these sediments. Although significant research has been conducted in the Smelterville Flats area concerning water quality and biota of the region, few studies have been undertaken on the distribution and chemical composition of these wastes in the lower Coeur d'Alene River valley.

1.4 River System

Mining wastes are transported from the mining district by river flow and flood events. The South Fork of the Coeur d'Alene River (Figure 1.1) drains the source area and is a swift flowing stream with only minimal deposition occurring along its banks (Mink, 1971). The gradient of the South Fork is about 5.7 m/km between Wallace at the eastern edge of the mining district and the confluence with the North Fork at Enaville downstream of the district (Norbeck, 1974). The 0.19 m/km gradient of the deeper and slower moving main stem below Enaville allows a higher percentage of suspended solids to settle out. Most of the water in the main stem of the Coeur d'Alene River is contributed by the North Fork, which is free of large-scale commercial mining activities (personal communication, Robert Harper, 1990).

The primary reason for the relatively flat gradient of the main stem below Enaville is Post Falls dam, which lies below Lake Coeur d'Alene on the Spokane River (personal communication, Hank Lubien, 1988). Water levels regulated at the dam for power generation and flood control may cause fluctuations of as much as 2.2 m in the Coeur d'Alene River. Because the lakes are directly connected to the Coeur d'Alene River by dredged channels, water level changes in the river directly influence the water levels of the lakes. Water levels in the river, and hence in the lateral lakes, are controlled by the dam unless the river discharge exceeds 85 cubic meters per second (personal communication, Hank Lubien, 1988). At discharges exceeding this value, water from the river flows into the lateral lakes, but at lower discharge rates water flows from the lakes into the river. Discharge from the Coeur d'Alene River to the lateral lakes generally occurs between February and April during spring runoff (personal communication, Hank Lubien, 1988).

Bells Lake was chosen as a control lake. It lies adjacent to the St. Joe River, which is unpolluted with respect to heavy metals and mining wastes (Mink, 1971). The river has been used primarily by the logging industry and has supported no major mining activities (Rabe and Flaherty, 1974). The St. Joe River has an average annual discharge of 2.45 billion cubic meters, which is slightly greater than the 2.28 billion cubic meters of the Coeur d'Alene River (personal communication, Hank Lubien, 1988). Post Falls dam influences the flow of the St. Joe River in the same way that it influences the flow of the Coeur d'Alene River (personal communication, Hank Lubien, 1988).

1.5 Lakes Studied

The premise upon which this study is based is that prior to the use of tailings ponds, mine wastes were carried downstream by flood events and river transport and were deposited in the lateral lakes and Coeur d'Alene Lake. Though a dam was constructed downstream of Smelterville to minimize transport of mining wastes in the 1930's, it breached only a few years later (personal communication, Hank Lubien, 1988). After construction of the tailings ponds, wastes currently in the river system may have been transported downstream during annual or semi-annual flood events. Figure 1.4 shows scouring above Killarney Lake after a flood event in April 1989.

A lake is a stable environment. Because there is little erosion of a lake bottom surface, sediments deposited during annual or semi-annual floods remain as a permanent record and may give some indication of sediment transport in the river system.

Killarney Lake is one of nine lateral lakes adjacent to the Coeur d'Alene River. This lake was selected for this study for the following reasons:

1) Killarney Lake is flooded and directly connected to the river in annual to semi-annual high water or flood conditions (Figure 1.4). Therefore, the sediments preserved on the lake bottom may provide a near-continuous record of flood events and deposition of mining and milling wastes.

2) Killarney Lake is the first lateral lake occurring downstream of the mining district that is directly connected to the Coeur d'Alene River by a wide, dredged channel. Therefore, it is one of the first sediment sinks downstream of the mining district, and probably served as a natural tailings pond prior to 1968. Rose Lake (upstream from Killarney Lake) is closer to the district, but there is no clear channel between the lake and the river. Since the construction of Idaho State Highway 8 in the 1920's, the road embankment has partially shielded Rose Lake from flood waters, hence only the highest flood events reach Rose Lake.

Figure 1.4. Flood Scouring Upstream of Killarney Lake, April, 1989 (from north)

Bells Lake, in the St. Joe River system, was chosen as a control lake for the following reasons:

1) The St. Joe River drains the same regional and geologic environment as the Coeur d'Alene River (Figure 1.3) but is free of mining activities or any known source of heavy metal contamination.

2) Bells Lake is also flooded by the river during annual to semi-annual high water or flood conditions. Bells Lake is connected to the St. Joe River by a small creek, unlike Killarney Lake, which is connected to the Coeur d'Alene River by a dredged channel.

3) Bells Lake was used as a control lake in an earlier study by Rabe and Bauer (1977), thus allowing a comparison of the two studies.

Although both lakes lie in similar environments, they differ in acreage. Bells Lake covers only 15 acres in comparison to the 508 acres of Killarney Lake (Milligan and others, 1983).

This study is intended to be a preliminary study of the heavy metal concentrations in lake bottom sediments in Killarney Lake. It also establishes methodologies for possible future studies.

2.0 PREVIOUS RESEARCH

Many studies have investigated the soils, water quality, and biota of the Coeur d'Alene region. Morilla (1975) reviewed the impact of mining operations on the water quality of the Coeur d'Alene River and concluded that gross pollution of the Coeur d'Alene River occurred prior to the construction and operation of mine-tailings ponds in 1968. In an extensive survey of heavy metal contamination in the Coeur d'Alene River valley, Ellis (1932) noted that the river was essentially devoid of life from the South Fork at Kellogg to the delta at Harrison. He also noted that three of the lateral lakes along the river supported only sparse plankton and benthos populations, conditions which he attributed to the toxic effects of mining wastes.

Although natural weathering and erosional processes may contribute some heavy metals to the valley, most heavy metal contamination has originated from the Coeur d'Alene mining district, particularly in the Kellogg and Smelterville Flats region (Figure 1.1). Point sources have included mining and processing activities in the forms of particulate matter from smelter stacks, dust from smelter operations, and dust and leachate from tailings ponds. Non-point sources have included all types of mining wastes occupying the valley floor (Johnson and others, 1976).

Mine tailings occupying the valley floor of the mining district represent a major source of downstream heavy metal contamination. From inception of the mining district in the 1880s to the 1930s, jig tailings, characterized by high Cd, Pb, and Zn concentrations, were dumped on the valley floor of the South Fork in the Kellogg-Smelterville area. In a study of the transport of uncontrolled tailings, Inoannou (1979) concluded that owing to high concentrations of Pb and Zn detected in suspended sediment samples, sediment transport from tailings piles to the South Fork of the Coeur d'Alene River (and thence to the river system) is a function of stream discharge. Galbraith (1971) found leaching of heavy metals by groundwater to be a mechanism that causes poor water quality in groundwater passing through these tailings piles. Norbeck (1974), however, concluded that groundwater movement through the tailings of the Smelterville Flats region had a minimal effect on the water quality of the South Fork.

Since the 1930s, flotation tailings have been stored primarily in settling ponds (Johnson and others, 1976), but these were designed to maximize ore recovery - not to improve sediment and water quality discharges. A dam was constructed in the early 1930's downstream of Smelterville at a constriction in the valley to minimize the transport of mine and milling wastes from the mining district; the dam breached in high water only a few years later (personal communication, Hank Lubien, 1988).

By 1968, tailings ponds, which were originally recommended by Ellis in 1932, were installed by mining companies under pressure from federal and state agencies (Rabe and Flaherty, 1974). The ponds had the effect of lessening environmental degradation by reducing the quantity of mining and milling wastes entering the river. Ellsworth (1972) noted that the tailings ponds effectively removed solids from the waste stream, but he questioned whether sufficient amounts of dissolved solids could be removed from the effluent to meet current (as of 1972) and future water quality standards. Mink (1971) showed that installation of the settling ponds had greatly improved the water quality of the South Fork and Main Stem, but water quality samples collected from 34 stations continued to show Cd and Zn concentrations above toxic limits for fish survival. Constituents such as dissolved Cd and Zn remained above toxic limits for most aquatic organisms (Rabe and Bauer, 1977).

Although the installation of tailings ponds reduced the sediment discharge and a portion of the suspended sediment discharge to the river system, millions of tons of material had already entered the system. Norbeck (1974) found that high heavy metal concentrations in the valley downstream of the South Fork could be correlated with mining operations and disposal practices. Bauer (1974) measured heavy metal concentrations in surface water and lake bottom sediments in the nine lateral lakes. Bells Lake was used as a control. However, he did not core the sediment, but simply took dredge samples of the top four centimeters. Lake bottom surface samples indicated that metal concentrations in each lake were greatest closest to the river. Cd and Zn concentrations in fish were significantly higher in the lateral lakes than in Bells Lake, and concentrations were greater in benthic insects than in fish. Funk and others (1975) found that heavy metal concentrations, particularly Zn, were higher in sediments of the Coeur d'Alene River and lateral lakes than in those from Bells Lake. Heavy metals were found in a layer varying from 30 cm to 80 cm in thickness in the Coeur d'Alene delta and lake bottom sediments, but were 5 cm in thickness towards the outlet to the Spokane River. Neither of these studies analyzed heavy metal concentration distributions with depth. Piske (1990) has found tailings deposits to a depth of 8 feet in the Coeur d'Alene delta. Although groundwater concentrations of As, Cd, Fe, Mn, Pb, and Zn are above the Environmental Protection Agency's drinking water standards, groundwater discharge from the tailings is negligible.

Sediment uptake of heavy metals from surface waters may affect the distribution of the contamination in the valley. Reece and others (1978) performed laboratory experiments on river bank samples from the Coeur d'Alene River and found that metals such as Cd, Mn, Pb, and Zn in sediments can reach saturation concentrations in water relatively quickly. Cd and Pb were much less soluble in water than Zn. Maxfield (1974) collected sediment samples from the Coeur d'Alene River delta area and found that variation of metal content is related to the nature of the sediments, with highest concentrations being found in the silt and clay fractions. In an unrelated study, Bourg (1974) explained that Zn uptake in clays increases rapidly as pH rises from 6.5 to 8. A recent study by Wai and Mok (1988) on As and Sb concentrations within the river system shows that these as well as other heavy metals, such as Ag, Cd, Cu, Hg, Mn, Pb, and Zn, are being leached to varying degrees by ground and surface waters. They state that interaction of water with the existing sediments in the valley is likely a major factor in the distribution of these metals and may control water quality of the Coeur d'Alene River.

In a study of water and sediment quality in Coeur d'Alene Lake and the Spokane River, Funk and others (1973) found that metal concentrations were "inhibitory" to some algal test organisms. They also found that algae in the Spokane River, which drains Coeur d'Alene Lake, were the prime concentrators of Cd, Fe, Hg, Mn, Pb and Zn. Although relatively high concentrations of Zn were found in the livers of fishes, this did not appear to have a significant impact on the fish. They too measured metal concentrations in aquatic life and found that metal concentrations decrease progressively up the food chain as the higher organisms actively excrete the metals. Metal concentrations in fish muscle tissue were two to three times higher than in fish found above Wallace, high in the Coeur d'Alene River drainage. Studies by Minter (1971) and Rabe and others (1973) investigated plankton populations in the St. Joe and Coeur d'Alene Rivers and found the physicochemical environment of the Coeur d'Alene River influenced plankton communities particularly with respect to discharge, turbidity, conductivity, and allocthonous material. Therefore, the presence of heavy metals in the waters of the Coeur d'Alene drainage affects the biota in the system.

A study by Towatana (1990) showed that in wastes deposited in the Smelterville Flats area, As, Ag, Cu, and Sb tend to form sulfides, whereas Cd tends to combine with organic species. Furthermore, the clays of the Smelterville aquitard act as a scavenger for Ag, As, Cd, Cu, Fe, Sb, and Zn but may be a source of Ca, Mn, and Mg. Water pH in the upper aquifer at Smelterville is buffered by carbonates and so plays a minor role in controlling metal solubility, and hence mobility of the metals. Anaerobic conditions are likely to increase the solubility of Cd, Pb, and Zn.

The Idaho Department of Fish and Game has collected over 15 years of data on waterfowl uptake of lead and other heavy metals. A report by Neufeld (1987) summarizing the data concluded that the most important contributor to swan mortality is the consumption of new sediments deposited on vegetation, and of sediments that may be utilized as grit. Swan mortality was found to be predictable and seems related to newly deposited sediments from winter flooding and low water levels. Baseline studies of soils and sediments throughout the Coeur d'Alene valley have indicated lead concentrations as high as 11,000 ppm, with a mean lead concentration of 2,500 ppm.

While significant environmental degradation has occurred in the waters, sediments, and aquatic life within the lower Coeur d'Alene River drainage; airborne and flood transport of heavy metals have also impacted the flora and fauna. Revegetation of the slopes around the mining district, which were decimated by fires in 1910, was inhibited by the emission of sulfur dioxide from smelter stacks. The loss of vegetation has contributed to the near-complete loss of soils on the steeper slopes of the valley (Johnson and others, 1976). A student study by Keely and others (1975) measured heavy metal concentration in soils to 4 inches in depth at over 150 sites within the Coeur d'Alene River drainage. Their results showed that mean heavy metal concentrations were higher in the top 2 inches than in soils from 2 to 4 inches in depth. The study showed a strong correlation between high concentrations in soils and heavy metal accumulation in plants, mice, and other biota. The results in turn correlated with distance from the mining district. In a study of waterfowl habitat in the Coeur d'Alene River valley, Chupp (1956) found that waterfowl mortality is caused by toxic levels of Cu, Pb, and Zn in soils, water, and vegetation. This contamination was attributed to mine wastes in the valley.

Mining wastes are still discharged to the river system. The EPA National Pollutant Discharge Elimination System (NPDES) allows mine operators to discharge nearly 11,000 pounds of lead annually (Neufeld, 1987), and as much as 20 pounds of lead per day were measured by the EPA (in press) in August 1986. Additionally, nonpoint sources of heavy metals, such as windblown soils and erosion of old mine tailings and river banks contribute to the discharge or redeposition of heavy metals throughout the valley.

Wai and others (1985) and Savage (1986) have summarized many of the studies on the environmental problems in the Coeur d'Alene basin. From these studies, one can conclude that 1) large quantities of heavy metals, particularly Cd, Pb, and Zn, have been deposited throughout the lower Coeur d'Alene drainage and lakes and have significantly changed the chemistry of the sediments and water in the valley; and 2) significant anomalies of heavy metals have been found in the flora and fauna of the valley.

There have been no previous studies on the variation of concentrations within the vertical thickness of lake bottom sediments in a basin such as Killarney Lake, downstream of the mining district and upstream of Coeur d'Alene Lake.

3.0 FIELD SAMPLING TECHNIQUES

3.1 Introduction

In this study, lake bottom sediments were cored to establish the depth of mining wastes at three sites in Killarney Lake. The first sampling objective was to core through lake bottom sediments to a known stratigraphic time indicator older than the mining wastes. Recent studies had indicated deposits of Mazama ash in the region (Smith and Westgate 1968; Merhinger and others, 1977). Positive identification of this ash in both Killarney Lake and the control lake (Bells Lake) would provide a definite time horizon in the two lakes. Accordingly, the first core in each lake was drilled to the Mazama ash. Later coring concentrated on the layers containing mining wastes. The second objective was to make a comparison of sediments deposited before mining operations in the valley, sediments deposited during mining, and sediments deposited after tailings ponds installation. With sufficient time stratigraphic indicators, sedimentation rates could also be estimated from the cores. Sampling sites at Killarney and Bells Lakes are shown in Figures 3.1 and 3.2, respectively.

3.2 Piston Core Sampling

3.2.1 Sample Sites

Piston core sampling in both lakes was performed in August, 1988. Killarney Lake sample locations are shown in Figure 3.1. Rationale determining the location of site KB in Killarney Lake was that it is near the center and deepest point in the lake (4.6 m); therefore, the site is located in the 'sink' of the lake. Care was taken also to locate the site beyond the historic valley walls of the Coeur d'Alene drainage in order to reduce the possibility of coring into historic river meanders and impenetrable sands and gravels.

Cores KC and KD were collected at the south and north ends of Killarney Lake, respectively (Figure 3.1). Site KC in a low-lying, marshy area frequently covered by water at high stages of the Coeur d'Alene River. Site KD is located at the north end of the lake approximately, 300 meters south of the shore and the mouth of Killarney Creek. This site, as well as site KB, is located where bedrock walls border the lake; flood waters which reach these sites are therefore a result of ponding of waters rather than direct, high-energy flooding. Sites KC and KD were cored to give some indication of the areal extent of the tailings in the lake as well as the chemical variability towards each end of the lake.

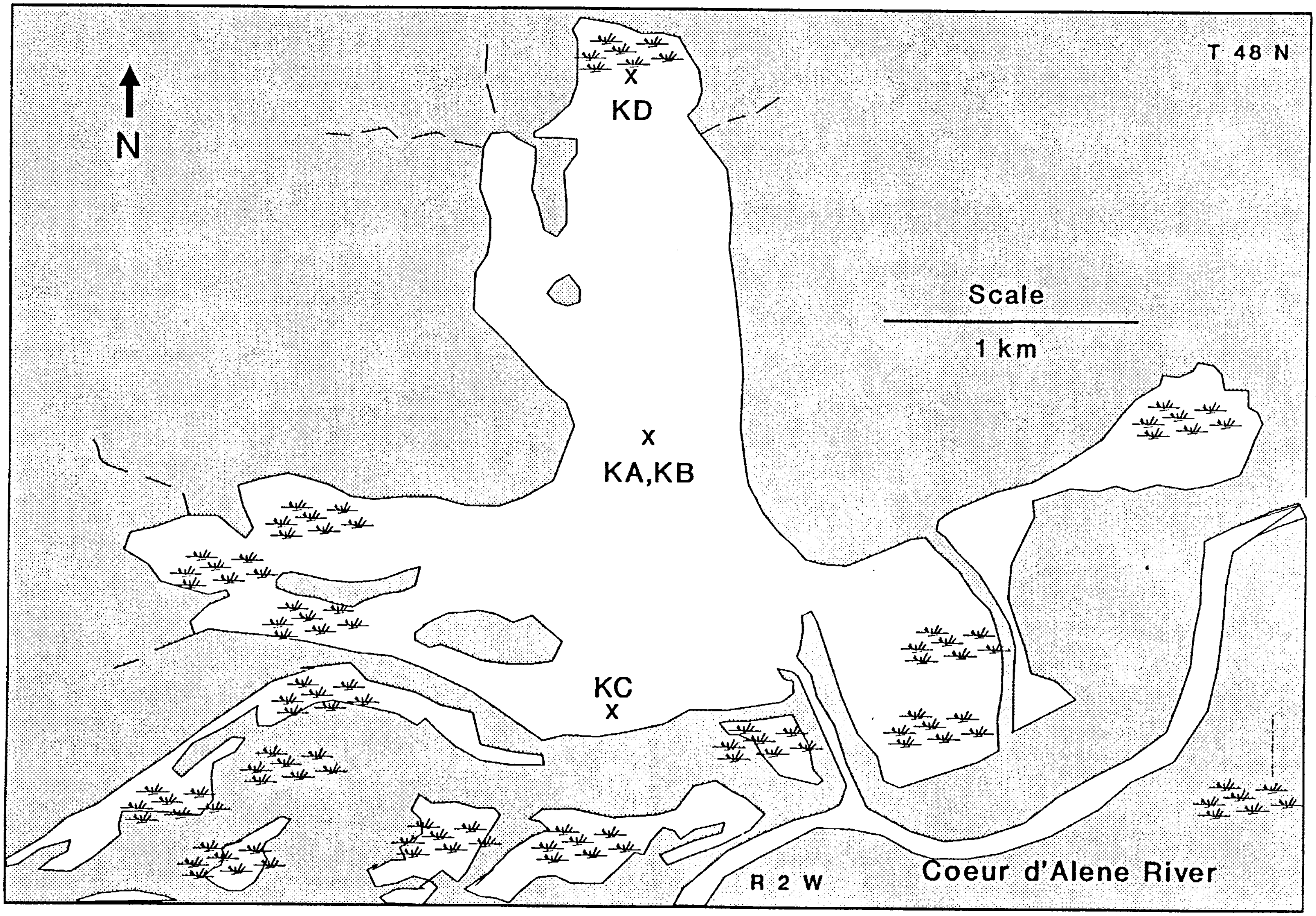


Figure 3.1. Killarney Lake Sampling Locations

In Bells Lake, drilling site BA was chosen in the deepest, flat portion of the lake (Figure 3.2). This location was optimal for it sampled from the bottom of the sediment sink while staying as far from the river as possible, reducing the chances of coring through impenetrable sands and gravels.

3.2.2 Method

The piston core sampler shown in Figure 3.3 was operated from two rafts on the lake surface (a similar apparatus without the rafts is commonly used on a frozen lake surface after being towed to the site by a snowmobile). The coring apparatus consists of several parts. The first is the core barrel. This is a 10.2 cm x two meter PVC sewer pipe, slightly tapered at one end to cut through the sediments. One and two meter pipe sections are connected in a continuous array to lower the sampler, and disconnected when tripping out. A two inch steel pipe, used to lower and raise the apparatus, is connected to the piston head, a brass fitting which is bored on the inside to allow a 3/4 inch steel pipe, called a 'stinger', to slip through. The stinger is attached to a rubber piston which creates a seal, or vacuum, inside the core barrel while coring.

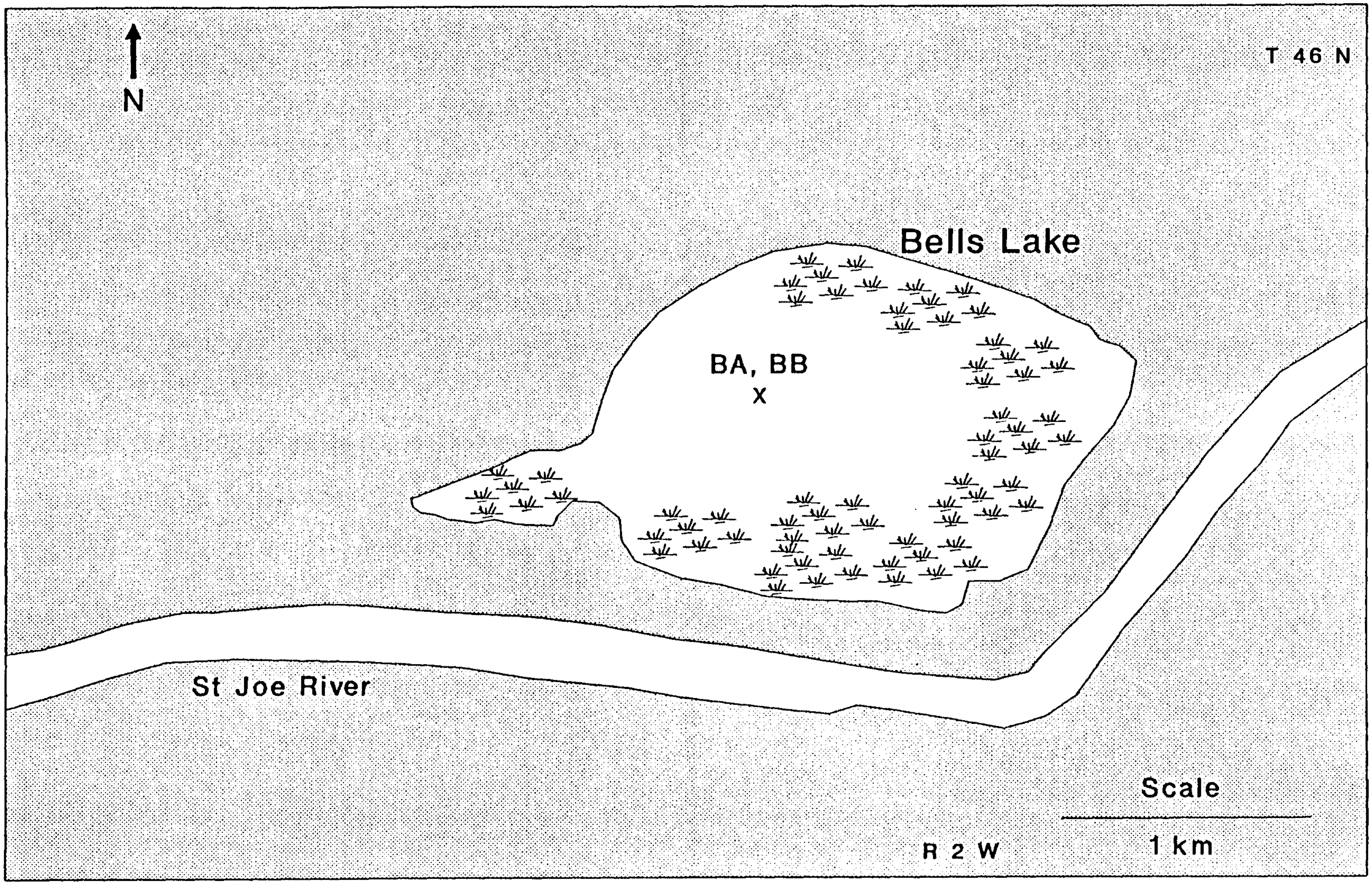


Figure 3.2. Bells Lake Sampling Location

Figure 3.3. Piston Core Sampler

The coring operation consisted of securely anchoring the rafts and measuring the depth of water by means of a steel tape with a weight at one end. A six-inch-diameter casing was then lowered to the lake bottom to ensure accurate placement of the core barrel in the bottom sediments. The core barrel was lowered inside the casing to the measured lake bottom surface, with the piston extended to the lower end of the barrel. Once the lake bottom surface was reached, the stinger was locked to a fixed position and the core barrel was manually driven into the lake bottom sediments. A near vacuum, created by pushing the core barrel down past the piston, ensured that the core would not slip out of the barrel after egress. Once the sampler was on the raft, the core and barrel were removed from the piston head, measured, labeled, capped at both ends, and stored with as little agitation as possible. Depth control in the hole was maintained by measuring lake depth and core length.

Core barrels were a maximum of two meters long and multiple cores were collected from each hole to reach the desired sampling depth. This required inserting and removing up to four core barrels per hole. Casing was used to maintain hole integrity at the lake bottom surface, and during coring, it appeared that the core hole remained open and fairly competent. Hole integrity was shown by the firm bottom of the hole felt when lowering the sampler. Hence little, if any, sloughing of sediments into the hole occurred. Hole integrity was probably due to the compact, silty nature of the sediments and hydrostatic pressure within the hole.

In order to document sloughing in the hole and to check for lithologic log distortion, additional cores KA and BB were drilled within three to six meters of each of the cores KB and BA (Figures 3.1 and 3.2). The good lithologic match between the main offset core in each lake suggested that negligible sloughing had occurred.

3.2.3 Results

Cores KA and KB were cored to depths of 493.0 cm and 607.5 cm below the lake bottom surface, and collected 13.5 cm and 30.0 cm of the Mazama ash, respectively. A full section of the ash was not retrieved because of the difficulty of manually driving this coring apparatus to penetrate any dense unit, such as ash, particularly where the glass shards are lying perpendicular to the direction of coring.

Depth to water at site KC was 1.52 m, and two cores were collected to a total depth of 356.5 cm. Depth to water at site KD was 1.23 m, and two cores were collected to a total depth of 351.5 cm. Vegetation was observed on the bottom and surface at both sites.

Depth of water at site BA was 4.6 m. Core BA penetrated to a total depth of 653 cm into the lake bottom, extending through 192 cm of Mazama ash as well as through an additional 82 cm of organic silt to a second unidentified ash. Core BB was extended 0.91 m into the lake bottom before coring, and consisted of 416 cm of samples to a total depth of 507 cm below lake bottom. This core also sampled 138 cm of Mazama ash before hitting an obstruction. The coring technique was improved upon reaching Bells Lake by hammering on the 2 inch steel pipe while pressing into the ash. The vibration in the core caused by the hammering, and the introduction of water into the ash layer through coring, may have loosened the compact ash shards causing a slurry which the core could penetrate. Upon retrieval, a dry ash had dictoclastic properties with the introduction of water. Identification of the Mazama ash is described in Section 5.5.

White-gray metallic silt interpreted to be mining wastes were visible in each of the three Killarney Lake piston core sites. Metallic silt thicknesses varied from 3 cm in core KB to 19.5 cm in core KC. Chemical analysis showed that high concentrations of heavy metals were found primarily in these gray silts. Whereas cores KC and KD had 19.5 and 17.5 cm of these silts, respectively; core KB had only 3 cm of the gray silt, even though core KB was located at the deepest part of the lake. On the basis of these data, it was concluded that either the piston core did not retrieve or adequately sample the upper, loose lake bottom sediments at site KB; and/or tailings deposits on the lake bottom are variable due to transport of the sediments by lake bottom currents. At coring locations KC and KD the water was shallow enough to visually observe the piston core sampling, which appeared to be successful. However at location KB, the lake bottom was not visible; and the coring device may have passed a thick accumulation of unconsolidated sediments which were not retrieved because they were not 'felt' by the corer.

Metallic silt were not observed in the Bells Lake cores. As explained in Chapter 4, the sediments above the Mazama ash consist of a near-continuous column of organic silt. Coring in Bells Lake may have missed the uppermost few millimeters of sediments, because a thin layer of ash found on top of the raft anchors was not found in the core.

3.3 Freezer Box Sampling

3.3.1 Method

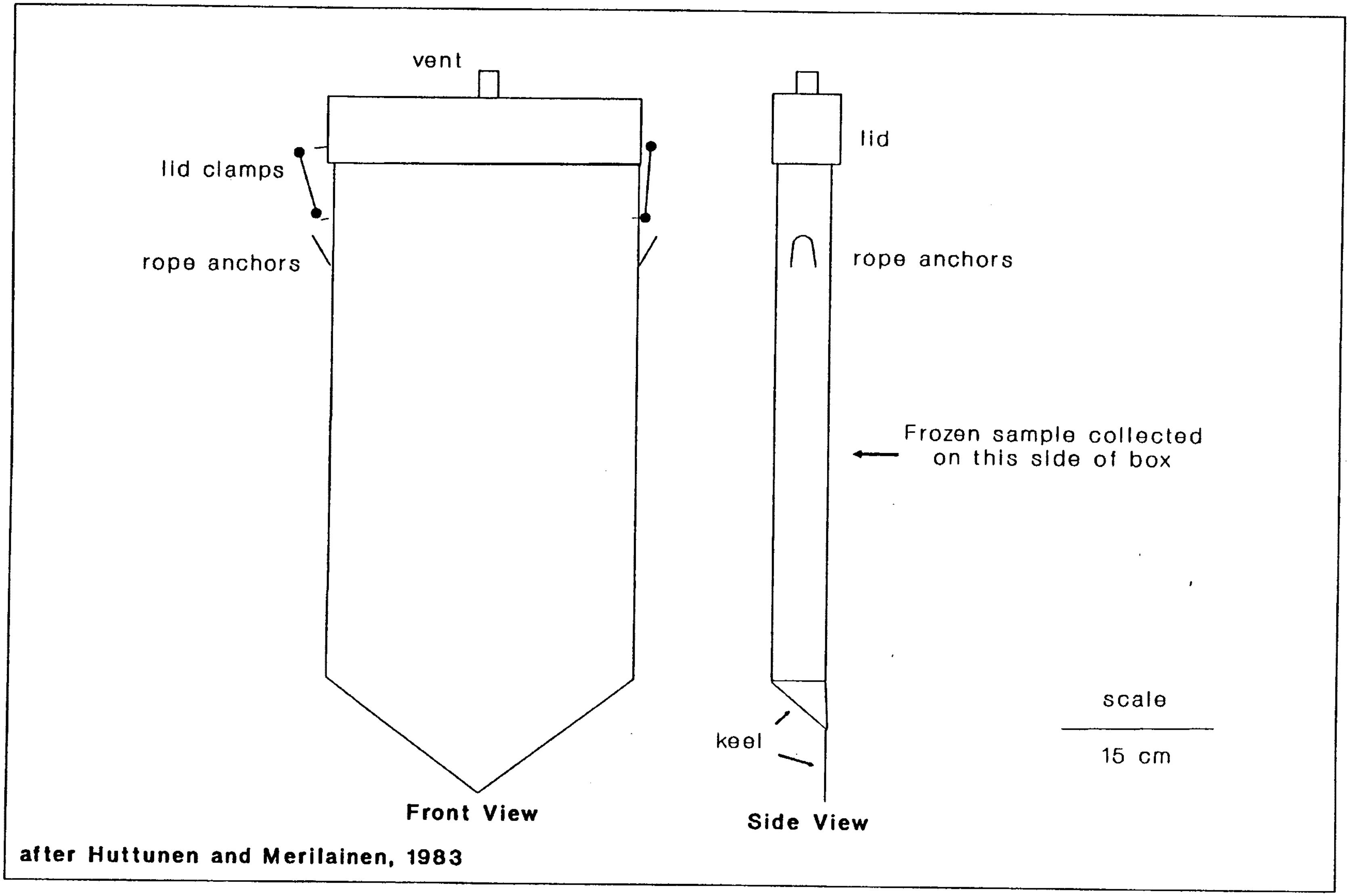
A freezer box sampler was used in early 1989 to supplement the core samples and to ensure collection of the uppermost sediments in both lakes. The freezer box is a hollow, stainless-steel box, pointed at one end, with the point offset to one side of the box. The geometry of this box allows for representative sampling, because the sediments displaced by the box are those that are not sampled. The sample is frozen to the flat, vertical surface of the box (Figure 3.4). The sampler is such that it will collect approximately 60 cm of sediments, preserving the original stratigraphy; and it can also collect a sample of bottom lake water by freezing it onto the box.

The box was filled with dry ice and isopropyl alcohol to cool its surface to below 0°C. It was then immediately lowered through a hole previously cut in the frozen lake surface. After approximately 30 minutes of freezing, the box was raised to the surface and filled with warm water to release the sample. After the frozen slab was removed from the freezer box, all loose or non-frozen material was scraped off the slab to leave a clean frozen surface (Figure 3.5). Any additional, non-representative parts, such as the corners of the slab, were broken off and discarded. The preserved sample was exclusively from the front panel of the box and included no foreign or physically disturbed section of the slab. The sample was then placed in a 30 gallon plastic bag inside a portable cooler. The samples were stored on campus in a freezer at -4°C.

3.3.2 Results

Three attempts were made to sample at site KB in Killarney Lake using the freezer box. The reason for the multiple attempts was to ensure retrieval of a complete section of metallic silt (bounded on both sides by relatively unpolluted, green organic silt). Because the box is 0.61 m long, one sample had to fit within this length. The resulting sample was 59.0 cm in length (sample KF). Comparison of the metallic silt unit in the three samples indicated that the thickness of the unit is fairly consistent in the region sampled; the first few sampling attempts missed bracketing the pollution with organic silt.

One freezer box sample was collected from Bells Lake. The method was similar to that used to collect sample KF in Killarney Lake to ensure retrieval of the uppermost layers of sediment and ash which had been missed by the piston corer. Hence, the box was simply pushed as far as possible into the sediments without exceeding the length of the box. The resultant sample was a 30 cm section of homogeneous organic silt with a thin layer of ash near the top of the section (sample BF). Again, there was no adequate reference for locating site BA, but the sample was collected within 30 m of the site.



after Huttunen and Merilainen, 1983

Figure 3.4. Schematic Diagram of Freezer Box Sampler

Figure 3.5. Freezer Box with Sample

3.4 Sample Handling and Preparation

3.4.1 Piston Core Samples

Before the piston cores were sampled, excess fluids were drained out of the ends of the core. These fluids were saved for future analysis, the volume varying from 0 to 200 milliliters. The core barrel was then sawn through longitudinally with a skill saw. The top half of the core barrel was removed and the core cut in half by running a piano wire along the top of the remaining core barrel and through the soft, silty organic cores. The top half of the core was then placed in the previously removed half core barrel. Except for the uncommon occurrence of a stick or twig, there was no apparent smearing or displacement of any core features.

The core was then logged using traditional grain size (silt, sand, etc.) and color conventions. After annotation, the core was photographed at 40 cm intervals. A Munsell color chart was not initially used in the annotations because one was not available until three months later, when it was then used for annotation. The core was sealed after the initial annotations, and no significant color changes occurred except for oxidation of some metallic fluids. Core logs can be found in Appendix A. A description of the lithology is included in the following chapter.

Core sampling and description started from the bottom of the core and worked upward to the lake bottom surface. Annotations started at the lower end so that in cores KA, KB, BA, and BB, the Mazama ash could be used as a reference; the same procedure was followed with the other shorter cores.

Sediment samples were collected from each core at 10 cm intervals. The sample volume equaled one half the core diameter (10.2 cm) by 2 cm wide, or 82 cm^3. Samples were collected such that a sample labeled 'KB-20' represented a sample from core KB collected 20 to 22 cm above the reference, in this case the top of the Mazama ash layer. Samples were cut from the core using a clean plastic knife, placed in labeled ziplock plastic bags, and refrigerated until analysis.

The core halves were wrapped in saran-wrap and enclosed in the core barrels. The core barrels and caps were then securely taped. Cores were stored in a cool, dry location.

3.4.2 Freezer Box Samples

Preparation for the analysis of freezer box samples began by cutting a 10-cm-wide section of the frozen slab with a band saw. The section was then washed in cool tap water. Washing removed any possible contamination from the band saw or from any materials which may have frozen to the section, and left a clear section which could be easily described. Figure 3.5 shows an unprepared section of alternating light and dark bands bordered by near homogeneous gray (visually green) sections. These alternating light and dark bands may or may not be varves as defined by O'Sullivan (1983) as annually laminated sediments. There is no certain way of stating whether the laminations represent annual (or semi-annual) events. However, in this text the term varve is used to mean a dark and light band sequence.

This section was then left to thaw and dry at room temperature. Experimenting with test sections showed that the best time to sample was when the section had lost most of its water but before it had completely dried.

Two sections from freezer box section KF (Killarney Lake) were sampled. The first sampling attempted to collect every varve, although occasionally these lines were too close together to obtain either an accurate, representative sample or an adequate sample volume. The second sampling was at continuous 2 cm intervals. This included the organic silt above and below the metallic silt as well as the metallic silts themselves. The Bells Lake section was sampled over continuous 2 cm intervals. Samples were placed in labeled ziplock bags, allowed to dry, and stored.

4.0 LITHOLOGY OF LAKE BOTTOM SEDIMENTS

4.1 Introduction

This chapter describes the general lithology of each core section. Sediments above the Mazama ash in each lake consist primarily of organic silt. Organic silt represents a near-homogeneous unit of organic materials within a silt matrix. The organic material was identified visually. The relative percentage of organic material and silt was not investigated. Killarney Lake sediments included a layer of metallic silt overlying the organic silt, whereas Bells Lake sediments did not. Metallic silt was identified by its gray color, relative absence of organics, and metallic smell. Metallic silt composition was verified through geochemical analysis on an atomic absorption spectrometer. Coring sites are shown in Figures 3.1 and 3.2.

Volcanic ash layers were identified by inspection of the sediments with a binocular microscope. The Mt. Mazama ash was specifically identified by chemical fingerprinting comparing electron microprobe analyses with established Mazama ash values supplied by Smith and Westgate (1968). This is discussed in Chapter 5.

Cores KA and BB were obtained to maintain quality control for cores KB and BA. As explained earlier, these cores were vertically offset to maintain a complete lithologic log in the event of sloughing in the open hole between core sections. No visible distortion could be detected in either core, but this may be due to the lack of abrupt changes in the core lithologies for which any comparison could be made. However, the depth to the Mazama ash in cores KA and KB is the same and during coring, a distinct bottom to the hole could be found each time a new section was added. Hence sloughing was unlikely and cores KA and BB are not discussed further.

4.2 Lake Lithologies

4.2.1 Site BA Lithology, Bells Lake

Coring at site BA was done in the deepest, flat-bottomed, portion of Bells lake where water depth was 4.6 m (Figure 3.2). Four core sections were used to establish the lithologic section (Table 4.1).

Table 4.1. Generalized Lake Bed Lithology at Site BA.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Description
0 - 253	253	organic silt	Green-brown organic silt grading into brown organic silt. Alternating light chocolate brown organic silt to dark chocolate brown organic silt in approximately 15-cm intervals above 145 cm. Distinct dark gray ash grading into chocolate brown organic silt at 145 cm.
253 - 260	13	clay	Gray, green-brown clay.
260 - 263	3	vegetation zone	Coarse brown pieces of vegetation - almost peat.
263 - 265	2	organic silt	Brown-green organic silt.
265 - 369	4	fine sand to coarse silt	Two distinct layers of light gray fine sands and dark-gray, coarse silt.
369 - 372	3	organic silt	Uniform, moist, brown-green organic silt.
372 - 374	2	clay	Light gray clay.
374 - 375	1	organic silt	Brown-green organic silt.
375 - 378	3	clay	Light gray clay.
378 - 380	2	sands	Dry, medium-gray "salt and pepper" sand.
380 - 381	1	organic silt	Brown-green organic silt.
381 - 571	190	Mt. Mazama volcanic ash	Light pink to medium gray, compact, volcanic ash. Grades from a very dry, dense ash, to a coarser, wet ash. Possible worm burrow at 487 - 501 cm filled with salt and pepper sand with micas.
571 - 651	80	organic silt w/lenses	Organic silt with moist, dark clay lenses of 2 to 4 cm in thickness. 2 cm sand lens at 633.
651 - 653	2	volcanic ash	Gray to gray-green, moist, volcanic ash.

The combined section was composed of 2 cm of an unknown volcanic ash; 80 cm of silt, organics, clays, and sand below the Mazama ash; 190 cm of Mt. Mazama ash; 6 cm of interlayered fine sand to coarse silt; 18 cm of interlayered clays and silts; and an uppermost 253 cm of organic silt.

Bells Lake sediments were deposited in a generally low-energy environment. Apart from three sand layers in the 128 cm above the Mazama ash, the nearly continuous low-energy fine-grained sediments suggest that the lake has been present since the Mazama ash fall. The absence of gravel and debris suggests that the St. Joe River did not migrate to the present lake location over the time period represented by the core. Occasional flooding possibly introduced the fine sand.

4.2.2 Site KB Lithology, Killarney Lake

At site KB in Killarney Lake (Figure 3.1), four core sections were used to establish the lithologic section. The core was retrieved from lake bottom sediments at the center of the lake in 4.6 m of water. Table 4.2 describes the lithologic section.

Table 4.2. Generalized Lake Bed Lithology at Site KB.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Description
0 - 3	3	metallic silt	Tan, yellow-brown, metallic smelling, fine silt interpreted as heavy-metal contamination.
3 - 574	571	organic silt	Green-brown organic silt grading to brown-green between 409 and 389 cm. Pine cone or tree knot at 197 cm. Bands of alternating dark chocolate to light chocolate brown organic silt above 164 cm.
574 - 575	1	vegetation layer	Brown to black, fibrous, laminated vegetation.
575 - 609	34	organic silt	Soft, moist, green-brown organic silt including two 3 mm thick ash layers at 607 cm and 578.7 cm.
609 - 639	30	Mt. Mazama ash	Light pink to medium gray, dry, compact volcanic ash. Includes occasional worm burrows filled with salt and pepper sand.

The section is composed of 3 cm of metallic silt, 606 cm of organic silt, and 30 cm of Mt. Mazama volcanic ash with a total core length of 639 cm.

The lithology of core KB depicts a low-energy environment of deposition. The lake received a thick deposit of Mazama ash, probably through both air-fall and stream transport. The additional thin layers of the ash may have flushed into this basin during high water events. Settling of organic silt continued throughout the rest of the lake history until deposition of the metallic silt. The data suggest that at site KB, a lake or calm water environment has been present since the eruption of Mt. Mazama approximately 6700 years before present.

4.2.3 Site KC Lithology, Killarney Lake

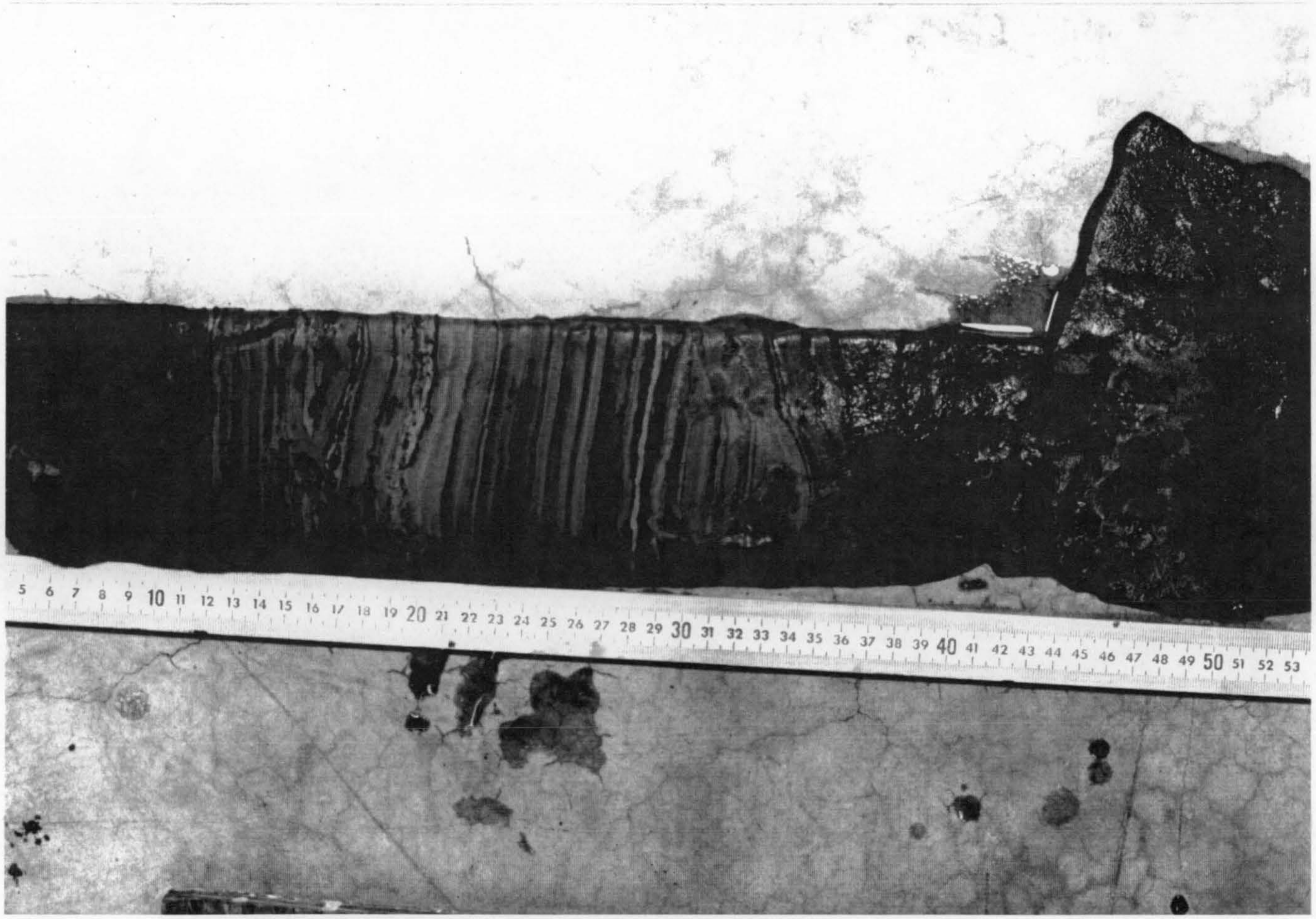
Site KC was located approximately 20 meters north of the southern end of the lake (Figure 3.1). This core was collected to compare metallic silt unit thicknesses and chemistries with cores from sites KB and KD. The shallow depth of the lake (1.2 m) provided visual assurance that the coring apparatus sampled the uppermost lake bottom sediments. Two core sections were used to establish the lithologic section, which is given in Table 4.3.

Table 4.3. Generalized Lake Bed Lithology at Site KC.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Description
0 - 19.5	19.5	metallic silt	Light and dark gray laminated fine silt with metallic smell interpreted as heavy-metal pollution.
19.5 - 28.5	9	peat/silt	Brown peat mixed with gray silt.
28.5 - 30.5	2	silt	Gray silt.
30.5 - 176.5	46	peat	Black peat grading into brown peat. Quartzite rock at 136 - 132 cm.
176.5 - 186.5	10	organic silt	Gray-brown organic silt grading into brown peat.
186.5 - 248.5	38	peat	Black peat. Above 226 cm, includes visible roots with mottled gray silt between 194 and 170 cm.
248.5 - 259.5	11	organic silt	Brown-gray silt and organics. Grades rapidly into overlying peat.
259.5 - 261.0	1.5	organic silt with silt	Two distinct 0.3 mm gray-brown silt layers separated by green-brown organic silt.
261.0 - 356.5	4.5	organic silt	Gray-brown silt increasing to approximately 40% organic material above 322.5 cm.

The combined section was composed of a lower section of 108 cm of silt and organics which may continue below the cored section; 229 cm of near continuous peat with interlayers of silt; and 19.5 cm of laminated metallic silt interpreted as heavy-metal contamination.

The substantial thickness of peat at this locality is due to the aquatic and surficial vegetation along the shore of the lake. The peat may indicate inward migration of the lake shore with time. This is somewhat substantiated by the 1903 U.S. Geological Survey Rathdrum quadrangle map, on which the lake shore is shown much closer to the river.


5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53

The metallic silt unit shows 16 light and dark laminations approximately 0.3 cm thick per sequence. It is unlikely that these varve-like sequences represent the complete sediment column of annual or semi-annual deposits because more laminations should be present for an accumulation of over 100 years. Additional evidence supplied through the heavy metal analysis shows that concentration profiles in this section are similar to the peaks observed in the lowermost metallic silt deposits at sites KB, KF, and KD. It is possible that these peaks correspond with the early tailings deposits, and later deposits have eroded off during high water events. Because site KC is near the river (0.75 km), flood scouring could be responsible for the removal of sediments.

4.2.4 Site KD Lithology

Site KD was located at the north end of the lake approximately 250 meters south of the shore and the mouth of Killarney Creek in 1.2 m of water (Figure 3.1). Vegetation was observed on the lake bottom surface. The shallow depth of the lake again provided visual assurance to successful coring of the uppermost lake bottom sediments. Two core sections were used to establish the lithologic section, which is given in Table 4.4.

Table 4.4. Generalized Lake Bed Lithology at Site KD.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Description
0 - 17.5	17.5	metallic silt and fine sand	Gray-tan coarse silt and fine sand with metallic smell. Oxidized rim.
17.5 - 118.3	100.8	peat	Coarse black and brown peat including silt lenses and large quartzite rock at 118 - 111 cm.
118.3 - 127.0	8.7	fine sand to coarse silt	Gray, fine sand to coarse silt.
127.0 - 214.0	13	organic silt	Light to medium brown organic silt increasing in organic content up the section.
214.0 - 257.3	43.3	fine sand to coarse silt	Light and dark gray, laminated, fine sand to coarse silt.
257.3 - 260.5	3.2	silt	Gray-brown silt including a 0.2 cm thick layer of vegetation.
260.5 - 351.5	9	fine sand to coarse silt	Light and dark gray, laminated, fine sand to coarse silt. 2.1 cm thick layer of volcanic ash at 334.1 cm with another distinct 0.5 cm thick layer at 288.7 cm. Some sand includes reworked ash.

The combined section of core KD included 43 cm of interlayered fine sand to coarse silt; 16 cm of silt or organic silt; 100.8 cm of peat; and 17.5 cm of metallic silt.

Killarney Lake sediments at site KD appear to have gone through transitions. Shoreline transgressions through time may be responsible for the sediment-type fluctuations between fine sand and coarse silt, to organic silt. A lake level lower than the present would foster the deposition of fine sand, possibly from Killarney Creek or other similar creeks at this locality, whereas lake levels similar or higher than the present level would facilitate deposition of sediments finer than sand. Thus the interlayers are probably due to lake level fluctuation.

4.2.5 Freezer Box Section KF

Site KF was probably within 50 m of site KB. The water depth was 4.5 m. The lithology of the freezer box section (KF) is given in Table 4.5, where 'wet' thicknesses are given. The section measured 59 cm in length when wet but shrank by about 12% to 52 cm during drying. Figure 4.1 shows section KF, still frozen, after it had been cut and washed.

Table 4.5. Generalized Lithology of Freezer Box Section KF (wet sample).

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Description
0 - 17.5	17.5	organic silt	Green-brown organic silt with pods or lenses of black fine silt and gray metallic silt. Ash layer of 2-3 mm at approximately 4 cm.
17.5 - 50.5	33	metallic organic silt	Gray metallic silt layers separated by one or more black organic layers (may be difficult to count or distinguish). Thicker sequences of metallic silt layers show gradational change from gray-black, to gray-brown, to gray, to white. Color changes not observed in all layers. Sequence thicknesses varied from less than 1 mm to 1.8 cm. Vegetation as grass and twigs from 37.9 to 37.5 cm.
50.5 - 59.0	8.5	organic silt	Green-brown organic silt with random pods or lenses of black fine silt and gray metallic silt.

The contact between the lower organic silt and the metallic silt is not distinct but somewhat gradational (Figure 4.1). Pods or lenses of gray, metallic silt are found at random locations and orientations in the lower silt and organic unit. These pods have parallel laminations similar to those in the metallic silt zone. These laminations are horizontal in the metallic silt zone, but are randomly oriented in the pods. This suggests that they are of higher density silt which have sunk into the organic layer below.

Within the metallic silt zone, 47 metallic silt/black organic cycles were observed. These sequences are interpreted as varves as defined by O'Sullivan (1983) as annually laminated sediments. Metallic silt was probably deposited during spring high water events or flooding, the black organic layers being deposited during winter when organisms died and settled under the frozen lake surface. Between 10 and 31 cm, the

Figure 4.1. Freezer Box Section KF.

varves are mottled and not distorted. The deformation of sediments between 31 and 42 cm may be due to loading, which could deform a thin cycle. Distortion may also be due to action from surface waves from weather, lake industrial activities, or recreation.

Though mine and milling operations continued 90 years without tailings ponds, only 47 distinct varves were observed. However, many additional dark surfaces were observed in the section, but were too thin to count with any confidence. These surfaces may represent years when the river did not flood into the lake, years when flood energy was too high to allow settling within the lake, or years when activities such as industry or recreation remobilized the sediments into the water column and subsequently transported them into another portion of the lake or into the river system.

The upper organic zone is composed of continuous organic silt except for small pods or lenses of metallic silt. At approximately 55 cm (4cm below the lake bottom surface), a 3-mm-thick ash layer occurs and is probably a deposit from the 1980 eruption of Mt. St. Helens. This ash was not found in core section KB. Time and cost constraints prevented the identification of the ash through electron microprobe analysis.

The lower silt and organic/metallic silt zone contact is present in both the core and freezer box samples. The freezer box sample may or may not represent an average deposit of mining wastes on the lake bottom. Variability certainly occurs as shown through the three piston cores. However, metallic silt was observed overlying a silt and organic zone in all three Killarney Lake cores and the freezer box section.

4.2.6 Freezer Box Section BF

The location of site BF was close to site BA. As with section KF (Killarney Lake), the exact location of the coring site was not known and as much as a 30 m difference in sampling locations is possible. The original section measured 30 cm in length when wet but shrank nearly 50% to 16 cm during drying. Table 4.6 describes the general lithology of section BF before drying.

Table 4.6. Generalized Lithology of Freezer Box Sample BF (dry sample).

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Description
0 - 30	30	organic silt	Uniform green-brown organic silt. Ash layer of 2-3 mm at approximately 1 cm.

The organic silt in the freezer box sample visually resembles those found in all of the core samples, and those of the Killarney Lake freezer box section. No visual or chemical references were found in freezer box sample BF or in core BA to identify the location of this sample in the Bells Lake lithologic section.

The ash found at approximately 1 cm again is believed to be a deposit from the 1980 eruption of Mt. St. Helens. This ash was not seen in the core section, but ash was found on top of the raft anchors. Because the coring apparatus missed the ash in both lakes, it must be concluded that it does not successfully retrieve unconsolidated sediments at the lake bottom surface.

4.3 Killarney Lake/Bells Lake Sedimentation Rates and Lithologic Comparison.

A comparison of Killarney Lake and Bells Lake lithologies is shown in Figure 4.2. The freezer box section is included on the Killarney Lake section because a visual contact between the organic silt and metallic silt zones in both core and freezer box samples was observed. The freezer box section is not shown in Bells Lake because no reference contact was seen in Bells Lake. During the freezer box sampling at Bells Lake, the box was pressed into the lake bottom sediments until high resistance was felt. The high resistance material should be corable material and may represent the top of core BA. If so, core BA may be up to 30 cm longer than shown in Figure 4.2.

In Killarney Lake at site KB, there are 606 cm of organic silt between the top of the Mazama ash and contaminated zone. Using 6700 years before present as the approximate date of the Mazama ash fall (Smith and Westgate, 1968), Killarney Lake had a mean deposition rate of 0.90 mm per year (without considering compaction). Using 90 years as the time period of active mining to the time of tailings pond installation, the mean sedimentation rate increased 400 percent to 3.6 mm per year. Sedimentation rates may have further increased to at least 8.7 mm per year since the installation of tailings ponds (calculated using 17.5 cm of organic silt above the metallic silt). Many factors, such as increased sedimentation due to logging practices could be responsible for this. These rates are similar to those found by Funk and others (1975) at the Coeur d'Alene River delta. It should be noted that the presence of 2.1 cm of the Mazama ash at site KD from 334 cm below lake bottom may suggest that there was more erosion or slower deposition of sediments at this site than at sites KB or BA.

In Bells Lake at site BA there are 381 cm of organic silt above the top of the Mazama ash. By superimposing freezer box section BF above core BA, a maximum of 411 cm of organic silt may be present above the Mazama ash. Over the last 6700 years, Bells Lake shows a minimum mean sedimentation rate of 0.57 mm per year and a maximum mean sedimentation rate of 0.61 mm per year.

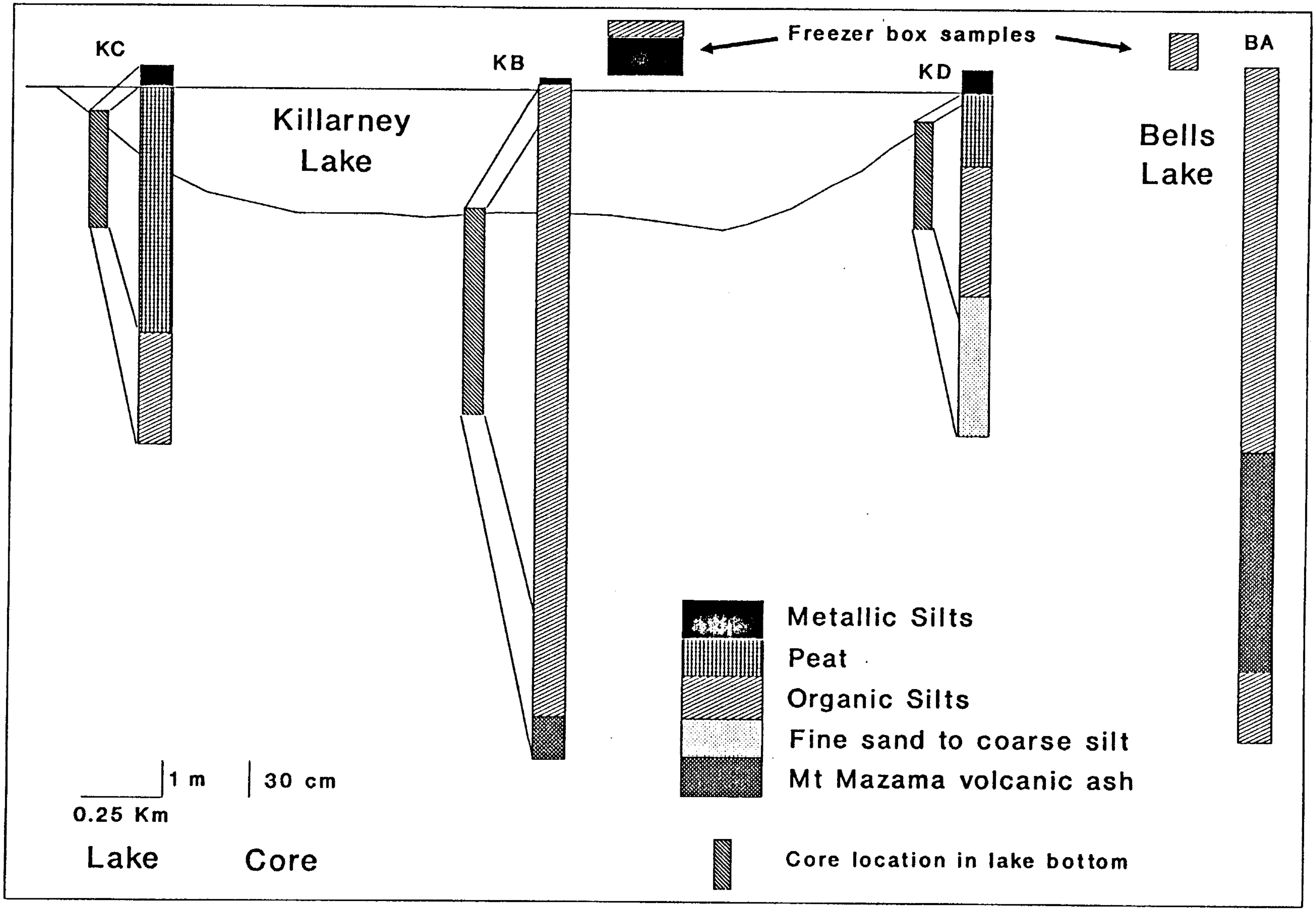


Figure 4.2. Generalized Stratigraphy of Lake Bed Sediments

The average sedimentation rate in Killarney Lake is 32 percent to 37 percent greater than that of Bells Lake. These comparisons are approximate for Killarney Lake exhibits a uniform 606 cm of organic silt; Bells Lake shows only 253 cm of continuous organic silt. Bells Lake is farther from the St. Joe River than Killarney Lake is from the Coeur d'Alene River, and higher floods may be required to inundate this lake than Killarney Lake. Though Bells Lake shows a rather different, changing environment in the earlier periods after the Mazama ash fall, the two lakes show a quiet water depositional period from that time until the introduction of mining in the Coeur d'Alene River valley.

5.0 GEOCHEMICAL METHODS AND RESULTS

This chapter discusses analytical methods, sample preparation, and quality control procedures used in the geochemical analysis of core and freezer box samples. Results from heavy metal analyses are provided after Section 5.4. Electron microprobe analysis of the Mazama ash is discussed in Section 5.5. Environmental Protection Agency (1987) test methods for evaluating solid waste were used throughout the analyses.

5.1 Sample Preparation

Samples were prepared for analysis by being dried, weighed, and digested. The same procedure was used for all solid sample analyses. These preparation techniques are outlined below.

Two water samples were obtained from the water frozen above the sediment column in freezer box sections KF and BF. These samples, which represented lake bottom waters in the winter, were allowed to melt at room temperature and refrigerated until analysis. The samples were not acidified.

Type II water (distilled and deionized) was used throughout the analyses as called for by EPA analytical methods (1987).

5.1.1 Sample Drying

Various methods were tested for drying the core and freezer box samples. Samples must be dry before digestion so that they can be weighed accurately. Any presence of water in the sample would result in a misleading weight, and hence metal concentration in the sample. The drying method must be such that metal ions are not washed or evaporated off the sample.

The first sample drying method tested consisted of placing an aliquot of each sample on a Whatman No. 4 or 41 filter paper and vacuum pumping the sample on a Buchner funnel while spraying the sample with acetone. The filter paper and sample were first sprayed with Type II water to inhibit movement of the paper on the funnel and to place an adequate medium on the paper surface to facilitate filtration. Reagent grade acetone was used to evaporate moisture from the sample. Care was taken in spraying with both liquids to ensure that no particle from the sample moved to the edge of the filter and subsequently through the funnel. Though this procedure removed most of the water from the sample, the sample still required some mixing and drying at room temperature to remove all of the moisture.

Though vacuum drying was adequate for timely removal of moisture, a yellow liquid resulted in the beaker draining the Buchner funnel. Because fluid color must represent either particulates, or organic or inorganic species in solution, this method was evaluated as inadequate on the basis that elemental concentrations were not preserved in the sample. Four of the vacuum-dried samples were analyzed by flame atomic absorption spectrometry. A comparison of vacuum-dried to air-dried sediment concentrations is shown in Table 5.1, showing that vacuum dried samples KB 470, KD 340, KD 350, and KC 350 were depleted compared with air dried samples in many of the heavy metals analyzed.

Table 5.1. Percent Difference in Elemental Concentrations of Air-Dried Aliquots and Vacuum-Dried Aliquots of Identical Samples (minus denotes greater concentration from vacuum dried sample).

	Ag	Cu	Cd	Fe	Mn	Ni	Pb	Zn
KB 470	0	-8	0	6	-9	5	23	-8
KD 340	20	3	8	1	7	7	12	5
KD 350	50	14	27	4	13	0	-16	18
KC 350	37	5	46	–	17	-3	-14	18

The second method tested involved drying the samples at room temperature or at a temperature less than 50°C. The procedure involved weighing a wet sample, drying the sample while periodically mixing it to avoid clotting, and then reweighing the dried sample. Samples were placed in plastic Dixie cups during drying. After drying they were placed in clean plastic bags and gently crushed with the fingers to break up any clumps of material. The samples were stored in the bags in a dry location until digestion. Samples were weighed before and after drying to determine water content and to see if a relationship existed between the percent water loss and amount of pollution in the sediments.

Freezer box samples KF and BF were air dried at room temperature. The cut section (Figure 3.5) from the slab was dried as a whole and then divided into separate samples. Partitioning an unfrozen, wet sample into individual aliquots was unsuccessful as the sample formed a slurry that was difficult to isolate. Test sections showed that it was best to dry the samples to the point that they were near dry, but still contained some water. Samples could then be cut with a knife without chipping and possibly mixing the sample, as occurred when cutting a very dry sample. Water content was not determined for these samples.

Figure 5.1 shows the relationship between percent water content and distance below lake bottom for selected core samples. The samples were those analyzed at 10 or 30 cm intervals from the preliminary, first-phase sampling. Sediments from Bells Lake (core BA) tend to increase in water content up the lithologic column towards the lake bottom surface. This is to be expected as there is less lithostatic pressure above the organic silt up the sediment column. Reduced lithostatic pressure permits water to enter pore spaces and absorb within the organic sediments. Variations from this trend (200 and 380 cm below lake bottom) in core BA may be due to the presence of clay (Table 4.1).

Water content of samples from Site KB in Killarney Lake generally decreases in water content similar to those samples from Site BA. This is probably a result of lithostatic pressure decreasing the pore space with depth. The abrupt change in water content in core KB at 3 cm below lake bottom occurs at the visual contact between metallic silt and the underlying organic silt (Table 4.2). Geochemical analysis of sample KB 606, above this contact, has shown that this silt does contain high concentrations of heavy metals.

Samples from cores KC and KD show the same abrupt changes in water content below the metallic silt as samples from core KB. A decreasing trend in water content below this zone is not apparent because these cores did not penetrate as deep as cores KB and BA.

These results may indicate that heavy metal contamination within the Coeur d'Alene River drainage in the form of metallic silt may be recognized by the abrupt decrease in water content. This change is probably a result of an increase in sedimentation rates of silt with a lesser percentage of organic material in the matrix. Chapter 6 discusses the chemistry of the silt.

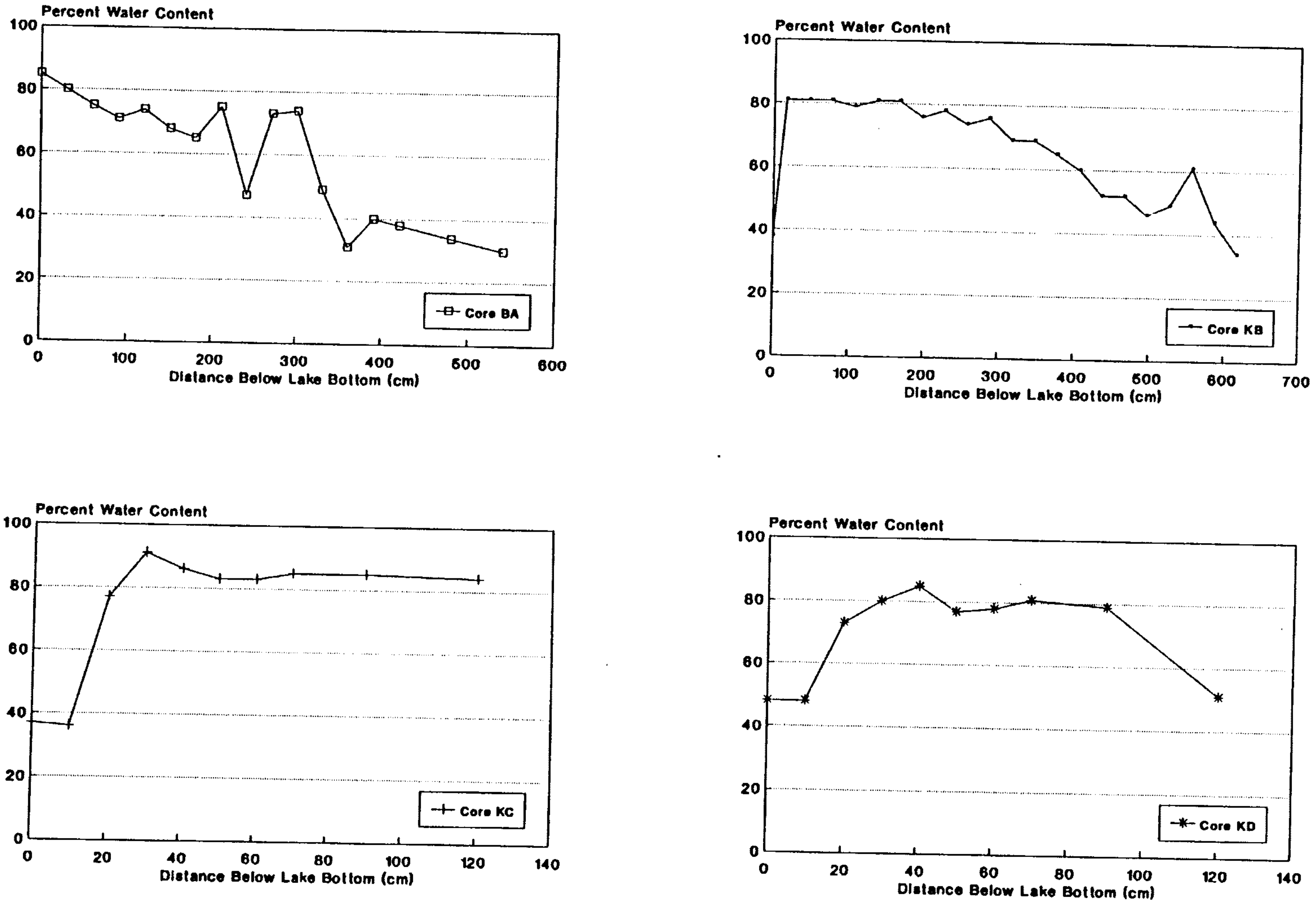


Figure 5.1. Water Content of Core Samples (by weight).

5.1.2 Sample Digestion

Digestion is required to place ions in solution and produce a suitable sample matrix for spectrometer analysis. For the analysis of Ag, As, Cd, Fe, Mn, Ni, Pb, and Zn, EPA Method 3050 (1987) was used for digestion. This method is specific for preparation of sediment, sludge, and soil samples for flame atomic absorption (FLAA) or graphite furnace atomic absorption (GFAA) analysis of heavy metals. Method 3050 is outlined below including specific procedures used for each digestate prepared in this study.

Method 3050

- Weigh a homogeneous sample to the nearest 0.01 gram and transfer to a conical beaker. A 1.000 gram sample was used in each digestate.

- Add 10 ml of 1:1 HNO_3, mix the slurry and cover with a watch glass. Heat and reflux the sample at 95°C for 10 to 15 minutes without boiling. Cool, add 5 ml of concentrated HNO_3 and reflux for 30 minutes. Repeat last step.

- Using a ribbed watch glass, evaporate the solution to 5 ml without boiling.

- Cool, add 2 ml of Type II water and 3 ml of 30% H_2O_2. Cover and heat to start the peroxide reaction. Heat until effervescence subsides. Continue to add 1 ml aliquots of 30% H_2O_2 until effervescence is minimal or sample appearance is unchanged.

To avoid bias, hydrogen peroxide was added in 1 ml aliquots until a total of 10 ml H_2O_2 had been added, the maximum volume allowed. This step also reduces any judgement error as samples tended to react differently with the addition of H_2O_2.

- For flame analysis of Ag, Cd, Fe, Mn, Ni, Pb, and Zn: add 5 ml concentrated HCL and 10 ml of Type II water and reflux for 15 minutes. For furnace analysis of As: cover with a ribbed watch glass and evaporate to approximately 5 ml.

- Filter solution through a Whatman No. 41 filter paper and dilute to 100 ml with Type II water. Sediments which accumulated on the filter were thoroughly washed on the filter. The rinsate was collected until the 100 ml volume was achieved.

The samples were then poured into brown, opaque, plastic 120 ml bottles and placed in a refrigerator until analysis. The samples were warmed to room temperature prior to analysis.

5.2 Atomic Absorption Spectrometry

Atomic absorption spectrometry (AAS) techniques were used to determine the heavy metal content of the sediments and water samples from Killarney and Bells Lakes. These techniques are simple and applicable to a large number of metals in sediments, waters, and domestic and industrial wastes (EPA, 1987). The atomic absorption spectrometer was used in this study because the instrument obtains results within the desired degree of accuracy, is inexpensive to use, and was readily available. Other instruments which were equally suited for the project, such as the inductively coupled argon plasma spectrometer (ICP), were too costly to run and were not readily available.

The heavy metal analysis was conducted on a Model 603 Perkin-Elmer Atomic Absorption Spectrometer. Flame atomic absorption spectrometry (FLAA) was used for the analysis of Ag, Cd, Cu, Fe, Mn, Ni, Pb, and Zn. Graphite furnace atomic absorption spectrometry (GFAA) was used for analysis of As.

In direct-aspiration, or flame atomic absorption spectrometry, a sample is aspirated and atomized in a flame. A light beam from either a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame onto a detector which measures the amount of light absorbed by the flame. The wavelength of the light is specific to the element being analyzed. During sample atomization, the amount of energy absorbed by the excitation of previously unexcited ground-state atoms is measured as the decreased energy reaching the detector. The light energy absorbed by the atomized sample is a measure of the concentration of the metal in that sample.

Elemental concentration is calculated when the quantity of light absorbed is within the linear range specific to the element. The linear range describes a range of intensities where the amount of energy absorbed is proportional to the concentration of the element. Concentrations above the linear range introduce an undesirable degree of error into the analysis. The error is a result of a decrease in the proportion of absorbed light in comparison to the concentration of the sample; above this range a linear relationship does not exist, and the spectrometer cannot accurately measure concentrations. Samples with concentrations above the linear range require dilution, which increases time of analysis and may increase the possibility of error.

As a greater percentage of available analyte atoms is vaporized and dissociated for absorption within the graphite tube rather than in an open flame, detection of lower concentrations of elements is possible than with FLAA. Using the graphite furnace, a representative aliquot of the sample is placed in a graphite tube in the furnace. Pre-set controls then evaporate the sample to dryness, char and atomize the sample. Detection is essentially the same as in direct aspiration. The intensity of the transmitted radiation from the light source decreases in proportion to the amount of ground-state elements in the vapor generated from the furnace.

Arsenic required analysis through GFAA because 1) the anticipated concentrations of As were low; and 2) because arsenic is a particularly volatile element, graphite furnace analysis reduces the undetected loss of the element which may occur during aspiration of the sample. A separate digestion is required for samples analyzed by GFAA. Analyses of many of the above elements is possible using GFAA, but this is a more costly and time-consuming technique. It was also anticipated that the elemental concentrations of most metals analyzed would be above GFAA detection limits. Graphite furnace analysis may lower the linear range for a particular element when compared to FLAA, making dilution necessary for many samples.

5.3 Flame Atomic Absorption Analysis

All 127 core, freezer box samples, and blanks were analyzed by FLAA for eight elements. The Model 603 Perkin-Elmer atomic absorption spectrometer requires single-element analysis, with manual introduction each sample. Analytical wavelengths, slit, flame, and use of background correction complied with Test Methods for Evaluating Solid Waste; Volume 1A, Lab Manual of Physical/Chemical Methods, EPA, September 1987. Calibration standards for the spectrometer were prepared according to the above specified EPA manual. These standards were periodically checked with commercial standards. Analytical wavelengths, specified and achieved sensitivities, specified detection limits, linear ranges, and use of background correction are shown in Table 5.2.

During analysis, each sample was aspirated approximately 3 to 5 seconds, or until the concentration reading on the spectrometer was fairly constant. Concentrations were read directly off the machine. Values which fluctuated rapidly due to machine noise or at analytical wavelengths which characteristically had noise, such as Fe, were estimated to the nearest significant digit.

After analysis of six samples, the first of the six would again be analyzed to check for instrument drift. If the concentration of the sample changed by a significant digit, the instrument would be recalibrated. If the analysis of an element for a suite of samples took over one day, or if a second suite of samples was to be analyzed, previously analyzed samples would be run again to check for deterioration of the standard, analytical lamps, or machine settings.

Table 5.2. Operating Parameters used during Atomic Absorption Spectrometry.

Element	Wavelength (nm)	Sensitivity (specified)	Detection Limit	Linear Range	Background
Ag	328.1	0.019 (.024)	0.06	1	on
Cd	229.4	0.025 (.016)	0.025	1	on
Cu	325.8	0.030 (.034)	0.1	2	off
Fe	252.7	0.32 (.21)	0.12	10	on
Mn	280.3	0.026 (.030)	0.05	2	off
Ni	342.4	0.23 (.17)	0.15	5	on
Pb	217.0	0.25 (.19)	0.5	3	on
Zn	213.9	0.014 (.011)	0.02	0.20	on
Graphite Furnace Analysis					
As	193.7	0.010 (.013)	0.2	1	on

Drying temperature = 100°C time = 19 seconds
Charring temperature = 200°C time = 14 seconds
Atomizing temperature = 2000°C time = 13 seconds

5.4 Graphite Furnace Atomic Absorption Spectrometry.

Graphite furnace atomic absorption analyses for arsenic were completed in one day. Thirty-six samples were analyzed. Due to the extra time necessary for a second digestion of the samples for arsenic alone, and the additional time required for instrumentation, only necessary samples in the polluted zone were analyzed with a few background samples.

For sample analysis, a fresh graphite tube was placed in the furnace. Each sample was analyzed twice and the mean value reported. Machine calibration was conducted after every five samples. Samples were introduced to the furnace through 1 - 100 microliter pipet tips using a 25 microliter applicator. Calibration of the spectrometer used the same pipets. Tables 5.3 through 5.8 show the results of the geochemical analysis.

Table 5.3. Bells Lake Bottom Sediment Concentrations, Site BA.

Sample	Dist blw Lk Btm	Concentration - ppm																	
		As	(+/-)	Ag	(+/-)	Cu	(+/-)	Cd	(+/-)	Fe	(+/-)	Mn	(+/-)	Ni	(+/-)	Pb	(+/-)	Zn	(+/-)
BA 100	553			<1	(1)	13	(1)	<1	(1)	3900	(200)	120	(10)	11	(4)	<2.0	(2)	100	(40)
BA 160	493			<1	(1)	12	(1)	<1	(1)	13400	(200)	240	(10)	15	(4)	<2.0	(2)	115	(40)
BA 220	433			<1	(1)	16	(1)	<1	(1)	7000	(200)	220	(10)	22	(4)	<2.0	(2)	117	(40)
BA 250	403	12	(1)	<1	(1)	26	(1)	<1	(1)	17400	(200)	340	(10)	27	(4)	30	(2)	259	(40)
BA 280	373			<1	(1)	33	(1)	<1	(1)	23600	(200)	350	(10)	38	(4)	10	(2)	370	(40)
BA 310	343			<1	(1)	26	(1)	<1	(1)	22800	(200)	360	(10)	36	(4)	<2.0	(2)	260	(40)
BA 340	313			<1	(1)	28	(1)	<1	(1)	25600	(200)	460	(10)	32	(4)	15	(2)	420	(40)
BA 370	283	32	(1)	<1	(1)	55	(1)	<1	(1)	25200	(200)	470	(10)	37	(4)	10	(2)	500	(40)
BA 400	253			<1	(1)	35	(1)	<1	(1)	24700	(200)	370	(10)	37	(4)	20	(2)	450	(40)
BA 430	223			<1	(1)	33	(1)	<1	(1)	30600	(200)	640	(10)	43	(4)	20	(2)	570	(40)
BA 460	193			<1	(1)	55	(1)	<1	(1)	27700	(200)	460	(10)	52	(4)	19	(2)	390	(40)
BA 490	163	27	(1)	<1	(1)	32	(1)	<1	(1)	29200	(200)	530	(10)	40	(4)	5	(2)	530	(40)
BA 520	133			<1	(1)	38	(1)	<1	(1)	31600	(200)	560	(10)	43	(4)	13	(2)	520	(40)
BA 550	103			<1	(1)	34	(1)	<1	(1)	28800	(200)	520	(10)	37	(4)	10	(2)	380	(40)
BA 580	73			<1	(1)	35	(1)	<1	(1)	30000	(200)	540	(10)	47	(4)	17	(2)	530	(40)
BA 610	43	18	(1)	<1	(1)	33	(1)	<1	(1)	30000	(200)	720	(10)	47	(4)	<2.0	(2)	540	(40)
BA 640	13			<1	(1)	34	(1)	<1	(1)	26600	(200)	490	(10)	49	(4)	<2.0	(2)	710	(40)

Error (+/-) based on detection limits and dilution factor.

Table 5.4. Bells Lake Bottom Sediment Concentrations, Freezer Box Section BF.

		Concentration - ppm																	
Sample	Dist b/w Lk Btm	As	(+/-)	Ag	(+/-)	Cu	(+/-)	Cd	(+/-)	Fe	(+/-)	Mn	(+/-)	Ni	(+/-)	Pb	(+/-)	Zn	(+/-)
BF 1	16			<1	(1)	36	(1)	<1	(1)	29700	(200)	625	(1)	39	(4)	180	(2)	396	(4)
BF 2	14			<1	(1)	34	(1)	<1	(1)	20800	(200)	500	(1)	40	(4)	72	(2)	274	(4)
BF 3	12			<1	(1)	37	(1)	2	(1)	50700	(200)	755	(1)	36	(4)	762	(2)	864	(4)
BF 4	10			<1	(1)	28	(1)	<1	(1)	28800	(200)	360	(1)	26	(4)	34	(2)	161	(4)
BF 5	8			<1	(1)	26	(1)	<1	(1)	28700	(200)	344	(1)	26	(4)	56	(2)	172	(4)
BF 6	6			<1	(1)	38	(1)	3	(1)	53700	(200)	1107	(1)	28	(4)	663	(2)	924	(4)
BF WATER				<1	(1)	<1	(1)	<1	(1)	22	(2)	102	(1)	<4.0	(4)	<2.0	(2)	<4	(4)

Error (+/-) based on detection limits and dilution factor.

Table 5.5. Killarney Lake Bottom Sediment Concentrations, Site KB.

Sample	Dist blw Lk Btm	Concentration - ppm																
		As	(+/-)	Ag	(+/-)	Cu	(+/-)	Cd	(+/-)	Fe	(+/-)	Mn	(+/-)	Ni	(+/-)	Pb	(+/-)	Zn	(+/-)
KB -10	616			<1	(1)	14	(1)	<1	(1)	14100	(200)	700	(10)	18	(4)	<2.0	(2)	170	(40)
KB 20	586			<1	(1)	27	(1)	<1	(1)	24300	(200)	750	(10)	32	(4)	<2.0	(2)	330	(40)
KB 50	556			<1	(1)	29	(1)	<1	(1)	27500	(200)	700	(10)	37	(4)	80	(2)	490	(40)
KB 80	526			<1	(1)	23	(1)	<1	(1)	24400	(200)	470	(10)	35	(4)	90	(2)	290	(40)
KB 110	496			<1	(1)	21	(1)	<1	(1)	22500	(200)	450	(10)	28	(4)	32	(2)	260	(40)
KB 140	466			<1	(1)	22	(1)	<1	(1)	28800	(200)	800	(10)	33	(4)	42	(2)	290	(40)
KB 170	436	42	(1)	<1	(1)	26	(1)	<1	(1)	29600	(200)	600	(10)	45	(4)	50	(2)	300	(40)
KB 200	406			<1	(1)	29	(1)	<1	(1)	30500	(200)	560	(10)	42	(4)	46	(2)	420	(40)
KB 230	376			<1	(1)	28	(1)	<1	(1)	25100	(200)	420	(10)	41	(4)	20	(2)	280	(40)
KB 260	346			<1	(1)	28	(1)	<1	(1)	21200	(200)	320	(10)	42	(4)	12	(2)	270	(40)
KB 290	316			<1	(1)	39	(1)	<1	(1)	26200	(200)	460	(10)	52	(4)	30	(2)	380	(40)
KB 320	286	31	(1)	<1	(1)	40	(1)	<1	(1)	24400	(200)	460	(10)	51	(4)	28	(2)	370	(40)
KB 350	256			<1	(1)	42	(1)	<1	(1)	25500	(200)	520	(10)	57	(4)	62	(2)	430	(40)
KB 380	226			<1	(1)	46	(1)	<1	(1)	22500	(200)	490	(10)	66	(4)	50	(2)	420	(40)
KB 410	196			<1	(1)	45	(1)	<1	(1)	23300	(200)	480	(10)	54	(4)	60	(2)	510	(40)
KB 440	166			<1	(1)	43	(1)	<1	(1)	19900	(200)	380	(10)	58	(4)	33	(2)	410	(40)
KB 470	136	40	(1)	<1	(1)	39	(1)	<1	(1)	22700	(200)	400	(10)	53	(4)	36	(2)	360	(40)
KB 470 (Split)	136			<1	(1)	40	(1)	<1	(1)	21500	(200)	330	(10)	58	(4)	28	(2)	390	(40)
KB 500	106			<1	(1)	41	(1)	<1	(1)	20300	(200)	360	(10)	55	(4)	61	(2)	430	(40)
KB 530	76			<1	(1)	39	(1)	<1	(1)	19100	(200)	300	(10)	53	(4)	35	(2)	430	(40)
KB 560	46			<1	(1)	43	(1)	<1	(1)	19000	(200)	270	(10)	63	(4)	39	(2)	480	(40)
KB 590	16			<1	(1)	38	(1)	<1	(1)	19200	(200)	370	(10)	57	(4)	35	(2)	530	(40)
KB 592	14			<1	(1)	53	(1)	<1	(1)	30000	(1000)	218	(1)	71	(4)	62	(2)	300	(40)
KB 594	12			<1	(1)	49	(1)	<1	(1)	28000	(1000)	172	(1)	66	(4)	48	(2)	205	(40)
KB 596	10			<1	(1)	48	(1)	<1	(1)	30000	(1000)	208	(1)	76	(4)	47	(2)	205	(40)
KB 598	8			<1	(1)	50	(1)	<1	(1)	28000	(1000)	200	(1)	68	(4)	46	(2)	235	(40)
KB 600	6	70	(1)	1	(1)	50	(1)	4	(1)	40000	(1000)	350	(25)	62	(4)	540	(40)	800	(40)
KB 602	4			15	(1)	220	(10)	64	(1)	76000	(1000)	4400	(50)	45	(4)	13100	(100)	14450	(200)
KB 604	2			16	(1)	220	(10)	65	(1)	111000	(1000)	8600	(50)	32	(4)	14000	(100)	17100	(200)
KB 606	0	122	(1)	13	(1)	183	(1)	74	(1)	107000	(1000)	13440	(50)	30	(4)	17460	(50)	17800	(80)

Error (+/-) based on detection limits and dilution factor.

Table 5.6. Killarney Lake Bottom Sediment Concentrations, Freezer Box Section KF.

Sample		Dist b/w	Concentration - ppm																	
		Lk Btm	As	(+/-)	Ag	(+/-)	Cu	(+/-)	Cd	(+/-)	Fe	(+/-)	Mn	(+/-)	Ni	(+/-)	Pb	(+/-)	Zn	(+/-)
KF2	0	52			3	(1)	46	(1)	10	(1)	45000	(1000)	390	(10)	57	(4)	600	(50)	3200	(200)
KF2	2	50			4	(1)	60	(1)	21	(1)	48000	(1000)	460	(10)	50	(4)	2600	(100)	7200	(200)
KF2	4	48	45	(1)	9	(1)	94	(1)	36	(1)	58000	(1000)	880	(10)	47	(4)	6900	(100)	10850	(200)
KF2	6	46			22	(1)	202	(1)	74	(1)	71000	(1000)	3250	(25)	39	(4)	25100	(100)	20300	1000)
KF2	8	44			37	(1)	475	(1)	120	(1)	75000	(1000)	6480	(25)	30	(4)	37400	(100)	32850	1000)
KF2	10	42	51	(1)	33	(1)	475	(1)	121	(1)	79000	(1000)	9020	(25)	28	(4)	32500	(100)	34150	1000)
KF2	12	40	70	(1)	24	(1)	275	(1)	74	(1)	79000	(1000)	8680	(25)	23	(4)	22250	(50)	20250	1000)
KF2	14	38	53	(1)	16	(1)	250	(1)	69	(1)	79000	(1000)	11430	(25)	23	(4)	21100	(50)	18450	1000)
KF2	16	36	93	(1)	13	(1)	200	(1)	44	(1)	76000	(1000)	11080	(25)	19	(4)	14450	(50)	14200	1000)
KF2	18	34	71	(1)	11	(1)	150	(1)	38	(1)	80000	(1000)	12450	(25)	27	(4)	11050	(50)	12500	1000)
KF2	20	32	159	(1)	11	(1)	150	(1)	44	(1)	76000	(1000)	9780	(25)	28	(4)	10750	(50)	13500	1000)
KF2	22	30	181	(1)	10	(1)	125	(1)	38	(1)	75000	(1000)	10920	(25)	26	(4)	9750	(50)	9750	1000)
KF2	24	28	156	(1)	9	(1)	125	(1)	35	(1)	77000	(1000)	10180	(25)	26	(4)	8950	(50)	9450	1000)
KF2	26	26	141	(1)	9	(1)	175	(1)	29	(1)	84000	(1000)	9780	(25)	25	(4)	8550	(50)	8500	1000)
KF2	28	24	83	(1)	9	(1)	175	(1)	34	(1)	79000	(1000)	8720	(25)	31	(4)	9600	(50)	8700	1000)
KF2	30	22	106	(1)	7	(1)	175	(1)	32	(1)	74000	(1000)	6600	(25)	28	(4)	8550	(50)	8025	(200)
KF2	32	20	131	(1)	6	(1)	150	(1)	25	(1)	75000	(1000)	6850	(25)	31	(4)	5750	(50)	6825	(200)
KF2	34	18	111	(1)	7	(1)	150	(1)	30	(1)	79000	(1000)	7520	(25)	31	(4)	6400	(50)	6975	(200)
KF2	36	16	150	(1)	11	(1)	200	(1)	50	(1)	83000	(1000)	9280	(25)	30	(4)	4900	(50)	8000	(200)
KF2	38	14	315	(1)	12	(1)	200	(1)	55	(1)	83000	(1000)	10720	(25)	37	(4)	4400	(50)	8875	(200)
KF2	40	12	315	(1)	17	(1)	183	(1)	65	(1)	103000	(1000)	7100	(50)	35	(4)	4200	(50)	9150	(200)
KF2	42	10	376	(1)	17	(1)	180	(1)	64	(1)	102000	(1000)	7050	(50)	36	(4)	4100	(100)	8900	(200)
KF2	44	8	203	(1)	17	(1)	180	(1)	63	(1)	103000	(1000)	7050	(50)	35	(4)	3950	(100)	8950	(200)
KF2	46	6			16	(1)	169	(1)	77	(1)	93000	(1000)	6150	(50)	37	(4)	4250	(100)	10300	(200)
KF2	48	4			14	(1)	154	(1)	73	(1)	85000	(1000)	5100	(50)	34	(4)	4550	(100)	9900	(200)
KF2	50	2			11	(1)	117	(1)	49	(1)	67000	(1000)	4000	(50)	33	(4)	4250	(100)	8000	(200)
KF	23.6	28			10	(1)	126	(1)	36	(1)	83000	(1000)	9325	(25)	31	(4)	7200	(50)	9500	(200)
KB H2O					<1	(1)	7	(1)	3	(1)	—	—	360	(10)	5	(4)	6	(2)	255	(40)

Error (+/-) based on detection limits and dilution factor.

Table 5.7. Killarney Lake Bottom Sediment Concentrations, Site KC.

Sample	Dist b/w	Concentration - ppm																	
	Lk Btm	As	(+/-)	Ag	(+/-)	Cu	(+/-)	Cd	(+/-)	Fe	(+/-)	Mn	(+/-)	Ni	(+/-)	Pb	(+/-)	Zn	(+/-)
KC 230	124			<1	(1)	17	(1)	<1	(1)	9200	(200)	180	(10)	21	(4)	25	(2)	180	(40)
KC 260	94			<1	(1)	17	(1)	<1	(1)	9550	(200)	260	(10)	24	(4)	33	(2)	190	(40)
KC 280	74			<1	(1)	15	(1)	<1	(1)	9300	(200)	310	(10)	21	(4)	32	(2)	170	(40)
KC 290	64			<1	(1)	15	(1)	<1	(1)	9500	(200)	320	(10)	20	(4)	36	(2)	160	(40)
KC 300	54			<1	(1)	15	(1)	<1	(1)	10000	(200)	320	(10)	22	(4)	33	(2)	190	(40)
KC 310	44	85	(1)	<1	(1)	15	(1)	<1	(1)	12090	(200)	520	(10)	22	(4)	66	(2)	350	(40)
KC 312	42			<1	(1)	18	(1)	1	(1)	19000	(1000)	420	(10)	23	(4)	156	(2)	237	(4)
KC 314	40			<1	(1)	20	(1)	1	(1)	10000	(1000)	400	(10)	20	(4)	98	(2)	420	(4)
KC 316	38			<1	(1)	19	(1)	2	(1)	14000	(1000)	400	(10)	21	(4)	153	(2)	900	(200)
KC 318	36			<1	(1)	21	(1)	2	(1)	17000	(1000)	430	(10)	20	(4)	307	(2)	1050	(200)
KC 320	34	46	(1)	<1	(1)	25	(1)	11	(1)	14000	(1000)	620	(20)	25	(4)	3540	(40)	5640	(200)
KC 330	24	32	(1)	15	(1)	134	(1)	146	(1)	29000	(1000)	1860	(20)	26	(4)	19480	(40)	19420	(200)
KC 340	14	95	(1)	11	(1)	141	(1)	70	(1)	96000	(1000)	13060	(20)	28	(4)	16800	(40)	17520	(200)
KC 350 (split	4	93	(1)	11	(1)	143	(1)	70	(1)	104000	(1000)	12720	(20)	28	(4)	17160	(40)	17820	(200)
KC 350	4			7	(1)	136	(1)	38	(1)	—	(1000)	10760	(20)	29	(4)	11000	(40)	14220	(200)
KC 352	2			9	(1)	164	(1)	45	(1)	103000	(1000)	6600	(50)	32	(4)	5300	(40)	7650	(200)
KC 354	0			10	(1)	172	(1)	63	(1)	108000	(1000)	7000	(50)	38	(4)	4150	(40)	7400	(200)

Error (+/-) based on detection limits and dilution factor.

Table 5.8. Killarney Lake Bottom Sediment Concentrations, Site KD.

Sample	Dist blw Lk Btm	Concentration - ppm As	(+/-)	Ag	(+/-)	Cu	(+/-)	Cd	(+/-)	Fe	(+/-)	Mn	(+/-)	Ni	(+/-)	Pb	(+/-)	Zn	(+/-)
KD 230	120			<1	(1)	19	(1)	<1	(1)	15400	(200)	320	(10)	26	(4)	23	(2)	180	(40)
KD 260	90			<1	(1)	23	(1)	<1	(1)	15300	(200)	570	(10)	46	(4)	13	(2)	390	(40)
KD 280	70			<1	(1)	20	(1)	<1	(1)	12200	(200)	560	(10)	37	(4)	14	(2)	320	(40)
KD 290	60			<1	(1)	21	(1)	<1	(1)	13700	(200)	540	(10)	29	(4)	15	(2)	300	(40)
KD 300	50			<1	(1)	19	(1)	<1	(1)	11400	(200)	510	(10)	21	(4)	33	(2)	210	(40)
KD 310	40			<1	(1)	20	(1)	<1	(1)	14200	(200)	680	(10)	29	(4)	70	(2)	310	(40)
KD 320	30	30	(1)	<1	(1)	21	(1)	1	(1)	17300	(200)	960	(10)	28	(4)	160	(50)	5600	(80)
KD 322	28			1	(1)	34	(1)	18	(1)	18000	(1000)	760	(10)	29	(4)	1150	(100)	2800	(80)
KD 324	26			1	(1)	47	(1)	27	(1)	18000	(1000)	980	(10)	28	(4)	1850	(100)	5200	(80)
KD 326	24			3	(1)	75	(1)	42	(1)	22000	(1000)	970	(10)	23	(4)	3900	(100)	5550	(80)
KD 328	22			4	(1)	94	(1)	60	(1)	24000	(1000)	990	(10)	27	(4)	5350	(100)	7600	(80)
KD 330	20	9	(1)	4	(1)	85	(1)	73	(1)	26100	(400)	1340	(20)	33	(4)	9080	(50)	19420	(80)
KD 340 (split)	10			5	(1)	107	(1)	102	(1)	42700	(400)	2900	(20)	43	(4)	4000	(50)	17540	(80)
KD 340	10	94	(1)	4	(1)	104	(1)	94	(1)	42500	(400)	2720	(20)	40	(4)	3540	(50)	15300	(80)
KD 350	0	50	(1)	1	(1)	65	(1)	86	(1)	34800	(400)	1340	(20)	38	(4)	1400	(50)	14220	(80)
KD 350 (split)	0			2	(1)	64	(1)	118	(1)	36100	(400)	1480	(20)	38	(4)	1220	(50)	17800	(80)

Error (+/-) based on detection limits and dilution factor.

5.5 Quality Control

Quality control was maintained throughout the analytical phase of the project. All sample containers, plastic bags, and sampling devices such as spoons and knives were thoroughly washed according to EPA procedures. All glassware used for sample digestion and dilutions were cleaned according to EPA procedures as listed below.

Glassware Cleaning Procedure (Method 3050)

- tap water rinse
- wash in Alconox soap
- tap water rinse 4 - 5 times
- wash in 6 N HCL
- tap water rinse 7 - 8 times
- wash in 6 N HNO_3
- tap water rinse 7- 8 times
- Type II water rinse 4 - 5 times

During analysis, concentration values were tabulated after every sample measurement. Dilution factors, where appropriate, were recorded on all bottles, glassware, and in the laboratory notebook. Type II water was used in all dilutions. All transfer of digestates or dilutions was between clearly marked beakers. Pipettes were used once only before washing.

Serial dilutions were performed when any sample exceeded the linear range for an element. The volume of the sample to be diluted was never less than 5 ml. Ratios of solute to solvent neither exceeded 1:20 nor were less than 1:1.

Instrument sensitivity checks were made prior to each element analysis. On the Model 603, this involved dividing 0.0044 by the absorption reading from aspirating a standard, and multiplying this value by the concentration of the standard. If this value was within 0.10 of the manufacturers specifications, the analysis proceeded. Because the instrument is over 10 years old, this is probably a valid error range.

The method of standard additions was used for each element. This procedure checks for matrix interferences. The method involves taking two equal aliquots of the sample and adding a known volume of the standard analyte to one of them. The same volume of Type II water is added to the other aliquot. The unknown sample concentration can then be calculated and checked against the concentration of the other sample. If the two values do not agree within error, matrix interference occurs. No significant interference was found throughout the analysis.

Type II water, reagent grade HNO_3 and HCL blanks were run through the digestion procedure. These acids were then analyzed by FLAA to determine if impurities within the solution affected the results. HNO_3 contained small quantities of the elements analyzed for, and so these were zeroed out on the instrument prior to analysis by aspirating a type II water/HNO_3 solution and calibrating the machine to ignore the small fraction (less than 0.5 ppm) contributed by the matrix.

After analysis, the concentrations were recorded on computer diskettes. Backup disks and superseded data files have been maintained throughout the project.

5.6 Microprobe Ash Analysis

Ash identification was needed to establish a time and lithologic base for the sediment cores from different lakes. Correlations were necessary to establish that Bells Lake received sediments similar to those of Killarney Lake from a referenced horizon, such as the Mt. Mazama ash.

Of particular interest was the Mt. Mazama ash. As mentioned previously, this thick, dense ash deposit was 609 cm below Killarney Lake and 383 cm below Bells Lake bottom. If the two ash deposits were chemically identical, then the unit can be used as a time level marker horizon for this and other studies throughout the valley. The Mazama ash, which is derived from the explosion of Crater Lake in southern Oregon and covers much of the Pacific Northwest (Smith and Westgate, 1968), has a reported age of 6600 - 6900 years before present (Merhinger and others, 1977).

Electron microprobe techniques were used to determine the chemistry of volcanic ash. With this instrument the composition of the volcanic glass can be determined more accurately than with other techniques such as comparison of the refractive index or phenocryst assemblage, or by bulk chemical composition, for microlites or bubbles in the glass shards can be avoided (Smith and Westgate, 1968).

Three ash samples were analyzed. These were: KB -10, BA 100, and KD 17.5. Sample KD 17.5 (334 cm below lake bottom at site KD) was the only sample, apart from the thick Mazama ash deposits which KB - 10 and BA 100 were from, of sufficient sample size for analysis. Samples had to be large enough to cover a petrographic slide after the non-ash fractions had been removed. Because most ash deposits found in the cores were only a few millimeters thick, an adequate volume was difficult to obtain.

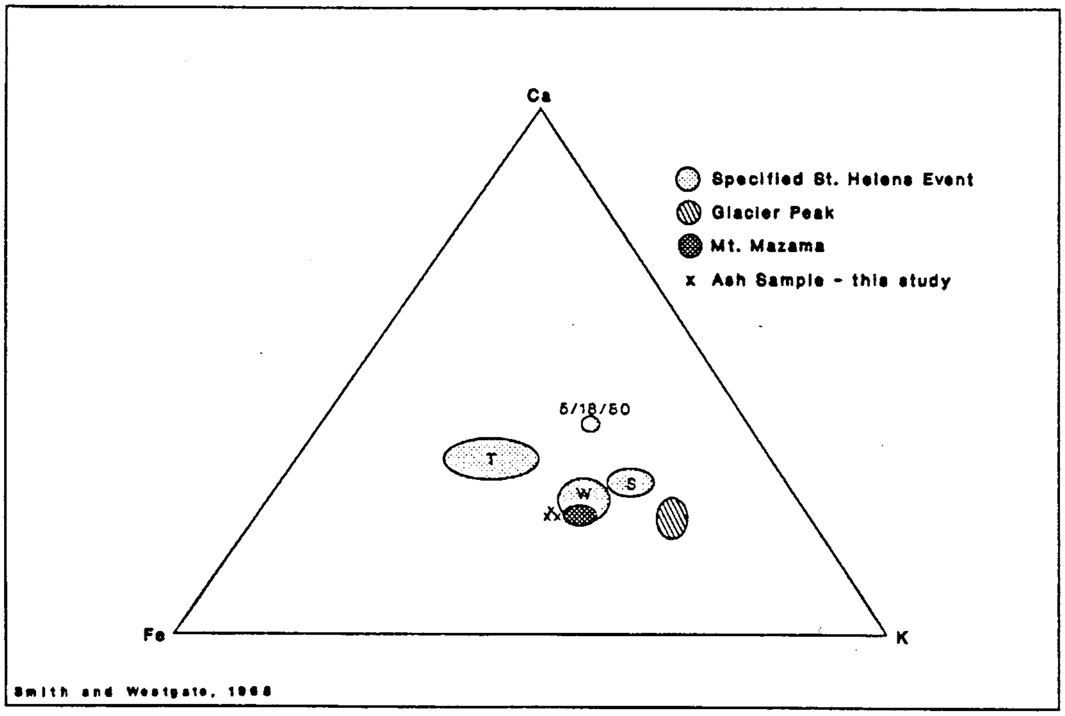
Glass shards were separated from the soil matrix by centrifuging the shards in a heavy liquid for three minutes. This liquid was a mixture of tetrabromoethane and acetone with a density of 2.92 grams per cubic centimeter. The centrifuge tubes were then placed in liquid nitrogen to freeze the lower, heavy fraction. The light fraction and liquid was filtered through Whatman No. 4 filter paper and washed with acetone. The glass shards were dried and mounted in an epoxy resin, and thin sections prepared. Conduction of the electron beam was facilitated by adding a thin film of carbon prior to the analysis. Elemental concentrations during analysis were obtained by reference to obsidian standard "University of Idaho Standard No. 1," equivalent to Smith and Westgate, 1968. Concentrations were determined by dividing the average radiated intensity of the shard by the intensity of the standard, and multiplying by the concentration of the standard. At least 10 shards were analyzed per sample per oxide. These concentrations as well as the average Mazama ash concentrations (Powers and Wilcox, 1964), are shown in Table 5.9.

The ash was identified by comparison of compositions with a suite of established Mazama ash samples compiled by Smith and Westgate (1968). The comparison was made with respect to the modal concentration of Ca, Fe, and K. As shown in Figure 5.2, Mt. Mazama, Glacier Peak, and several Mt. St. Helens eruptions have distinctive, consistent, compositional groupings which identify them on a triangular diagram. As seen in Figure 5.2, the analyzed samples lie very close to the Mazama composition, although they are slightly depleted in potassium and calcium, and enriched in iron with respect to the average Mazama ash. Further evidence that these samples are Mazama ash is seen in the glass shards which have the characteristically thick walls of the Mazama ash whereas the compositionally similar Mt St. Helens 'W' eruptive sequence (approximately 1800 years before present) characteristically has thin walled shards (personal communication, C.R. Knowles, 1989). Mazama ash is also characterized by the ash thicknesses found in both lakes; 190 cm of ash was found in Bells Lake and over 30 cm of ash were retrieved from Killarney Lake. These deposits are much greater than observed St. Helens 'W' deposits found in the Pacific Northwest (personal communication, Charles R. Knowles, 1989).

Table 5.9. Electron Microprobe Results (percent).

	K	K_2O	Ca	CaO	Fe	FeO
KD 17.5	1.89	2.28	1.06	1.48	1.65	2.11
KB (-10)	1.92	2.32	1.04	1.44	1.69	2.16
BA 100	2.01	2.42	1.07	1.48	1.69	2.31
Mazama*		2.67		1.58		1.27

*mean Mazama Ash analysis from Powers and Wilcox (1964)



Smith and Westgate, 1968

Figure 5.2. Triangular Diagram of Killarney and Bells Lake Ash Chemistries Compared to Those From Other Pacific Northwest Events.

6.0 RESULTS

This chapter presents the results of the geochemical analysis of Killarney Lake and Bells Lake bottom sediments. The first section addresses pre-mining sediments; subsequent sections discuss the upper 80 cm of lake bottom sediments from each lake. For comparison, crustal averages of igneous rocks (Hurlbut and Klein, 1977) for each element are provided. A summary of the conclusions reached in this study is presented at the end of the chapter.

6.1 Bells Lake and Killarney Lake Pre-mining Sediments

Sediments from Bells Lake and Killarney Lake were analyzed to determine background heavy metal concentrations. This section discusses the results of background sediment chemistry analysis. Bells Lake was used as a control for lake bottom sediment analysis because this drainage is free of commercial mining practices, although airborne contaminants from the smelter in the Silver Valley conceivably could have been deposited in the drainage. To determine if Bells Lake is indeed an adequate control for the Coeur d'Alene River drainage, deeper Killarney Lake bottom sediments were compared with Bells Lake sediments.

The graphs in Figure 6.1 show Bells Lake and Killarney Lake element concentrations below a depth of 80 cm below lake bottom. Concentrations for each core are shown below 80 cm because no measurable concentration anomalies associated with heavy metal contamination from the mining district were observed below this depth. The depth criterion is arbitrary; it was chosen to allow the comparison of pre-mining sediment chemistry with mining-related sediment chemistries in the following section. Figure 6.1 displays concentrations for each element in two columns. The scale on the ordinate varies with the maximum concentration of the element.

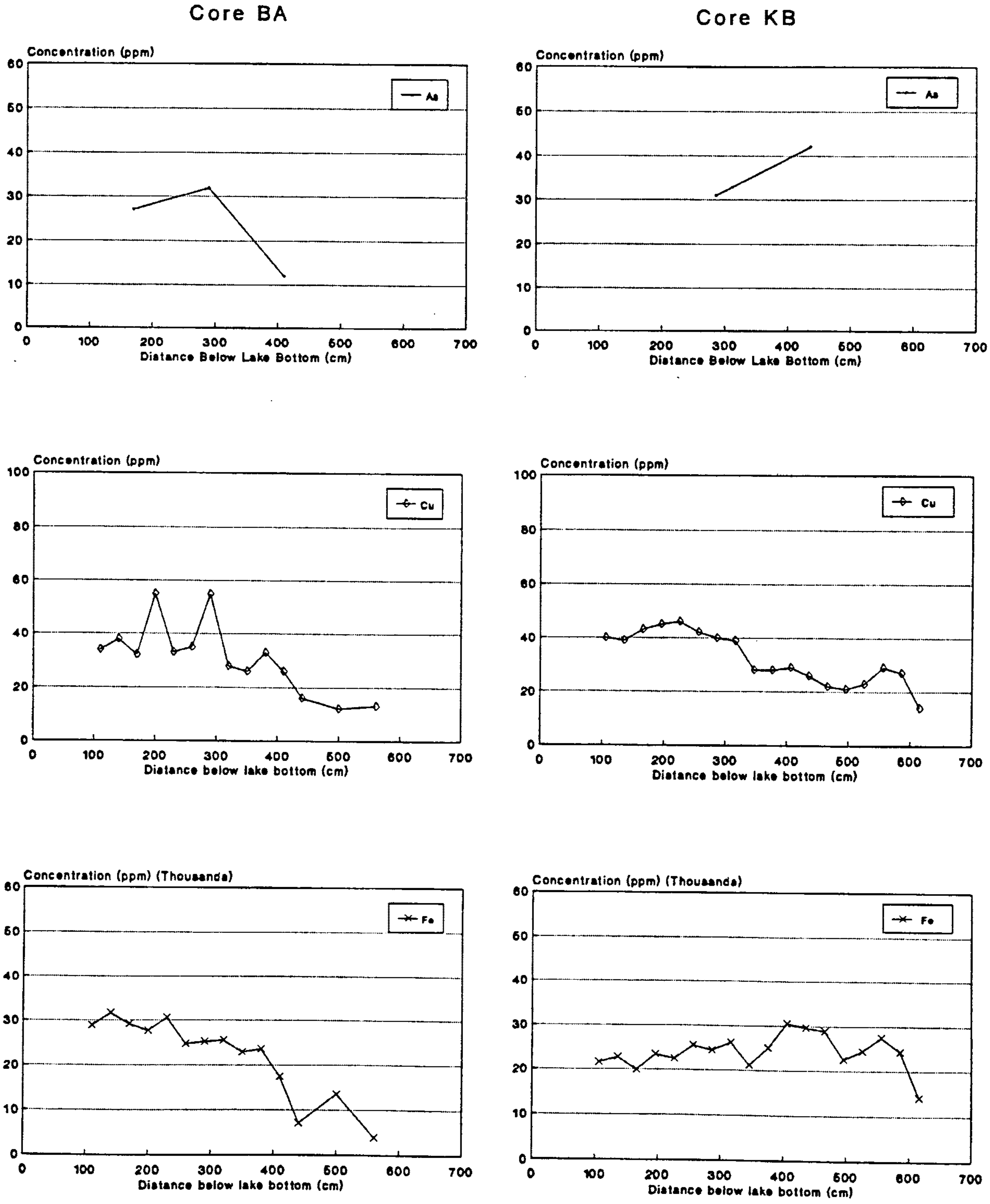


Figure 6.1. Element Concentrations from Core BA (left) and Core KB (right).

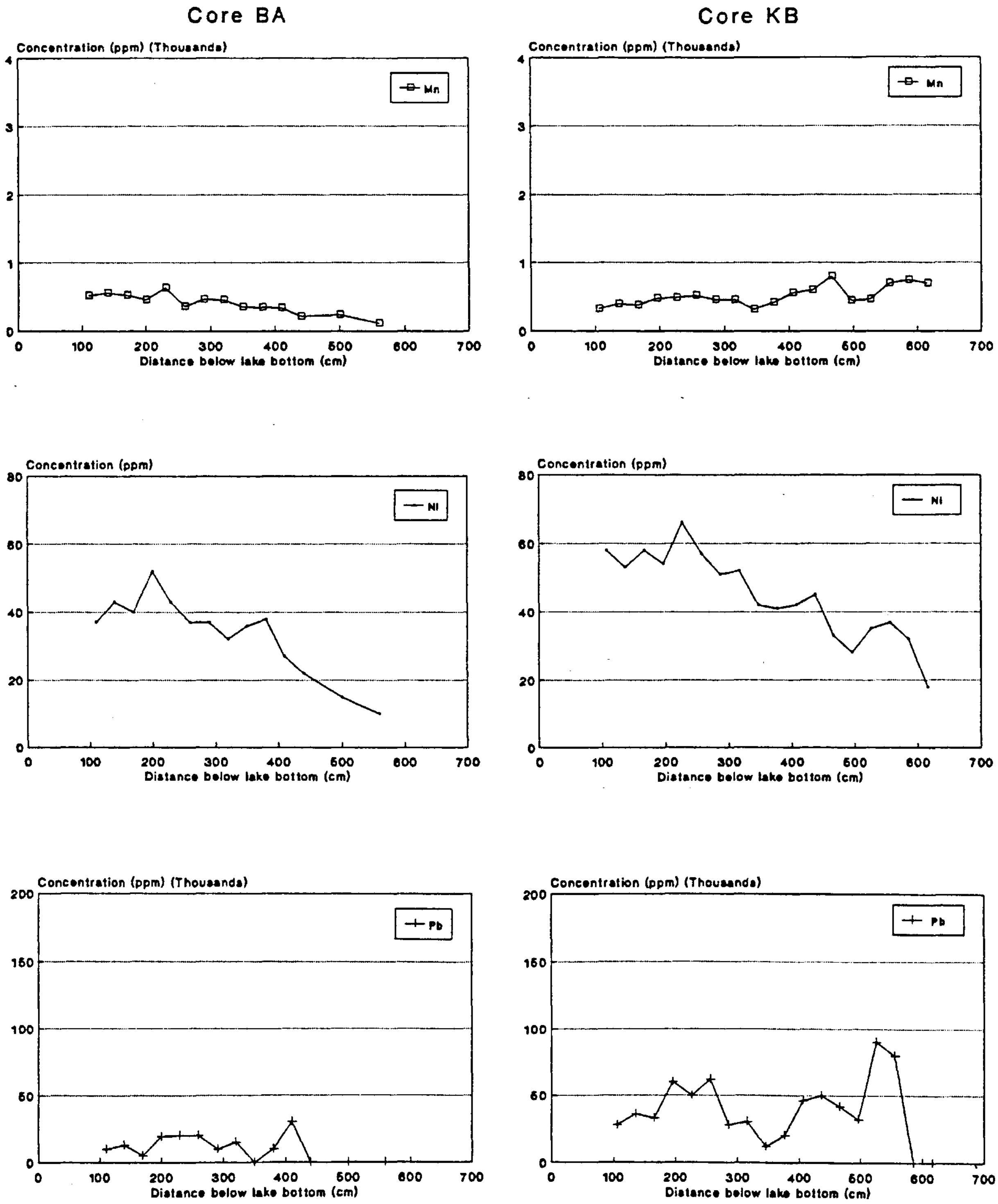


Figure 6.1 (cont.). Element Concentrations from Core BA (left) and Core KB (right).

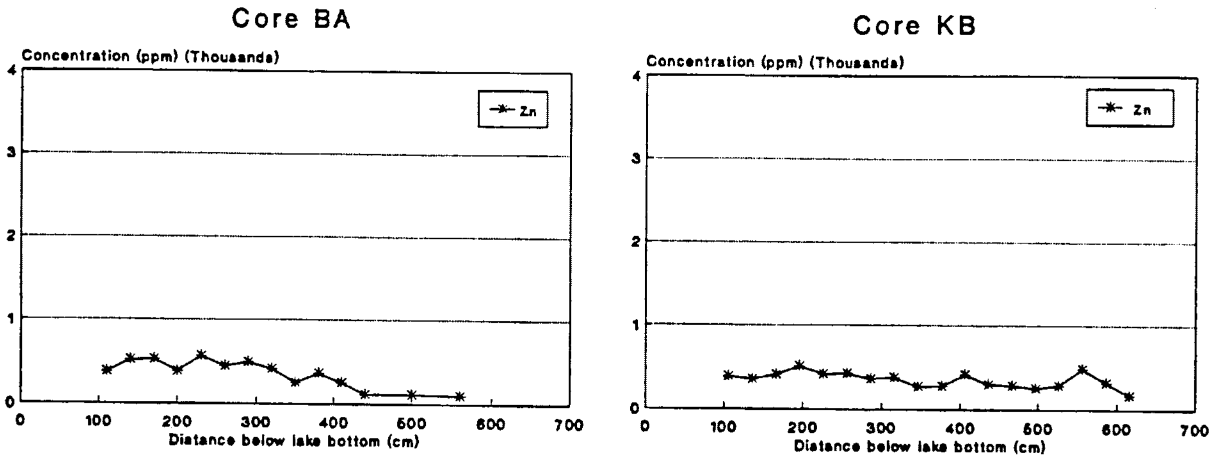


Figure 6.1 (cont.). Element Concentrations from Core BA (left) and Core KB (right).

6.1.1 Silver Background Concentrations

Ag concentrations in both cores were below detection (1 ppm). The crustal average for Ag is 0.07 ppm; and because this value is below FLAA detection limits, there are no means of comparing background concentrations with this value.

6.1.2 Arsenic Background Concentrations

Measured concentrations of As varied between 18 and 32 ppm in core BA and between 31 and 42 ppm in core KB. The crustal average for As is 1.8 ppm. Although only six samples were analyzed from the sediments in the two lakes, concentrations appear to be similar. Sediment concentrations are more than one order of magnitude greater than the crustal average.

6.1.3 Cadmium Background Concentrations

Cd concentrations in both cores were below detection (1 ppm). The crustal average for Cd is 0.20 ppm, and there is no means of comparing background concentrations with this value.

6.1.4 Copper Background Concentrations

Cu concentrations varied from 12 to 55 ppm in core BA and from 14 to 46 ppm in core KB. These concentrations are very similar; both appear to slightly increase in concentration towards the lake bottom surface. The crustal average for Cu is 55 ppm. Sediments from both lakes fall at or slightly below this value.

6.1.5 Iron Background Concentrations

Fe concentrations varied from 3,900 to 31,600 ppm in core BA and from 14,100 to 30,000 ppm in core KB. The lower concentrations found near the bottom of both cores are samples from the Mazama ash, and concentrations above the ash are very similar in both cores. The crustal average for Fe is 50,000 ppm, and sediment concentrations from both cores fall below this value.

6.1.6 Manganese Background Concentrations

Mn concentrations varied from 120 to 640 ppm in core BA and from 320 to 800 ppm in core KB. Lake bottom concentrations are similar in both cores. The crustal average for Mn is 13 ppm, and sediment concentrations from both cores are generally one order of magnitude above this value. No apparent trends are found in the lake bottom sediment concentrations for manganese.

6.1.7 Nickel Background Concentrations

Ni concentrations varied from 11 to 52 ppm in core BA and from 18 to 66 ppm in core KB. Again, lake bottom sediment concentrations are very similar in both cores. Sediment concentrations in each core have similar trends, increasing in concentration towards the lake bottom surface. The crustal average for Ni is 75 ppm, and concentrations in both cores are slightly below this value.

6.1.8 Lead Background Concentrations

Pb concentrations varied from below detection to 20 ppm in core BA and from below detection to 90 ppm in core KB. Lake bottom sediment concentration trends are similar in both cores but sediment concentrations from Killarney Lake are generally higher than those from Bells Lake. The crustal average for Pb is 13 ppm, and sediment concentrations from both lakes bracket this value.

6.1.9 Zinc Background Concentrations

Zn concentrations vary from 100 to 570 ppm in core BA and 170 to 510 ppm in core KB. These concentrations are very similar. The crustal average for Zn is 70 ppm, and sediment concentrations from both cores are greater than this value.

6.1.10 Summary of Results for Background Sediment Concentrations

Lake bottom pre-mining sediment concentrations for Bells Lake and Killarney Lake are similar in magnitude for each respective element analyzed. As, Mn, and Zn sediment concentrations in each lake fall above the crustal average. Cu, Fe, and Ni sediment concentrations fall below the crustal average. Pb concentrations approximate the crustal average, and Ag and Cd concentrations are below detection. Trends in the data, whether constant or increasing, are also similar.

A comparison of the pre-mining sediments in this study and Bells Lake dredge samples of Rabe and Bauer (1977) is presented in Table 6.1. Data obtained during the present study are similar to those of Rabe and Bauer. Differences in Cu, Pb, and Zn between the two studies may occur because Rabe and Bauer collected only one lake bottom sample at each station, whereas this study collected many samples with depth at each station.

Table 6.1. Comparison of Non-polluted Sediment Concentrations (ppm).

	As	Ag	Cu	Cd	Fe	Mn	Ni	Pb	Zn
Bells Lake	12 - 32	<1	12-55	<1-3	3900-31600	120-1107	11-49	<2-762	100-924
Killarney Lake	31-42	<1	14-53	<1	19000-30500	172-800	28-76	<2-90	205-530
Bells Lake, Rabe and Bauer (1976)	---	---	4-9	<2	20000-22000	---	---	30	52-100

6.2 Shallow Lake Bottom Sediments

This section compares lake bottom sediment concentrations above a depth of 80 cm in both lakes. As explained above, the comparison of sediment concentrations above this depth allows comparison of pre-mining and mining sediment concentrations in all core sections. Freezer box sections BF and KF did not sample below 80 cm and may not necessarily show pre-mining sediment concentrations.

The discussion compares lake bottom sediment concentrations for Bells Lake and Killarney Lake for each element. The following graphs show elemental concentrations for the four core sections and two freezer box sections. Sediment concentrations in the cores are displayed independent of the freezer box sections because there are no definitive lithologic horizon markers to match sediments from the core with those from the freezer box sections. Recall from Chapter 4 that site KB contained 3 cm of metallic silt; site KF contained 33 cm of metallic silt in the wet sample; core KC contained 19.5 cm of metallic silt; and core KD contained 17.5 cm of metallic silt. If 33 cm of metallic sediments are present at site KB they were missed by the core sampler, and it is probable that the core retained only the lowest, more compacted portion of the contaminated sediments at this site. However, at sites KC and KD the sections are believed be complete because the lake bottom was visible. The metallic silt in freezer box section KF was both overlain and underlain by organic silt and is believed to show the entire metallic silt section at site KF.

6.2.1 Ag Concentrations in Shallow Lake Bottom Sediments

Ag concentrations in lake bottom sediments above a depth of 80 cm are shown in Figure 6.2. Pre-mining silver concentrations in sediments from all cores were below detection, as were those in the sediments from Bells Lake section BF. In core KB, the deepest elevated silver concentration was measured in sediments from 6 cm below lake bottom, 3 cm below the sharp visual contact between organic silt and metallic silt. Silver concentrations were above background in the lowermost sediments sampled from section KF, 8.5 cm below the silt and organic/metallic silt contact. Recall that pods of metallic silt were found in the organic silt below this contact; density differences in the two sediment types may have allowed metallic silt pods to migrate into the less dense metallic silt. In section KF, silver concentrations reach their peak of 37 ppm at the lower organic silt/metallic silt contact. From this point, silver concentrations generally decrease towards the lake bottom. A rise in concentration then occurs to a maximum of 17 ppm in the organic silt overlying the section. Sediment silver concentrations in core KC are less than those in sections

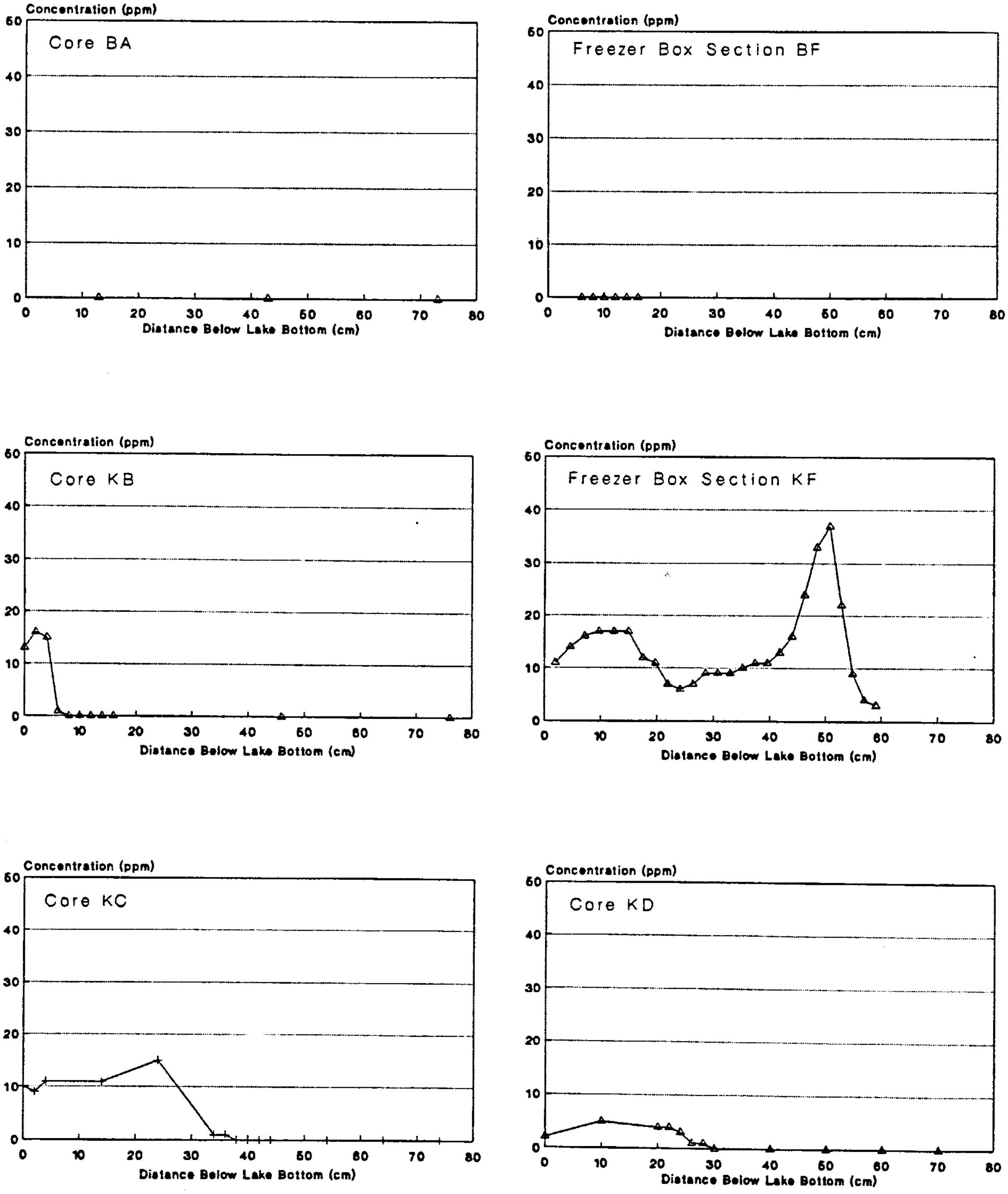


Figure 6.2. Silver Concentrations from Respective Sites
Crustal Average = 0.07 ppm

KB and KF, and concentrations in KD yet lower. All sediment concentrations above background are approximately three orders of magnitude above the crustal average concentration of 0.07 ppm.

6.2.2 As Concentrations in Shallow Lake Bottom Sediments

As concentrations in shallow lake bottom sediments are shown in Figure 6.3. As explained in Chapter 5, As analysis required a separate digestion and analysis, and hence fewer sediments were analyzed. Only one sample was analyzed in the top 80 cm of lake bottom sediments in core BA, it has an As concentration of 18 ppm which is similar to that in samples below 80 cm depth. No samples were analyzed for As in freezer box section BF. Only 2 samples were analyzed in section KB, and these samples show a two to threefold increase in concentration over those sediments analyzed lower in the section. Sediments from section KF show an increase in concentration towards the lake bottom to a maximum concentration of 376 ppm at 10 cm below lake bottom. The only sample analyzed above this point was from the organic silt unit and it had a lower concentration of 203 ppm. In cores KC and KD, As concentrations measured in the sediments above 80 cm averaged 70 ppm and 48 ppm, respectively. However only 5 samples were analyzed from KC and only 4 from KD. All sediments analyzed in these sections fall one to two orders of magnitude above the crustal average of 1.8 ppm.

6.2.3 Cd Concentrations in Shallow Lake Bottom Sediments

Cd concentrations from sediments above 80 cm depth in all sections are shown in Figure 6.4 Sediment concentrations in Bells Lake are either below detection, in core BA, or just above detection, in section BF. As shown in Section 6.1, cadmium concentrations were below the detection limit in sediments deeper than 80 cm. The presence of Cd concentrations up to 3 ppm in lake bottom sediments 3 to 6 cm deep in Bells Lake suggest that they may be a natural variation in drainage sediment Cd concentrations, that air fall from smelter emissions reached Bells Lake, or there may be some other local anthropogenic Cd source. In core KB sediment Cd concentrations peak in the uppermost sediments retrieved from the core, first increasing at 6 cm below lake bottom, 3 cm below the visual organic silt and metallic silt contact. In section KF, the Cd concentration profile is similar to the Ag profile. Concentrations are above background in the sediments below the metallic silt contact and peak at 121 ppm at the contact. Cd concentrations in sediments from cores KC and KD rise abruptly above background at 18.5 cm and 12.5 cm below the visual metallic silt contact, respectively. Concentrations in core KC peak abruptly at 146 ppm, the highest Cd concentration measured in any section, and then decline abruptly to approximately 70 ppm in the top 24 cm. Concentrations in core KD peak at 118 ppm at the lake bottom surface. All sediments above 80 cm in

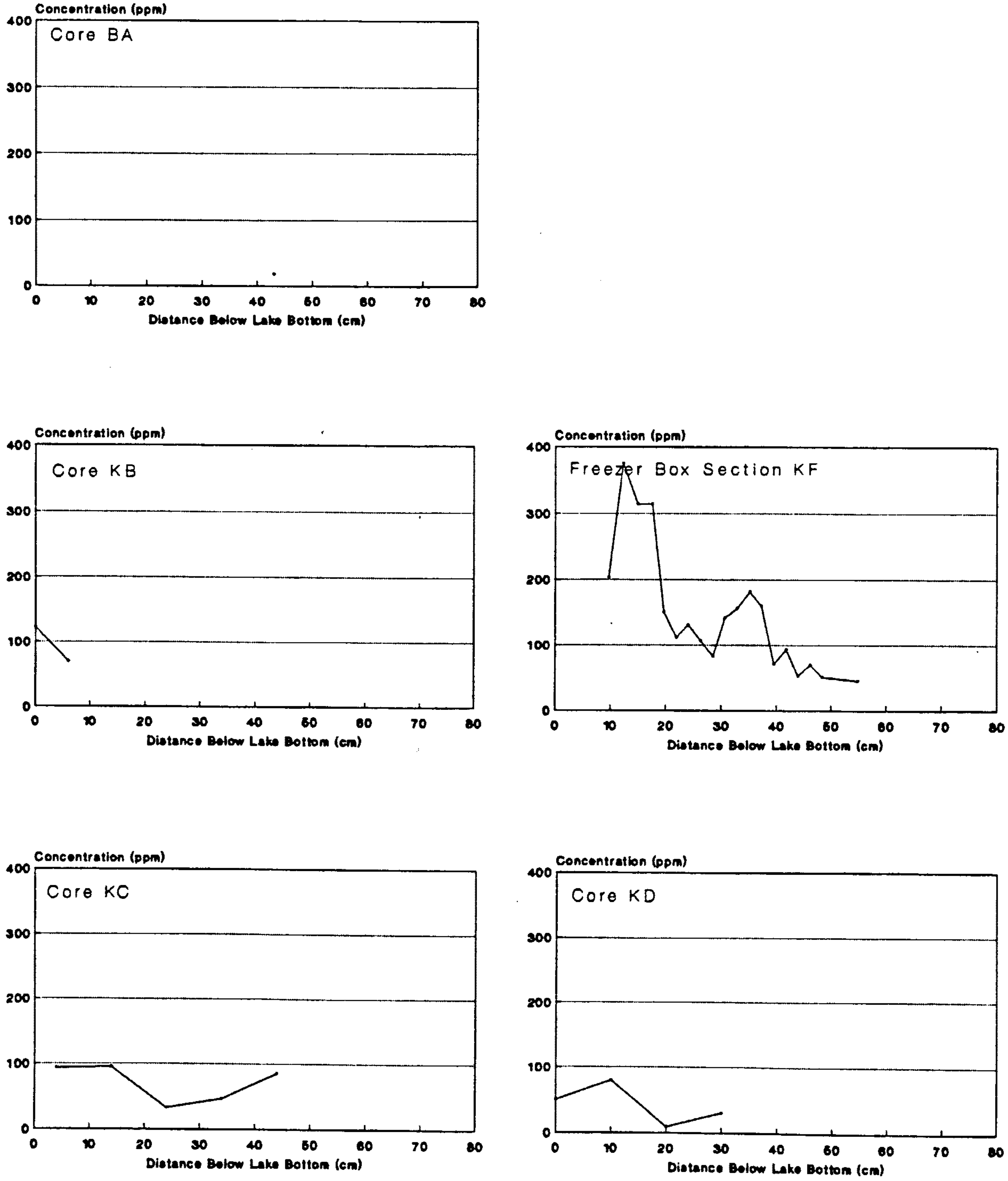


Figure 6.3. Arsenic Concentrations from Respective Sites
Crustal Average = 1.8 ppm

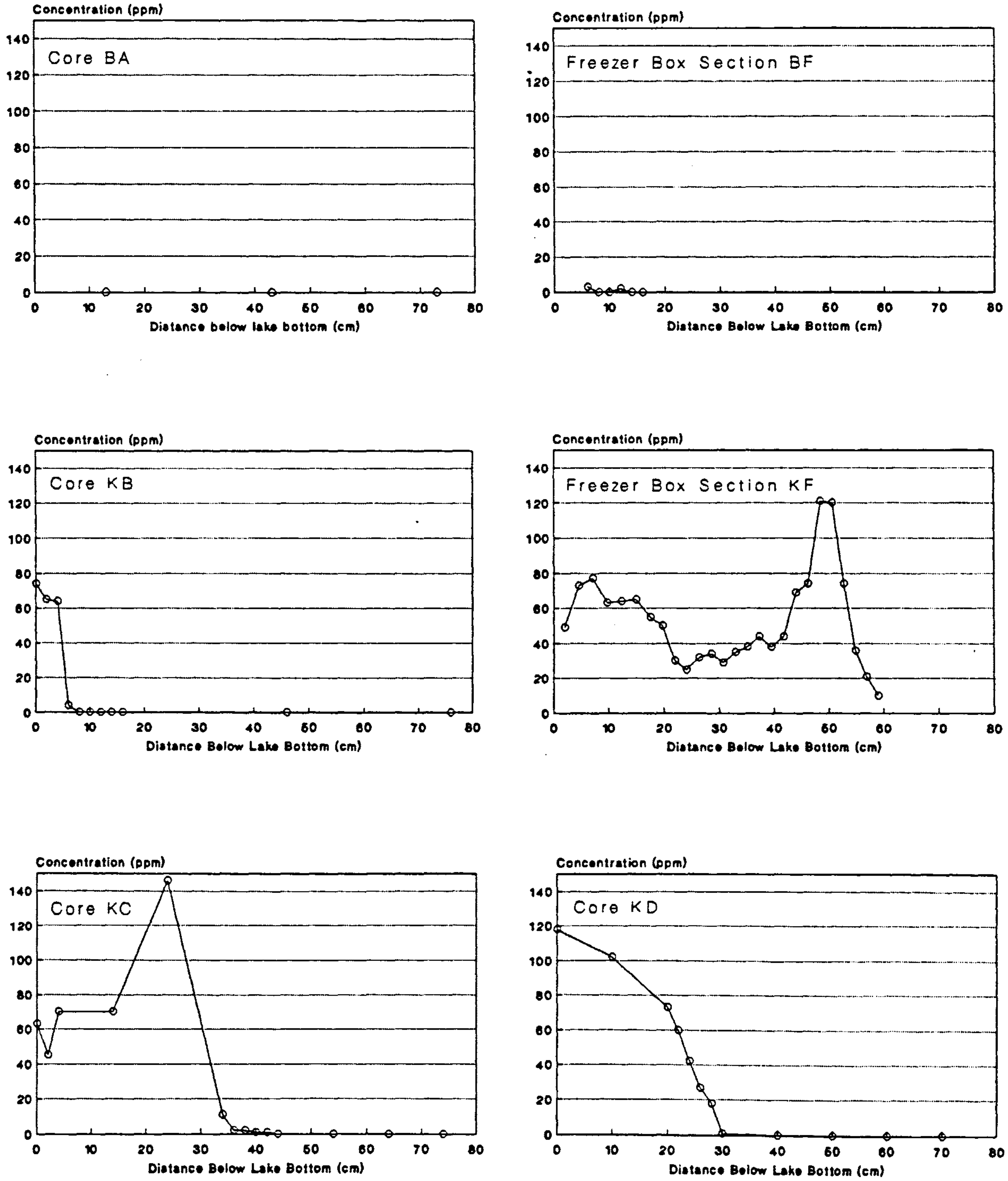


Figure 6.4. Cadmium Concentrations from Respective Sites
Crustal Average = 0.20 ppm

Killarney Lake have Cd concentrations more than one order of magnitude greater than background or the crustal average.

6.2.4 Cu Concentrations in Shallow Lake Bottom Sediments

Cu concentrations in shallow lake bottom sediments from all sections are shown in Figure 6.5. In core KB, sediments below 6 cm (interpreted as pre-mining) have Cu concentrations similar to those below 80 cm (shown in Figure 6.1), below or close to the crustal average of 55 ppm. A significant increase in Cu concentration to 220 ppm is seen 1 cm below the visual contact with the metallic silt. However, as shown in Figures 6.2 to 6.4, the highest concentration in core KB is less than one-half the highest concentration in core KF. Sediment concentrations at the bottom of section KF are similar to background concentrations but peak at 475 ppm, 6 cm above the bottom of the section and near the metallic silt contact. The average Cu concentrations in section KF are approximately three times that of background and the crustal average, but they peak at nearly one order of magnitude greater than background. In cores KC and KD, Cu concentrations increase 24 and 28 cm below lake bottom, respectively, to values 2 to 3 times greater than background.

6.2.5 Fe Concentrations in Shallow Lake Bottom Sediments

Lake bottom Fe concentrations are shown in Figure 6.6 (note that concentrations are in thousands of ppm). Fe concentrations within Bells Lake sediments are equal to or slightly greater than the deep sediments shown in Figure 6.1. The concentration profile from section BF is variable, and samples at 3 and 6 cm depth are more than twice as concentrated as the crustal average, the remaining concentrations approximate or are below the crustal average of 50,000 ppm. These two small peaks are observed in all elements analyzed above detection with the exception of nickel (section 6.2.7). There are no lithologic indicators to explain this chemical variation. Section KB Fe concentrations rise above background 11 cm below the visual metallic silt contact and peak at 111,000 ppm 1 cm above the contact. This profile is similar to those of elements previously discussed. The profile of Fe concentrations in section KF differs somewhat from the elements previously discussed. Although Fe concentrations in the section begin near the crustal average, there is no peak at the initial metallic silt contact. Fe concentrations peak at 103,000 ppm at 8 cm depth within the upper organic silt. They are nearly twice that of the crustal average. Cores KC and KD concentration profiles are more similar to profiles previously discussed at these sites. The profile from section KC gradually increases in concentration 22 cm below the metallic silt contact and peak at 108,000 ppm at the lake bottom surface. Fe concentrations in core KD began to deviate from background between

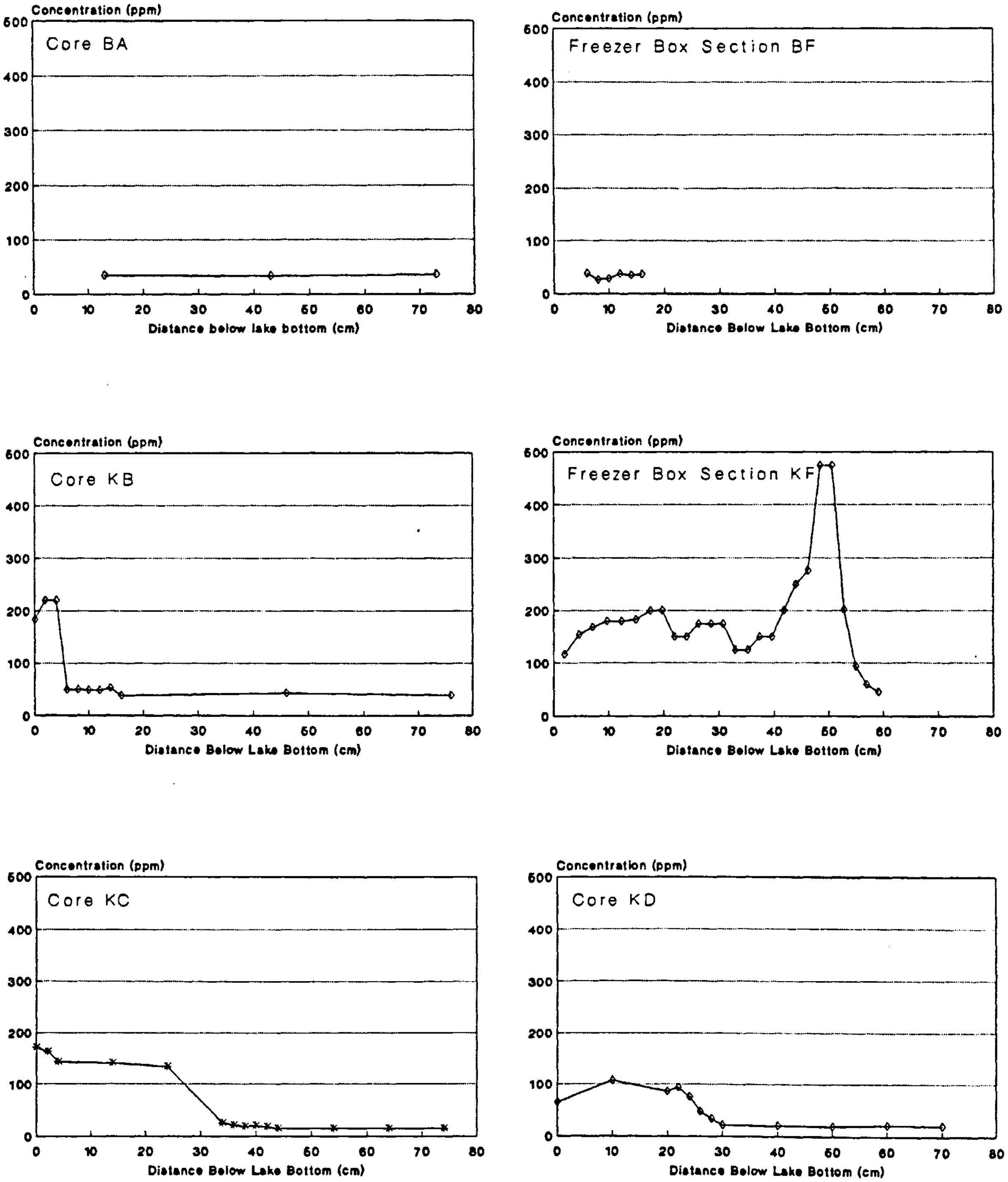


Figure 6.5. Copper Concentrations from Respective Sites
Crustal Average = 55 ppm

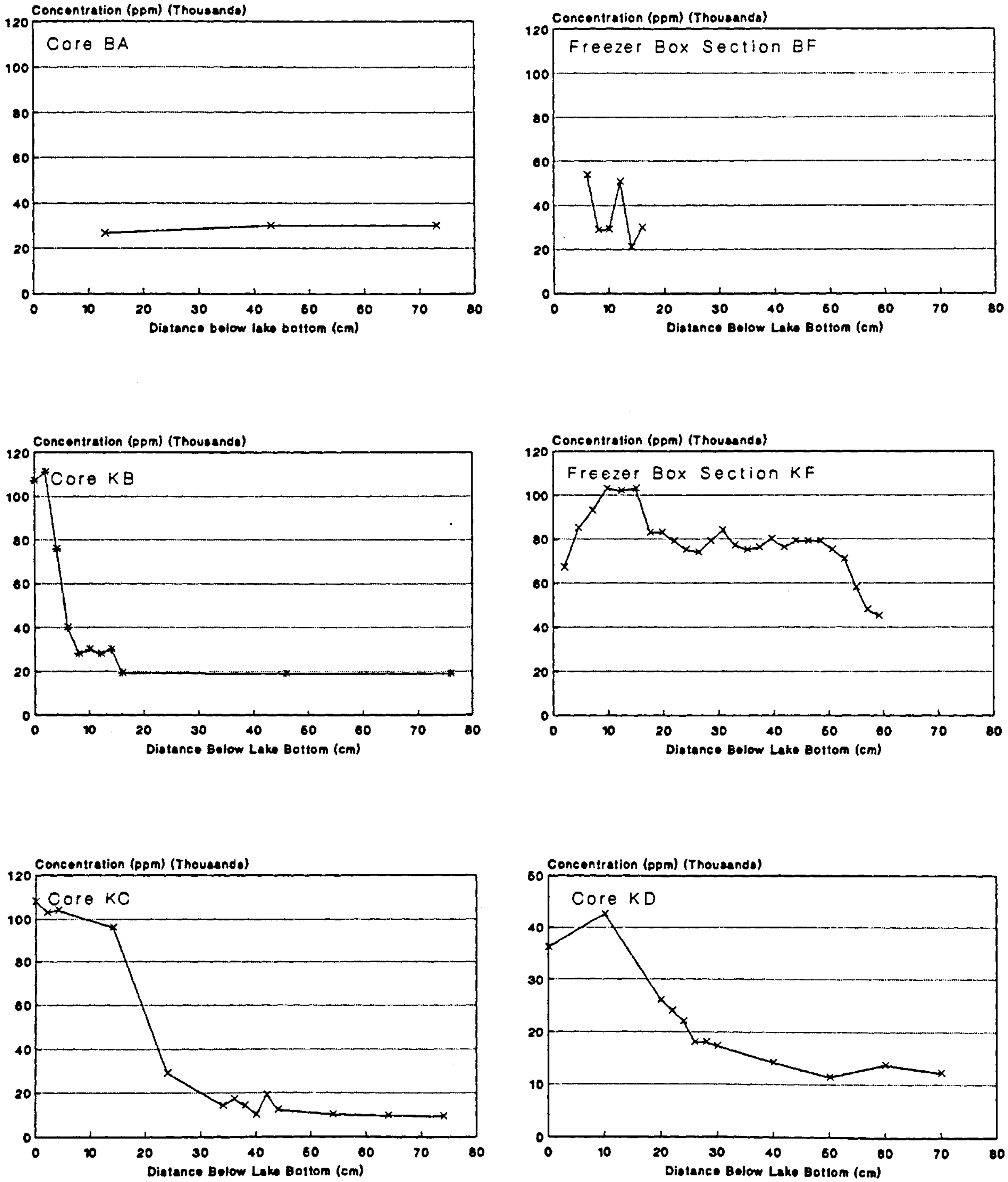


Figure 6.6. Iron Concentrations from Respective Sites
Crustal Average = 50,000 ppm

12 and 22 cm below the metallic silt contact, concentrations peak at 42,700 ppm at 10 cm depth. Fe concentrations in samples from Killarney Lake all peak over 2 times the concentrations of background or the crustal average.

6.2.6 Mn Concentrations in Shallow Lake Bottom Sediments

Lake bottom concentrations above 80 cm depth for Mn are shown for all sites in Figure 6.7. Mn concentrations in Bells Lake sediments are generally less than the crustal average of 900 ppm. One small peak in Mn concentration of 1107 ppm is observed at the lake bottom surface. Mn concentrations in core KB generally decline from the bottom of the core (Table 5.5, Figure 6.1) but rise abruptly to 13,440 ppm 1 cm below the visual metallic silt contact, the highest Mn concentration observed at all of the sites. Core KF Mn concentrations peak at 12,540 ppm (1.2% by weight) above the metallic silt contact and again peak at 10,720 ppm just below the upper contact. Concentrations then decline in the organic silt above the contact. Concentration profiles for cores KC and KD are quite different. Although there is only one relatively small Mn concentration peak in core KD of 2900 ppm, it is only 3 times the crustal average. Concentrations in core KC are much higher within the metallic silt and peak at 13,060 ppm within the metallic silt at 14 cm depth. Concentrations rise 2.5 cm below the metallic silt contact in core KD and between 5 and 15 cm below the contact in core KC.

6.2.7 Ni Concentrations in Shallow Lake Bottom Sediments

Ni concentration for shallow lake bottom sediments are shown in Figure 6.8. Reference to Figure 6.1 shows nickel concentrations increasing towards the crustal average of 75 ppm in cores KB and BA, peaking around 200 cm below lake bottom and decreasing thereafter. Ni concentrations in core BA average 37 ppm in the section but decrease to an average of 27 ppm at the lake bottom surface in section BF. Concentrations in core section KB dramatically increase at approximately 11 cm below the metallic silt contact to a peak of 76 ppm at 10 cm depth and rapidly decrease to 32 ppm in the metallic silts. The profile of section KF also appears depleted with respect to Ni in the metallic silt zone. The concentration at the bottom of the profile is approximately that of pre-mining sediments (37 ppm), where it then drops to a low of 25 ppm, less than one-half of background, and slowly increases towards the lake bottom surface. Concentration profiles in cores KC and KD are not definitive but tend to show an increase in Ni concentration within the metallic silt zone. Both of these sections appear depleted with respect to pre-mining sediments and the crustal average.

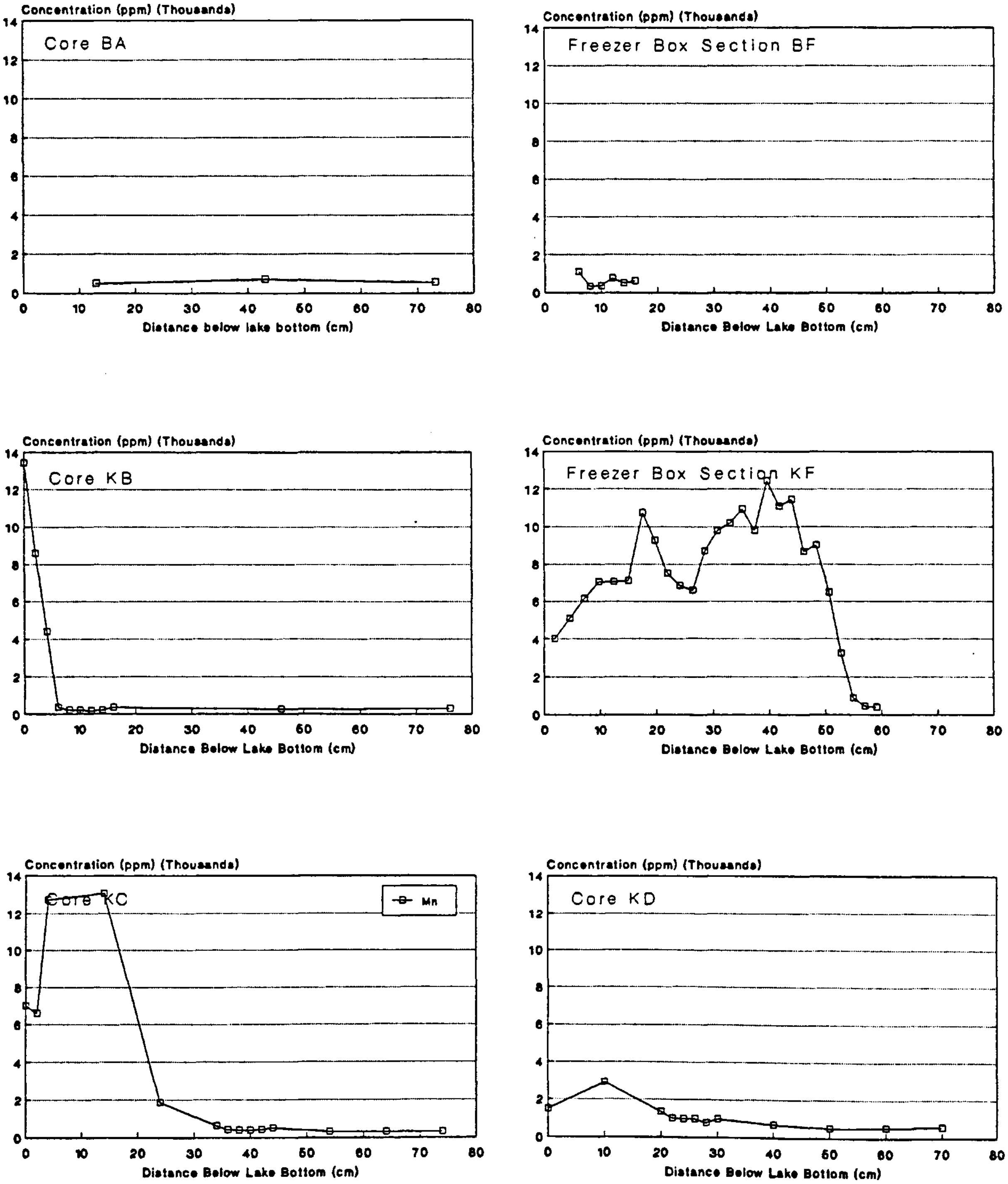


Figure 6.7. Manganese Concentrations from Respective Sites
Crustal Average = 900 ppm

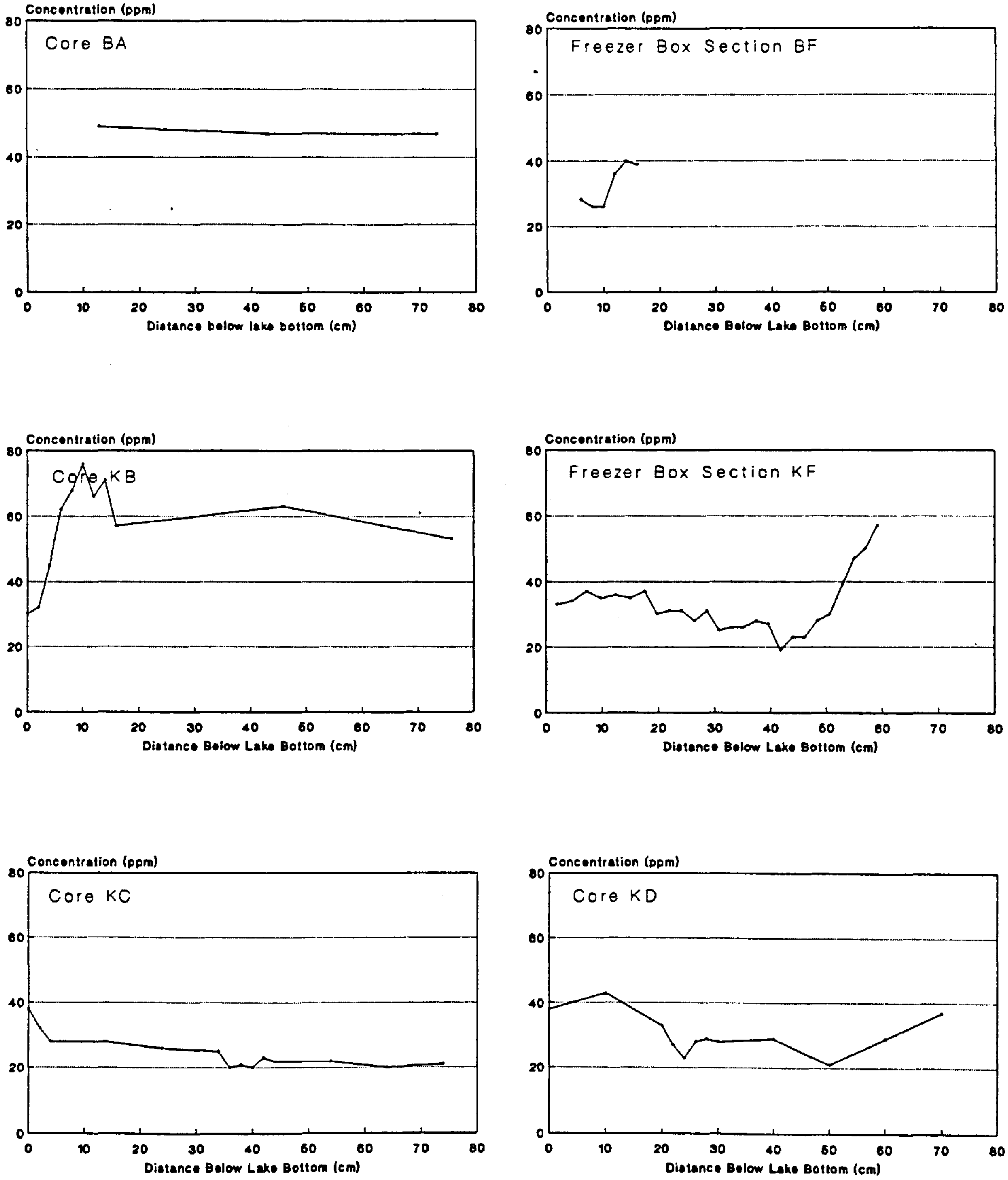


Figure 6.8. Nickel Concentrations from Respective Sites
Crustal Average = 75 ppm

6.2.8 Pb Concentrations in Shallow Lake Bottom Sediments

Pb concentrations in thousands of ppm from all sites are shown in Figure 6.9. In this case, concentrations in core BA and freezer box section BF differ significantly. Concentrations in core BA bracket the crustal average of 13 ppm from below detection to 20 ppm. Pb concentrations in section BF vary from 34 to 762 ppm. Again, the two peaks at 6 and 12 cm below lake bottom are observed. These peaks cover a concentration range of over one order of magnitude; differences in concentration are significant and again may be attributed to chemical changes in the sediments of the basin, local anthropogenic factors, or air fall from smelter or automobile emissions, or laboratory error. Core KB Pb concentrations average 42 ppm throughout the section to 3 cm below the metallic silt contact and peak at 17,460 ppm at the lake bottom surface. This is approximately one-half of the maximum Pb concentration observed in section KF, which peaks at 37,400 ppm at the lower metallic silt contact. In this sample from core KF, Pb constitutes 3.74% by weight of the sediments. Concentrations in this profile again follow the geometry seen for most elements, but the profile does not rise again in the organic silt above the metallic silt. The Pb concentration profile in cores KC and KD follow the same pattern observed previously and peak at 19,480 ppm, 4.5 cm below the metallic silt contact in core KC, and 9,080 ppm at 2.5 cm below lake bottom in core KD. All peak concentrations are a minimum of 3 orders of magnitude greater than that of the crustal average.

6.2.9 Zn Concentrations in Shallow Lake Bottom Sediments

Zn concentrations for all sites are shown in Figure 6.10 in thousands of ppm. Pre-mining Zn concentrations are approximately 5 times that of the crustal average and are relatively consistent except for the two small peaks observed in section BF. Cores KB, KC, KD, and section KF all have familiar concentration profiles. Section KB peaks at 17,800 ppm at the lake bottom surface; core KF peaks at 34,150 ppm at the lower metallic silt contact; core KC peaks at 19,420 ppm 4.5 cm below the metallic silt contact; and core KD peaks at 19,420 ppm, 2.5 cm below the metallic silt contact. These section maximum concentrations range from 1.8% to 3.4% Zn by weight in the sediments sampled.

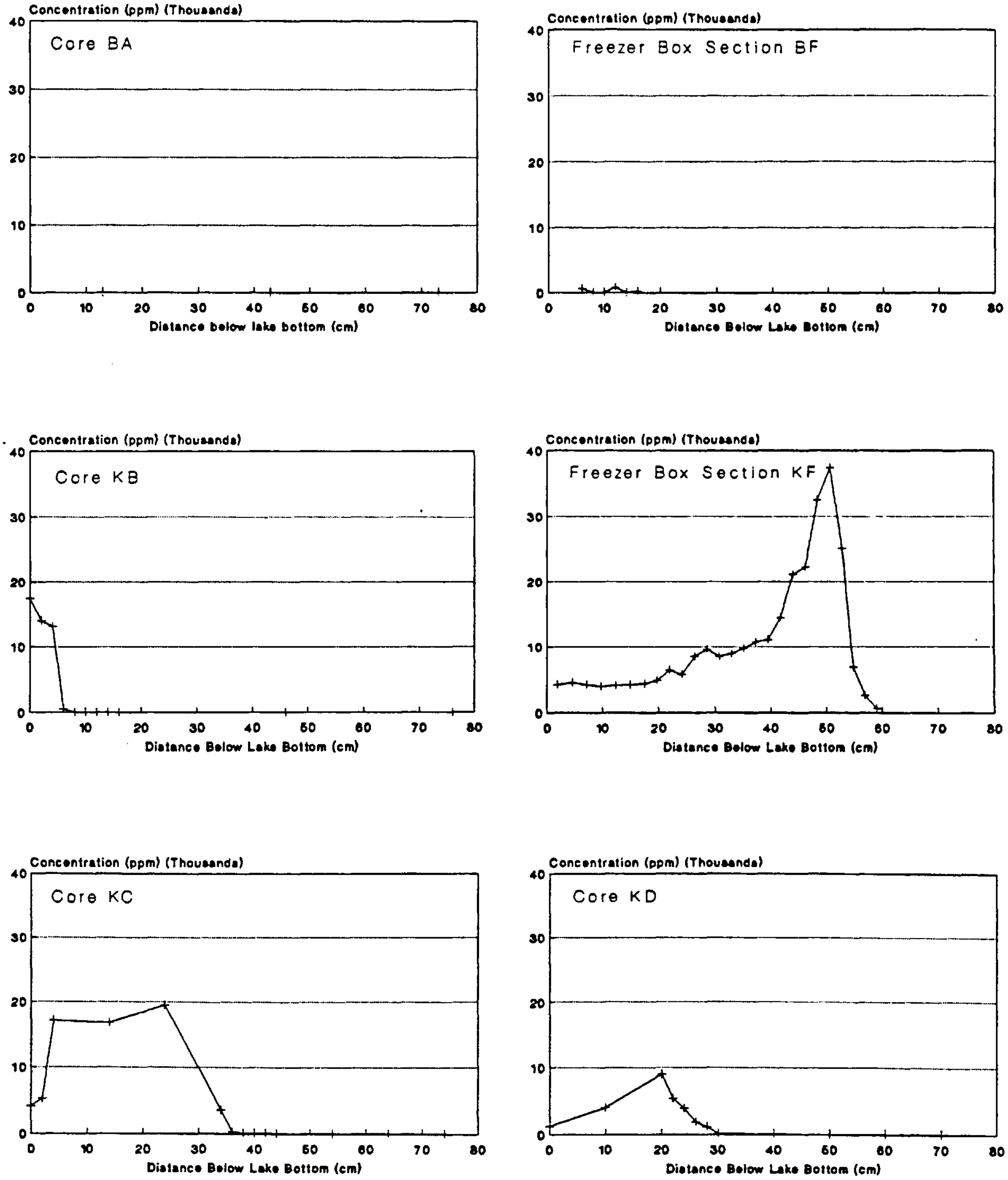


Figure 6.9. Lead Concentrations from Respective Sites
Crustal Average = 13 ppm

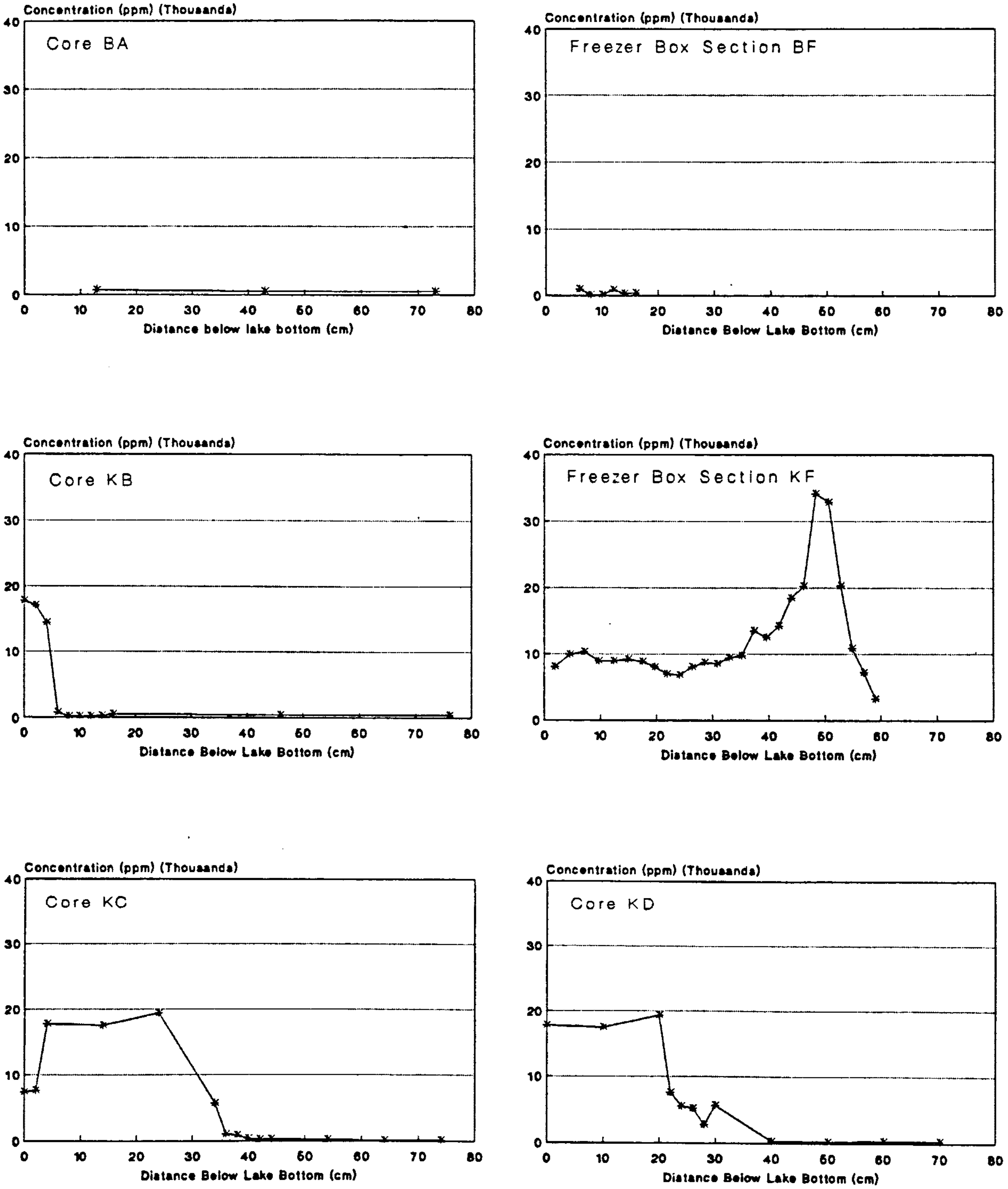


Figure 6.10. Zinc Concentrations from Respective Sites
Crustal Average = 70 ppm

6.2.10 Discussion of Metal Concentrations in Sediments above 80 cm Depth

Shallow lake bottom sediment concentrations in Bells Lake were used as a control for the evaluation of sediment concentrations in Killarney Lake. The two minor peaks observed in freezer box section BF from Bells Lake for elements Cd, Cu, Fe, Mn, Pb, and Zn, peaks may indicate a change in the St. Joe River drainage sediment chemistry, local anthropogenic influences in Bells Lake, air fall of particulates from the smelter in the mining district, or laboratory error. The peaks do not occur in all elements analyzed and they vary in occurrence vertically in the freezer box samples. Apart from these peaks, metallic concentrations in Bells Lake sediments were similar to uncontaminated sediments below 80 cm in Killarney Lake. These metallic concentrations are taken as "background" levels.

In shallow Killarney Lake sediments, metallic concentrations were significantly greater than those of "background" sediments as described above for all elements analyzed except Ni. Metallic concentrations for all elements except Cu, Fe, and Ni varied from 1 to 3 orders of magnitude greater than background. Cu concentrations were found over two times background with peaks just less than one order of magnitude greater than the crustal average. Fe concentrations were greater than one and one-half to twice that of background. Ni appeared depleted in the metallic silt zones. All elements analyzed except Ni showed concentrations greater than background in sediments below the sharp visual contacts observed in the cores and freezer box section from Killarney Lake. The maximum observed depth of concentrations above background which occurred below the visual metallic silt contact was 10.5 cm for Ag, 22.5 cm for Cd, 6.5 cm for Cu, 8.5 cm for Fe, 4.5 cm for Mn, 18.5 cm for Pb, and 18.5 cm for Zn. The presence of metallic concentrations above those of background would indicate that vertical sediment transport of heavy metals has occurred.

The presence of elevated heavy metal concentrations below the base of the metallic silt zone may be influenced by sediment mixing, bioturbation, chemical diffusion, and/or groundwater discharge. Reference to Table 5.6 shows that some of the highest elemental concentrations in section KF are from the organic silt just below and above the base of the metallic silt at 50.5 cm below lake bottom. Mixing of sediments appears to have occurred as metallic silt pods up to 0.5 cm in diameter are found within the underlying organic silt zone.

Sediment mixing could also been accomplished by bioturbation. Small red worms were found in the freezer box samples from both lakes. These and other organisms in the sediments may have a role in transporting sediments within, above, and below the metallic silt unit. Bioturbation was evident in the Mazama ash section collected from Bells Lake. The depth or extent of transport which can be attributed to bioturbation is dependent on the rate of sedimentation within the lake and the mixing rate, which is influenced by the number and size of the organisms (Jones and Bowser, 1978). Bioturbation rates are typically lower than fluid diffusion rates (Jones and Bowser, 1978).

Chemical diffusion through pore waters is another mechanism for the presence of heavy metals in the sediments bordering the metallic silt unit. Towatana (1990), states that anaerobic conditions are likely to increase the solubility of Cd, Pb, and Zn. The factors affecting the rate of diffusion are the porosity of the sediments, the tortuosity of the pore space, the concentration gradient, and groundwater flow and direction (Lloyd and Heathcote, 1985). Diffusion may also have distributed heavy metals within the metallic silt unit and affected the geochemical results of this study. Because the freezer box sample was air dried, precipitates from pore waters may have formed on the sediments before it was sampled at the two cm interval. Hence, transport mechanisms may have affected the results of this study even while it was being done.

Metallic silt concentrations were generally greater at sites KB and freezer box section KF in the center of the lake than at sites KC and KD on opposite ends of the lake. All elements except Cd and Fe had greater concentrations at these sites. The fact that the highest concentrations occur in the center of the lake is reasonable because it is the deepest point, and hence the sediment sink of the lake. The thickest section of metallic silt was collected at site KF (33 cm). Sediment concentrations were greater at site KC than KD. This is partially a function of distance from the river as higher energy floods are required to transport sediments to the north end of the lake. Therefore the concentration and depth of metallic silt are a function of lake geometry and proximity to the river.

Similar geochemical profiles were observed in most of the chemical analyses from Killarney Lake. At site KF, the highest elemental concentrations were at or near the base of the metallic silt unit for all but As, Fe, and Ni. Concentrations decreased from this point upward through the metallic silt section, but increased at or above the top of the metallic silt zone. This profile may in part be evidence of the advances in mill extraction techniques in the mining district. Ore recovery was relatively poor in the early days of jig tailings when compared to the extraction techniques used before tailings pond installations, and hence one would expect that heavy metal concentrations in tailings would decrease with time. The increase in concentrations observed at and above the top of the metallic silt zone, is possibly evidence of tailings being eroded and redeposited in Killarney Lake through annual to semi-annual flooding events. Hence, it may be possible to discern the period of time where the tailings were discarded from the mining district by their geochemical profile.

A comparison of sediment concentrations from section KF, which generally showed the highest elemental concentrations in this study, with other studies along the main stem of the Coeur d'Alene River and Bells Lake is shown in Figure 6.2. Elemental concentrations from section KF are greater than those of the other studies and much greater than those from Bells Lake. As discussed in section 6.1, elemental concentrations may differ from Rabe and Bauer's (1977) because the present study analyzed the lake bottom sediments with depth, rather than analyzing lake bottom surface samples. Because of poor mining and milling practices in the early days of mining, the sediments with the highest heavy metal concentrations are likely to be low in the mining sediment profile. This study has shown that the best method to characterize heavy metal contamination in the drainage is to analyze sediments with depth.

Table 6.2. Range of Concentrations Found within Freezer Box Section KF Compared with Other Studies and with Bells Lake (ppm)

	As	Ag	Cu	Cd	Fe	Mn	Ni	Pb	Zn
1) Section KF	45-376	3-37	46-475	10-121	45000-103000	390-12450	19-57	600-37400	3200-20250
2) Killarney Lake	---	---	87-140	50-130	46000-93000	---	---	2550-4600	4000-5200
3) Coeur d'Alene River delta sediments	---	6-15	90-150	16-75	---	6200-12500	---	3000-6300	3200-4700
4) Coeur d'Alene River delta, Core 1	0-0.23	10-23	8-89	4-26	4700-16700	335-1900	172-574	232-1890	255-1020
5) Bells Lake	12 - 32	<1	12-55	<1-3	3900-31600	120-1107	11-49	<2-762	100-924

1 = Freezer box sample (6 - 50 cm) from center of Killarney Lake (this study).
2 = Dredge samples of the top few centimeters of lake bottom sediments from three sites in Killarney Lake similar to this study (Rabe and Bauer, 1977)
3 = Core samples from the Coeur d'Alene River delta and nearby Coeur d'Alene Lake bed sediments (Maxfield, 1974).
4 = Core sample from the Coeur d'Alene River delta sediments (Funk and others, 1973).
5 = Piston core sample from the center of Bells Lake (this study).

6.3 Summary of Conclusions

Killarney Lake, one of nine lateral lakes within the Coeur d'Alene River drainage, has received mine and milling wastes from the Coeur d'Alene mining district for over a century. Lead and zinc sediment contamination was found above 3.4% in the center of the lake, over one order of magnitude greater than background concentrations. High concentrations of contamination by other metals such as As, Ag, Cu, Cd, Fe, and Mn also exist between one and three orders of magnitude greater than background concentrations. Sediments analyzed in Bells Lake from a separate drainage basin, show no such heavy metal contamination. Mining wastes have settled to the bottom of Killarney Lake and may affect the chemistries of natural sediments. Although not discussed in this study, the contaminated sediments may affect vegetation, fish, and biota of the region (Rabe and Bauer, 1977). Because the thickest accumulations of metallic silts are in the center and deepest portion of the lake, they will probably remain in Killarney Lake. However, it appears that flooding has removed some of the sediments at site KC. Hence, portions of the lake which are shallow and directly exposed to the flooding, and not recessed within the bedrock surrounding the northern portions of the lake, may contribute sediments to flood waters and transport wastes farther downstream. Killarney and other lateral lakes of the Coeur d'Alene River may act both as a sediment sink and as a temporary holding basin of contaminated sediments. The most important findings of this study are listed below.

Sediment Collection. Sediment collection using a piston core was successful for collection of semi-consolidated sediments, but not for the upper, loose, highly saturated lake bottom sediments. Sample collection using a freezer box was successful for retrieving the upper lake bottom sediments while still preserving stratigraphy. A further advantage of the freezer box is that a sample of lake bottom water is also obtained.

Ash/Sedimentation. Ash from the Mt. Mazama eruption approximately 6700 years before present was geochemically identified. At Killarney Lake, more than 609 cm of sediments lie above the ash at site KB, and 334 cm at site KD. At site BA (Bells Lake), more than 381 cm of sediments lie above the ash. Sedimentation rates in Killarney Lake are greater than rates in Bells Lake.

Control Lake. Comparison of lithologic and geochemical results confirms that pre-mining sediment chemistries, and trends of chemistries between Bells Lake and Killarney Lake sediments are similar and that Bells Lake is an adequate control lake for this and other studies of the Coeur d'Alene mining district.

Metallic Silt. Within Killarney Lake, metallic silt could be distinguished from natural organic silt both by visual color and by density contrasts. Additionally, comparing the percent water loss of samples collected from the two matrices showed that the metallic silt could be identified by its relatively low water content. More than 33 cm of metallic silt were found in the center of the lake at site KF, and 19.5 cm, and 17.5 cm of metallic silt were found at sites KC and KD in Killarney Lake, respectively. There are no visible or anomalous concentrations of metallic silt in Bells Lake.

Elemental concentrations in the metallic silt were 1 to 3 orders of magnitude greater than background for most analyzed metals elements. These concentrations indicate gross heavy metal contamination of the sediments in the lake, particularly of Pb and Zn which constitute 3.7% and 3.4% of the sediments by weight at their highest concentrations, respectively. Similar geochemical variation with depth was observed for most elements from Killarney lake. The profile generally showed the highest concentrations at the base of the metallic silt; concentrations then decreased towards the lake bottom surface. Many of the elements showed a second peak at the upper metallic silt contact. This profile may be used to discern the time period which the tailings were milled. Higher heavy metal concentrations were found in the center of Killarney Lake (sites KB and KF) than at the ends (sites KC and KD).

Mechanism of Transport. Annual to semi-annual flooding is the probable mechanism of transport of heavy metals from the Coeur d'Alene mining district and Coeur d'Alene River banks and beds to Killarney Lake and possibly other lateral lakes within the Coeur d'Alene drainage system. Flooding is shown by annual to semi-annual laminations in the sediments from the center of Killarney Lake. These laminations are composed of light bands of metallic silt separated by dark bands of organics.

Migration of Heavy Metals. Anomalous heavy metal concentrations were observed below the visual metallic silt and silt and organic contact for all elements analyzed. The greatest depth observed below the contact was 22.5 cm for Cd. The presence of heavy metals below this contact would indicate that vertical elemental transport has occurred. Transport may have been facilitated by sediment mixing, bioturbation, chemical diffusion, and/or groundwater discharge.

APPENDIX A - CORE LITHOLOGIES

Appendix A-1. Lake Bed Lithology at Site BA.

Distance Below Lake Bottom (cm)	Thickness (cm)	Unit	Munsell Color Chart	Description
0 - 3	3	organic silt	5 Y, 2.5/1	Dark chocolate brown organic silt.
3 - 9	6	organic silt	5 Y, 2.5/2	Light chocolate brown organic silt.
9 - 19	10	organic silt	5 Y, 3/1	Dark chocolate brown organic silt.
19 - 36	17	organic silt	5 Y, 2.5/1	Light chocolate brown organic silt.
36 - 43	7	organic silt	5 Y, 2.5/1	Dark chocolate brown organic silt.
43 - 54	11	organic silt	5 Y, 2.5/1	Light chocolate brown organic silt.
54 - 71	17	organic silt	5 Y, 2.5/1	Dark chocolate brown organic silt.
71 - 85	14	organic silt	5 Y, 2.5/1	Light chocolate brown organic silt.
85 - 102	17	organic silt	5 Y, 2.5/1	Dark chocolate brown organic silt.
102 - 109	7	organic silt	5 Y, 2.5/1	Light chocolate brown organic silt.
109 - 126	17	organic silt	5 Y, 2.5/1	Dark chocolate brown organic silt.
126 - 133	7	organic silt	5 Y, 2.5/2	Light chocolate brown organic silt.
133 - 145	12	organic silt	5 Y, 2.5/1	Dark chocolate brown organic silt.
145 - 179	34	ash, organic silt	5 Y, 2.5/1	Dark gray volcanic ash grading into dark chocolate brown organic silt.
179 - 190.5	11.5	organic silt	5 Y, 3/1	Dark Brown organic silt.
190.5 - 202.5	12	organic silt	5 Y, 3/1	Gray-brown organic silt.
202.5 - 217.5	15	organic silt	5 Y, 3/1	Light brown organic silt.
217.5 - 251.5	34	organic silt	5 Y, 3/1	Brown organic silt, wood fragment at 231 cm.

(Appendix A-1, continued)