A

THESIS

entitled

SECONDARY DISPERSION OF SULPHUR FROM SULPHIDE DEPOSITS IN THE NOTRE DAME BAY AREA NEWFOUNDLAND

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ABSTRACT

Exploration for concealed mineralization in glaciated terrain is particularly difficult because of the complex mechanical and saline dispersion of elements within the overburden. Sulphur is one element that has been slightly neglected in geochemistry because of its difficult analytical chemistry, but in line with recent advances in vapour geochemistry indicating that sulphur dioxide vapour in particular is a potentially useful guide to buried sulphide ores, interest in the dispersion of sulphur has increased. In order to investigate processes involved in the secondary dispersion of sulphur, field areas were selected in the Notre Dame Bay mining district of Newfoundland, where disseminated and massive base metal deposits are located beneath various thicknesses of glacial debris and forest soils, and a study of the distribution of sulphur in soils, stream and lake sediments, surface water, and soil air was undertaken.

Anomalous levels of total sulphur were found in soils overlying sulphide mineralization, and examination of the soil profile showed a marked enrichment of sulphur in the humus. Sulphur concentrations were also found to be enhanced in stream and lake sediments in the drainage system of mineralized areas. Because of the high correlation between total sulphur and organic matter content of the soils and sediments, it was concluded that interpretation of total sulphur patterns must be made on the basis of the organic content of the samples. The concentration of sulphate in surface-waters was found to vary with seasonal changes in precipitation and run-off. Investigations on the distribution of sulphur compounds in soils and sediments were aided by analysis using a microwave-induced argon plasma emission system.

Sulphur dioxide levels in air were determined using a modified West-Gaeke colorimetric method which provided a detection limit of less than 1 ppb. under the field conditions adopted. Detectable patterns of sulphur dioxide (in the 1-10 ppb. range) in soil air pumped from auger holes were found to occur over pyrite and chalcopyrite located in a shear zone covered by shallow ground moraine. Samples collected above ground level largely fell below the detection limit, indicating that evolved sulphur dioxide is rapidly diluted in the open air. This was confirmed by measurements over sulphide dumps and tailings derived from former mining activity. Soil air sampling appears to be more useful than atmospheric sampling under the climatic conditions of the field area, which are generally unfavourable to the production of large amounts of sulphur dioxide from the pyritic deposits.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Mineral exploration geochemistry to the present time has concentrated on the detection in the environment of the specific metals derived from ore deposits. Base metal deposits, in particular, consist primarily of these metals in the form of sulphides, frequently occurring together with pyrite. Although sulphur is the one element common to all sulphide deposits, it has been somewhat neglected because of its non-specific nature and the shortage of sufficiently rapid techniques for the analysis of sulphur compounds.

Although the non-specific nature and difficult analytical chemistry of sulphur are slight disadvantages to its application in the exploration for sulphide deposits, an advantage is that some sulphur compounds are more mobile in the geochemical environment than associated metals and may indicate the presence of otherwise hidden sulphide deposits. Examples are large hydrogeochemical sulphate anomalies and the production of gaseous sulphur dioxide anomalies over oxidizing sulphides. Moreover, being non-specific is not a prohibitive disadvantage in the case of sulphur as less specific properties of ore deposits have been successfully applied in geophysical prospecting for many years.

Vapour geochemistry has gained increasing application in recent years as improved techniques of remote sensing of metal and petroleum deposits are sought. The variety of applications include helium, methane and other gas surveys in the U.S.S.R., radon surveys for uranium deposits in Canada and the U.S., and Hg and sulphur-containing gases over base metal deposits, studied in a number of areas (Bolotinkova, 1966; Kravtsov and Fridman, 1965; Barringer, 1966; Edelman, 1971; Dyck, 1971; Ovchinnikov, et al. 1972; McCarthy, 1972). Rouse and Stevens (1971) reported anomalous concentrations of sulphur dioxide in the soil air and atmosphere over various types of oxidizing sulphide deposits in North America, and McCarthy (1972) and Bristow and Jonasson (1972) discuss sulphur dioxide in recent reviews of vapour geochemistry. The application of vapour geochemistry, of which only sulphur dioxide is considered in this project, thus has been shown to have some potential in exploration for buried sulphide deposits.

The origin and role of sulphur in the formation of various types of ore deposits has been the source of much debate and study among economic and mining geologists and subsequently much has been written on the genesis of sulphide ores. Much information is also available on sulphur in general, as studied in several scientific fields, namely, works on sulphur chemistry, sulphur isotopes in relation to sedimentation and sulphide ore deposition, biology and geochemistry of sulphur bacteria, agricultural and soil science studies of sulphur in soils, and pollution investigations on sulphur compounds in air and water. Comparatively little is known, however, on the subject of the secondary dispersion of sulphur from sulphide deposits and one of the

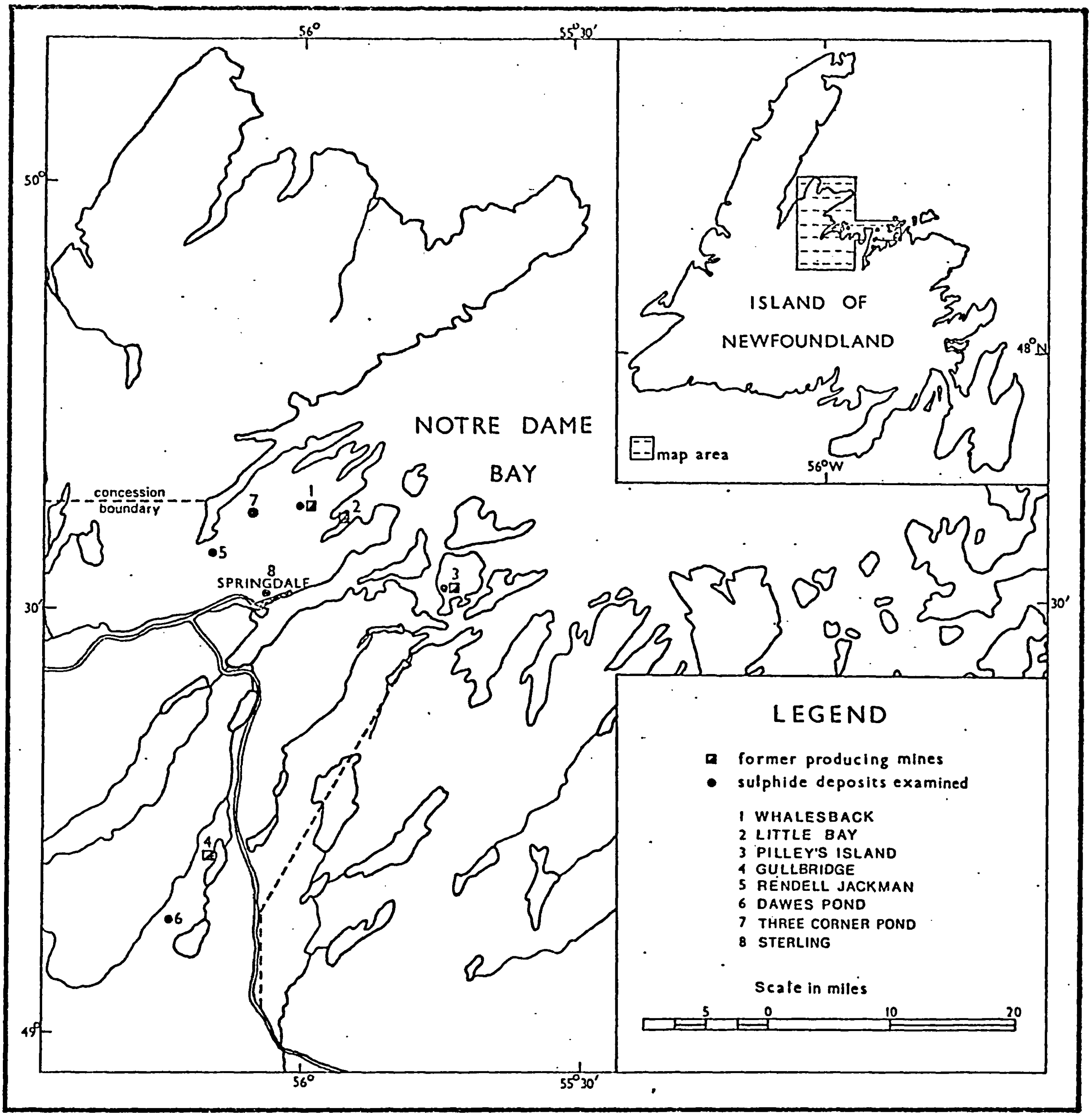

Figure 1. Location of studies in Newfoundland.

aims of the research described in this thesis was to contribute some information in that respect to the growing study of applied geochemistry.

1.2 SCOPE OF RESEARCH

The aim of the research project was primarily to investigate the secondary dispersion of sulphur from sulphide deposits in the Notre Dame Bay area, Newfoundland (Figure 1) and secondarily to evaluate the use of sulphur in geochemical exploration and particularly in the exploration of buried sulphide deposits in glaciated terrain.

The initial objectives were to determine the levels of total sulphur and of various sulphur compounds in background areas and in the vicinity of sulphide occurrences to provide basic data on the range of values to be expected and the effect of sulphide mineralization on the distribution of sulphur in the surface environment.

Detailed investigations in the vicinity of a number of sulphide occurrences within the Notre Dame Bay area were then carried out to provide information on the dispersion of sulphur compounds in the soils, sediments, waters and air adjacent to these deposits. In the case of sulphur dioxide, emissions from sulphide dumps and mine wastes were also examined in an attempt to determine the physical and chemical variables affecting the dispersion of the gas in the atmosphere.

1.3 LOCATION AND DESCRIPTION OF THE FIELD AREA

Field investigations were carried out in the Notre Dame Bay area of Newfoundland, mainly on property located at the western end of Notre Dame Bay which is held as a mineral concession (the Halls Bay Concession) by British Newfoundland Exploration Ltd. (BRINEX). The area contains numerous occurrences of mainly pyritic sulphides with several former producing mines, and has been an active mining and exploration district since 1875. Of the deposits examined within the area, three are held by parties other than BRINEX in Fee Simple grants, viz., Pilley's Island, Sterling, and Rendell Jackman prospects. The Halls Bay Concession comprises some 765 square miles within latitudes 49° 0' - 49° 40' N and longitudes 55° 35' - 56° 30' W, and is indicated on the location map (Figure 1).

1.3.1 Geology

The geology of the Notre Dame Bay area has been described by a number of authors, notably Williams (1964, 1969), Neale and Nash (1963) and Maclean (1947), and the geology and setting of the sulphide deposits within the region by Douglas, et al. (1940), Maclean (1947), Williams (1963), Peters (1967) and Kennedy and DeGrace (1972), among others. A brief description of the general geology of the district is presented here.

The rocks of the Notre Dame Bay area form part of the Central Paleozoic mobile belt of the Newfoundland Appalachians, the mountain system which extends some 2000 miles southwest into the United States (Williams, 1969).

They consist mainly of a thick Lower to Middle Ordovician eugeosynclinal sequence of basaltic pillow lavas and pyroclastics with associated greywackes and cherts, of marine deposition, overlain by a Silurian accumulation of volcanics, conglomerates and sandstones, largely of terrestrial deposition (Figure 2).

The Ordovician rocks of the Lush's Bight and Western Arm Groups (Marten, 1971) are strongly altered, sheared, and folded into a steeply-dipping, northeast trending belt intruded by frequent sills and dykes. The overlying Silurian rocks are generally of the same NE trend but less altered and not as severely deformed. Most of Newfoundland was affected by the Acadian orogeny in the Devonian period evidenced by folding, regional metamorphism and numerous granitic intrusions.

Within the region, and mainly in the basic volcanic sequence of the Lush's Bight Group, numerous disseminated and massive pyrite deposits occur, containing varying amounts of pyrrhotite, chalcopyrite, sphalerite and magnetite. These are found almost entirely as lenses, veins and impregnations in chlorite schist zones within the volcanic pile. The sulphides are considered by most of the recent authors to be volcanogenic in origin but concentrated in stratigraphic traps, i.e. stratigraphically controlled deposition, and later remobilized during subsequent metamorphism to give enrichment, particularly by chalcopyrite, in fold hinges within the shear zones (Kennedy and DeGrace, 1972, Peters, 1967, and Williams, 1963). The Pilley's Island deposit of pyrite, chalcopyrite, sphalerite and galena is an exception to this general rule, occurring in rhyolites and tuffs of the

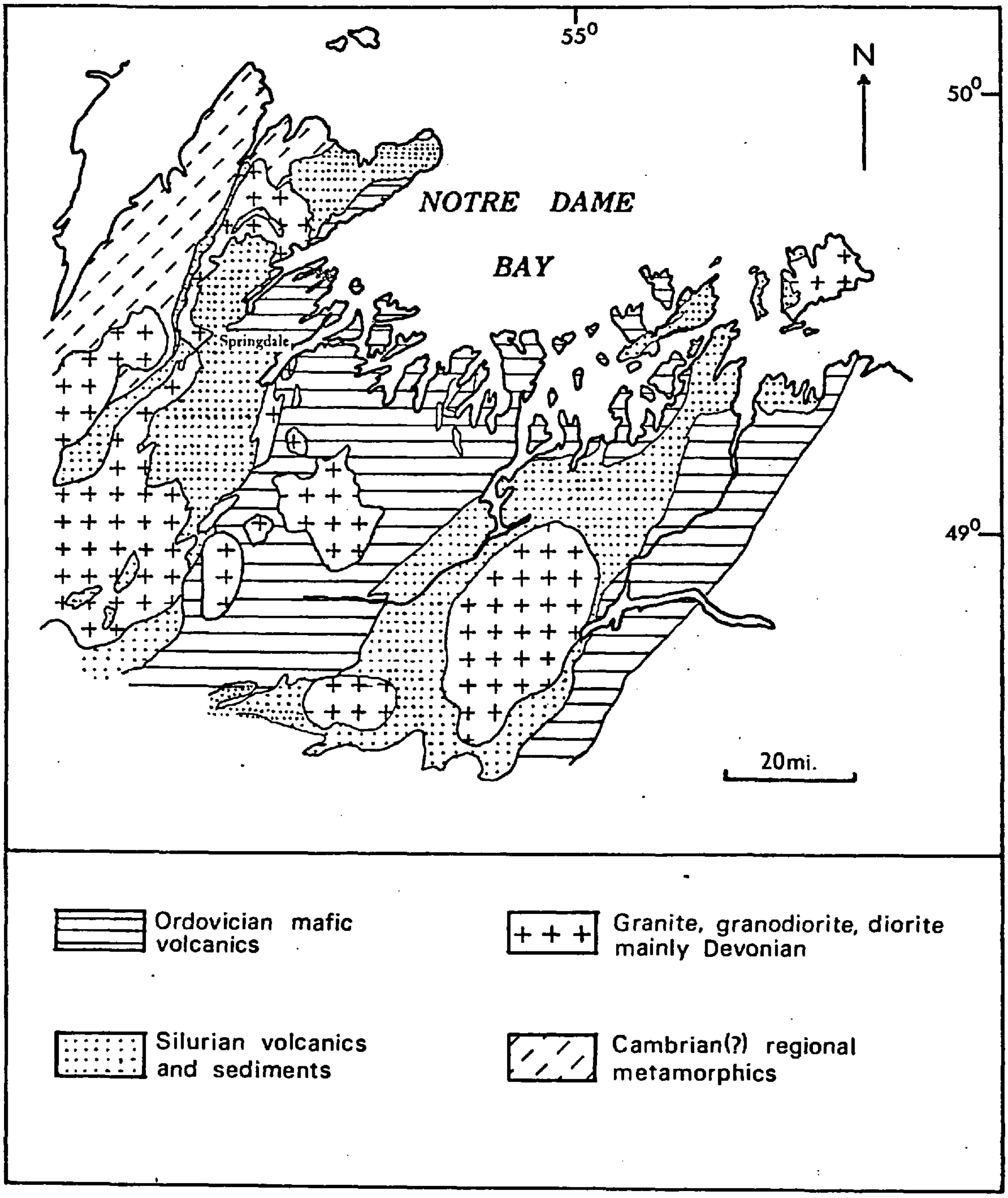

Figure 2: General geology of the Notre Dame Bay area.

Silurian (?) Roberts Arm Group and believed to be of syngenetic volcanic exhalative origin.

1.3.2 History of Mining

Of the scores of sulphide occurrences in the district, at least twelve have a record of production (Peters, 1967), sporadically over the period 1878 to 1972. The Pilley's Island deposit was first discovered in 1875 but the earliest producing mine was at Little Bay, in 1878. Most of these mines have produced low grade pyritic ore containing 1-3 per cent copper, with a few pods and lenses producing high grade copper (10-12 per cent) being selectively exploited. The most recent mines, Whalesback, operated by British Nfld. Exploration Ltd., and Gullbridge Mines Ltd., of First Maritime Mining Corporation Ltd., closed in 1972 and 1971 respectively. Over the nearly one hundred years of mining in the Notre Dame Bay area more than 65,000 tons[1] of copper have been produced from these low grade ores.

1.3.3 Glaciology

The Pleistocene geology of insular Newfoundland has been described

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[1] 65,000 = 60,500 (from Peters, 1967) + estimated 4500 tons for 1967-1972.

in parts and generally by a number of workers, notably MacClintock and Twenhofel (1940) and Jenness (1960). Northeastern Newfoundland glaciology, covering the Notre Dame Bay area, was the subject of a short study by Lundqvist in 1962 (Lundqvist, 1965) as a joint project for Brinex and the Boliden Co.

The region was entirely glaciated during the Wisconsin glaciation period, in the early stages by the Labrador ice sheet and later by radially moving ice from the local Newfoundland ice cap. The latter has produced most of the glacial features observed in the Notre Dame Bay area.

Evidence of glaciation is found as striae at many locations and the area is more or less covered with till, which tends to be thinner on the hilltops and towards the coast. Valley deposits are generally thicker and of rather compact basal moraine type. Some drumlinoid forms occur, oriented in a NE-SW direction, coinciding with the main strike of the bedrock and the general topography. These plus the striae reflect a general NE movement of the ice towards the coast. Other glacial features such as hummocky ablation moraine on the highlands and small ridges on the valley bottoms have been formed where it is considered the ice sheet was rather stagnant (Lundqvist, 1965).

Prominent glaciofluvial deposits occur at a number of coastal localities in the form of deltas, the two largest at Springdale and South Brook forming terraces 200-250 feet above present sea level. Eskers are rare and the small ones observed, oriented in a NW-SE direction, are considered to have been formed subaerially in ice crevasses and do not provide an indication of the direction of ice movement.

1.3.4 Physiography

A characteristic feature of the landscape of northeast Newfoundland is the long, narrow fiord-like bays running SW from the coast, some of which are fiords in the true sense of the word in that they have steep sides and are quite deep, with a rise in the bottom near the mouth of the bay, caused by the terminal moraine. The topography is marked by NE-SW trending ridges and valleys. Elongate lakes are common in the valleys and most rivers follow the topography NE to the sea.

Elevations generally decrease northeastward from about 1000 feet above sea level in the south. The rounded hilltops reach average elevations of 500-800 feet and tend to be less well forested than the sides of the ridges and the valleys.

Swamps or bogs are common, occurring along the margins of some of the lakes and forming extensive areas of peat on the poorly drained uplands.

1.3.5 Vegetation

The area is still largely under forest cover of mixed coniferous and deciduous trees, with conifers predominating. Of these, spruce (*Picea mariana* Mill.) and fir (*Abies balsamea* L.) are most common, with lesser amounts of pine (*Pinus strobus* L.), white spruce (*Picea gluca* Moench.) and larch (*Larix lariciana* Du Roi). Of the deciduous growth white birch (*Betula papyrifera* March), poplar (*Populus tremuloides*) and alder (Alnus rugosa) predominate, but a variety of lesser species are known to occur.

The forest cover is best developed on the freely drained soils, with the poorly drained regions supporting smaller growth of spruce, alder or larch frequently interrupted by areas of peat bog. These bogs are predominantly of the blanket type and support Sphagnum (Pollett, 1968). Ericaceous shrubs are more common on shallow, turfy soils, on drier parts of the peat bogs, and on tufts above the Sphagnum mat constituting the bulk of the bog material.

This vegetation is fairly typical of the boreal coniferous forest belt (in which the region lies) which covers most of the Canadian Shield areas and much of Scandinavia and the U.S.S.R.

1.3.6 Climate

The climate of the island of Newfoundland may be generally described as cool and maritime. It is also classified by Thornthwaite (1948) as humid to perhumid on the basis of moisture index. The greatest single influence on the climate is the ocean, particularly the cold Labrador current, which brings Arctic ice south along the coasts in the spring and this ice in turn keeps the temperatures cool, causing late springs and limiting the growing season (temperature above 6.1°C) to about 150 days. Another important factor is the prevailing southwesterly and westerly winds which average 10-15 m.p.h. and tend to have a cooling effect even when air temperatures are high.

The Notre Dame Bay area can be said to be somewhat drier than the south and east parts of the island, but the precipitation rate is still relatively high at greater than 35 inches per annum (Figure 3). Mean January temperatures for the region are about -7°C and mean July temperatures 15-17°C (Figure 4).

The maritime climate, with long, cold winters and short, mild to warm summers, tends to limit the exploration field season as well as the length of the growing season to about the four months from June to September.

1.3.7 Pedology

Since any post-Carboniferous deposits which may have existed were removed from the underlying bedrock by the Wisconsin glaciation, all the soils of the region are relatively young (less than 10,000 years) and are largely developed in the top 1-2m. of glacial till. In areas other than those covered by blanket peat deposits, shallow soils have developed under coniferous forest and are predominantly podzolic. Coniferous trees and high rainfall are the outstanding causes of podzolization, of course, as conifers do not return large amounts of nutrients to the soil surface as leaf litter, and rainfall promotes the leaching process.

No comprehensive soil survey of Newfoundland has been conducted to date but the forest soils of central Newfoundland have been described in a government report by Bhure and Page (1971), in which the five major soil types and their properties are briefly examined (Table 1). A soil

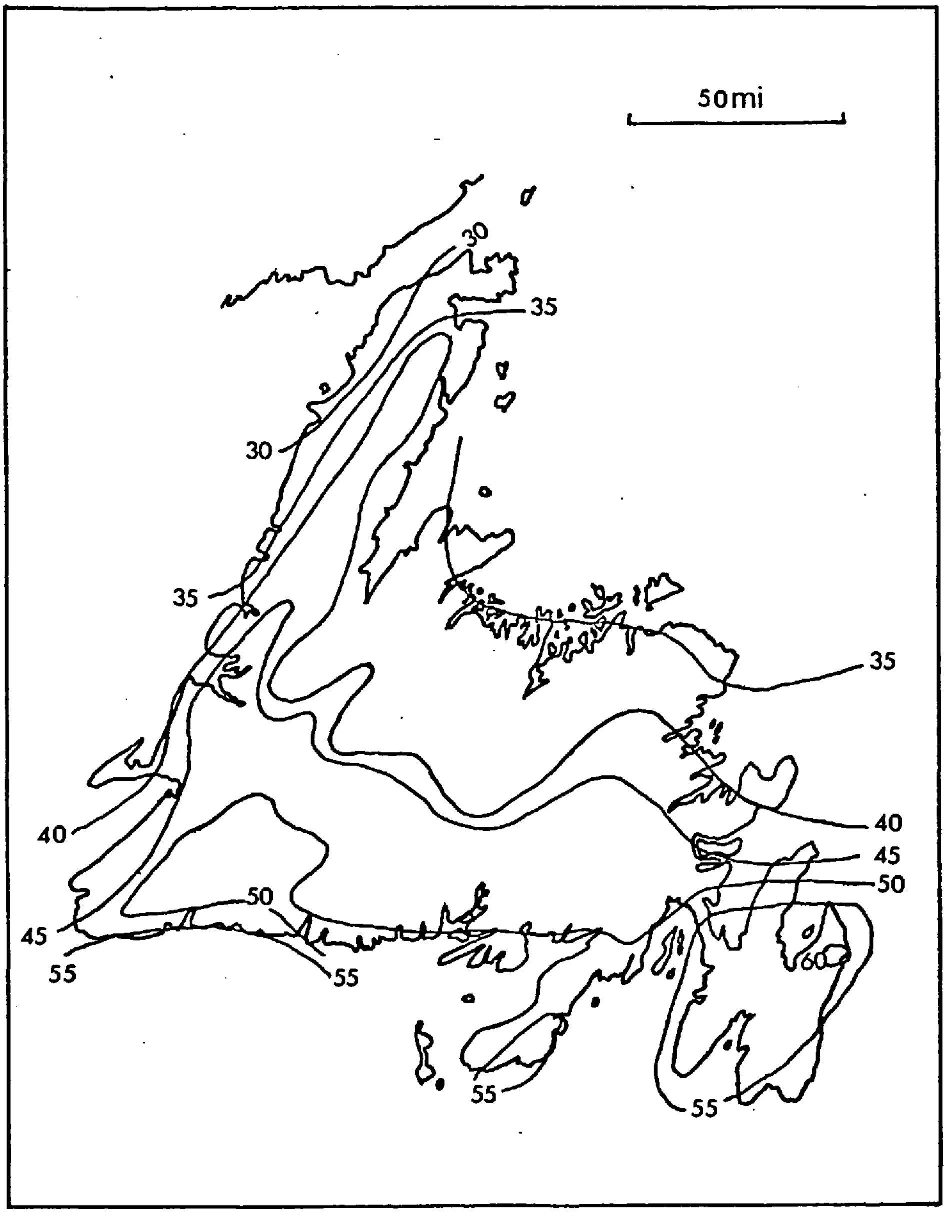

Figure 3: Mean annual precipitation for Newfoundland, in inches (after Pollett, 1968).

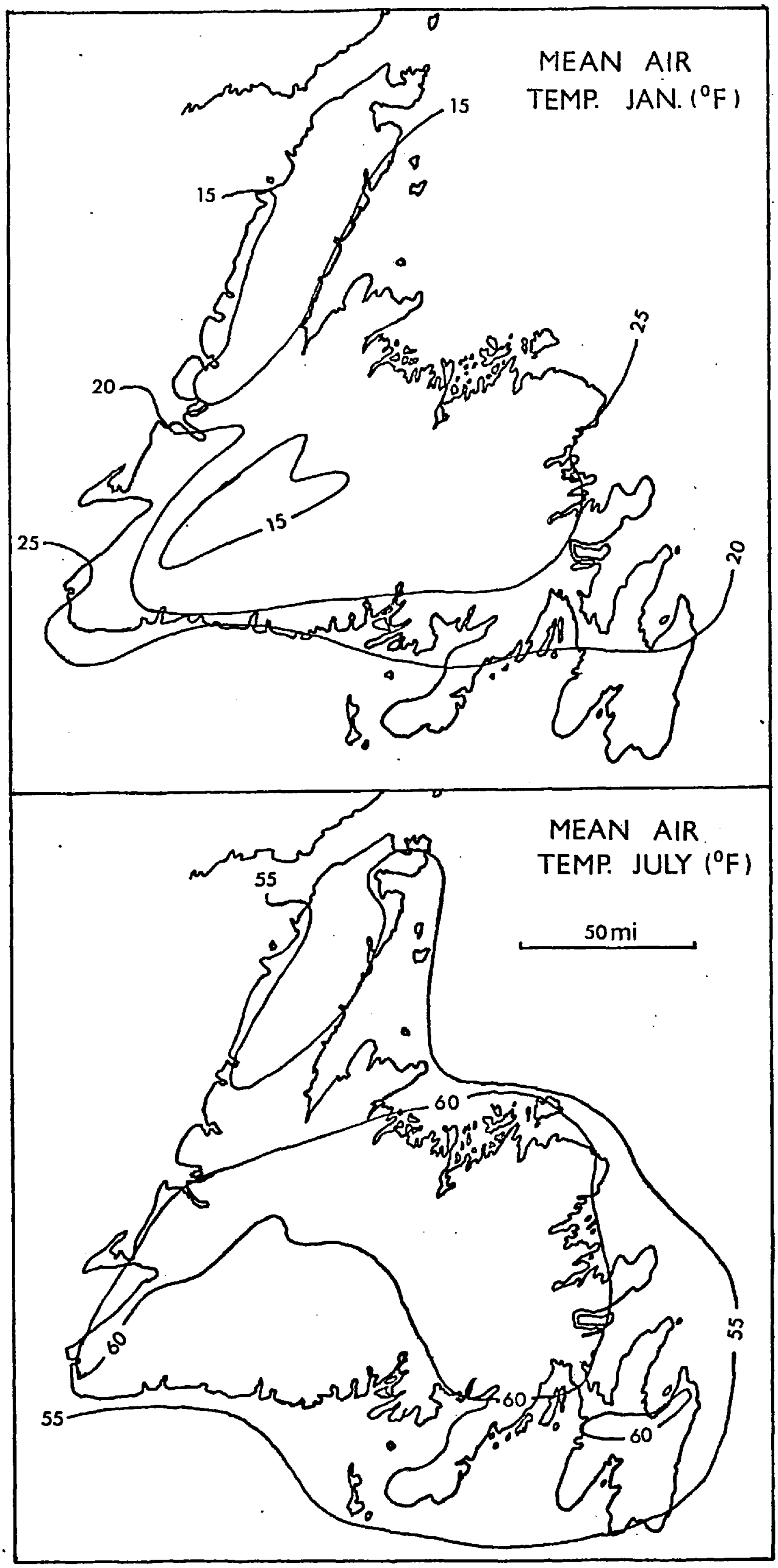

Figure 4: Mean air temperatures for Newfoundland (after Pollett, 1968).

survey of the Indian Brook - Sandy Lake area was also conducted by P.J. Murray (Murray, 1944) as a reconnaissance survey of the agricultural potential of the area.

It is observed from these publications and information gathered during geochemical soil surveys by Brinex that the majority of the soils are orthic podzols, consisting of an organic mat (2-5 in.) of leaf litter and partially decomposed humus overlying a grey, leached A_e horizon and an iron rich B horizon (Bf, Bfh, or Bhf).

Some humic podzols occur, characterized by a thicker accumulation of surface organic material and a humus rich upper B horizon, as well as acid brown wooded soils, characterized by the lack of an Ah horizon, with a shallow organic zone occurring above a yellow-brown Bm horizon.

Most podzols and acid brown wooded soils occur where the drainage is free to excessive, but where drainage is restricted in lower parts of the profile, some gleying may occur, giving rise to gleyed podzols and, where drainage is poor, to gleysols. The gleyed soils are much less common than the podzols.

The chemical characteristics of the forest soils of central Newfoundland such as pH, texture, and available nutrients are presented in Tables 1 and 2.

During geochemical soil surveys conducted by Brinex, an attempt was made to sample the B horizon of the usually podzolic profile, as this horizon has been shown to accumulate metals such as Cu, Pb, and Zn by illuviation and better reflects the underlying geology than do the surface horizons (Hawkes and Webb, 1962). Occasionally where the B horizon

Table 1: Average Values for Soil Factors by Soil Types from Newfoundland (after Bhure and Page, 1971)

Soil type and number of samples	Horizon	Depth of horizon (inches)	pH	% organic matter	% sand	% silt	% clay	Textural class
Acid brown wooded soil (1)	LFH	1.5	4.6	66.1	-	-	-	-
	Bm$_1$	4.0	5.0	15.5	38	46	16	Loam
	Bm$_2$	6.5	5.1	11.8	38	46	16	Loam
	C	11.5	5.4	5.4	47	38	15	Loam
Orthic podzol (18)	LFH	2.6	3.9	78.9	-	-	-	-
	A$_e$	2.9	3.9	3.1	41	50	9	Loam
	Bf/Bfh/Bhf	9.8	4.9	10.2	48	42	10	Loam
	C	11.1	5.1	3.4	59	34	7	Sandy Loam
Humic podzol (5)	LFH	3.4	3.9	79.4	-	-	-	-
	A$_e$	3.1	4.1	4.0	38	53	9	Silty Loam
	Bh	4.9	4.6	16.9	49	44	7	Sandy Loam
	Bf^1	6.0	4.8	12.9	56	39	5	Sandy Loam
	Bg^1	3.7	5.0	11.0	41	52	7	Silty Loam
	C (g)	17.0	5.1	2.3	49	40	11	Loam
Gleyed podzol (9)	LFH	2.9	4.0	89.1	-	-	-	-
	A$_e$	3.3	4.2	3.7	35	56	9	Silty Loam
	Bf/Bfh/Bhf^1	5.6	4.7	7.0	47	44	9	Loam
	Bg	7.0	4.7	6.9	49	41	10	Loam
	Cg	8.3	4.9	3.8	45	44	11	Loam
Gleysol (6)	LFH	3.2	4.2	85.2	-	-	-	-
	Aeg^1	5.0	4.8	9.5	39	56	5	Silty Loam
	Bg	9.5	5.0	3.7	44	40	16	Loam
	Cg	8.3	5.2	3.5	57	35	7	Sandy Loam

[1] Horizons not always present.

Table 2: Average available and total nutrient contents in upper 10 inches of soil profile (after Bhure and Page, 1971)

Soil type and number of samples	Available nutrients (lbs. per acre)					Total nutrients (lbs. per acre)				
	N	P	K	Ca	Mg	N	P	K	Ca	Mg
Acid brown wooded soil (1)	31.8	1.9	187.9	567.7	83.6	4,332	548	5,479	5,126	13,753
Orthic podzol (18)	26.5	14.5	76.3	63.5	45.9	3,550	1,299	10,122	1,458	4,677
Humic podzol (5)	47.4	19.9	118.0	70.4	43.8	6,899	1,128	11,429	2,358	5,646
Gleyed podzol (9)	25.7	19.3	62.8	248.5	73.2	2,892	758	12,058	2,947	5,604
Gleysol (6)	30.7	34.9	41.6	414.0	40.6	2,520	789	10,556	3,245	5,689

Table 2B: Comparison of Terms Used to label Podzol Horizons according to Different Soil Classification Schemes.

Conventional (as used by Hawkes and Webb)	Bhure and Page, 1971 (Soil Survey Handbook, 1960)	Description
A_{oo}	L	Fresh leaf litter
A_o	F	Partly decayed litter, roots
A_1	H A_h	Largely decayed humus, brown/black.
A_2	A_e	Eluviated (leached) material, grey/white.
B_1	B_t, B_h, B_f, B_g	Illuvial, oxide-rich, red/orange/brown. Textural, humic, ferric, gleyed characteristics.
C	C	Mixed, oxides, clays, and weathered bedrock.

was poorly developed or absent the humus was sometimes sampled and labelled A_1, which generally corresponds to the LFH of Bhure and Page's orthic podzols (Bhure and Page, 1971). A simplified comparison of the terminology of different soil classification schemes used to describe podzol horizons has been given in Table 2B.

CHAPTER 2

GENERAL ASPECTS OF THE GEOCHEMISTRY OF SULPHUR AND SULPHUR IN MINERAL EXPLORATION

2.1 THE DISTRIBUTION OF SULPHUR IN NATURE

Sulphur is fairly abundant in the earth, estimated as comprising 520g/ton as an average for all rocks by Rankama and Sahama (1950). It exists in four main valence states, S^{+6}, S^{+4}, S^{0} and S^{-2}, and forms a great variety of compounds both organic and inorganic, in which the sulphur atom can act either as cation or anion, e.g. H_2S or SO_2. Consequently, the host of chemical and biochemical reactions involved in the transformation and distribution of sulphur in the environment is immensely complex. This is evident simply from a list of the more common stable compounds: sulphides, polysulphides, isothiocyanates, oxides, sulphones, sulphonates, sulphamates, proteins, vitamins, amino acids, enzymes, sulphoxides, sulphates and elemental sulphur. Of the remaining twenty-five or more ionic and molecular species which have been isolated, most are not stable in the geochemical environment and do not occur in large amounts in natural substances.

2.1.1 Hydrosphere

The hydrosphere is estimated to contain approximately 0.06% sulphur by weight. Sea water, which constitutes more than 98% of the hydrosphere, contains 884g/ton sulphur (.097%), making it the sea's fourth most abundant element and sulphate the second most important anion (Newham, 1962).

The remaining 1-2%, distributed as circulating groundwater, surface water in lakes and streams, and water vapour/precipitation in the atmosphere, contains lesser amounts of sulphur, almost entirely as sulphate (SO_4^{2-}) ion. Data reviewed by Hutchinson (1957) show that sulphate is an important anionic constituent of almost all natural waters (Tables 3 and 4). Rain water approximates very dilute lake waters in anionic composition but in most lakes the composition is more dependent on the ions of influent streams and the composition of the rocks in the drainage basin. Near the sea, chloride is enriched with respect to sulphate in precipitation as a result of sea spray in the air.

It may be noted that although SO_4^{2-} is by far the predominant inorganic ion of sulphur in the hydrosphere, under the reducing conditions found near some lake bottoms, near the sea floor, and in the vicinity of fumaroles or hot springs, significant concentrations of HS^- and S^{2-} are known to occur. In the case of waters near sea and lake bottoms, the dissolved H_2S is produced by sulphate reducing bacteria in the sediments. In the surface environment and freely circulating waters the reduced forms are rapidly oxidized to sulphate.

Table 3: Composition of rain and dilute lake water, (after Hutchinson, 1957).

	Rain Water (Provisional Estimate) mg/l	Rain, Mean, Lake District mg/l	Rain, Uncontaminated, Lake District mg/l	Min. Concentration, Wisconsin Lakes, mg/l
Cl	0.5	3.3	5.1	0.1
Br	0.03	...	...	...
I	0.001	...	...	...
SO_4	2.0	3.2	1.7	0.75
B	0.01	...	...	...
Na	0.4 or more	1.9	3.1	0.13
K	0.03 or more	0.2	0.2	0.25
Mg	0.1 or more	0.3	0.3	0.5
Ca	0.1 - 10	0.2	0.2	0.13
N. NH_3	0.5	...	...	0.01
N. NO_3	0.2	...	...	0.004

Table 4: Mean equivalent proportions of cations and anions in certain natural waters, (after Hutchinson, 1957).

	Mean Igneous Source Material	Mean Sedimentary Source Material	Water from Igneous Rocks	Wisconsin Soft Waters	Uppland	Central Europe	Mean River	N. German Soft Waters
Na^+	20.1	4.8	30.6	10.9	13.6	4.5	15.7	43.0
K^+	9.8	8.0	6.9	4.8	2.2	1.9	3.4	6.7
Mg^{++}	33.1	34.0	14.2	37.7	16.9	25.4	17.4	14.3
Ca^{++}	37.1	53.2	48.3	46.9	67.3	68.2	63.5	36.0
$CO_3^=$	...	93.8	73.3	69.6	74.3	85.4	73.9	42.4
$SO_4^=$	...	6.2	14.1	20.5	16.2	10.8	16.0	14.1
Cl^-	...	0 (?)	12.6	9.9	9.5	3.9	10.1	43.5

2.1.2 Biosphere

Sulphur is required for the metabolism of all living organisms and is an essential nutrient for plant growth (Freney, 1967, and Tabatabai and Bremner, 1972). It is therefore a significant constituent of all organic material, which in geochemistry concerns organic soils, plants, peat, organic sediments, and material associated with petroleum.

The inorganic sulphur forms involved in biological processes are sulphate chiefly, followed by sulphide and elemental sulphur. Other compounds are formed during the transformation of these simpler ions into complex organic molecules via the metabolic processes of plants, animals and bacteria, but these are the basic forms in which sulphur is obtained by the organism from the environment.

The amount of inorganic sulphur involved in the biosphere is small, however, in comparison to the amount of sulphur in organic combination. This is particularly evident in the case of studies of sulphur fractions in soils (Lowe 1964, Tabatabai and Bremner, 1972). The principal organic sulphur forms are the amino acids cysteine[1] and methionine (Freney, 1967, and Postgate, 1968). As amino acids are the basic units of proteins, these sulphur-containing compounds are involved in the metabolism of a great number of plants, animals and, especially, bacteria.

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[1] Cystine is the disulphide dimer of cysteine and may be considered an equivalent compound in these discussions.

Other organic sulphur compounds occur and will be discussed later in more detail in relation to soils. The composition of some natural organic sulphur compounds are given in Table 5.

2.1.3 Lithosphere

Most igneous and metamorphic rocks contain small amounts of sulphur as sulphides and in some cases sufficient accumulations occur to be of economic significance i.e. ore bodies. Some shales deposited under anaerobic conditions may also contain appreciable amounts of sulphides. Sulphide is the predominant form of sulphur under anaerobic or reducing conditions. Elemental sulphur is also formed under reducing conditions in special environments such as the caps of salt domes, but many deposits of elemental sulphur are believed to be largely due to the work of anerobic sulphate reducing bacteria (Jensen, 1962).

Non-marine sediments, evaporites, and most sedimentary rocks deposited under aerobic and/or oxidizing conditions contain sulphur as sulphates. Sulphides occur in clastic material derived from other sources, of course, but under oxidizing conditions sulphate is the stable form.

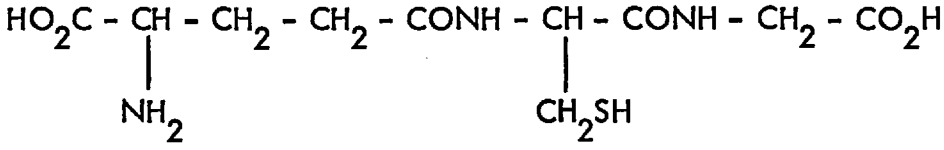
Organic compounds containing sulphur occur particularly in association with petroliferous deposits but these are of minor significance in the overall discussion of sulphur geochemistry.

Table 5: Chemical composition of some common organic sulphur compounds, (after Postgate, 1968).

Cysteine : $SH - CH_2 - CHNH_2 - COOH$

Methionine : $CH_3S - CH_2 - CH_2 - CHNH_2 - COOH$

Glutathione:



$$HO_2C - \underset{NH_2}{\underset{|}{CH}} - CH_2 - CH_2 - CONH - \underset{CH_2SH}{\underset{|}{CH}} - CONH - CH_2 - CO_2H$$

From the point of view of exploration geochemistry the compounds occurring in the sample are metal sulphides and some sulphates in rocks and stream sediments, while sulphide grains, sulphates and organic sulphur compounds are found in soils and lake sediments. Sampling of plant material involves sulphate and organic sulphur, and natural waters contain sulphate and/or dissolved H_2S. The sulphide and sulphate from decomposing rocks, the sulphate of surface waters and sulphur of organic origin may be found in different proportions in the materials of the surface environment depending on the composition of the source and the physico-chemical conditions of the local environment.

2.1.4 Atmosphere

Jensen and Nakai (1961) and Junge (1960) have presented discussions of sulphur in the atmosphere and it is evident that apart from particulate or ionic SO_4 in aerosols and rain, atmospheric sulphur consists of SO_2 and

H_2S gases, the former being very much more abundant than the latter.

All the H_2S in the atmosphere is of natural origin, the sources being mainly the bacteria of coastal or tidal sediments (the release of H_2S taking place when the muds, etc. are exposed to the atmosphere at low tide) and volcanic emanations. Atmospheric H_2S is being continually oxidized to SO_2 and thus coexists with SO_2 in the atmosphere for a relatively short time.

Sulphur dioxide, on the other hand, is partly of natural origin and partly anthropogenic, i.e., from industries. The natural sources are biochemical reactions, volcanic emanations, and the oxidation of H_2S in the atmosphere. Also, it is known that small amounts of SO_2 are released from oxidizing sulphide deposits (Rouse and Stevens, 1971, McCarthy, 1972). The main source relating to man's activity is the combustion of fossil fuels, of which SO_2 is a product. All the industrial plants burning coal and oil emit SO_2 to the atmosphere, as well as such industries as paper mills, ore smelters and petroleum processing plants. These contributors, plus the automobile, make SO_2 the principal pollutant of the atmosphere of industrial cities. Consequently, in recent years much attention has been paid to the measurement of small quantities of SO_2 in industrial and urban atmospheres in an effort to control this form of pollution, and this has increased substantially the information available on sulphur compounds in the air.

Junge (1960) points out that some of the SO_2 in the atmosphere is oxidized to SO_4 by either of two processes, namely, photochemical oxidation in sunlight or catalytic oxidation in cloud droplets. Oxidation of SO_2 in the atmosphere appears to be a fairly slow process, however, and most SO_2 is stable in the air for at least several days.

2.1.5 Factors Influencing the Distribution of Sulphur Compounds

The stability fields of the various ionic species of sulphur are defined by the oxidation potential (Eh), pH, temperature and pressure conditions of the environment. Since water is involved in the movement of ions in almost all natural habitats, a fair representation of the stability fields of various sulphur species is given in Figure (5) (after Garrels and Naeser, 1959) for ions in water under equilibrium conditions.

For non-aqueous environments, of course, these conditions do not apply such as in the magmatic environment, if one is considering conditions of ore deposition or the like, or in the case of gaseous sulphur compounds in the atmosphere. The magmatic environment is a very reducing one (Mason, 1949), so sulphide would be the dominant ion of sulphur, but which particular mineral is formed is entirely dependent on pressure – temperature conditions and the chemical composition of the material involved. The atmosphere, though not completely non-aqueous, is an environment in which other variables affect the distribution of sulphur compounds, such as the potential for catalytic or photochemical oxidation or the amount of water vapour in the air, the amounts released by sources of the compounds, wind conditions, temperature and pressure.

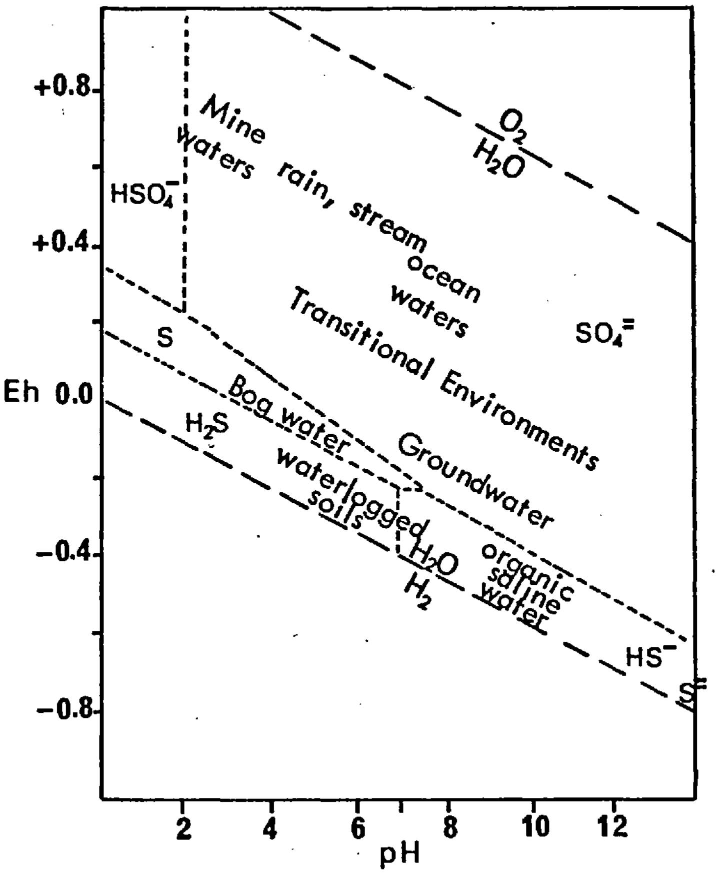


Figure 5: Natural environments and the distribution of some sulphur species in water under equilibrium conditions at 25°C and 1 atm. pressure for an activity of dissolved sulphur of 10^{-1} (after Garrels and Naeser, 1959).

From the point of view of exploration geochemistry, the stability fields shown in Figure (5) cover most of the "aqueous" domain of the surface or near surface environment.

The Eh-pH conditions of the local environment also determine the solubility of various compounds or ions and subsequently influence the mobility of those compounds in the environment. Other variables affecting solubility are the concentration of the ions concerned, the type and concentration of other ions in the solution, the solubility product of the compounds formed and the pressure - temperature conditions in that locality. An example of the influence of solubility is lead solubility with respect to sulphide in a Pb - S - H_2O system. Under increased pressure and decreased temperature, the solubility of H_2S is increased. With more H_2S in solution, the concentration of Pb in solution increases as well (Hemley, 1953). A simpler example is the restricted mobility of Ba as $BaSO_4$ because of its insolubility in water.

The preceding discussion concerned the distribution of inorganic sulphur species, but much of the sulphur in nature is held in organic combination in both plant and animal matter. The form in which the sulphur occurs is dependent on the metabolic processes involved in the particular organisms but they are usually complex molecules such as amino acids, proteins, enzymes, ester sulphates and polysaccharides, the biochemistry of which is quite complex and in some cases little understood as yet.

From the geochemist's view point, organic sulphur compounds are involved in the distribution of total sulphur in soils, sulphur in plants, and sulphur in organic stream and lake sediments. For example, the amount of total sulphur occurring in a particular soil or sediment sample is dependent firstly on the proportion of organic to inorganic material, as organic tends to be sulphur-rich, and, secondly, on the type of vegetation or other organic matter in the sample. For instance, needles of conifers have small amounts of sulphur, about 0.1 per cent, whereas tamarix, crucifers and crops such as onions and radish may have 0.5 to 0.7 per cent (Thomas, et al. 1950).

One of the most important controlling factors in the distribution of both organic and inorganic sulphur is the abundance of bacteria which metabolise it. Sulphur is both oxidized and reduced by microbes. The sulphate reducing bacteria are the most common and most studied, and the majority of forms belong to the genus Desulfovibrio or to a lesser extent Desulfotomaculum, both of which are anaerobic and perform dissimilatory sulphate reduction, i.e., they ingest sulphate, producing a sulphide product (Postgate, 1968). Other sulphate reducing bacteria are assimilatory, building up the sulphur - containing organic materials of their body proteins from inorganic sulphate. Escherichia coli of the genus Clostridium is such a type.

These sulphate reducing bacteria are important particularly to the economic geologist in that they reduce sea water sulphate to sulphide in marine sediments (and sometimes in lake sediments under reducing conditions), the H_2S formed by the bacteria reacting with ferrous iron and other metals in the sediments to produce metal sulphides (Jensen, 1962; Berner, 1962, Sandqvist, 1964).

Sulphide oxidizing bacteria largely belong to the genus Thiobacillus and are mostly aerobic organisms, though a few varieties can oxidize sulphide under anaerobic conditions if nitrate is present or by a photoreduction of CO_2 at the same time (Postgate, 1968). These are quite effective in the oxidation of sulphide ore deposits, especially pyritic ores, producing a sulphate product, and are influential throughout the surface environment. The possibility of using these bacteria to decompose low-grade sulphide ores has been considered for some time but never applied on a large scale (Duncan and Drummond, 1973; Kramarenko, 1969). The obvious economic advantage is well expressed by Jensen, (1962): "Insoluble copper sulphide at depth or in waste dumps might be oxidized by anaerobes to form soluble copper sulphate which would be leached to a draw point where it could be pumped to the surface. And then, of course, bacteria work 24 hours a day, they do not organize, take coffee breaks, form unions, go on strike, and so forth."

2.2 THE GEOCHEMICAL CYCLE OF SULPHUR

Many elements occurring in several oxidation states and existing in a variety of stable inorganic and organic forms are transformed by natural processes from one state to another and back again or form a complex cycle via the activities of living organisms. Such cycles as the carbon/oxygen cycle in all photosynthetic plants or the nitrogen cycle are well known. Similarly sulphur is cycled in nature through a variety of both biological, chemical and geological processes. Two representations of the cycling of sulphur are discussed below as well as the special case of sulphur cycling in lakes.

2.2.1 The Transportation Cycle of Sulphur

Holster and Kaplan (1966) have represented the geochemical cycle of sulphur in terms of the masses of sulphur transported by various processes from one reservoir to another (Figure 6). The largest single transport mechanism is fresh water flowing to the sea, carrying sulphate; so other processes, such as weathering, crystallization, and volcanism are represented as a proportion of that one, on a basis of 100. Other important features of the sulphur cycle included in this diagram are the masses of sulphur in each "reservoir"; the general division of the sites into those containing predominantly reduced forms and those containing oxidized; and the general environments in which predominate sulphur compounds containing heavy and light isotopes.

It can be observed from this diagram that most rocks contain reduced sulphur forms, namely sulphides, whereas evaporites and bodies of water contain oxidized, mainly sulphates. Also, sea water sulphate is enriched in the heavy sulphur isotope S^{34} with respect to the terrestrial environments. The surface water cycle involving sea spray, rain, and streams is a short-term one compared to the other cycling processes.

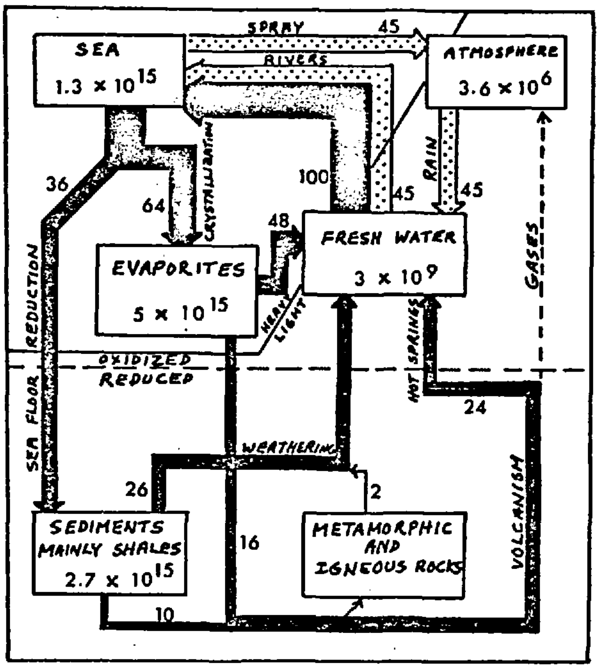


Figure 6: The transportation cycle of sulphur in the environment (after Holster and Kaplan, 1966).

Masses are in metric tons. Most material above dashed line is oxidized to sulphate, below, reduced to sulphide. Above the solid line, sulphur of heavy isotopic composition dominates, below, light sulphur. Long-term (dark) and short-term (stippled) fluxes between reservoirs are indicated on the basis of 100 for the long-term component of fresh water sulphate flowing to the sea.

2.2.2 The Transformation Cycle of Sulphur

Representation of the chemical processes involved in the transformation of sulphur compounds into other forms is another means of illustrating how sulphur is cycled in nature, as is done by Postgate (1968). This representation, given in Figure 7, shows that in the upper part of the cycle the sulphur may be organic or inorganic whereas in the lower part it is entirely in organic combination. Bacteria in the water, soil, or sediment may contribute to each transformation and in fact are very important throughout the sulphur cycle.

2.2.3 The Sulphur Cycle in Lakes

Hutchinson (1957) has discussed sulphur in lakes quite comprehensively in his treatise on limnology and according to his data there is a continual flux of sulphur compounds through most open lakes. Depending on whether the lake is thermally stratified and on how often the waters are circulated there may in fact be a complete cycling of sulphur in different forms within a single lake. As Postgate points out, such a closed cycle involving microbes is termed a sulfuretum (Postgate, 1968). Most lakes are not true sulfureta but most do have some flux of sulphur compounds. An illustration of sulphur in a typical lake is given in Figure 8.

The sources of sulphur to a lake are rain water (1-2 mg/litre) and sulphate brought into the lake by influent streams, the amount depending on the lithology of the drainage area. Two sources which give rise to high

Figure 7: The Transformation Cycle of Natural Sulphur (after Postgate, 1968).

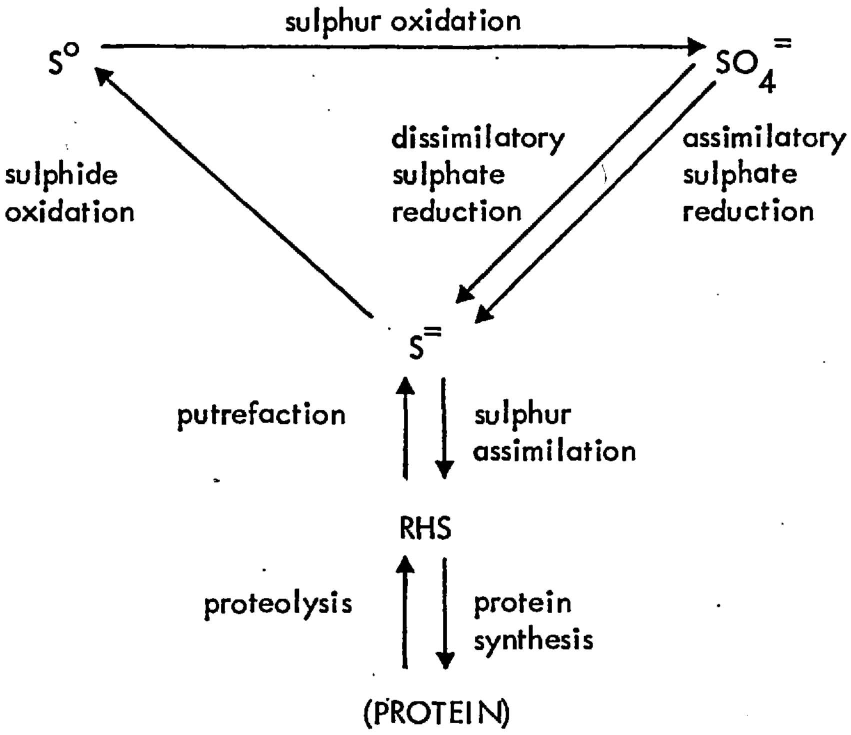
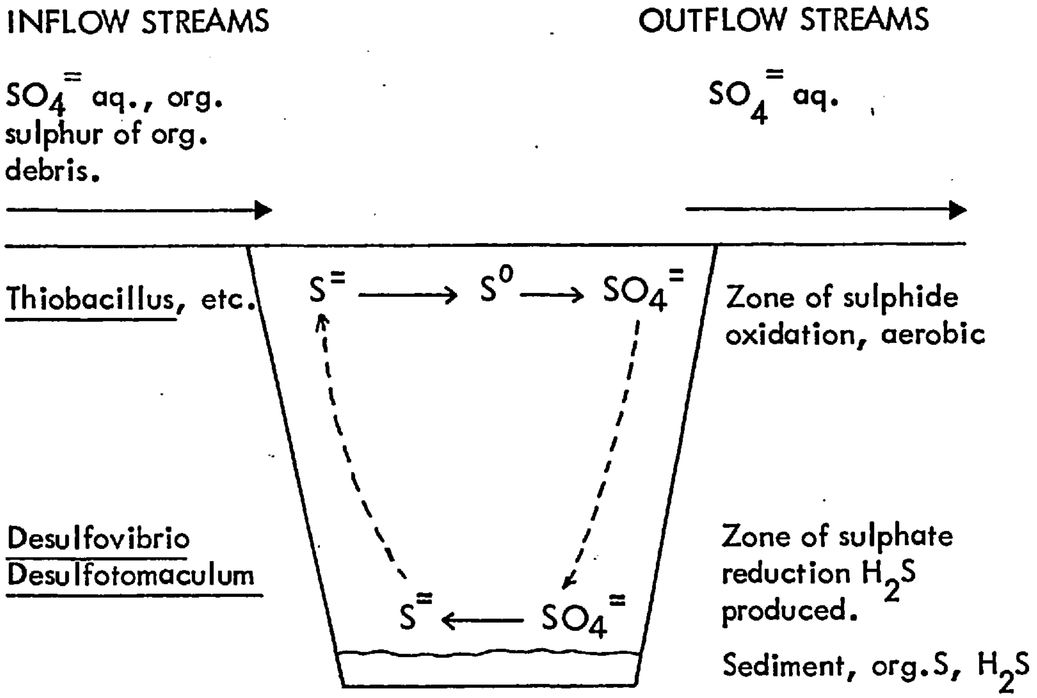


Figure 8: Sulphur in a typical lake (modified, after Postgate, 1968).



SO_4^{2-} concentrations if they occur in the drainage basin are deposits in gypsum or pyritic sulphides.

If oxygen is depleted in the deeper waters (the hypolimnion) of the lake during summer stagnation, some of the sulphate of the lake water near the bottom is used by bacteria in the sediment in the oxidation of organic matter and H_2S is produced. Some of his H_2S reacts with ferrous iron in the mud to produce sulphides and some is released to the lake water. In lakes in which anaerobic conditions do not exist year round, the waters circulate freely once or twice a year and most of the H_2S produced is oxidized to SO_4 again. Little H_2S is released to the air from lakes as most of it reacts with ferrous compounds in the sediment or is oxidized to sulphate (Hutchinson, 1957; Stuiver, 1967).

Other inorganic sulphur forms than SO_4 and H_2S have not been known to occur in most fresh water lakes and are probably quickly oxidized but small amounts of sulphur - containing organo-colloids may occur. Their significance has not been much investigated (Hutchinson, 1957).

2.3 ABUNDANCE OF VARIOUS FORMS OF SULPHUR

2.3.1 Rocks and Sediments

Table 6, compiled from data by Nikolayeva (1968) and Vinogradov (1962) shows the average contents of some sulphur forms in some common

Table 6: Abundance of Sulphur in Rocks and Marine Sediments (Wt. %). Modified after (1) Nikolayeva (1968) and (2) Vinogradov (1962).

	Rock	Sulphide	Sulphate	Free	Total
(1)	Clays	0.40	0.10	<0.10	0.50
	Clastics	0.15	0.10	0.04	0.30
	Siliceous carbonates	0.45	0.06	....	0.50
	Marine and Oceanic Sediments	0.41	0.15	0.025 (0.06 org.)	0.60
(2)	Mafic				0.03
	Intermediate				0.02
	Sedimentary				0.30

rock types. Nikolayeva's 0.50% total sulphur in clays is considerably higher than Vinogradov's 0.3% for sedimentary rocks, consisting of clays and clay shales, but the discrepancy may be largely due to the difference in the suites of samples analysed. In fact, Nikolayeva's estimates seem somewhat high throughout, whereas the data of Vinogradov compares favourably with the results of a computer study of elemental abundances conducted by Horn and Adams (1966), presented in Table 7.

The general conclusion derived from this data is that the total sulphur content of sediments derived from the common rock types will have mean values in the 400-2000 ppm range, except in the cases of carbonate, evaporite or organic rich materials, where the levels would be considerably higher. Most of the total sulphur is held as inorganic sulphide in the rocks (sulphate in the case of evaporite) but sediments containing organic material would be expected to hold a significant proportion in organic combination. Data from the field area will be shown later to support the predictions based on these observations.

2.3.2 Waters

Background contents of sulphate ion in surface waters varies with the lithology of the drainage basin but in areas uncontaminated by sources of sulphate such as gypsum or sulphide deposits or by sea spray, the background values are expected to be in the 0-50 mg/l range. Jensen and Nakai (1961) found values in this range for samples from Sweden and Japan (Table 8). Hutchinson (1957) gives values of 0.75 to 3.2 mg/l

Table 7: Computer Derived Sulphur Abundances, after Horn and Adams (1966) Sulphur in ppm.

	Igneous	Shale	Sandstone	Carbonate	Evaporite	Oceanic Clay	Oceanic Carb.
Rock Types	410	1850	945	4550	26,800	3450	1300

	Continent - Shield	Mobile belt - Shelf	Hemipelagic	Pelagic
Sedimentary Domains	2780	2330	3240	3150

for rain and dilute lake water in Wisconsin and the English Lake District and from 0.75 to 44.8 mg/1 for a number of American and European lakes. Ginzburg (1960) shows that in areas of oxidizing sulphides $SO_4^=$ levels can increase to as high as 200 mg/1 but in background areas are generally less than 50 mg/1.

Hutchinson (1957) also indicated that increased amounts of dissolved H_2S occur in the low-oxygen water at depth in some lakes but in aerated surface waters, levels are low, less than 0.25 mg/1, and usually 0.0.

Table 8: Concentration of sulphate in some natural waters and precipitation in Sweden, Japan, and the seas (after Jensen and Nakai, 1961).

	$SO_4^=$ mg/1
Snow	1.5 - 4.0
Rain	1.3 - 18.8
Lake Water	9.6 - 47.0
Sea Water	450.0 - 2740.0

2.3.3 Soils

The total sulphur content of soils varies with the soil type and insufficient surveys have been carried out to produce average values for particular types. However, a number of workers have analyzed soils for both total sulphur and sulphur fractions, particularly from the field of agriculture/soil science, and produced a great deal of information on sulphur in soils.

Lowe (1965, 1969) has presented data for Podzolic, Gleysolic and Chernozemic soils which show that in these soil groups most of the sulphur is organic and a large part of the organic sulphur is directly bonded to carbon. A small amount of sulphur may be held, particularly in the mineral horizons, by adsorption onto hydrous Al and Fe oxides and clays (Chao, et al., 1962). The subject of sulphur distribution in soils is treated in more detail in chapter 4.

Pertaining to the Nfld. field area where soils are largely of the Podzolic order, background total sulphur concentrations expected, based on data from Lowe, and others, were in the range of 50-500 ppm. for mineral horizons and in the 500-2000 ppm. range for organic and peaty soils. These estimates were substantiated by the field data and, again, are discussed with the presentation of the field data in chapter 4.

2.3.4 Atmosphere

Sulphur dioxide and hydrogen sulphide occur naturally in low concentrations throughout the atmosphere. In non-industrial areas the background levels of SO_2 are quite low, less than 5 ppb.* (Rouse and Stevens, 1971). However, over industrial centers and large cities like London, New York,

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* Everywhere in this thesis 1 billion = 10^9

and Los Angeles concentrations can be considerably higher. Craxford, et al. (1966), cite values of 200-500 ug/m^3 for London, which corresponds to the average winter value of 0.2 ppm. given by Smith, et al. (1961).

By comparison with sulphur dioxide, hydrogen sulphide concentrations in the atmosphere are extremely low (Smith, et al., op. cit.). Jacobs, Braverman and Hochheiser (1957) determined an average value for New York for 1956 of 2.0 ppb, which is approximately two orders less than the probable SO_2 levels. Smith, et al. (1961) determined values of 0.1 to 0.3 ppb. for rural, non-industrial areas in Wales against up to 1.4 ppb. for city centers and several ppb. near industrial plants. The silver nitrate method recommended by Smith, et al. (op. cit.) is capable of determining as little as 10^{-4} ppm. with a 2 hr. sampling time but no methods are presently available to measure concentrations of this order in times practical for geochemical surveys.

2.4 ISOTOPIC FRACTIONATION

The four stable isotopes of sulphur are distributed in the following proportions: 95.1% ^{32}S, 0.74% ^{33}S, 4.2% ^{34}S and 0.016% ^{36}S (Nickless, 1968). In general, sea water $SO_4^{=}$ is enriched in the heavier isotope ^{34}S with respect to the meteoric standard whereas the sulphur of sulphide deposits of magmatic origin contains more ^{32}S, i.e., they have a higher $^{32}S/^{34}S$ ratio. The variation of ratios with different compounds is given in Figure (9). A displacement of the natural ratios of abundances of the isotopes by enrichment in a particular isotope is called fractionation. Studies of fractionation and sulphur isotope ratios have been made over many years to aid in determining the genesis of sulphide and petroleum deposits as well as in a variety of other geologic problems.

In a review of the uses of sulphur isotope studies, L.N. Grinenko and V.A. Grinenko (1967) present the following points of importance applying to geochemistry:

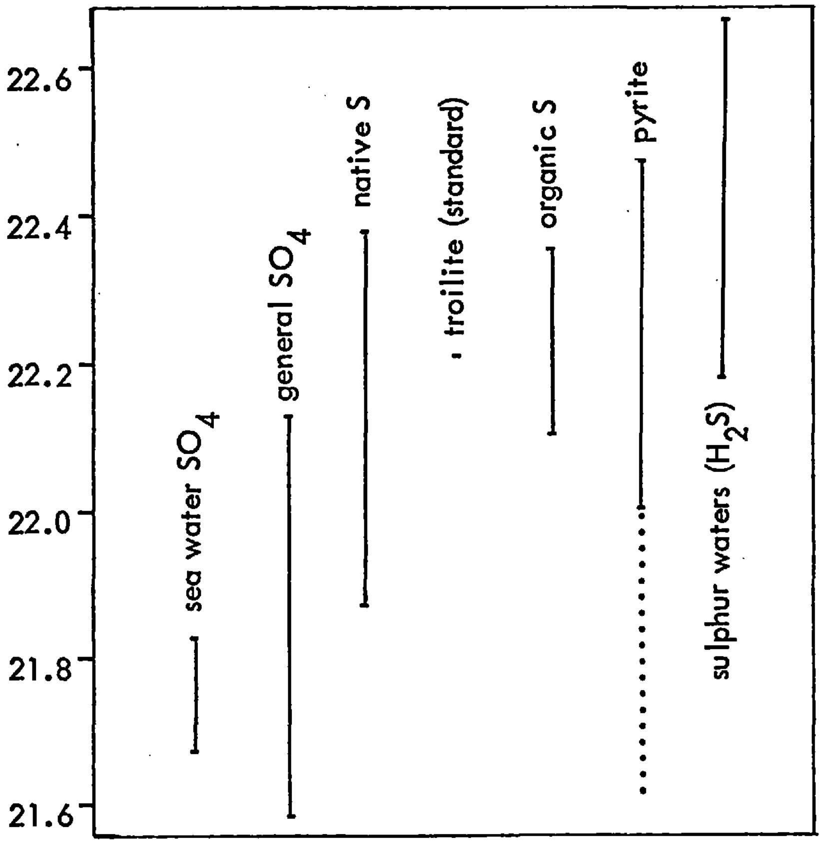
(1) Fractionation of sulphur isotopes can be caused by sulphate reducing bacterial activity as well as by isotope exchange reactions.

(2) Variations in the sulphur isotopic composition of evaporites can be related to depositional conditions and sedimentary cycles.

(3) Isotopic composition of sulphide sulphur of magmatic-hydrothermal origin varies within a restricted range as compared with much greater ranges observed for sulphide sulphur of biogenic origin.

(4) Sulphur of hydrothermal sulphides is commonly isotopically similar to sulphur of meteorites, thus suggesting the possibility of upper mantle origin.

Figure 9. Variation of Sulphur Isotope Ratios with Compounds from Different Environments (after Newham, 1962).



(5) Some investigators postulate that the deviation of hydrothermal sulphides from meteoric sulphides in isotopic composition is caused, in part, by differentiation of crustal rocks.

Although isotope studies are quite useful in the solution of some geologic problems, there are some difficulties in the interpretation of the significance of observed ratios. To mention two, the ratios for sediments can be scattered over a wide range, meaning that a particular observed ratio may not be directly indicative of the mode of origin; and, secondly, microbes are so widely distributed that they influence the distribution of sulphur compounds in almost all spheres and complicate the pattern of isotope ratios. The proceedings of a symposium on sulphur isotopes in geochemistry describing a variety of applications is presented by Jensen (1962).

2.5 RECENT TRENDS IN MINERAL EXPLORATION GEOCHEMISTRY

During recent years the number of new ore deposits with any surface expression enabling them to be detected by standard surface exploration techniques has diminished, so exploration research has concentrated on the development of new techniques to permit the detection of ore deposits which are at greater depth or otherwise obscured. A short review of some of the recent developments aimed at improving capabilities for the detection of buried deposits is presented below.

Other research has been conducted on the development of improved statistical techniques for the analysis of single and multi-element data so that true anomalies may be discriminated from false ones and element associations or trends which may indicate mineralization but may not be evident from the raw data may be determined. The statistical techniques that have been applied are factor analysis, cluster and discriminant analysis, linear and multiple regression, and trend surface analysis. These methods have much wider application than to the problems mentioned, of course, but serve to illustrate immediate purposes for application of these techniques in mineral exploration.

2.5.1 Guides to Buried Deposits

The difficulty with concealed deposits is of course that the overlying rock or exotic overburden prevents the geochemical dispersion to the surface of the metals which normally indicate the presence of ore, and detection must then involve either elements or compounds which are much more mobile than the metals, in particular gaseous compounds, or properties which are more independent of the cover material. Techniques of vapour sensing have thus been widely developed and increased attention is being given to hydrogeochemical methods.

In recent reviews of vapour geochemistry, Bristow and Jonasson (1972) and McCarthy (1972) discuss the detection of volatile Hg and sulphur dioxide over base metal deposits; as well as H_2S, CO_2, O_2, halides, and noble gases, especially helium and radon. Jonasson and Boyle (1972), McCarthy (1972), Barringer (1966), Evans (1971) and Edelman (1971), to name a few, all report anomalous concentrations of Hg in the atmosphere or soil gas above various sulphide deposits in Canada, U.S., Rep. of Ireland and the U.S.S.R. Similarly, Rouse and Stevens (1971) found SO_2 anomalies in atmosphere and soil air over several oxidizing sulphide deposits in the U.S. These illustrate that, despite various thicknesses and types of overburden, several types of gaseous haloes may exist around sulphide deposits, Hg and SO_2 being the ones so far studied. Bristow and Jonasson (1972) mention the possibility that others such as of H_2S, hydrides of arsenic or antimony, and organomercurials may also exist, but adequate methods for analysis of most of these are as yet undeveloped.

Some investigations have also been made into the potential of hydrogeochemical methods for the detection of hidden ore deposits. Boyle, et al. (1971) show that sampling of deep groundwaters in drill holes has some potential use in the exploration of hidden deposits at depth. In addition, the analysis of surface lake and spring waters may be useful in areas where standard techniques do not work as well, such as the Canadian Shield.

Other investigators have concentrated on the idea that anionic constituents are more mobile than the metals and form larger haloes in surrounding waters (Polykarpochkin, et al., 1965). Dall'Aglio and Tonani (1972) show that SO_4 in relation to other ionic constituents may be a useful indicator of mineralization. A number of Russian workers have also conducted hydrogeochemical surveys for ore deposits and report variable success, but demonstrate the applicability and potential of this particular technique in the exploration of concealed deposits (Ivanov, 1969; Vostroknutov, 1968; Yushkov, 1968).

2.5.2 Exploration in Glaciated Terrain

2.5.2.1 The Problem

The detection of concealed or buried mineralization is particularly pertinent to areas which have been glaciated and covered with transported - as opposed to residual - overburden. In these areas any existing soil development is juvenile and soil forming processes have not greatly influenced geochemical dispersion. Geochemical anomalies in till and shallow soils on till may then be of three main types:

(1) Those caused by mineralized material in the sample medium, having been mechanically transported by the ice, displaced and unrelated to underlying geology.

(2) Hydromorphic dispersion anomalies from mineralized material in the till, again displaced and unrelated to underlying geology.

(3) Hydromorphic dispersion anomalies from the underlying bedrock mineralization up into the till.

The location and size of a particular geochemical anomaly in till is dependent, in the case of transported anomalies, on how far the till/soil has been displaced by the ice from its original location and the amount of mixing or dilution that has occurred in the process. In the case of hydromorphic dispersion from mineralization in the bedrock below the till, the surface expression is dependent on the thickness and permeability of the till, the grain size, and movements of aqueous/saline solutions through the material (Mehrtens, 1966; Mehrtens, et al., 1973; Band, 1969; Cazelet, 1973).

2.5.2.2 Methods of Prospecting in Glaciated Areas

Some techniques of prospecting in glaciated terrain as applied in Scandinavia, Canada and Ireland have been described by various authors in a recent IMM publication of the proceedings of a symposium on the subject held in Trondheim, Norway, in August, 1973 (Prospecting in Areas of Glacial Terrain, 1973).

The conventional and most widely used technique is boulder tracing, which has been aided recently by the use of trained dogs in Sweden, Finland, and the U.S.S.R. (Nilsson, 1973). Other techniques include the geochemical analysis of rocks and till, especially by sampling till at depth by pitting or drilling (Wennervirta, 1973; Eriksson, 1973), photogeologic methods (Talvitie and Paarma, 1973), and a variety of geophysical techniques. The application of biogeochemical methods has also been reported (Wolfe, 1971).

The application and improvement of exploration techniques in glacial terrain is being actively pursued by the Geological Surveys of Sweden and Norway and a special program for the development of geochemical methods for the exploration of the Canadian Shield has been followed by the Geological Survey of Canada (Allan and Hornbrook, 1970; Allan, 1971; Boyle, et al., 1971).

2.5.2.3 Sulphur Dispersion in Glaciated Areas

The dispersion of sulphur compounds in areas which have been glaciated, such as the field area of this project in Newfoundland, is of particular interest in mineral exploration from three aspects. Firstly, hydrogeochemical sulphate anomalies can occur in waters circulating in the vicinity of sulphide mineralization which are distinguishable over larger areas and possibly through thicker overburden than cation anomalies. Secondly, gaseous SO_2 and H_2S can form haloes above sulphide deposits underneath considerable overburden, up to several hundred feet according to Rouse and Stevens (1971). Thirdly, soils through which more mobile sulphur forms are dispersed may have a significantly higher total sulphur content reflecting the presence of mineralization.

It should be pointed out, however, that the dispersion of SO_2 from oxidizing sulphides is dependent largely on oxidation rates and the moisture content and permeability of the overlying till, as very wet overburden, or till containing quite impervious clay horizons may restrict the movement of soil gases considerably.

CHAPTER 3

FIELD AND ANALYTICAL METHODS

3.1 FIELD TECHNIQUES

3.1.1 Soil Sampling

The soils of the Notre Dame Bay area are largely Podzolic and less than 2m. thick, and as most of the samples are taken from the top 50 cm. in forested areas, the most practical tool has been found to be the grubber, or mattock. For sampling peat bogs an auger or Hiller sampler was sometimes preferred.

Samples were normally collected in Kraft wet-strength paper bags, oven-dried, sieved through 80 mesh (.177 mm) stainless steel screen, and the -80 mesh portion retained for analysis. Both the samples taken during Brinex soil surveys and those taken by the author were collected and processed by the same techniques. Descriptive field data was recorded at each site on standard coded data forms facilitating data handling for any computer analysis.

3.1.2 Stream Sediments

Stream sediment samples were also collected in Kraft wet-strength paper bags using large stainless steel kitchen spoons to scoop the sediment from the active part of the stream. In the field area larger or faster streams carry considerable sand and silt as sediment but the very small and slow streams tend to accumulate organic material, especially where peaty soils occur in the drainage area.

As with the soils, the samples were dried and sieved, and the -80 mesh fraction retained for analysis. Sufficient sample was collected at each site to yield at least several grams of -80 mesh for analysis, which meant collecting larger samples if the sediment was very coarse or organic. Both soil and sediment samples were stored in small plastic vials after sieving.

3.1.3 Water

Water samples for the sulphate in water study were collected in 250 ml polyethylene bottles with screw caps. This was sufficient sample as only 50 ml were required for the sulphate determination. Several larger samples were collected in 1 litre polypropylene bottles from various depths in Three Corner Pond for several analyses but this type of material is not considered as good as polyethylene for general water sampling purposes and is unsuitable if Hg analysis is required.

In the water survey only surface water from the top 0-15 cm was sampled at each site. The samples taken from the small streams are considered representative of all the water in the stream (Boyle, et al., 1971) but the surface samples from the lakes are not necessarily representative of waters elsewhere in the lake with respect to sulphate concentration.

At each site the pre-cleaned plastic bottle was rinsed two or three times with the water being sampled to neutralize any other possible contamination and then immersed to fill.

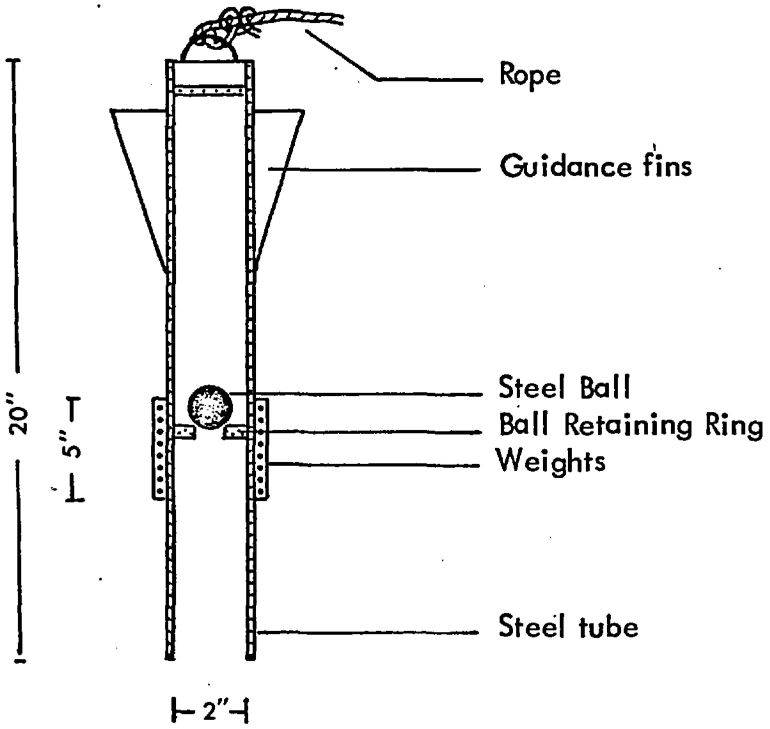
3.1.4 Lake Sediment

Samples of bottom sediment were obtained by using a sampler of original design consisting of a weighted steel tube 2 inches in diameter and 20 inches long attached to a small rope. A ball mechanism within the tube prevents water from washing out the sediment as the sampler is raised to the surface. The design is shown in Figure 10.

As most ponds and lakes in the Notre Dame Bay area contain sediments consisting of silt/clay underneath 0-3 feet of organic ooze or gyttja, and depths vary from 10-60 feet in the smaller lakes, it was found desirable that the sampler be weighty enough to be able, when plunged into the lake, to pass through the organic debris and reach the underlying silt. This was not always possible because of the thickness and texture of the organic sediment and in those cases the organic was sampled. The sampler worked very well, however, retrieving samples with greater than 90% success. Only if the bottom was very rocky was there difficulty in obtaining sediment.

The lake sediment sampling was conducted both from rubber raft or

Figure 10: Design of Lake Sediment Sampler.



canoe in the summer and through the ice in the winter. In both cases the same sampling method was used.

The sediment samples were oven-dried and sieved through 80 mesh (.177 mm) screen prior to analysis. In the case of some lake sediments from Three Corner Pond the samples were split, one portion oven-dried and the other air dried, to determine the effects, if any, of oven drying on the sulphur content of the sediments. The results are presented later in chapter seven.

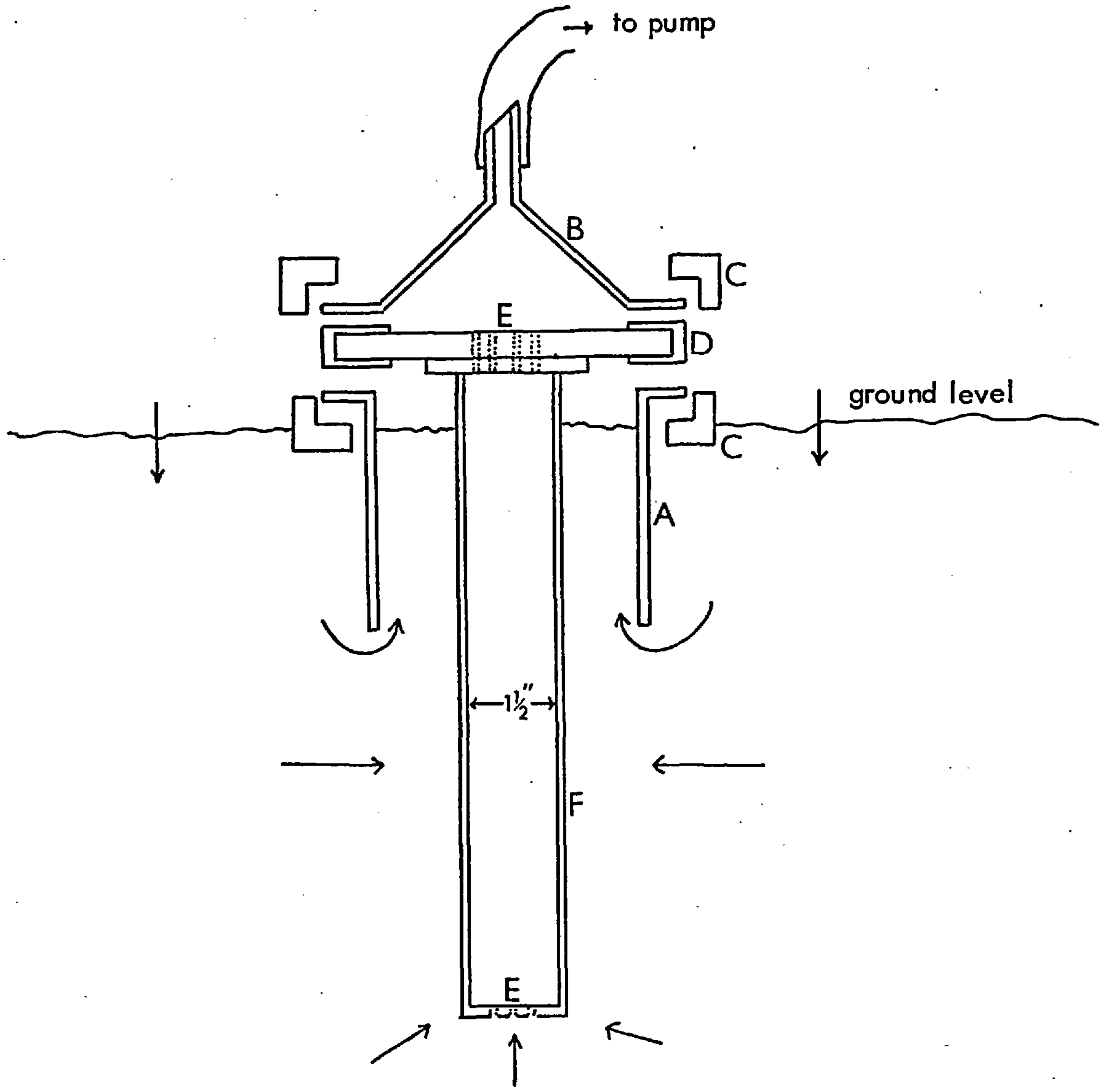
3.1.5 Soil Gas and Atmospheric Sampling

Samples of soil gas were obtained by using a Capex Mark I pump (Charles Austen Pumps Ltd., Surrey, Eng.) operated by a 12V battery attached to a probe inserted in auger holes in the soil. The probe/capping apparatus consisted of a perspex probe 1½ inches in diameter x 12 inches long attached to a stainless steel funnel-shaped hood 4 inches in diameter (Figure 11). When the probe is pushed into a 1½ inch auger hole, the hood is pressed into the soil around the probe helping to make a fairly tight seal so that as little air as possible gets in around the probe from the surface.

Soil air samples were generally taken from holes of 16-24 inches depth but in a few cases this was impossible because of high water table in poorly drained areas.

Apart from the use of the probe attachment for soil air, the method is the same for both soil air and atmospheric sampling. Sulphur dioxide

Figure 11: Diagram of Capping Apparatus for Obtaining Soil Gas Samples.



Directions of air flow (⟶)

Label	Item	Material
A	Tube	Stainless Steel
B	Funnel	Stainless Steel
C	Retaining rings	Stainless Steel
D	Sealing ring	Silicone
E	Grid plates, with holes	Perspex
F	Probe	Perspex

is determined by a modified West-Gaeke (1956) procedure in which a measured volume of air is bubbled through a tetrachloromercurate absorbing solution in a Gelman midget impinger. Air flow was regulated by a needle valve attached to a flow guage. A rate of 2 1/min was normally used but rates of up to 5 1/min may be used provided no entrainment occurs, as the absorbent is extremely efficient. Sample times varied from 10 minutes to 1 hour but normally a time of 15 or 20 minutes was used and this is recommended. The system was cleaned by rejecting the first two samples at the start of each sampling day as some adsorption of SO_2 onto the glassware tended to occur during storage.

The disulfito-mercurate (II) complex formed by absorption of the sulphur dioxide is stable for several days, permitting analysis of the samples in the laboratory at the end of a field day. The colorimetric procedure for determination of the SO_2 concentration in the solutions is discussed in a later section.

3.2 ANALYTICAL METHODS

3.2.1 Total Sulphur by LECO Combustion

Total sulphur in soils and stream sediments was determined by iodine titration of the sulphur dioxide evolved from sample combustion in the oxygen stream of a LECO (Laboratory Equipment Corp., St. Joseph, Michigan) induction furnace. Tin was added to the sample (200 mg) - iron mixture to assist complete combustion. The LECO technique is versatile and can be adapted to analyze such materials as steel, rocks, soils, sediments and a variety of organic substances such as hydrocarbons.

Modifications to the standard LECO method for sulphur analysis of soils included the dilution of the potassium iodate titrant, calibration of the instrument over the soil/sediment range of 0-10,000 ppm, the assignment of a correction factor to account for colour dilution where large volumes were involved, and the determination of optimum combustion rates for different types of sample. A diagram of the apparatus is given in Figure 12 and the dilution correction scale in Table 9.

The instrument was calibrated over the 0-10,000 ppm. range using natural standards prepared by dilution of a standard of known concentration with low-sulphur sand. The curve obtained (Figure 13) is quite linear over this range.

The precision of the technique was determined by ten replicate analyses of several natural standards in random order and calculation using the formula $P = \sqrt{\frac{\sum(A-\bar{A})^2}{N-1}} \times \frac{200}{\bar{A}}$ (A.G.R.G. Tech. Comm. No. 46).

The precision was found to be less than ±5% at the 95% confidence level over this range (Table 10). The method was found to have a sensitivity of about 20 ppm. and a detection limit also of 20 ppm., making it quite applicable to the determination of sulphur in soils and sediments for geochemical exploration purposes.

It was found that the combustion of organic soil samples had to be

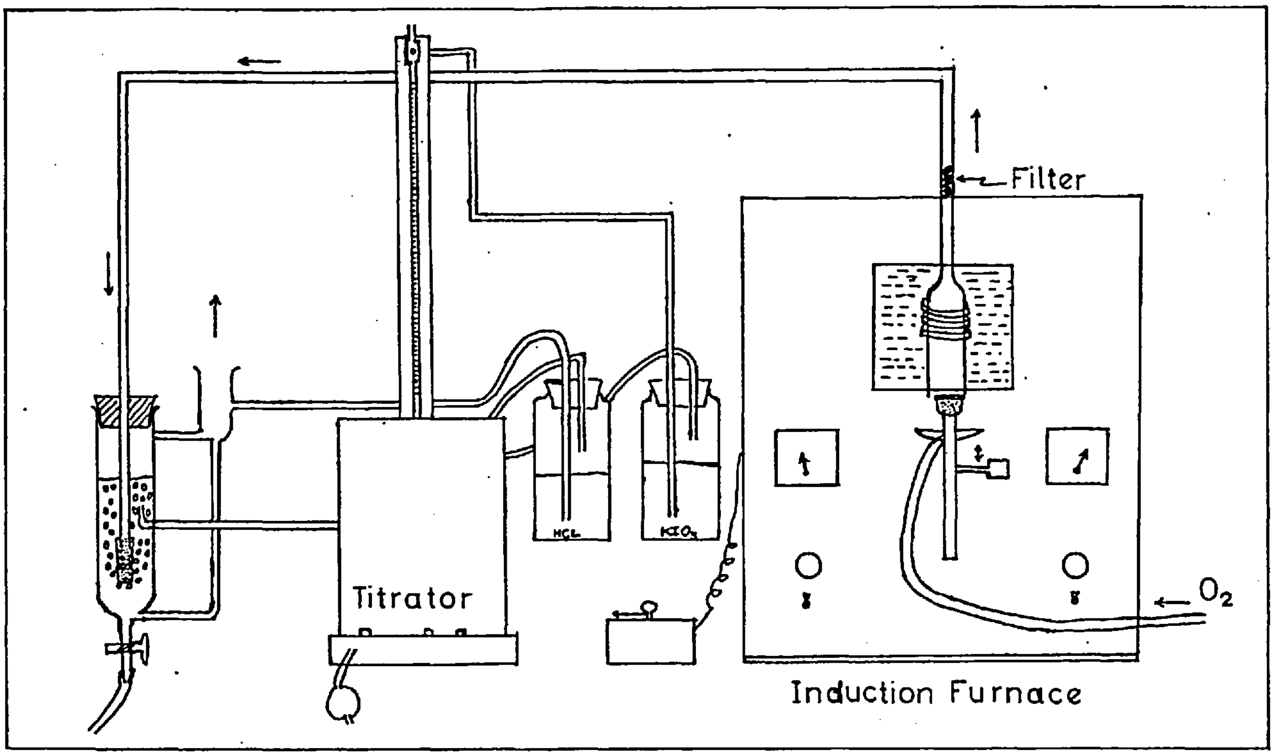


Figure 12: Diagram of the Leco Apparatus for Total Sulfur Analysis

KIO_3 added to give blue colour	Initial Volume of Solution	Final Volume of Solution	Dilution Correction*
.010	30 ml.	40 ml.	.003
"	"	50 ml.	.006
"	"	60 ml.	.009
"	"	70 ml.	.013
"	"	80 ml.	.016
"	"	90 ml.	.019
"	"	100 ml.	.022
.005	30 ml.	40 ml.	.001
"	"	50 ml.	.003
"	"	60 ml.	.004
"	"	70 ml.	.006

* This is a correction to be subtracted from the readings.

Table 9: The Dilution Correction Scale Used in the Total Sulfur Analyses.

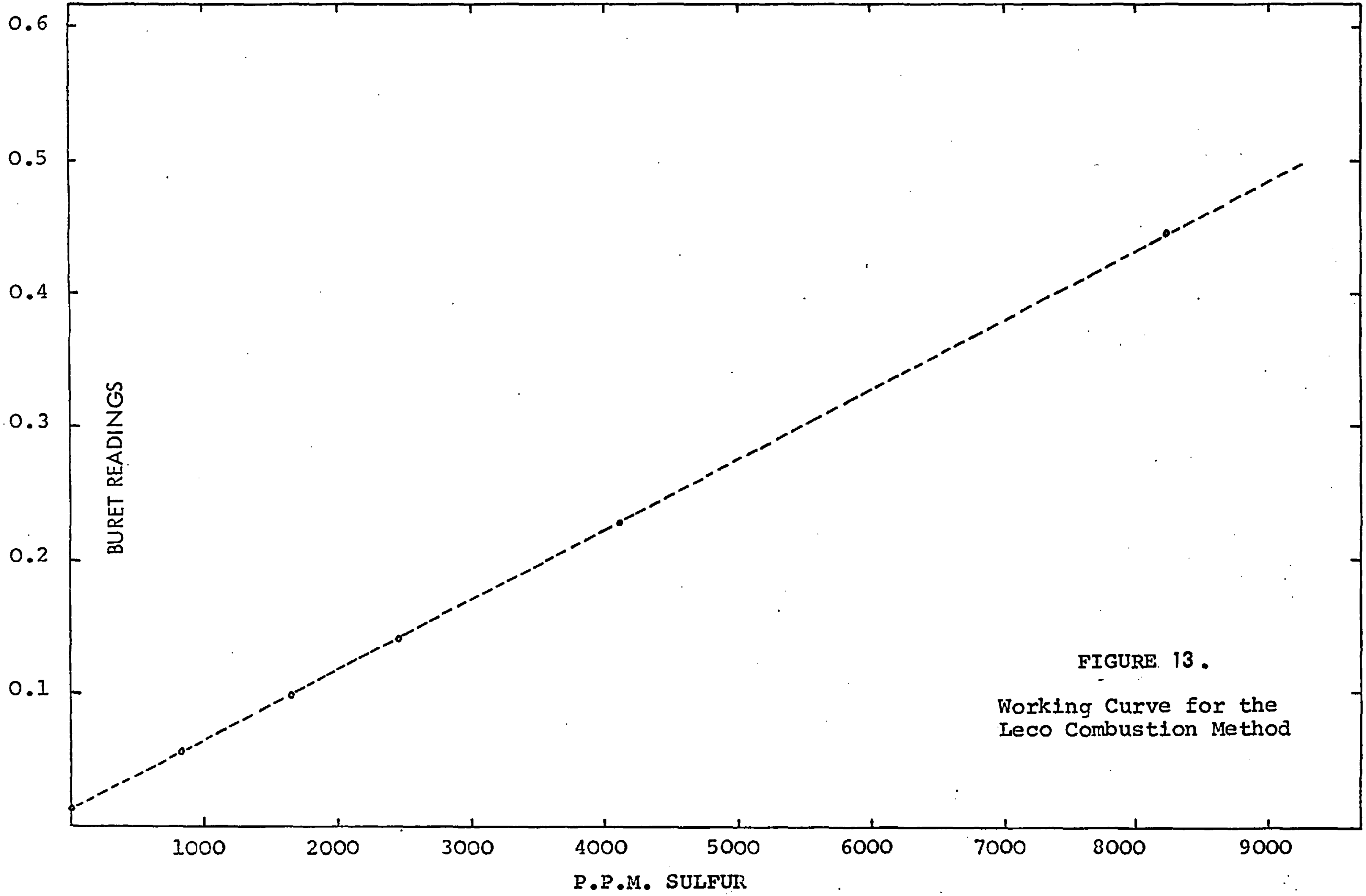


FIGURE 13.

Working Curve for the Leco Combustion Method

Table 10: Precision of the LECO Combustion Method.

No. of Analyses	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
1	.055	.096	.138	.233	.420
2	.055	.098	.135	.230	.422
3	.057	.101	.135	.231	.425
4	.056	.095	.134	.230	.419
5	.054	.101	.133	.230	.426
6	.056	.099	.135	.227	.425
7	.058	.095	.132	.226	.427
8	.057	.099	.134	.226	.422
9	.056	.095	.132	.229	.421
10	.058	.097	.134	.227	.423
Mean	.056	.098	.134	.228	.423
Standard Deviation[1]	.0013	.0024	.0018	.0025	.0027
Precision[2]	± 4.6%	± 4.9%	± 2.7%	± 2.2%	± 1.3%

[1] Standard deviation is calculated using $S = \sqrt{\frac{\sum d^2}{N - 1}}$

[2] Precision is calculated using $P = \sqrt{\frac{\sum (A-A)^2}{N - 1}} \times \frac{200}{\bar{A}}$

at the 95% confidence level (Tech. Comm. No. 46, A.G.R.G.).

carried out more slowly than for inorganic samples to prevent excessive accumulation of smoke, water vapour, and other combustion products in the system and to avoid spitting of the melt from the crucible. Also, if many organic samples are analyzed, it is necessary to clean the apparatus regularly to prevent contamination by adsorption of the combustion products onto the tubing. Together, cleaning and slower heating rates make the analysis of organic samples more time consuming than inorganic analysis, but it still requires less than 10 minutes per sample, an acceptable rate for routine analysis.

Application of the LECO technique for total sulphur determinations in soils is also described by Searle (1968) and Tabatabai and Bremner (1970).

3.2.2 Determination of Sulphate in Natural Waters

The sulphate content of surface water was determined using an adaptation of the indirect method for sulphur dioxide of Rose and Boltz (1969). This technique involves the addition of a known amount of excess lead as lead perchlorate to the water sample followed by the removal of lead sulphate by the use of a centrifuge. As sulphate concentrations were in the 0-30 mg/l range, the addition of 2 mg. Pb to a final volume of 100 ml. yielded lead concentration in the supernate in the 2-20 ug/ml range, which is the best concentration range for Pb determinations by atomic absorption. The lead remaining in the solution was measured using a

Techtron AA4 atomic absorption spectrophotometer, the amount consumed by precipitation of the $PbSO_4$ being proportional to the sulphate in the sample. A 50 ml. sample aliquot was used with 25 ml. ethanol added to minimize the solubility of lead sulphate.

Standard sulphate solutions were prepared from reagent grade ammonium bisulphite, oxidized to sulphate by H_2O_2. It was necessary to prepare fresh standards daily, as sulphite solutions are somewhat unstable, as well as Pb standards in ethanol since ethanol causes some enhancement. The method gave a detection limit of 0.2 mg/l which was satisfactory for the range of sulphate levels found in the surface waters of the Notre Dame Bay area.

3.2.3 HCL - Extractable Sulphate

A number of soils and sediments were analyzed for HCL - extractable sulphate by the method described in the Applied Geochemistry Research Group (AGRG) Technical Communication No. 33 (1965). In this technique 1g. of sample is digested in IM HCL on a sand tray for 1 hour and an aliquot taken for determination of the sulphate in solution. The determination is made turbidimetrically by the addition of $BaCl_2$ to produce a white $BaSO_4$ precipitate. The addition of acid-salt buffer and gum acacia to stabilize the precipitate is also required.

In this procedure adsorbed and easily soluble sulphates are released plus a partial solution of sulphides and sulphates such as lead and calcium sulphate in some cases. In the case of organic samples some organically held sulphur may also be released. The result obtained is only an estimate of the more soluble sulphate content and must not be considered as a determination of total sulphate.

3.2.4 Reducible Sulphur as H_2S

A small number of soil and sediment samples were analyzed for sulphide by an adaptation of the lead acetate method with 3M HCL in the presence of Al metal reducing strips. The H_2S produced from the reaction diffuses upwards from the test tube through a small glass tube in which is situated a strip of filter paper moistened with 0.1M lead acetate. The length of the dark PbS stain produced on the paper strip is an estimate of the sulphide content of the sample.

It may be noted that this method is only semi-quantitative as a measure of sulphide since the sulphides present may be only partially attacked and other sulphur compounds present which are reducible to sulphide will also be measured. Also, organic samples are difficult to analyze because of foaming.

3.2.5 Organic Carbon

The method used for the determination of organic carbon in soils was a modified oxidation technique after Schollenberger (1927), as in A.G.R.G. Tech. Comm. No. 32 (1967). The sample is decomposed with a potassium dichromate - sulphuric acid mixture and the excess dichromate titrated with ferrous ammonium sulphate. The amount of dichromate required to oxidize the carbon is thus determined, from which the carbon content is calculated. Application of and improvements in this method has been discussed by Walkley and Black (1934), Tinsley (1950), Allison (1960) and Bremner and Jenkinson (1960).

3.2.6 Organic Matter by Loss On Ignition

An estimate of the organic material content of some stream and lake sediments and soils was obtained by determining loss on ignition. For some samples, a rough estimate was obtained after ignition in a muffle furnace at 450°C for 5 hours by expressing weight lost as a percentage of the dry weight of the sample. A better estimate was obtained for other soils by first drying at 110°C for 1 hour, weighing, and then igniting overnight at 375°C for 16 hours. Ball (1964) has shown that under these conditions loss on ignition correlates well with organic carbon determined by oxidation methods for soils which are low in carbonates, as are the samples from the Notre Dame Bay area.

A good positive correlation was found for soil samples from this area containing up to 4% organic carbon (Figure 14). Above 4% org. C and 15% L.O.I. there is an increase in the proportion of total organic material compared to carbon. This may be due to low results in the organic carbon determination in this range or to the retention of water by the humus material during the drying stage of L.O.I. determination,

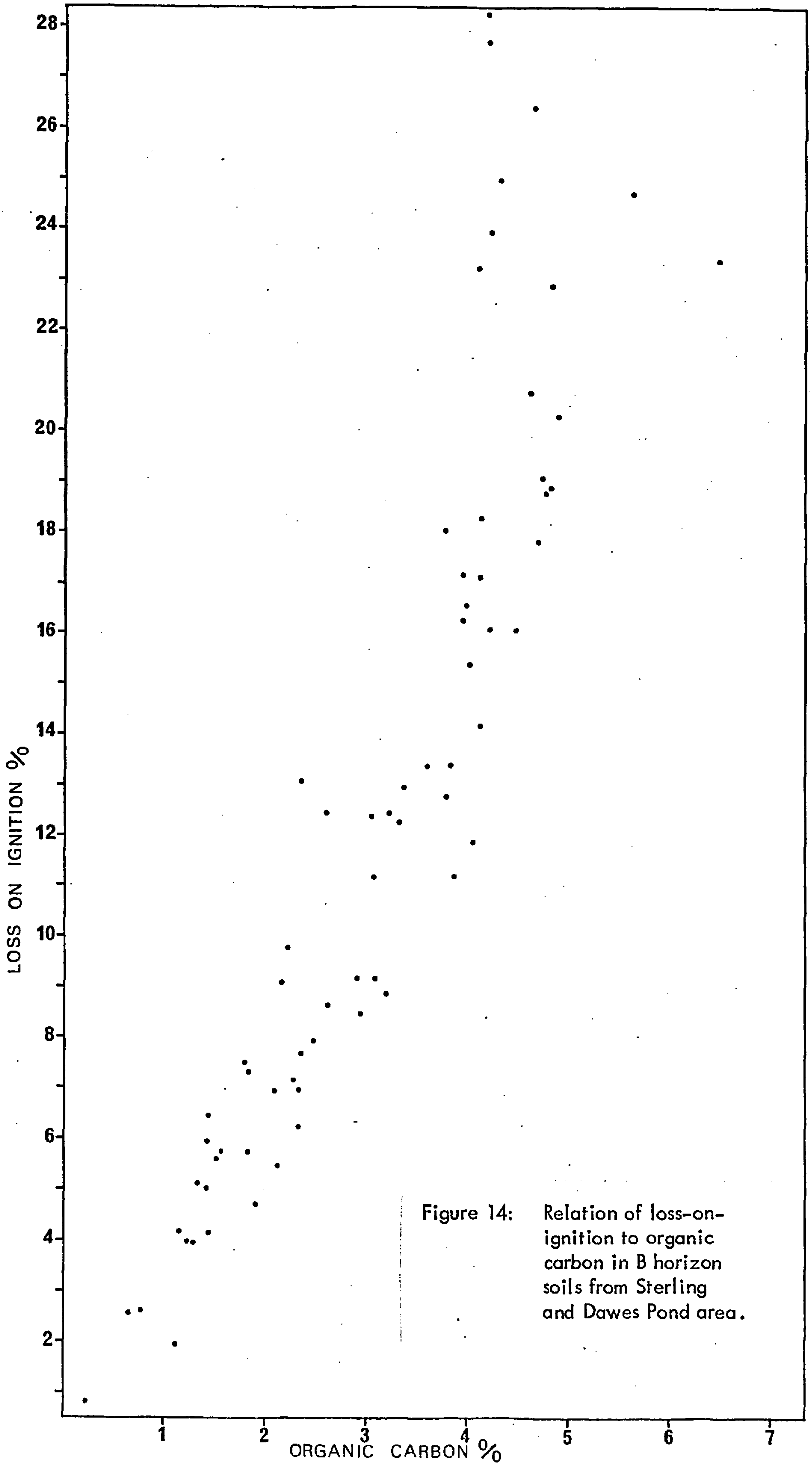


Figure 14: Relation of loss-on-ignition to organic carbon in B horizon soils from Sterling and Dawes Pond area.

yielding high L.O.I. values. Also, it seems over-optimistic to expect a very strong correlation between these two variables over a wide range of organic contents and soil and plant types.

3.2.7 Atomic Absorption Spectrophotometry

The principles of atomic absorption techniques are described by Angino and Billings (1967) for most of the common applications in geology. Some soils and sediments were analyzed according to the procedure outlined in Tech. Comm. No. 50 (1965) with hot HNO_3/ $HCLO_4$ acid attack followed by IN HCL leach, and determination on the Perkin Aylmer 403 spectrophotometer. The more common elements Cu, Pb, Zn, Ni, Mn and Fe were determined directly on the leach, whereas Co and Mg required the addition of 1% lanthanum in IN HCL to minimize interferences.

The foregoing procedure was followed for analysis by atomic absorption at the A.G.R.G. laboratories. Other samples were analyzed at the Brinex laboratory (now Atlantic Analytical Services Ltd., Springdale Nfld.) where determination was made on a Techtron AA4 spectrophotometer after digestion of the sample with hot 1:1 nitric acid. For Mo, an $HCLO_4$ attack was used as it yielded better results than other acids.

Both instruments and procedures have been demonstrated elsewhere as reliable and precise for routine analysis of common trace elements in soils and sediments (Urquidi, 1973; Closs, 1972). Estimated detection limits and precisions for a number of elements have been given in Table 11.

Table 11: Analytical precisions for various elements by atomic absorption, A.G.R.G. and Brinex laboratories.

Element	Estimated Detection Limit (ppm.)	Precision (%)	
Cu		18.9	(1)
Fe		15.0	
Ni		20.0	
Pb		7.6	
Zn		16.6	
Zn	10	8.34	(2)
Cu	5	20.57	
Pb	5	25.89	
Ag	0.1	51.70	
Ni	5	12.90	
Co	5	11.83	
Ba	10	57.16	
Mn	150	23.51	
Fe	0.5%	17.38	

(1) after Urquidi, 1973. A.G.R.G. laboratory, Perkin Elmer 403. Precisions calculated at 95% confidence level from 34 pairs of duplicate samples.

(2) after Closs, 1972. Brinex laboratory, Techtron AA4. Precisions calculated at 95% confidence level from 121 duplicate pairs.

3.2.8 Emission Spectrography

Emission spectrography (photographic) was used for semi-quantitative analysis of some soil samples for a large number of elements. For instance, about one hundred soils from the Rendell Jackman property were analyzed for fourteen elements, viz., Ag, Ba, Cu, Co, Cd, K, Mo, Mn, Fe_2O_3, Ni, Pb, Sn, V, and Zn.

The method is basically that of Nichol and Henderson-Hamilton (1965). Germanium (400 ppm.) is added to each sample as an internal standard and replicate analysis is used for control. All samples were ignited for 5 hours at 450°C prior to analysis.

The operating parameters and instrument specifications are presented in Table 12 and precisions and working ranges for various elements outlined in Table 13.

3.2.9 Determination of Sulphur Dioxide in Air

After absorption of sulphur dioxide from the air by the tetrachloromercurate solution, determination is made colorimetrically using pararosaniline as the indicator. The procedure is essentially that of West and Gaeke (1956). Scaringelli, et al. (1967) have shown that 0.04M potassium tetrachloromercurate is slightly better to use than 0.1M sodium TCM, so this reagent was used for most determinations.

To 10 ml. of the exposed absorbant is added 1 ml. of 0.2% formal-

Table 12: Specifications for manual spectrograph (after Nichol and Henderson-Hamilton, 1965).

Source Unit	Hilger and Watts F S 131
Spectrograph	Hilger and Watts Large Quartz F S 55
Arc Stand	Hilger and Watts F S 56
Comparator	Hilger, J.A. Co. Ltd. 90
Wavelength Range	2800-4950 Å
Emulsion	Ilford N.30
Anode	Morganite SG. 305H - 5 mm carbon 2.91 mm diameter and 5 mm crater
Cathode	Morganite SG. 305H - flat ended
Exposure	20 seconds
Gap	3 mm.
Arc Current	12.5 amp
Slit	15μ.
Collimator	Internal
Step Sector	Two steps giving three intensities in proportion $1 : \frac{1}{4} : 1/16$
Processing	5 min. Kodak developer at 20°C, 10 sec. stop, 10 min. fix, wash 30 min.
Sample Buffer	Spec-pure graphite, lithium carbonate, germanium dioxide mixture. Mixed 1 : 1 with ignited sample.

Table 13: Wavelengths and working ranges for various elements on the Hilger and Watts manual emission spectrograph (after Evans, 1971).

Element	Wavelength (Å)	Range (ppm.)	Precision
Ag	3382.9	0.2-1,000	48%
Ba	4554.0	20-10,000	36%
Bi	3067.7	5-200	-
Co	3453.5	5-10,000	89%
Cr	4254.3	2-500	46%
Cu	3274.0	2-200	65%
Cu	2961.2	200-10,000	
Fe_2O_3	3233.1	1% - 30%	
Ga	2943.6	2-10,000	62%
Mn	4034.5	2-500	
Mn	2933.0	500-10,000	
Mo	3170.3	2-10,000	68%
Ni	3414.8	5-200	34%
Ni	3050.8	200-10,000	
Pb	2833.1	2-100	
Pb	2873.3	100-10,000	
Sn	2840.0	5-10,000	-
Sr	4077.7	20-10,000	68%
Ti	3377.6	50-10,000	46%
V	3185.4	2-10,000	64%
Zn	3345.0	50-10,000	

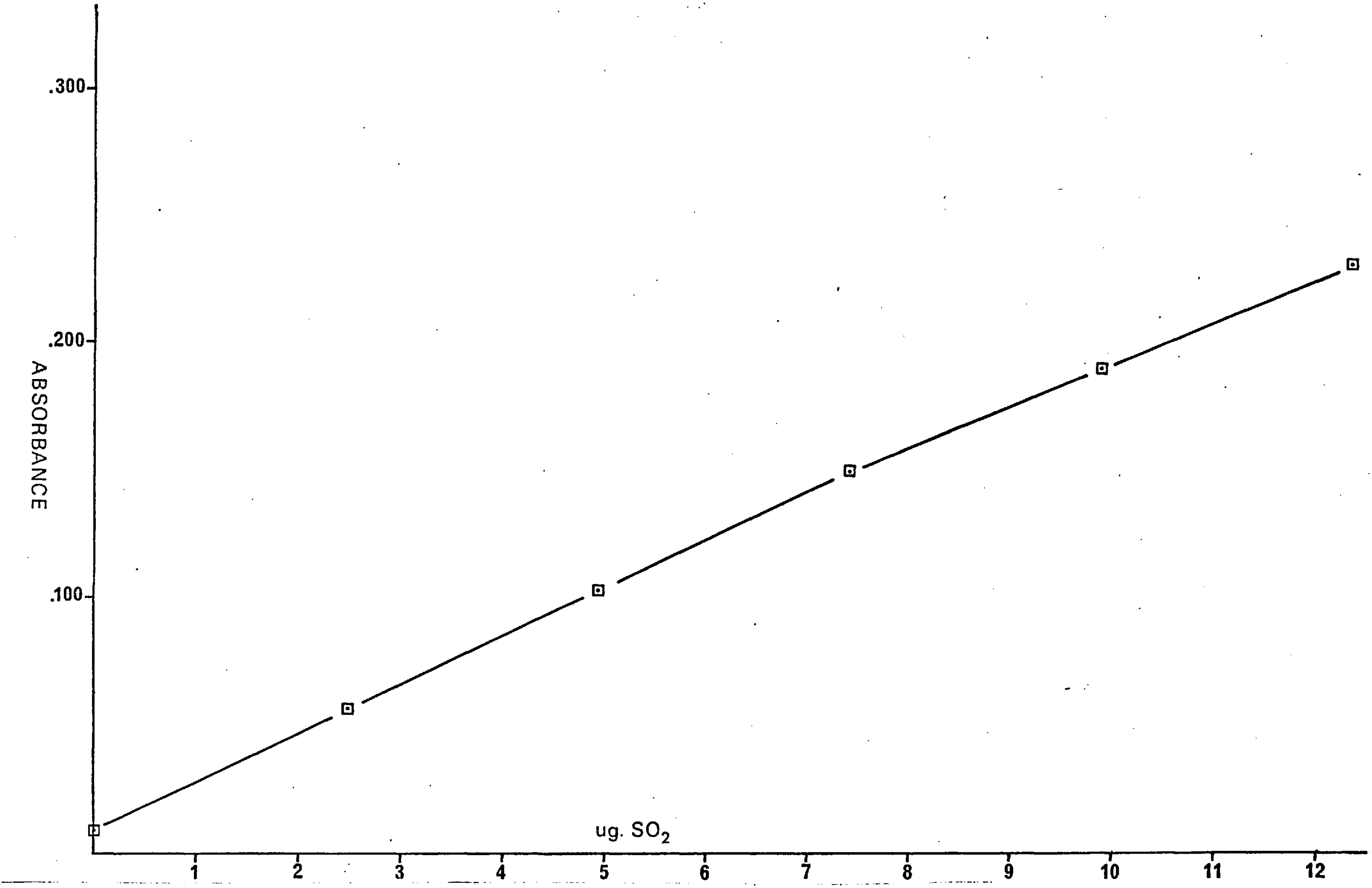


Figure 15: Calibration curve for SO_2 determinations by the colorimetric West and Gaeke procedure.

dehyde and 1 ml. of HCl - bleached p-rosaniline (.04%, prepared by mixing 4 ml. of 1% aqueous p-rosaniline hydrochloride with 6 ml. conc. HCl and diluting to 100 ml.) About 30 minutes is allowed for colour development and absorbance measured on a Klett-Summerson colorimeter. Maximum absorbance of the red-violet para-rosaniline methyl sulphonic acid complex formed upon addition of the dye occurs in the 548-575 mu range, the exact position of the peak depending on pH.

Standard sulphite solutions were prepared using ammonium bisulphite and from these good calibration curves were derived covering the range of 0-12 ug SO_2 (Figure 15). Sulphite solutions are quite unstable, so new standard solutions must be prepared each day.

The addition of dimethyl formamide in the determination has been suggested by Huitt and Lodge (1964) as a means of increasing sensitivity, but this did not prove advantageous as high blanks and other difficulties arose, probably due to impurities, so this possibility was not pursued further.

The West-Gaeke procedure is highly specific for the bisulphite ion formed by absorption of sulphur dioxide and with improvements suggested by Scaringelli, et al. (1967), is quite sensitive and reproducible in the ppb range. Under controlled conditions, the detection limit may be considerably less than 1 ppb (10^6 ng/m^3) but under field conditions values of less than 0.5 ppb were not considered to be significant, on a sample volume of 20 litres. The West-Gaeke method is the most widely used method for the detection of small quantities of SO_2 in the atmosphere.

CHAPTER 4

SULPHUR IN SOILS

4.1 SOIL SULPHUR CHEMISTRY

Since this chapter is primarily concerned with soil sulphur in relation to sulphide deposits, it is considered appropriate to orient the discussion by first considering aspects of the chemistry of sulphur in soils, beginning with its release to the soil by oxidation of sulphides and following with a review of the influences on its secondary dispersion. Other sources of sulphur to the soils of some areas are deposits of gypsum or barite, or evaporite formations particularly. Such occurrences are rare in the Notre Dame Bay area. It is important to note that much of the discussion concerns the dispersion of sulphur compounds independent of the source but attempt is made to maintain the context of sulphide mineralization as the source with which we are most concerned.

4.1.1 Oxidation of Sulphides

4.1.1.1 Decomposition Reactions

In many cases sulphide deposits consist of a mixture of several sulphide minerals and iron sulphides frequently occur. Consequently, it is not surprising that the oxidation of most other metal sulphides is related to the oxidation of pyrite where they occur together. Most sulphides will oxidize slowly on air to form sulphates, such as lead sulphides (Lamey, 1966): $PbS + 4O \longrightarrow PbSO_4$

However, as Buehler and Gottschalk (1912) point out, the solubility of other sulphides is increased in the presence of pyrite or marcasite and oxidation is promoted. Lamey (1966) has outlined these reactions involved in the oxidation of pyrite:

$$FeS_2 + 7O + H_2O \rightarrow FeSO_4 + H_2SO_4 \quad (1)$$

$$2FeSO_4 + H_2SO_4 + O \rightarrow Fe_2(SO_4)_3 + H_2O \quad (2)$$

$$6FeSO_4 + 3O + 3H_2O \rightarrow 2Fe_2(SO_4)_3 + Fe_2(OH)_6 \quad (3)$$

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + H_2SO_4 \quad (4)$$

The production of ferric sulphate by (2) and (3) and H_2SO_4 by reactions (1) and (4) is the important factor as these are oxidizing agents which promote the further decomposition of other sulphides, which may be oxidized by these reactions:

chalcocite

$$Fe_2(SO_4)_3 + Cu_2S \rightarrow CuSO_4 + 2FeSO_4 + CuS \quad (5)$$

$$Fe_2(SO_4)_3 + CuS + 3O + H_2O \rightarrow CuSO_4 + FeSO_4 + H_2SO_4 \quad (6)$$

galena

$$Fe_2(SO_4)_3 + PbS + 3O + H_2O \rightarrow PbSO_4 + 2FeSO_4 + H_2SO_4 \quad (7)$$

sphalerite

$$2Fe_2(SO_4)_3 + ZnS + 3O + H_2O \rightarrow ZnSO_4 + 2FeSO_4 + H_2SO_4 \quad (8)$$

chalcopyrite

$2Fe_2(SO_4)_3 + Cu\,Fe\,S_2 \rightarrow CuSO_4 + 5\,Fe\,SO_4 + 2S$ (9)

bornite

$Cu_5FeS_4 + H_2SO_4 + 18O \rightarrow 5\,CuSO_4 + FeSO_4 + 2H_2O$ (10)

Equation (9) is interesting because the sulphur produced may be oxidized to H_2SO_4 or to SO_2, which may escape to the surrounding air. Reactions of this type may contribute to the production of SO_2 haloes about sulphide deposits.

Many of these reactions produce ferrous sulphate and sulphuric acid. The ferrous sulphate is oxidized to ferric in the presence of oxygen and sulphuric acid and the ferric sulphate can in turn attack more sulphide, repeating the process.

4.1.1.2 Role of Bacteria

Bacteria occur throughout the surface environment and thrive in the acid conditions of oxidizing sulphide deposits. The presence of bacteria of the genus Thiobacillus and the genus Ferrobacillus promote the decomposition of sulphides considerably (Mulder and van Veen, 1968; Starkey, 1966). The species Thiobacillus ferrooxidans and Thiobacillus thiooxidans are most important but Ferrobacillus ferrooxidans and Thiobacillus concretivorous also often contribute (Lamey, 1966). Their essential functions are the oxidation of ferrous sulphate to ferric sulphate and elemental sulphur to sulphuric acid:

$$4\,FeSO_4 + 2\,H_2SO_4 + O_2 \xrightarrow{bacteria} 2\,Fe_2(SO_4)_3 + 2\,H_2O \qquad (11)$$

$$2S + 3O_2 + 2H_2O \xrightarrow{bacteria} 2H_2\,SO_4 \qquad (12)$$

The amount of decomposition due to the action of microbes is considerable and studies have been made of the feasibility of using microbes to leach metals from low grade ores and mine dumps (Lamey, 1966, Duncan and Drummond, 1973). Kramarenko (1969) found that ten times more copper dissolved from chalcopyrite and one hundred times more iron plus eight times more copper from pyrite ore in the presence of T. ferrooxidans than without the bacteria.

Sutton and Corrick (1963) have shown that bacteria are effective in dissolving copper from several copper minerals as well as oxidizing iron and sulphur (Table 14). In addition, other work has shown that sulphides such as sphalerite and molybdenite may also be attacked and significant amounts of metals dissolved (Lamey, 1966). It is evident that the importance of bacteria in the oxidation and supergene enrichment of sulphide ore deposits is frequently underestimated.

4.1.1.3 Rate of Oxidation

The rate of oxidation of a sulphide deposit is dependent mainly on two factors: (1) the pH and (2) the position of the groundwater table, apart from usual pressure-temperature effects, of course. The pH determines the activity of the hydroxyl ion (Garrels, 1954), the solubility of ions or compounds concerned, and influences the activity of

Table 14: Results of Leaching of Copper Minerals by Various Microbes (after data of Sutton and Corrick, 1963).

		Material Oxidized		Some Results	
Bacteria	pH Conditions	Ferrous Iron	Elemental Sulphur	Greatly Accelerate Dissolution of Iron from Pyrite and Chalcopyrite	Can bring about dissolution of significant amounts of copper from chalcocite, covellite and bornite
Ferrobacillus ferrooxidans	Active if pH below 4.5	x		x	x
Thiobacillus ferrooxidans	Active if pH 6.0	x	x	x	
Thiobacillus concretivorous			x		

the bacteria. Under acid conditions Thiobacillus and Ferrobacillus are much more efficient in decomposing sulphides (Figure 16, after Sutton and Corrick, 1963).

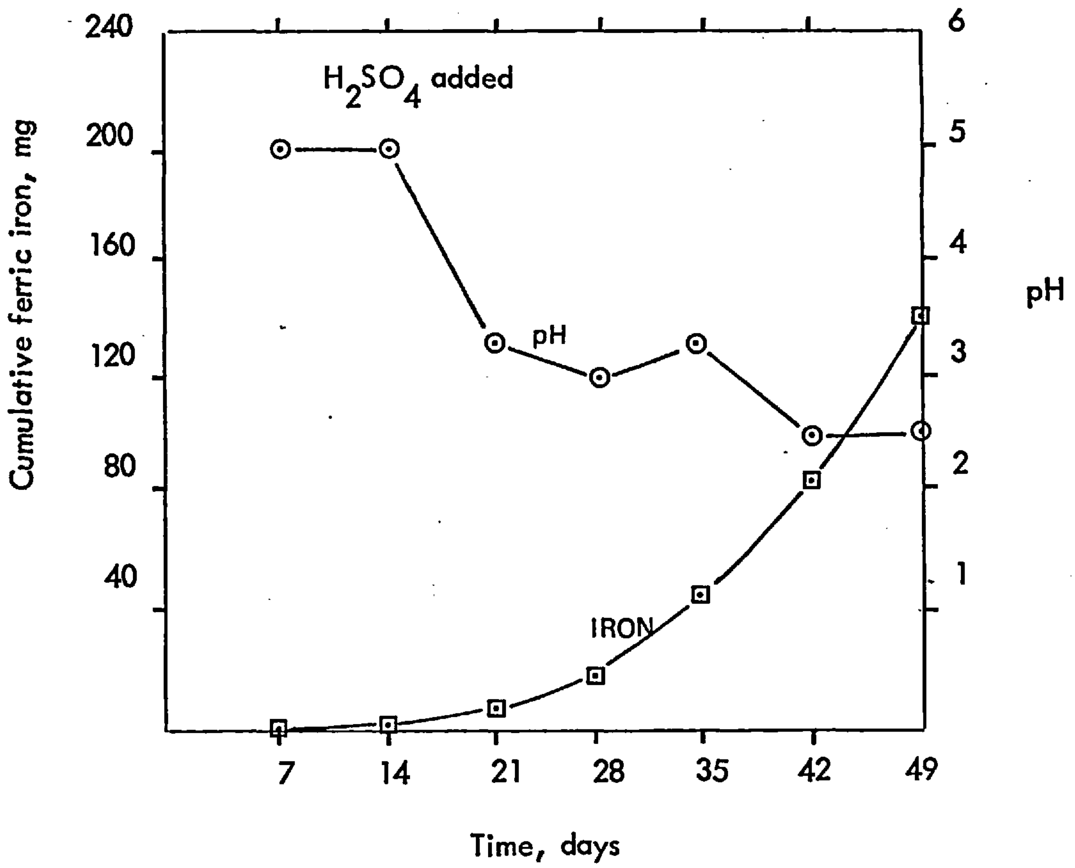
The position of the groundwater table influences the amount of oxygen in contact with the sulphides and the ions available to neutralize the H_2SO_4 produced. Generally, parts of a sulphide deposit below the groundwater table or in contact with CO_2-rich waters are very slowly oxidizing or stable under reducing conditions, whereas above the water table conditions are strongly oxidizing. The greatest rates of oxidation occur where the water table fluctuates frequently or at least where there are alternating wet and dry periods.

4.1.1.4 Sulphur Compounds Released to the Environment

Sulphur is released to surrounding waters from oxidizing sulphide mineralization as sulphate, partly as H_2SO_4, and is dispersed in aqueous solution over distances dependent on the solubility of the various ions in solution. For example, if cations such as lead or barium are abundant in the waters, insoluble sulphates may precipitate fairly close to the original deposit. Generally, however, sulphate is maintained in solution and fairly widely dispersed in surrounding waters.

Sulphate dispersed in groundwater may be absorbed or bonded to various compounds in surrounding soils or taken up by plants and used for nutrition and recycled biochemically. Some sulphate remains in solution in surface waters and is carried by surface drainage to the sea.

Figure 16: The effect of pH on the ability of <u>F.ferrooxidans</u> to oxidize iron in chalcopyrite (after Sutton and Corrick, 1963)



Under oxidizing conditions some SO_2 is produced from sulphides above the water table and this may be held in the air in the pores of overlying soils or released to the atmosphere.

4.1.2 Dispersion of Sulphur Compounds in Soils

4.1.2.1 Mechanisms

The principal mechanism for the dispersion of sulphur in soils is aqueous transport of sulphate in capillaries and pore spaces of soils, in circulating groundwaters, and in surface drainage. Hydromorphic dispersion is supplemented to a limited extent by mechanical dispersion of sulphide grains by streams as sediment and movement of grains by gravity downslope from a deposit after release by weathering processes. In arctic regions the action of frost and freezing of groundwaters may give rise to a movement of sulphide grains and sulphate away from weathering bedrock into overlying soils or surrounding drainage channels.

4.1.2.2 Biogeochemical Dispersion

Considerable amounts of sulphur are taken up as sulphate by plants from groundwater and mineral constituents of soil and used as a nutrient. (Esminger and Freney, 1966).

Bondarenko (1968) has shown that humic and fulvic acids of organic soils can dissolve considerable amounts of sulphides with the formation of chelates of metals with these acids and precipitation of sulphates. In general, however, plants receive sulphur as sulphate and form reduced sulphur compounds in a variety of organic combinations during metabolic processes (Allaway and Thompson, 1966). The sulphur is returned to the soil in organic form in leaf litter, plant residues and so on.

The importance of plants in the distribution and movement of sulphur in soils is illustrated by Bertramson, et al.,(1950) in a study of sulphur in soils and crops in Indiana. It is pointed out that the sulphur balance of a soil involves the following factors: (1) sulphur brought down by precipitation; (2) sulphur removed by crops; (3) the total sulphur reserves in the soil and its availability for crop use; (4) sulphur directly absorbed by the soil from the atmosphere; (5) sulphur absorbed by the plants from the atmosphere; (6) sulphur leached from the soil; (7) loss by erosion; and (8) sulphur returned to the soil as plant residues, manures, and fertilizers.

Once sulphur compounds are released in solution from an oxidizing sulphide deposit and into the soils, secondary biogeochemical dispersion via plants is a major influence on its distribution.

4.1.3 Iron and Aluminium Hydroxides and Clays

4.1.3.1 Adsorption of Sulphate

Sulphate from the oxidation of sulphides or other sources is held in the soils by adsorption onto hydrous Fe and Al oxides (Chao, et al., 1962, 1964), making the B horizon potentially the most suitable for geochemical sampling. Chao, et al., (1962) and Harward and Reisenauer (1966) have shown that minor amounts of sulphate are also adsorbed by clays, with kaolinite adsorbing more than montmorillonite, illite, or bentonite. In forest soils the proportion of sulphate adsorbed by clay minerals is usually small compared to the effect of Fe and Al hydroxides.

A mechanism for the adsorption of sulphate by Al hydroxides is proposed by Chang and Thomas (1963) involving replacement of OH^- ions by $SO_4^=$ coupled with neutralization of these OH^- ions by H^+ ions formed by the hydrolysis of Al. Retention in abundant small pores in soils rich in Fe and Al oxides may also contribute to the total amount held (Harward and Reisenauer, 1966).

The amount of inorganic sulphate adsorbed is related to the content of Al and Fe oxides, clays, and to the pH of the soil. Chao, et al. (1964, 1965) found that sulphate adsorption increases for the Fe system with decreasing pH and the Al adsorption gives a maximum at pH 4.0. At lower pH values, dissolution of the hydrous Al oxide phase decreases the sulphate adsorption capacity of the soil.

4.1.4 Organic Matter

4.1.4.1 Organic Sulphur Compounds

The organic matter content of any soil directly influences the total sulphur content of the soil because virtually all soil organic material contains sulphur in one form or another. L.E. Lowe (1964) found in studying the sulphur fractions of some Canadian soils that organic forms accounted for over 97% of the total sulphur of organic soils and from 53-90% of the total in mineral soils. Only in the C horizons of some Chernozemic profiles did inorganic sulphate reach very significant levels (Lowe, 1965).

Carbon-bonded sulphur is the dominant single component of most organic soil whereas the organic sulphate fraction, consisting of ester sulphates and alkyl sulphones, may predominate in mineral soils (Lowe, op. cit.). Of the carbon-bonded sulphur, a large part (30-40%) is in the form of amino acids, cysteine and methionine chiefly, and the remainder is undetermined but probably associated with humic acids, being inert to extraction even with hot H_2O_2 or HF (Lowe, 1965, 1969). A small amount of sulphated polysaccharides may occur in some surface horizons but usually accounts for less than 2% of the total sulphur of the soil.

The sulphur fractions of some soils of the Chernozemic, Podzolic, and Gleysolic orders in Quebec and Alberta are presented in Table 15, from data by L.E. Lowe (1964, 1965, 1969). The fractions designated are explained as follows: "Carbon-bonded" represents all organic forms other than ester sulphates and alkyl sulphones; "HI-reducible" is organic sulphates plus inorganic sulphur; and "adsorbed plus soluble" is essentially inorganic sulphate. Tabatabai and Bremner (1972) divided the "HI-reducible" fraction into inorganic S and ester

Table 15: Distribution of sulphur fractions in soils of the Gleysolic, Chernozemic and Podzolic orders (range, with means in parentheses). After Lowe (1969, 1964).

Soil Order	Hor.	No. of Samples	Total S (ppm.)	Easily soluble sulphate (ppm. S)	HI-S (ppm.)	C-S (ppm.)	N: total S	N: C-S
Gleysolic	LH	3	599-4020 (2183)	20-160	589-1723	363-1788 (1008)	6.3-15	9-24 (19)
	Ah	8	187-5010 (1539)	13-257	194-1510	137-1770 (708)	3.0-30	7-39
	Bg	11	72-869 (205)	2-634	33-1072	8-162 (60)	1.3-10	7-46 (24)
Chernozemic	Ah	8	262-576 (435)	8-27	142-353	42-126 (74)	5.4-9.6	38-50 (43)
	Bm	8	101-431 (273)	5-162	57-371	10-30 (22)	2.7-6.9	42-86 (58)
Podzolic	LH	7	279-1094 (700)	5-75	111-296	55-331 (190)	11-15	33-64 (50)
	Bt	7	60-110 (80)	0-10	19-52	7-19 (12)	3.5-9.3	25-64 (40)
Peat			(4580)	(27)	(2312)	(2160)		
Muck			(6450)	(88)	(3240)	(3710)		

sulphates. They found that for 37 Iowa soils inorganic S accounted for 1-5% of the total S, ester sulphate 50% and carbon-bonded 11%.

It is quite evident from Table 15 that the bulk of the sulphur in soils is contained in the surface horizons and held in organic combination, and this must be borne in mind in the interpretation of any studies of sulphur in soils in relation to sulphide deposits.

4.1.4.2 Adsorption

Organic matter content also affects significantly the amount of sulphate adsorbed by any particular soil. Chao, et al. (1962) found that removal of organic matter from a soil reduced its sulphate adsorption capacity by one-third to one-half, but in the light of the data from Lowe (op. cit.) at least some of the sulphate may not be actually adsorbed but bonded in organic molecules and still extractable with the solvents used. At any rate, the amount of sulphate retained by organic matter is significant in relation of total adsorption capacity.

4.1.4.3 Decomposition

Circulation of the sulphur in soils, especially that in organic form, is accomplished by return to the soil as leaf litter and plant remains. These materials help make soil humus, and the organic sulphur compounds decompose, yielding sulphate as the dominant end product of the decomposition (Freney and Stevenson, 1966). Frederick, et al.

(1957) found that cystine (eine), taurine, sulfosalicylic acid, and thiamine, when added to soil, decomposed under aerobic conditions to give sulphate. Methionine, on the other hand, did not yield sulphate on decomposition, but volatile methylthiol and dimethyl disulphide. The latter point may be significant as a source of volatile organic sulphur forms involved in the dispersion of Hg in soils (Evans, 1971; Booer, 1944; and Jonasson, 1970).

4.1.5 Leaching

Leaching of the soil, important in the case of podzols, affects the sulphur distribution in two ways: Firstly, leaching tends to remove free or adsorbed sulphate from the mildly acid surface horizons (Harward and Reisenauer, 1966). Secondly, sesquioxides are leached from the near surface horizons where the redox potential is higher and precipitated at lower depths in the B and C horizons of the profile (McKenzie and Erickson, 1954). This gives the mineral B and C horizons an increased adsorption capacity for sulphate and leaves the leached A_2 horizon in particular with a low adsorption capacity. What sulphur is contained in the A_2 horizon therefore is held in the little organic material remaining or adsorbed onto the positively charged edges of clay particles.

Bertramson, et al. (1950) found that on agricultural land in Indiana, some 37% of soil sulphur was removed annually by leaching and erosion. This appears to be a great amount of loss but it must be weighed against the amounts added to the soil from groundwaters, the atmosphere and, in this case, as fertilizer. Even on forest soils, however, leaching certainly has a significant affect on the redistribution of sulphur compounds.

4.1.6 Variations of Soil Sulphur Distribution with Region and Soil Type

Factors in the foregoing discussion such as leaching apply to podzols more than to some other soil groups, but on the other hand, adsorption onto clays may be more important in a soil developed on deposits of clay or derived from clay-rich bedrock. It is expected that sulphur distribution in the Chernozems of the plains of America and the U.S.S.R., which contain thick accumulations of organic material, is much more dependent on vegetation type, depth of root penetration, degree of humification and similar factors than on Fe oxide content for example, as those soils would contain the bulk of the sulphur in organic form and adsorption unto oxides would be of less significance. Also, in the case of gleysols the sulphur distribution is dependent on the level of the gleying, as this usually marks the boundary between areas with oxidized or reduced forms.

The soils of the Newfoundland field area are largely forest soils of the Podzol group, to which the factors discussed in the previous sections especially apply.

4.2 PRESENTATION OF DATA - RENDELL JACKMAN AREA

The potential application of sulphur dispersion in soils as a guide in the exploration for sulphide deposits was investigated in four areas, namely the Rendell Jackman, Sterling, and Pilley's Island prospects, and a mineral occurrence known as the Dawes Pond showing (see Figure 1 for location).

4.2.1 Geology and Mineralization

The Rendell Jackman prospect is a small lenticular deposit of massive banded pyrite-chalcopyrite mineralization occurring in schist zones in Ordovician tuffs of the Lush's Bight Group (De Grace, 1971). It is situated about 1 mile south of the town of King's Point, about 10 miles west of Springdale. Exploration shafts were sunk on the deposit during 1910-12 and again in the 1930's and more than 11,000 tons of low grade ore located, though none was shipped. Diamond drilling was conducted by Brinex, Kontiki Mines Ltd., and the Geol. Surv. of Nfld., but failed to locate further concentrations of ore beyond the two lenses already discovered.

The mineralization is predominantly pyrite, with bands of chalcopyrite, and minor amounts of sphalerite and gold, with grades in the extracted ore averaging about 1.0% copper. The ore is thought to have been emplaced early in the genetic sequence and remobilized into the schist zones during later tectonism, with some enrichment of chalcopyrite in the fold hinges (Kennedy and DeGrace, 1972).

The area is covered by shallow glacial moraine with a moderately developed podzolic profile. The soil has been disturbed by mining activity in the immediate vicinity of the deposit but elsewhere is in place under original forest cover.

4.2.2 Large Scale Coverage

A total of 661 samples from a soil survey of the Rendell Jackman area conducted by Brinex in 1966 were analyzed for total sulphur content by Leco combustion and a summary of the results is presented in Table 16. The samples were taken at intervals of 100 ft. on lines 800 feet apart, and cover an area of 1.72 sq. mi. mainly west of the Rendell Jackman deposit.

4.2.2.1 Distribution in the Vertical Profile

The data from the survey confirmed the predicted enhancement of sulphur in the humus coupled with depletion in the A_2 horizon (Figure 17). Comparison of the mean contents shows a six-fold decrease from the A_1 to the B horizon, which reflects the difference in organic matter content. The grey, leached material of the A_2 horizon is conspicuously low in sulphur, with 32% of the A_2 values falling below the detection limit of 20 ppm. This is indicative of the low adsorption capacity of this horizon and the effect of leaching on the sulphur distribution in podzols.

Soil Horizon	Total Sulphur, ppm.			Number of Samples
	Arithmetic Mean	Range	Standard Deviation	
A_1 Humus	1330	100-6000	817	222
A_2 Leached	75	0-600	86	121
B Oxide-rich	237	0-1400	187	318

Table 16: Concentration of sulphur in Podzol soil horizons, Rendell Jackman area.

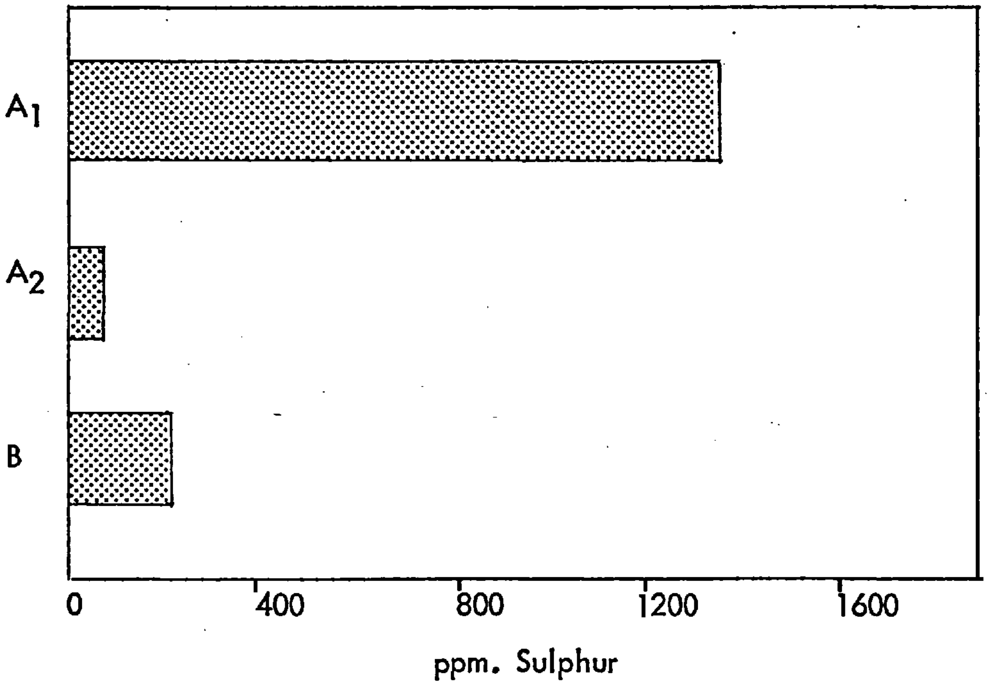


Figure 17: Mean contents of total sulphur in various soil horizons, Rendell Jackman area.

4.2.2.2 Treatment of Data

The "less than" cumulative frequency distributions of total sulphur values for the different horizons using raw data have been plotted in Figure 18. Plotted on log-probability paper, the linearity of the main portions of the plots indicates that the distributions in each case approximate to lognormal distribution.

To facilitate the interpretation of the data, and to attempt to correct for the difference in the sulphur content of the horizons due to difference in organic content, the sulphur values for the A_1 and A_2 groups, plus a few samples containing mixed A_1-A_2 material, were expressed as B horizon equivalents. This conversion was carried out on $\log_{10}$ transformed data using the following expression (after Meyer, 1969):

$$X_{iB} = 10^{\left(\frac{\text{Log}_{10} X_i \; - \; \bar{X} \text{ Log}_{10} A}{\sigma \text{Log}_{10} A} \right) \sigma \text{Log}_{10} B \; + \; \bar{X} \text{ Log}_{10} B}$$

where X_{iB} = Element value (p.p.m.) of alternate horizon expressed as B horizon equivalent.

$\text{Log}_{10}\ X_i$ = Log of element p.p.m. from alternate group.

$\sigma\text{Log}_{10}\ A$ = Standard Deviation of Log Data for alternate group.

$\sigma\text{Log}_{10}\ B$ = Standard Deviation of Log Data for B horizon.

$\bar{X}\ \text{Log}_{10}\ B$ = Mean log of B horizon data.

$\bar{X}\ \text{Log}_{10}\ A$ = Mean log of alternate group.

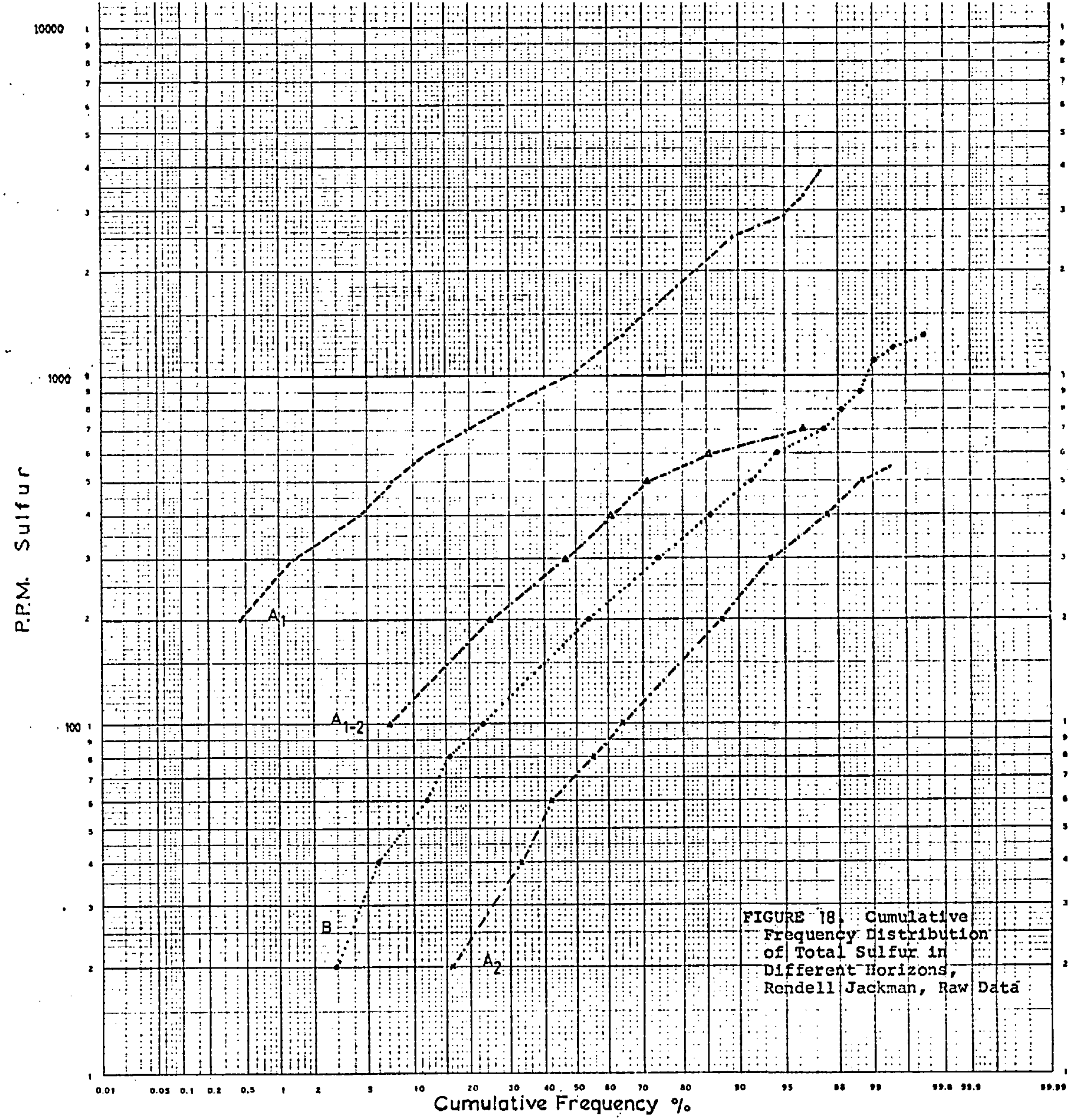


FIGURE 18. Cumulative Frequency Distribution of Total Sulfur in Different Horizons, Rendell Jackman, Raw Data

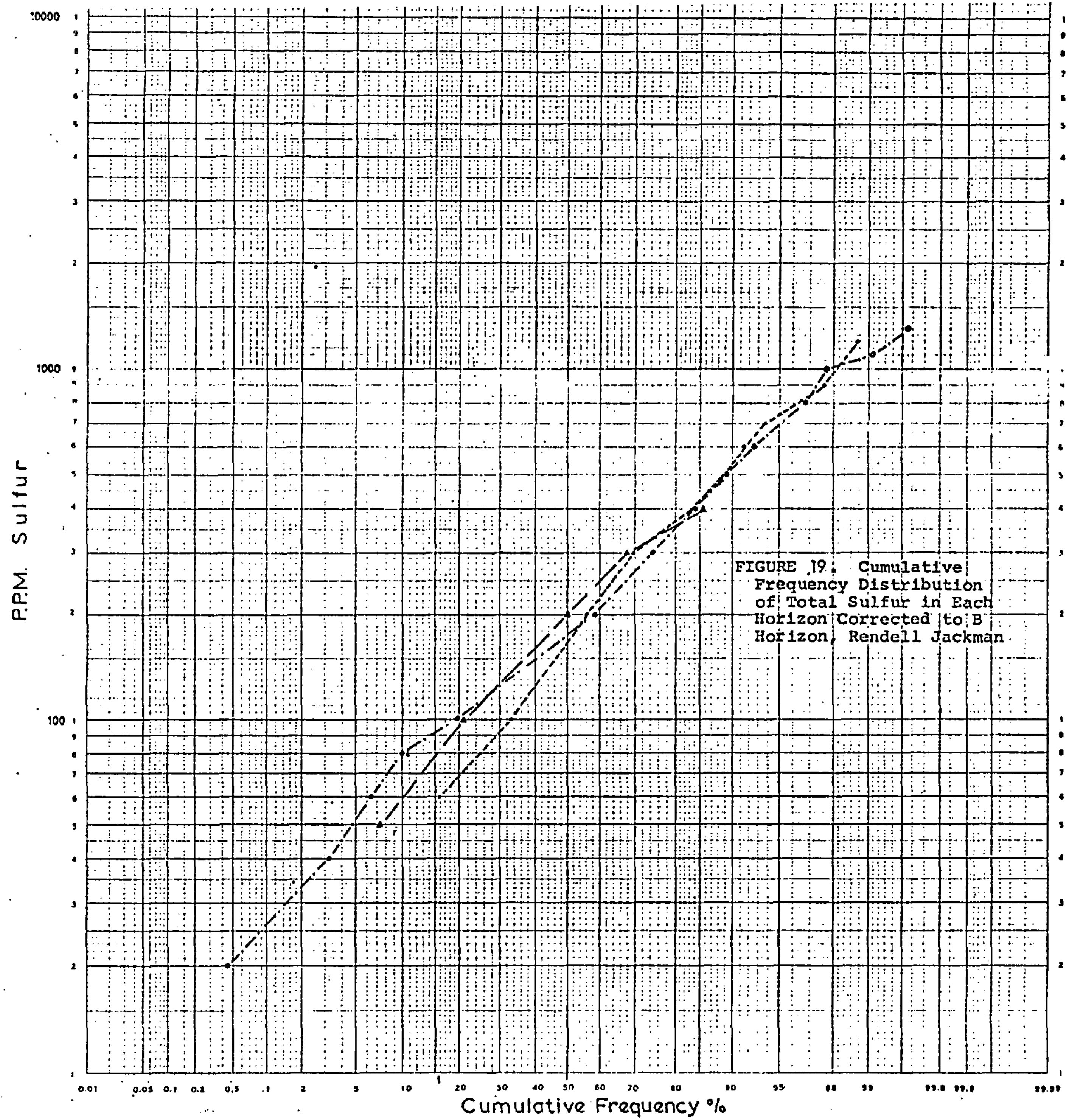


FIGURE 19. Cumulative Frequency Distribution of Total Sulfur in Each Horizon Corrected to B Horizon, Rendell Jackman

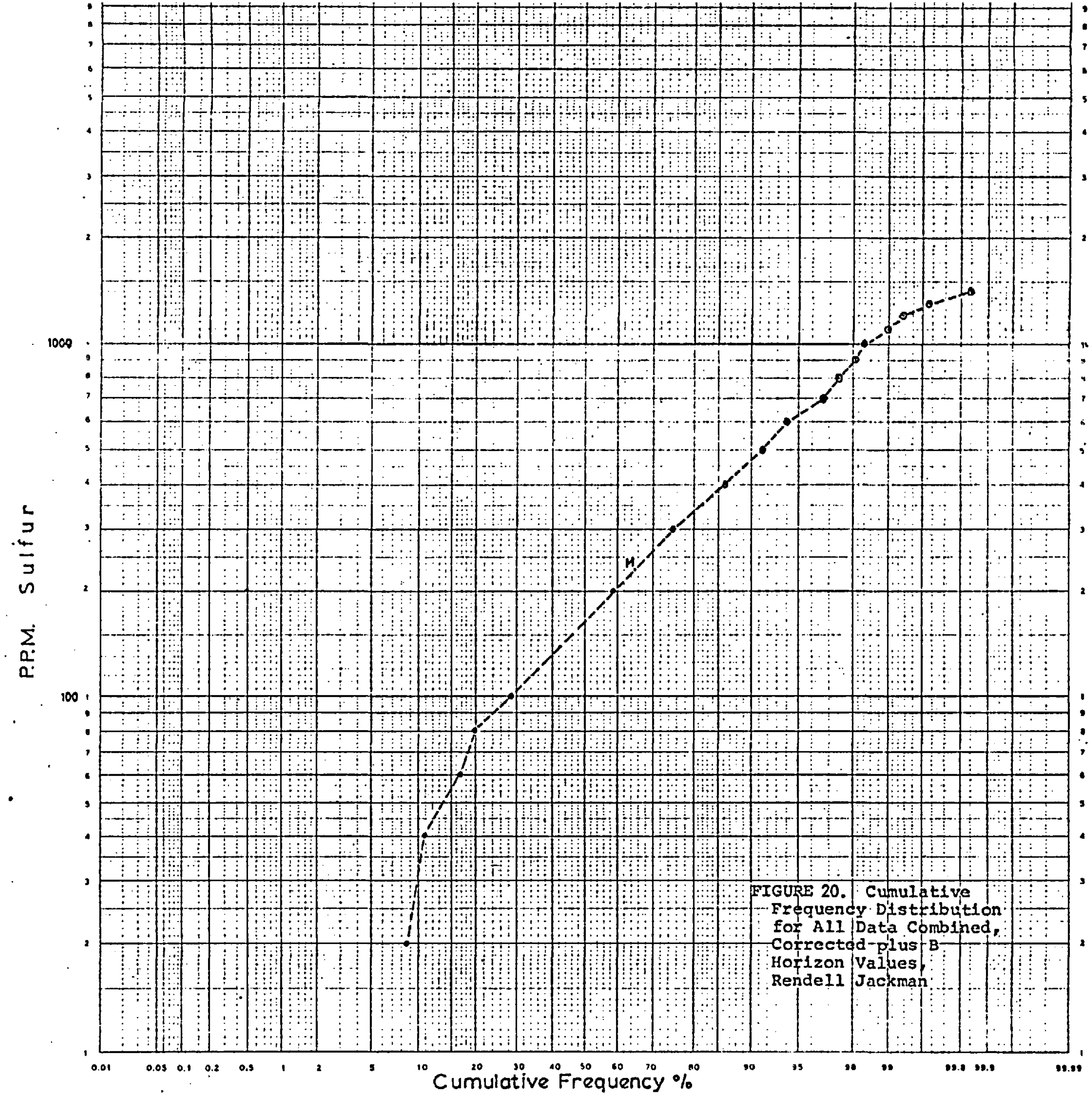


FIGURE 20. Cumulative Frequency Distribution for All Data Combined, Corrected plus B Horizon Values, Rendell Jackman

Interpretation of the sulphur patterns produced by expression of all the data as B horizon equivalents in this manner does not adequately correct for the variance in sulphur due to organic matter content and had organic carbon estimates been available for this survey a more valid interpretation could have been made using a regression of sulphur in terms of organic content as discussed in section 4.2.4. The corrected data does, however, show more meaningful patterns than the raw data.

Figure 19 gives the cumulative frequency distribution of the data for each group expressed as B horizon equivalents and Figure 20 is a similar plot for all data combined.

4.2.2.3 Interpretation of Patterns Produced - Correlation with Other Variables

The corrected total sulphur patterns and copper highs from this survey are shown on the map in Figure 21. Two trends of moderate copper values occur across the south portions of lines 24E, 32E and 40E which have corresponding sulphur build-up in the 500-600 ppm. range. Elsewhere, however, the correlation is not good, as the copper high on line 88E north of Bean Pond has no sulphur anomaly with it, and many sulphur highs occur without the association of any discernible copper.

Most of the anomalous sulphur values can be seen to coincide with swampy or boggy areas. These in most cases support moss, grasses, bushes and shrubs, but in some instances are marginally to almost completely wooded. The latter areas are classed as "seasonal forest swamps" (Meyer, unpublished report, Brinex, 1966) because restricted drainage promotes

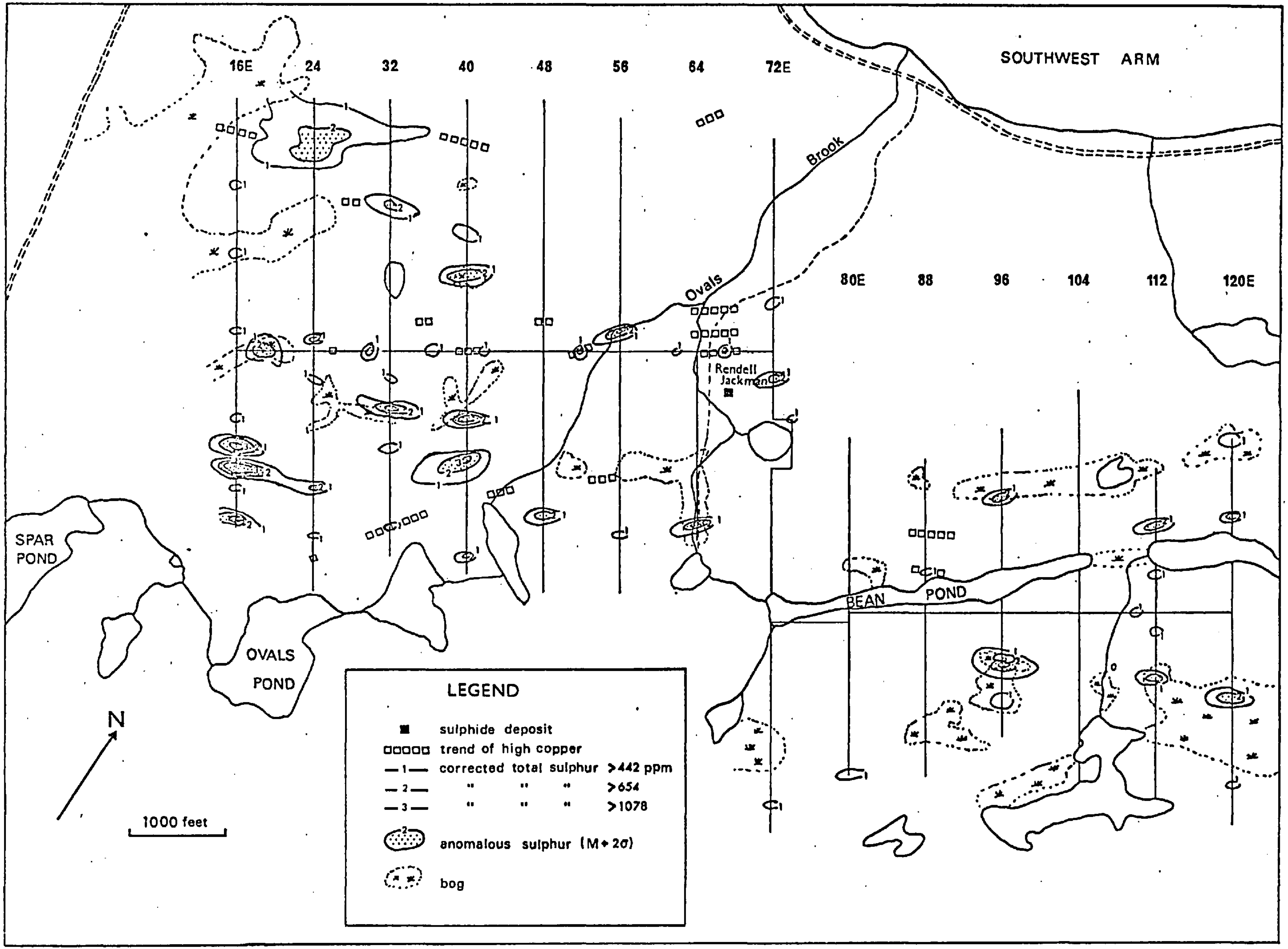


Figure 21: Total sulphur (corrected) and copper patterns from the 1966 soil survey in the Rendell Jackman area.

flooding of these areas in the spring, but the surface may dry during summer.

It is suggested that samples from bogs have abnormally high sulphur content for two reasons: 1) a very high proportion of the sample is organic material and 2) the vegetation types from which the bog material is derived contain more sulphur than those contributing to forest soil. That is to say, Sphagnum moss, grasses and Ericaceous shrubs appear together to retain more sulphur in their structures than do the coniferous and deciduous trees contributing organic debris to the forest soils. Restricted drainage in bogs may also play an important role, as samples from bogs occasionally smell of H_2S.

High organic content accounts for higher sulphur values in the humus horizons of forest soils as well as in bogs, but after a statistical correction is applied there are still residual sulphur anomalies occurring in some bog areas. These are considered due to the second factor, vegetation type, and although insufficient data was obtained to produce reliable estimates of the sulphur in the mosses and shrubs of the bogs in the Rendell Jackman area, determination of a factor based on the average contents of these plants in the area of a particular survey should discriminate between sulphur from this source and that which may arise from mineralization.

Two areas of high sulphur found in the soils of the Rendell Jackman area were considered significant, however, from the point of view that the source may possibly be sulphide mineralization. The first (area A) is a wide, low-amplitude anomaly near the north end of line 24E, occurring in a rather flat-lying area with an arc of bog to the NW, W, and S sides. It is developed in good B horizon soil and although it has no coincident copper anomaly, it is significant in relation to an I.P. anomaly just to the west (Tikkanen , unpublished report, Brinex, 1967).

The second (area B) occurs near the south end of line 16E. Although some of the high values occur in a seasonal forest swamp, the anomaly is considered significant because of its high relief and because of a trend of copper values across the lines to the east. Both areas A and B were followed-up with detailed sampling and the results are presented in section 4.2.3.

4.2.3 Detailed Investigations

4.2.3.1 Sulphur and Metals in Soils Adjacent to the Rendell Jackman Prospect

Soil samples collected from the B horizon at intervals of 100 feet across the axis of the sulphide mineralization provide striking evidence of the improvement in contrast and width shown by sulphur when compared to copper, lead and zinc (Figure 22). This strong sulphur pattern is not surprising in view of the ratio of sulphur (30-35%) to copper ($< 2\%$) and other metals in the ore. The increased width may be due to a primary halo of disseminated pyrite, a feature common to many sulphide deposits (Shishakov, et al. 1968) which could provide the advantage of a larger primary source when applying sulphur analysis in geochemical exploration.

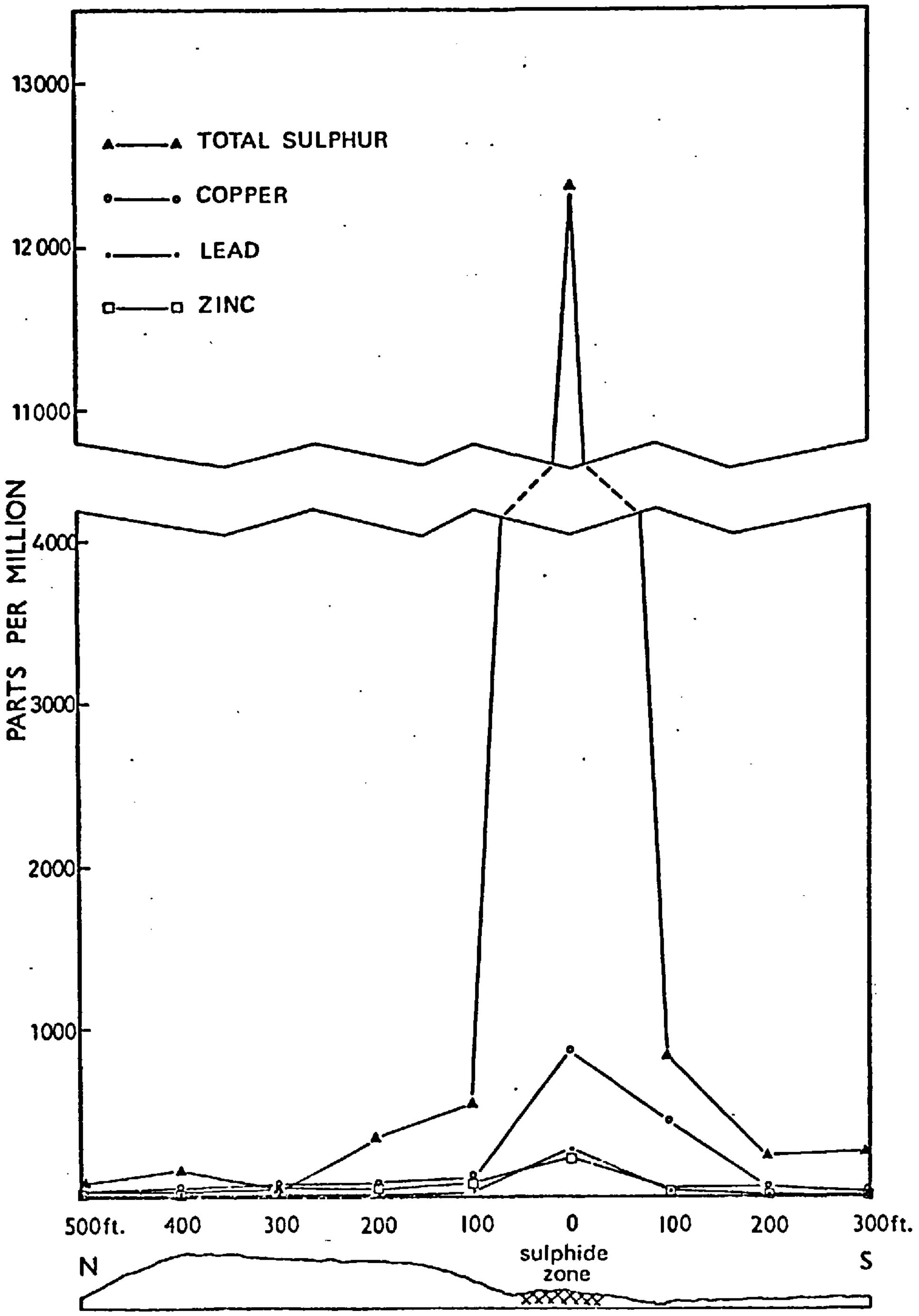


Figure 22. Total sulphur, copper, lead and zinc in B horizon soils collected across sulphide zone at Rendell Jackman prospect.

The total sulphur values on this traverse were corrected for organic matter content using the regression derived from data from the large scale survey (see section 4.2.4) and the corrected data shown in relation to the original values in Figure 23. It is evident from the similarity of the two plots that in this area the enhanced sulphur values are due almost entirely to the presence of sulphides and not to organic matter.

4.2.3,2 Follow-up in Line 16E - 24E Area

The broad sulphur anomaly at the north of line 24E was investigated by sampling at 100 ft. intervals across the area between L16E and L24E in the vicinity of the anomaly to see if it was continuous to the west and north and whether it could be related to the induced polarization (I.P.) anomaly occurring on L16E. The results are plotted in Figure 24 and show that there is a broad area of moderate sulphur values across this region.

Diamond drilling by Brinex in 1967 on the I.P. anomaly on L16E (see Figure 24 for location of holes) intersected a narrow zone of pyrite, pyrrhotite and magnetite mineralization at a depth of about 320 feet and it appears probable that this zone of iron sulphides may extend to the northeast and be responsible for both the I.P. anomaly and the moderate sulphur build-up in the area. Without further drilling, however, this conclusion could not be established.

No Cu, Pb or Zn anomalies were found in the follow-up sampling.

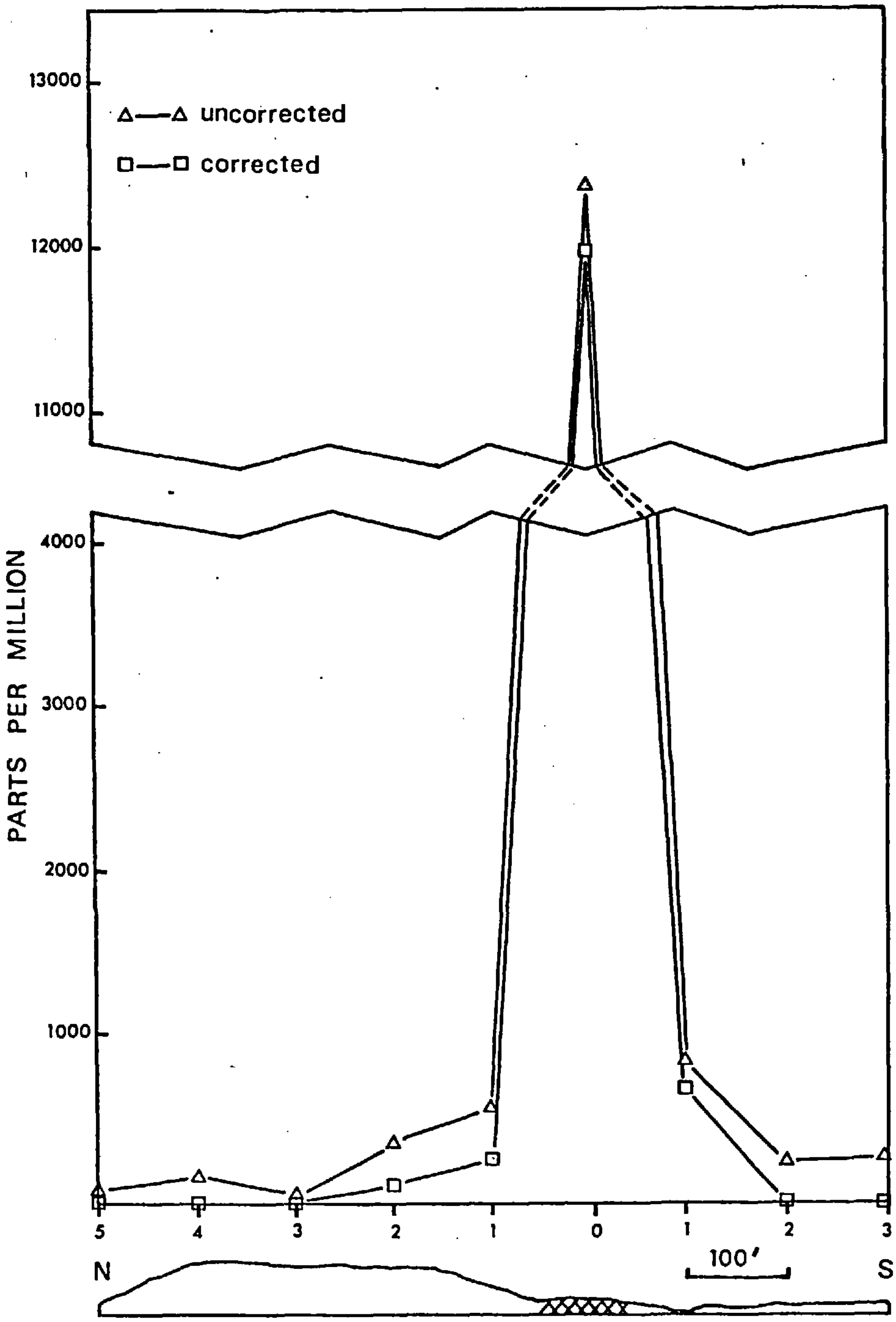


Figure 23. Corrected total sulphur data in relation to original values in B horizon soils across a sulphide zone at Rendell Jackman.

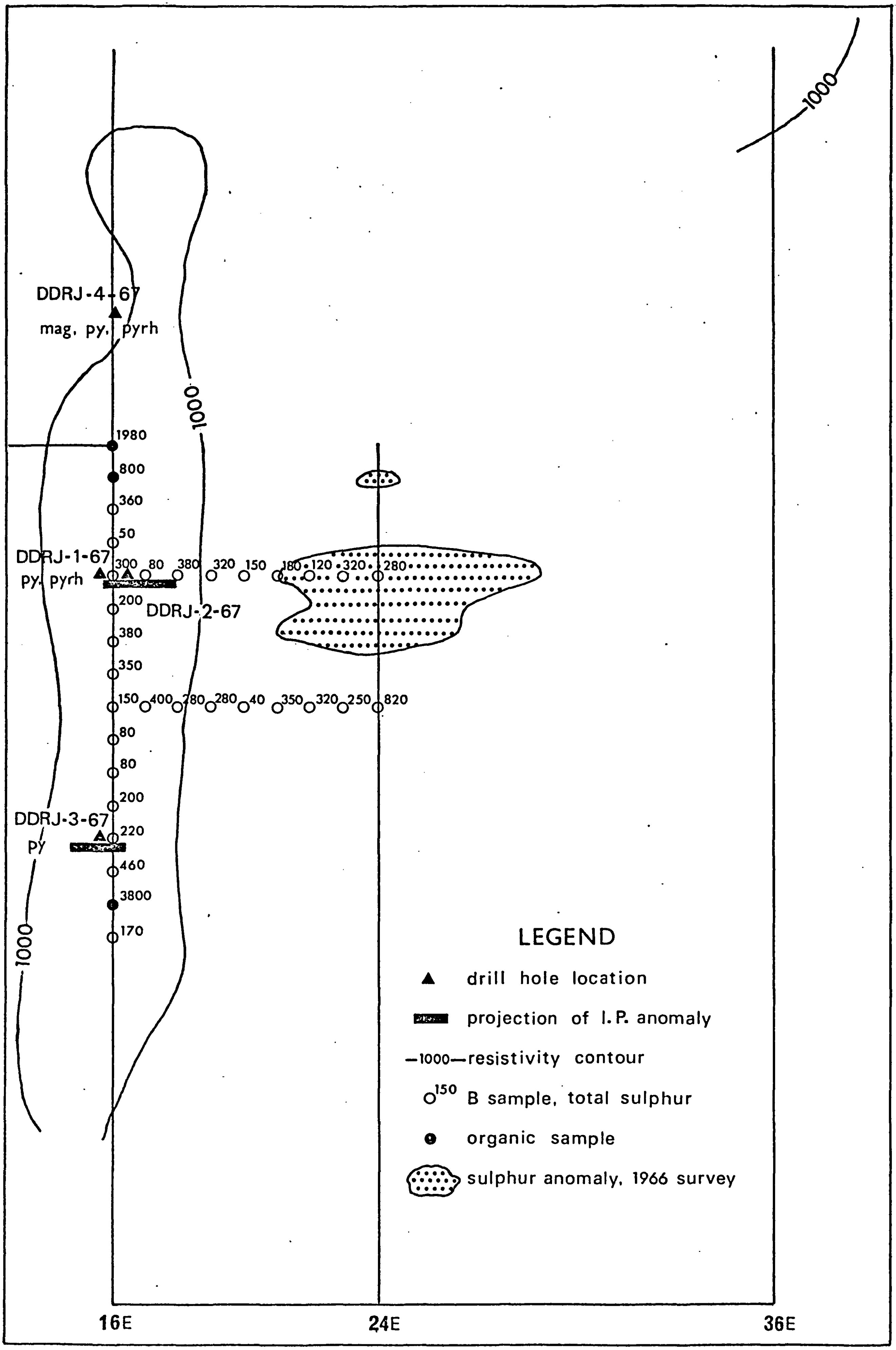


Figure 24: Total sulphur in detailed samples in the L16E-24E area, Rendell Jackman.

4.2.3.3 Vertical Profiles in Bogs

Several bogs in the Rendell Jackman area were sampled at various depths to obtain data on sulphur distribution in peat bogs as these were shown in the large scale survey to be conspicuously high in sulphur content, and this was not purely a function of organic matter content but also of factors peculiar to bogs such as plant type, restricted drainage and local chemical conditions. Interpretation of sulphur patterns from a soil survey in this type of terrain must take into account these differences between the peat bog environment and that of the forest soil.

Table 17 shows that in each case total sulphur content increased with depth in the bogs, which is opposite to the case of podzols, where sulphur generally decreases with depth as a function of organic matter content (see sections 4.2.2.1 and 4.4.4). The increase with depth is interpreted as due to humification or decay of the organic material, during which there may be an increase in the proportion of sulphur relative to total organic matter. An increase in the carbon content and in the carboxyl activity with increasing humification is noted by Visser (1964) but no data was available on sulphur-containing groups. As most of these bogs are waterlogged and mildly acid, these conditions may promote stabilization of the organic molecules containing sulphur relative to say nitrogenous compounds.

In case 3 grey glacial clay occurring beneath the peat contained only 140 ppm. sulphur compared to 3550 ppm. in the lower sections of the peat.

Table 17: Samples from Different Depths in Bogs of the Rendell Jackman area.

Profile	Sample Depth	Description	pH	Total Sulphur ppm
1	6 in.	Fresh plant material grass and moss, brown	5.15	800
	12 in.	Brown, partly decayed org. matter	5.20	1,500
	18 in.	"	5.28	2,400
2	6 in.	Partly decayed org. brown	5.85	2,080
	12 in.	"	5.63	4,060
3	8 in.	"	5.15	3,100
	12 in.	"	5.17	3,550
	14 in.	grey clay	-	140

It is evident that the sulphur in this peat was not derived from the underlying till clay in any great extent but accumulated with the decay and humification of the bog vegetation.

4.2.3.4 Detailed Sampling in the Ovals Pond Area

Two soil traverses were made in an E-W direction just north of Ovals Pond to determine whether the trends indicated by sulphur and copper in the large scale survey and by the I.P. survey on the south parts of lines 16E, 24E and 28E would lead to an anomaly in that region. The results presented in Figure 25 show that there are some high sulphur and copper values in the area but these are not considered indicative of the presence of much sulphide mineralization.

4.2.4 Regression Analysis of Soil Data

From the large scale 1966 survey fifty B horizon samples were selected at random and analyzed for organic content by loss-on-ignition, sulphur by LECO combustion, and twelve other elements using the emission spectrograph. Sulphur exhibits a strong linear correlation with organic carbon (L.O.I.) and is also significantly correlated with zinc, copper and iron at the 95% confidence level (Table 18).

The variance of the total sulphur values in the soil was analyzed by developing step-wise a regression (computer program devised by Health Sciences Computing Facility, U.C.L.A.) in which the variance of sulphur

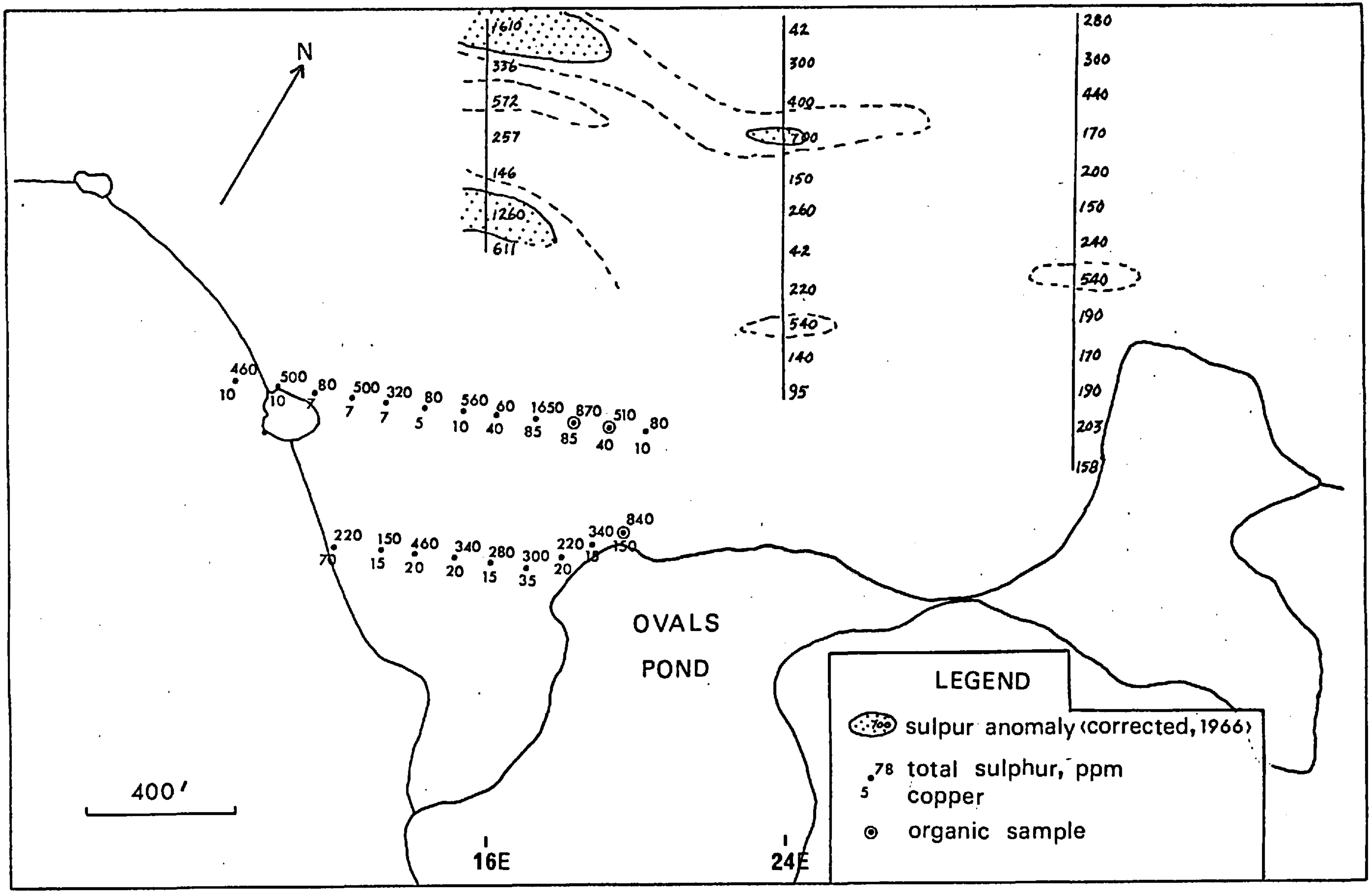


Figure 25. Detailed sampling in the Ovals Pond area.

Table 18 Correlation matrix for 14 analytical variables from analysis of 50 *B* horizon soil samples, Rendell Jackman area. Correlation coefficients greater than ±0.235 are significant at 95% confidence level

Variable	Ag	Ba	Co	Cu	Fe	K	Mo	Mn	Ni	Pb	V	Zn	S	Loss on ignition
Ag	1.000	–0.026	0.008	0.325	0.124	–0.044	–0.065	0.173	0.033	0.129	0.154	0.174	0.205	0.228
Ba		1.000	–0.278	–0.081	0.022	0.338	0.383	0.174	–0.214	0.510	–0.134	0.064	–0.225	–0.238
Co			1.000	0.442	0.088	–0.315	–0.031	0.410	0.708	–0.307	0.360	0.172	0.078	0.017
Cu				1.000	0.125	–0.143	–0.064	0.273	0.346	–0.190	0.197	0.400	0.372	0.445
Fe					1.000	–0.200	–0.073	–0.028	–0.001	0.012	0.337	0.355	0.266	0.281
K						1.000	0.146	–0.051	–0.159	0.504	–0.315	–0.125	–0.077	–0.115
Mo							1.000	0.013	–0.019	0.343	–0.134	–0.126	–0.135	–0.104
Mn								1.000	0.591	0.078	0.324	0.222	–0.154	–0.174
Ni									1.000	–0.281	0.328	0.080	–0.075	–0.057
Pb										1.000	–0.114	0.141	0.103	0.100
V											1.000	0.297	0.042	0.094
Zn												1.000	0.425	0.466
S													1.000	0.790
Loss on ignition														1.000

is estimated in terms of the other thirteen variables. It was found that 60.8% of the variance of sulphur in these samples is accounted for by organic content (L.O.I.) and 23.0% by a combination of Zn and Cu terms, if L.O.I. is ignored. The expression applied to data from several areas in Notre Dame Bay expressing sulphur in terms of L.O.I. is as follows: ppm.S = 16.73 (% L.O.I.) - 26.14.

Conceivably, interpretation of sulphur results from geochemical surveys should best be made on the basis of the variance not accounted for by organic matter content. Examples of the application of the technique are given in sections 4.2.3.1, 4.3.3 and 4.4.2. Brundin and Nairis (1972) have outlined a similar procedure using linear regression for the interpretation of data from stream sediment surveys.

Some element associations significant at the 95% confidence level determined by having mutual correlation coefficients greater than 0.235 (Table 18) are as follows: Ni-Co-Mn-Cu, Pb-Ba-K, Ni-Co-Mn-V, S-L.O.I.-Zn-Cu, and S-L.O.I.-Zn-Fe. With a large number of samples, some of these associations may not hold as well as in these cases but the S-L.O.I.-Zn-Cu and the S-L.O.I.-Zn-Fe appear to be most interesting with respect to dispersion of sulphur and metallic elements from sulphide mineralization.

4.3 STERLING PROSPECT

4.3.1 Geology

The Sterling property is situated about one mile north of the town of Springdale (Figure 1) and is underlain by strongly cleaved basalts and andesites of the Lush's Bight Group of Ordovician volcanics (Smitheringale, 1967). Several small deposits of semi-massive to disseminated pyrite-chalcopyrite mineralization occur within these units, mainly localized in shear zones. Considerable amounts of sulphides have been located by diamond drilling in the area by Brinex but to date the deposits remain uneconomic. Some ore was extracted in the early part of this century from shallow shafts in the Sterling deposit itself but the deposits have not been worked since then.

Although some glacial smearing has taken place in the area, bedrock exposure is fairly plentiful and shallow podzolic soils make up the principal cover.

4.3.2 Relationship of S, Cu and Fe patterns in A and B Horizons to Mineralization.

Sampling of both A and B horizons at each site was carried out at Sterling, in an area just north of Sterling Pond (Figure 26) where a narrow zone of pyrite-chalcopyrite mineralization occurs, trending approximately NE-SW. Disseminated sulphides occur at various other

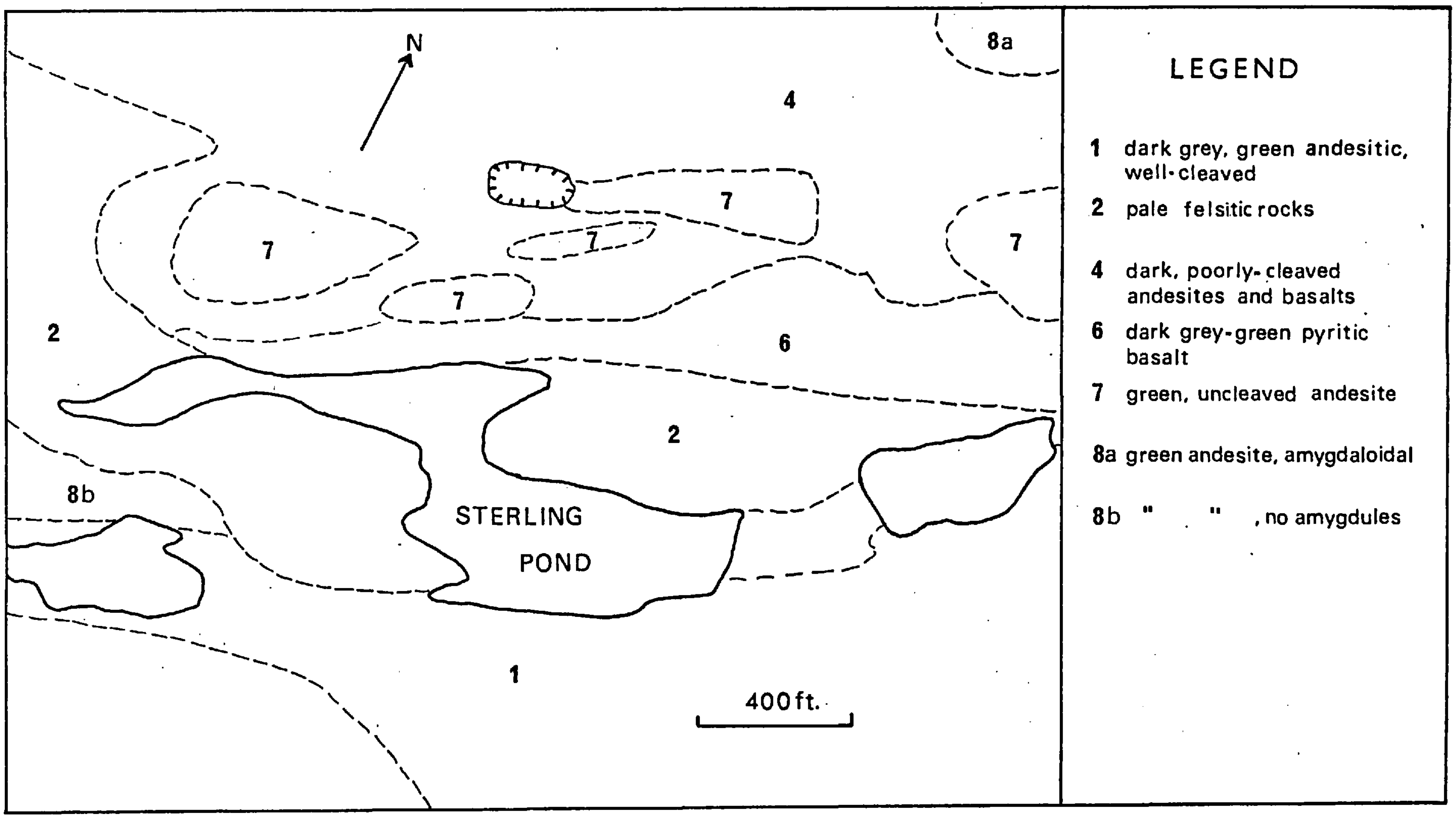


Figure 26. Geology of the Sterling Pond area (after Smitheringale, 1967).

localities eastward from this deposit. Figures (27 and 28) and show that the B horizon samples and, to a lesser extent, the A_1 samples, give high sulphur and copper concentrations over this area of mineralization. High sulphur in both the A_1 and B horizons at L60W, at the baseline, has no associated high copper, but 9.7% Fe in the B sample indicates that it may be due to pyrite only.

The humus samples show the greatest accumulation of sulphur, and some copper, in the area trending southwest from the ore dump. A small bog covers part of this area and the drainage is in that general direction on a gentle slope. Thus sulphur from the dump accumulating in the humus and bog material could account for this anomaly. Samples from below 6 in. depth in this bog were noted as smelling of H_2S.

Other low order build-ups of sulphur in the B horizon samples are believed due to pockets of disseminated sulphides. Mainly because of the anomaly over the known sulphides but also because of the soil chemistry, the B horizon sulphur is considered a better indicator of underlying mineralization than the humus sulphur.

Comparison of the Cu, Fe and S values using scatter diagrams indicates that there is a weak positive correlation between sulphur and copper but little between sulphur and iron. The Sterling data confirms only that the correlation between these elements is better close to pyrite-chalcopyrite mineralization where the mineralization is the largest source of these elements to the soil, but away from it this relationship is obscured by the introduction of sulphur from organic matter and iron from mafic minerals for example.

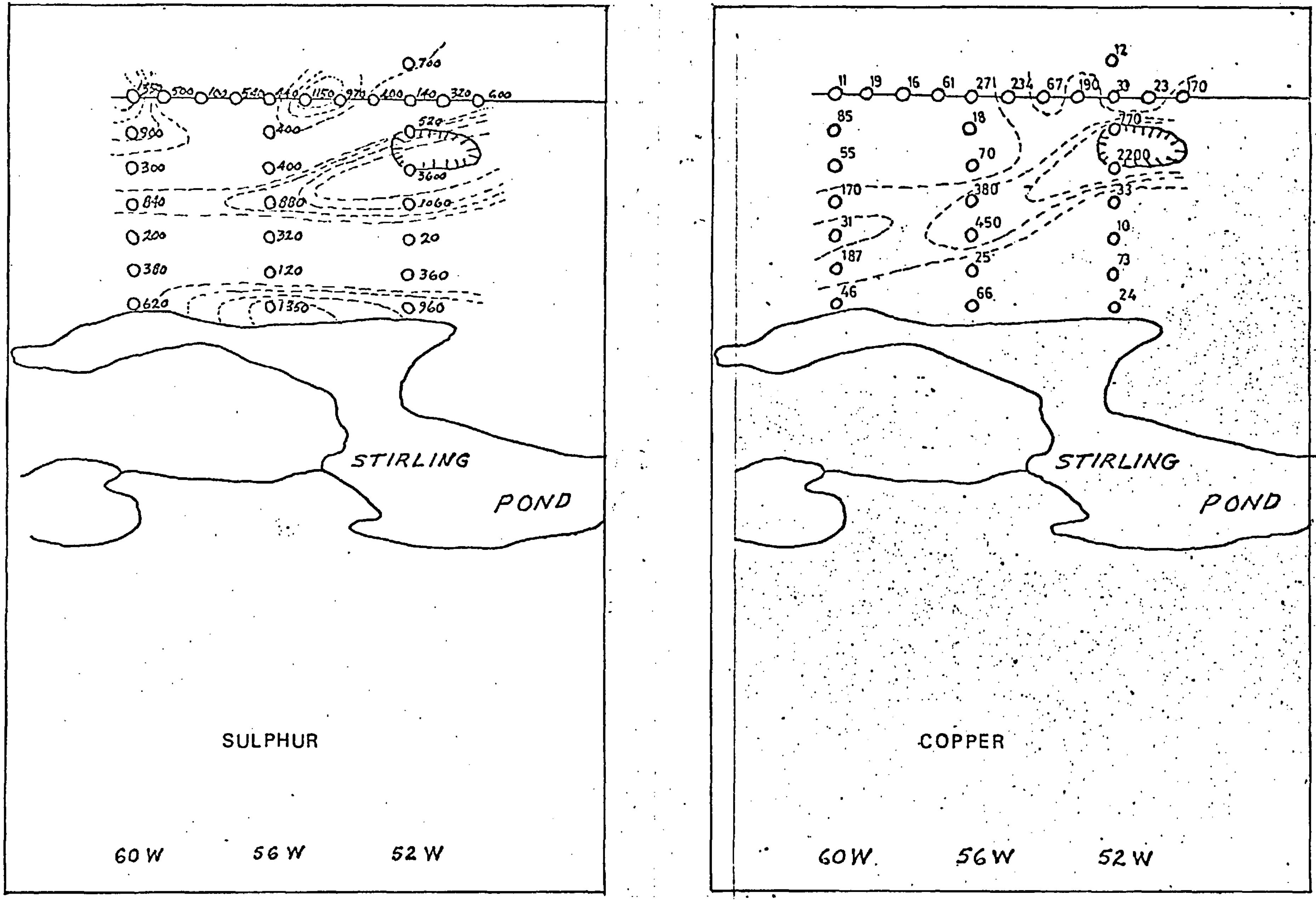


Figure 27: Total sulphur and copper concentrations in the A_1 horizon, Sterling area.

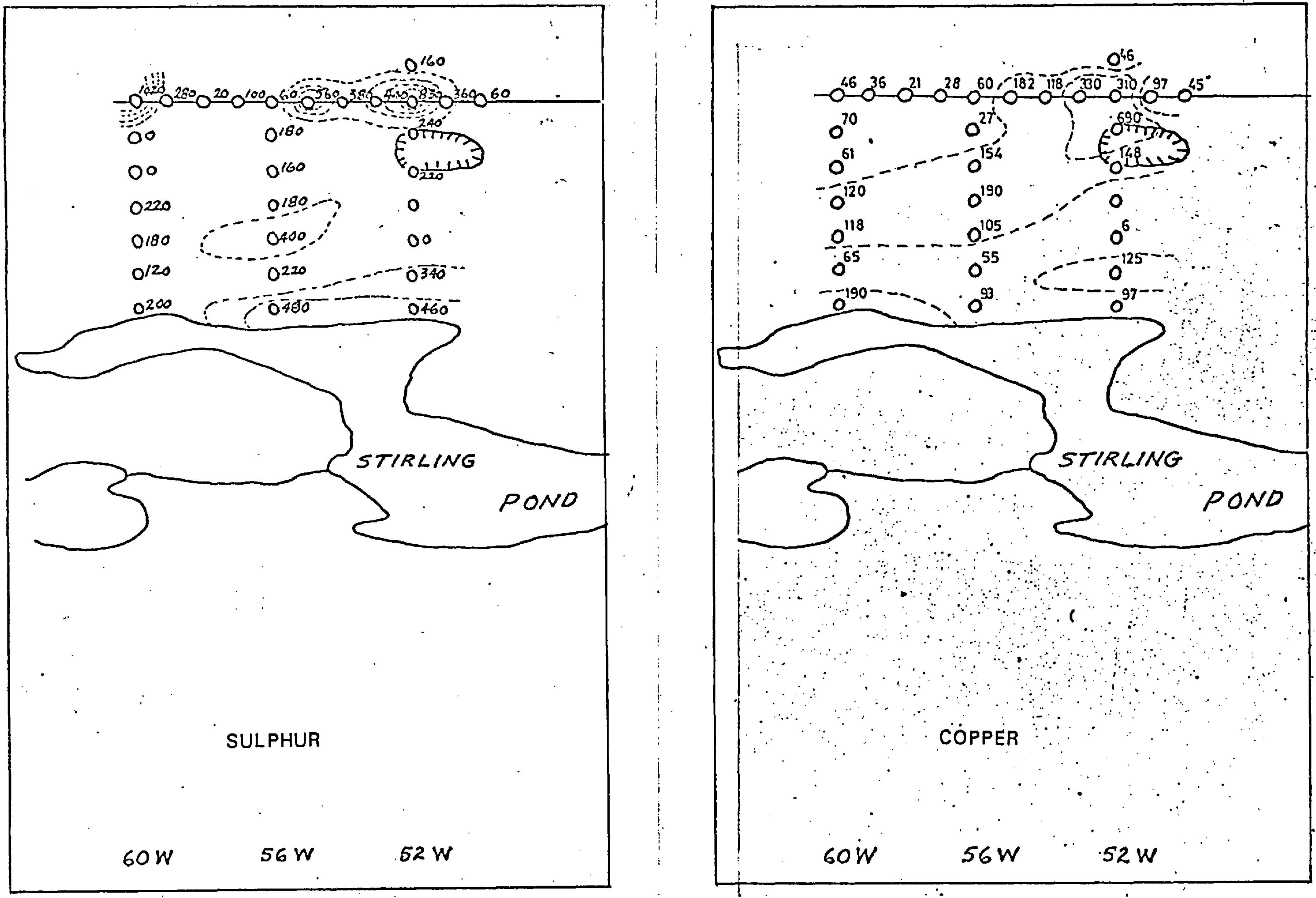


Figure 28: Total sulphur and copper concentrations in the B horizon, Sterling area.

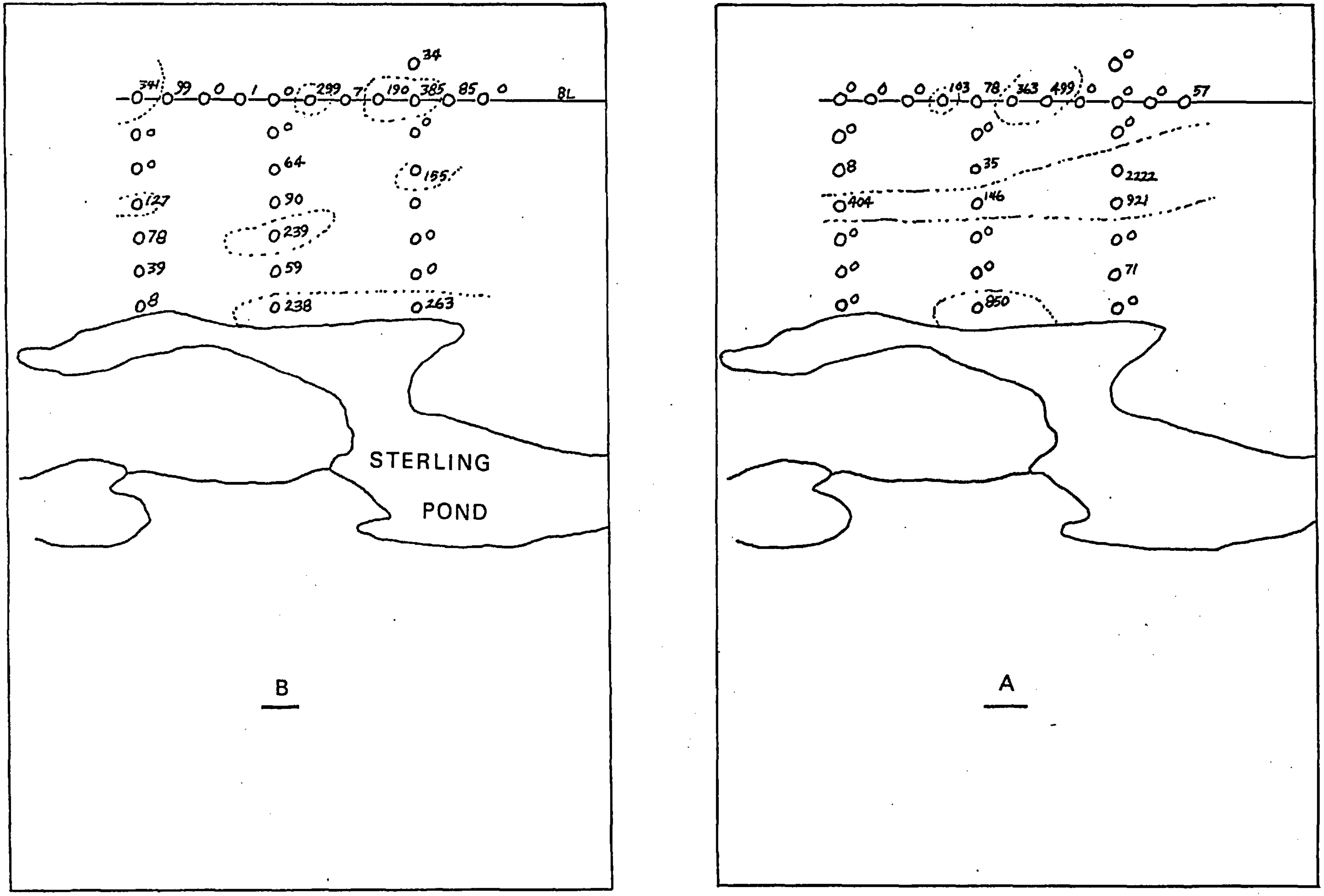


Figure 29: Residual sulphur patterns after correction for organic content in A and B horizon soils, Sterling area.

4.3.3 Interpretation of Sulphur Patterns after correction for Organic Content

The total sulphur values from the detailed sampling of the Sterling area were regressed against loss-on-ignition using the expression ppm. S = 16.73 (% L.O.I.) - 26.14 and the residual sulphur values for the A and B horizons plotted in Figure 29. It can be seen that in the B horizon all the anomalous sulphur areas remain and in the A horizon three of the anomalous sulphur areas remain, whereas that at 60W, at the baseline, disappears. The conclusion is that, with the exception of the latter case, most of these anomalies in both soil horizons are not due to organic matter content but to other sources, namely sulphides.

4.4 THE DAWES POND SHOWING

4.4.1 Description of the Area

A small zone of disseminated pyrite with some chalcopyrite was discovered during geochemical soil surveys carried out by Brinex in 1969 in the region of Dawes Pond (see Figures 1 and 30 for location), in a schist zone in deformed Ordovician basic volcanics. As DeGrace (1971) noted for the Rendell Jackman and other deposits in the Notre Dame Bay area, there is some enrichment here of sulphides in the hinges of folds, particularly in the trench exposure at line 20W, 2S.

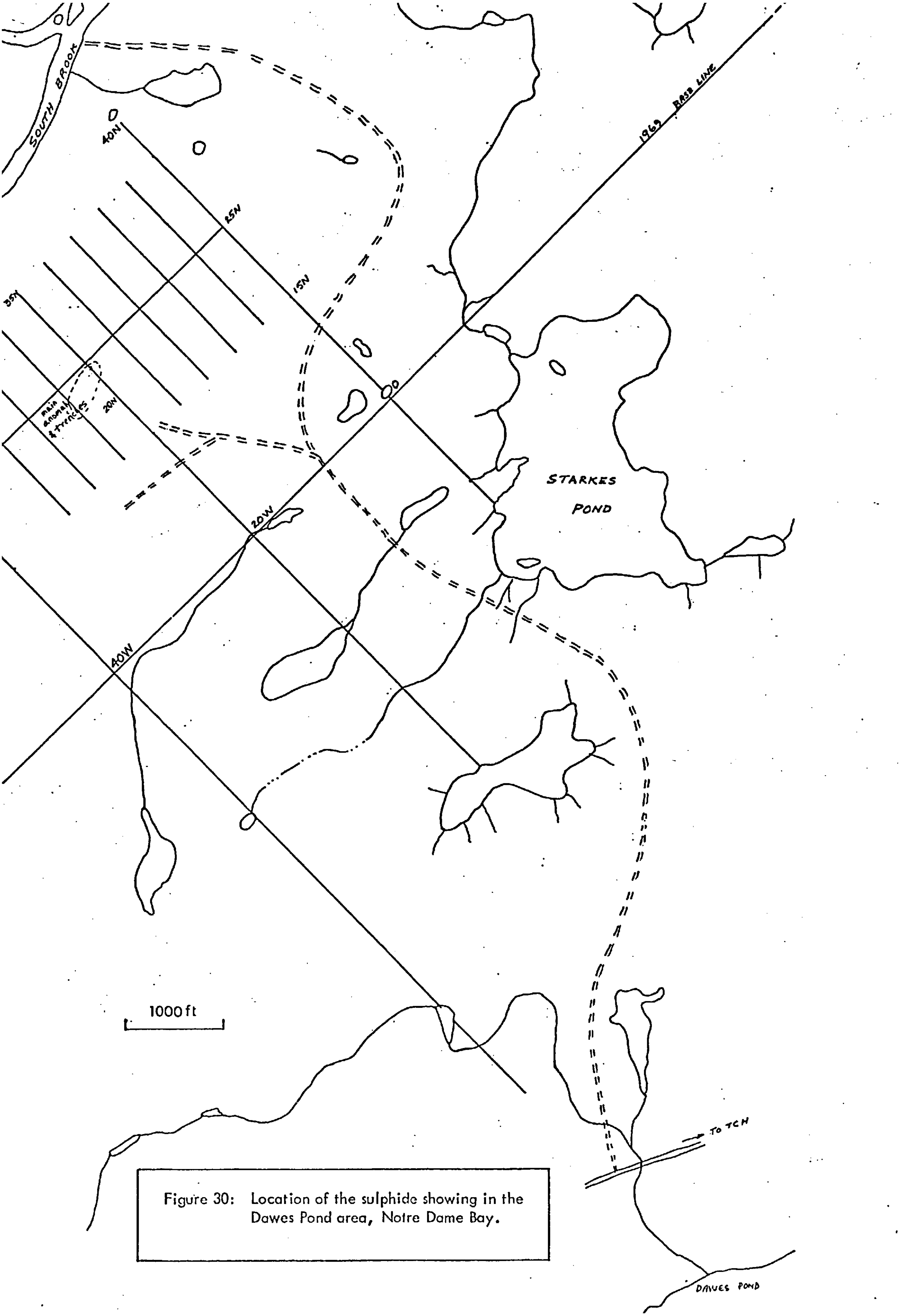


Figure 30: Location of the sulphide showing in the Dawes Pond area, Notre Dame Bay.

The mineralization has also been exposed in a trench at line 24W but elsewhere the bedrock is overlain by poorly sorted glacial till varying from 1 - 15 ft. depending on the topography. At several localities in the region of Dawes Pond moraine mounds exceed 50 feet in thickness but at this particular locality the glacial material is shallower on the tops of the hills. The upper 2 feet has developed into podzol under mainly coniferous forest cover.

4.4.2 S, Cu, Fe, Pb, and Zn in Dawes Pond Soils

Sampling of the B horizon from 4 to 36 in depth on lines 200 feet apart and at 100 feet intervals in the vicinity of the mineralization showed enhancement in these elements, particularly of S and Fe. The patterns produced for S, Cu and Fe are presented in Figures 31, 32 and 33 and it is observed that (1) the sulphur anomalies have either high copper or iron associated; (2) the iron and sulphur patterns delineate the zone of known mineralization fairly well, supporting the fact that the mineralization is largely pyrite; and (3) copper is displaced downslope in the freely drained soils of the hillside and enriched in the humus at the base.

Comparison of the plots in Figures (31 and 33) show that in areas A and B the sulphur and iron highs coincide. Copper, on the other hand, does not correlate with sulphur as well. In area A the copper anomaly is extended northward from the sulphur high, approximately 100 feet further downslope. In area C there are coincident copper and sulphur highs occurring in the black humus forming a deposit of greater than 3 feet

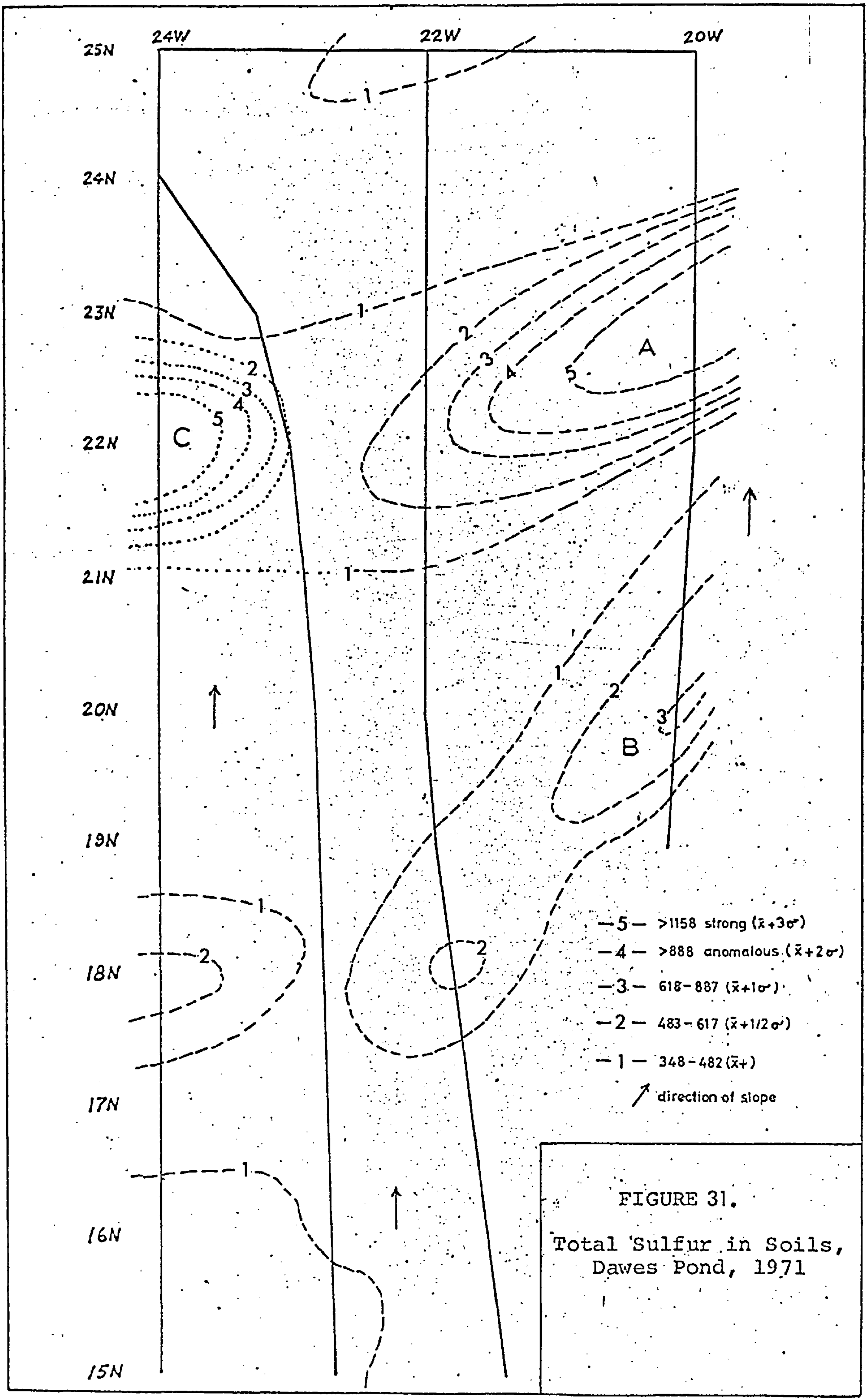


FIGURE 31.

Total Sulfur in Soils, Dawes Pond, 1971

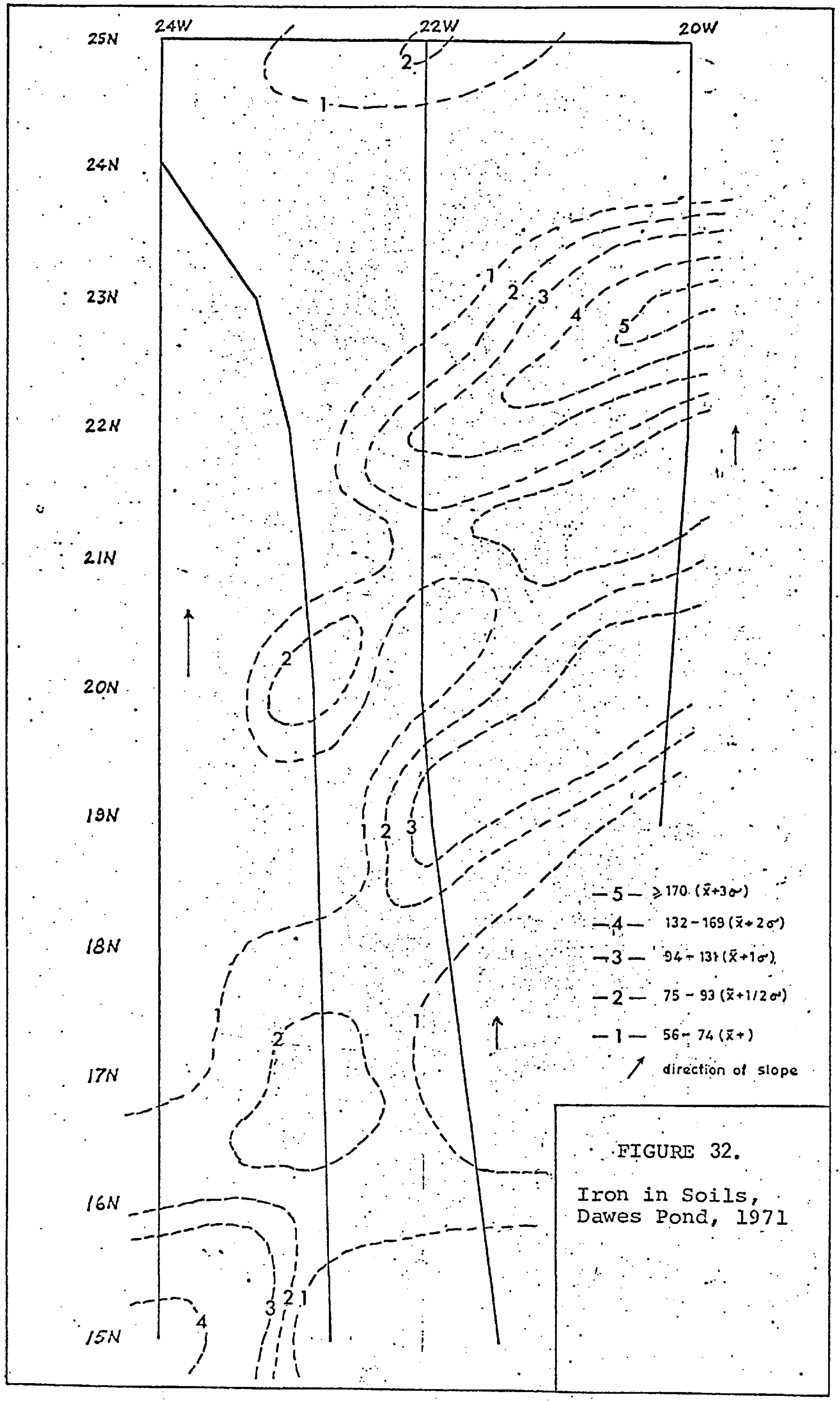


FIGURE 32.

Iron in Soils, Dawes Pond, 1971

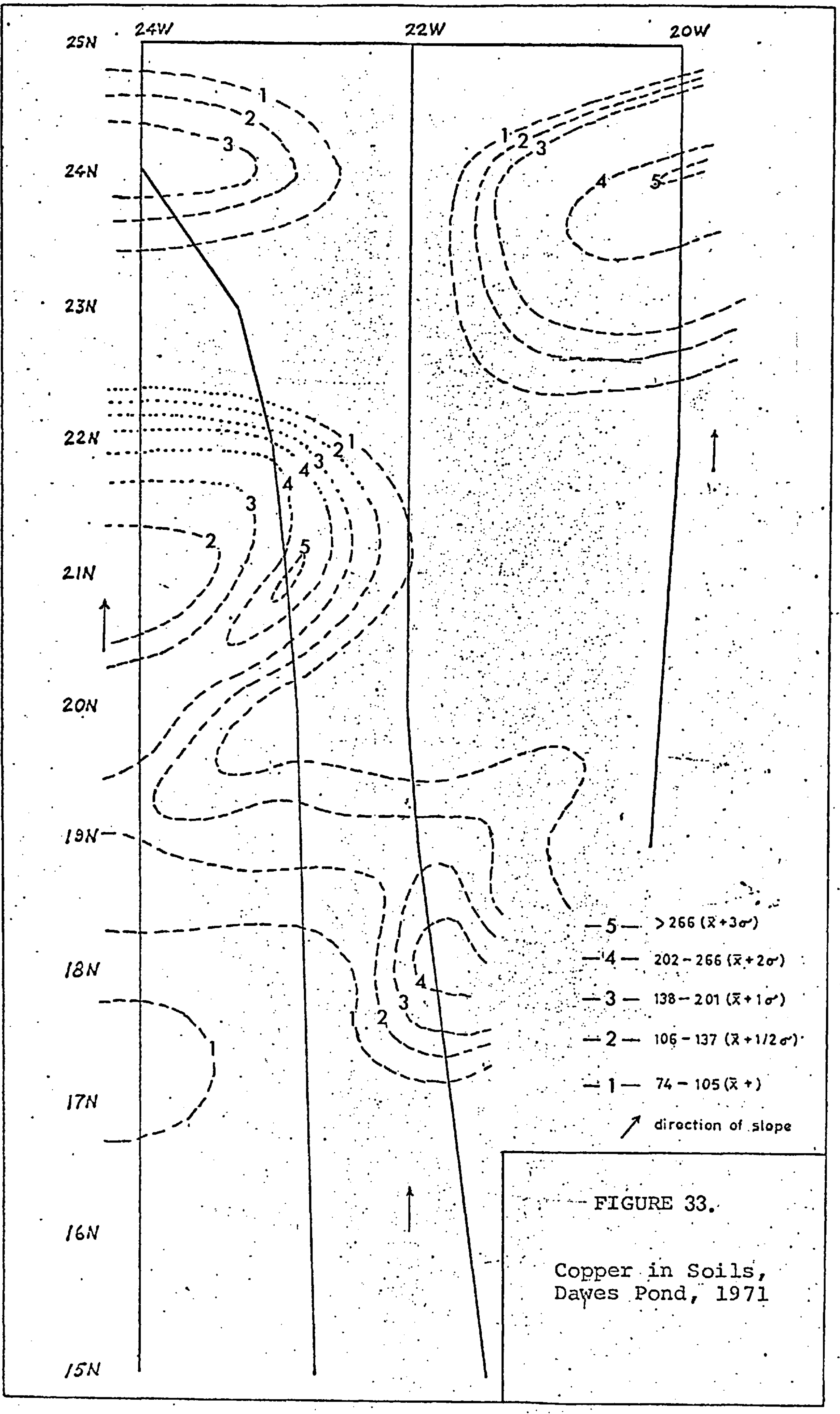


FIGURE 33.

Copper in Soils,
Dawes Pond, 1971

thickness at the base of the slope where known mineralization occurs. The high copper persists eastward in this organic material. It is evident that at both A and C areas copper brought down in the ground drainage from the mineralization on the slope is being fixed by the organic material at the base. Although it is theoretically possible that the copper derives from mineralization underlying the humus, that possibility does not seem as likely as the former because drainage from the slope accumulates easily in this area whereas there are several feet of till underneath the humus which would tend to limit dispersion from that source.

Sampling of the humus accumulation at area C at various depths showed that the black organic mud at the base of the humus contained more sulphur than less decomposed material nearer the surface (Table 19). The brown sandy till beneath the humus contains 350 ppm sulphur. Copper shows a general increase with depth but is considerably enriched in the organic material relative to the till underneath. Only Cu shows such an enhancement in this material, which suggests stability of a Cu-organic complex relative to the other elements determined.

The state of decomposition of the humus material in this area suggests that it may be considerably older than most of the surface humus and may possibly have formed in a peat basin soon after glaciation and later gave way to forest cover as the basin drained.

In the profile across the axis of the mineralization zone at line 20W shown in Figure 34, the improved contrast of total sulphur in relation to copper, iron and zinc is illustrated. A subsidiary anomaly

Table 19: Analysis of Humus Deposit at Area C, Dawes Pond.

Sample Number	Depth	Description	pH	ppm Cu	ppm Pb	ppm Zn	% fe	ppm S
PA-72-69	0- 6 in.	Black/Brown, partly decomposed humus	6.18	1050	5	615	0.38	460
70	6-12 in.	Black, decomposed humus	6.18	3000	10	360	0.68	220
71	12-18 in.	Black organic mud	6.10	2650	15	520	1.40	740
72	18-24 in.	Brown sandy till	6.35	260	10	580	1.50	350

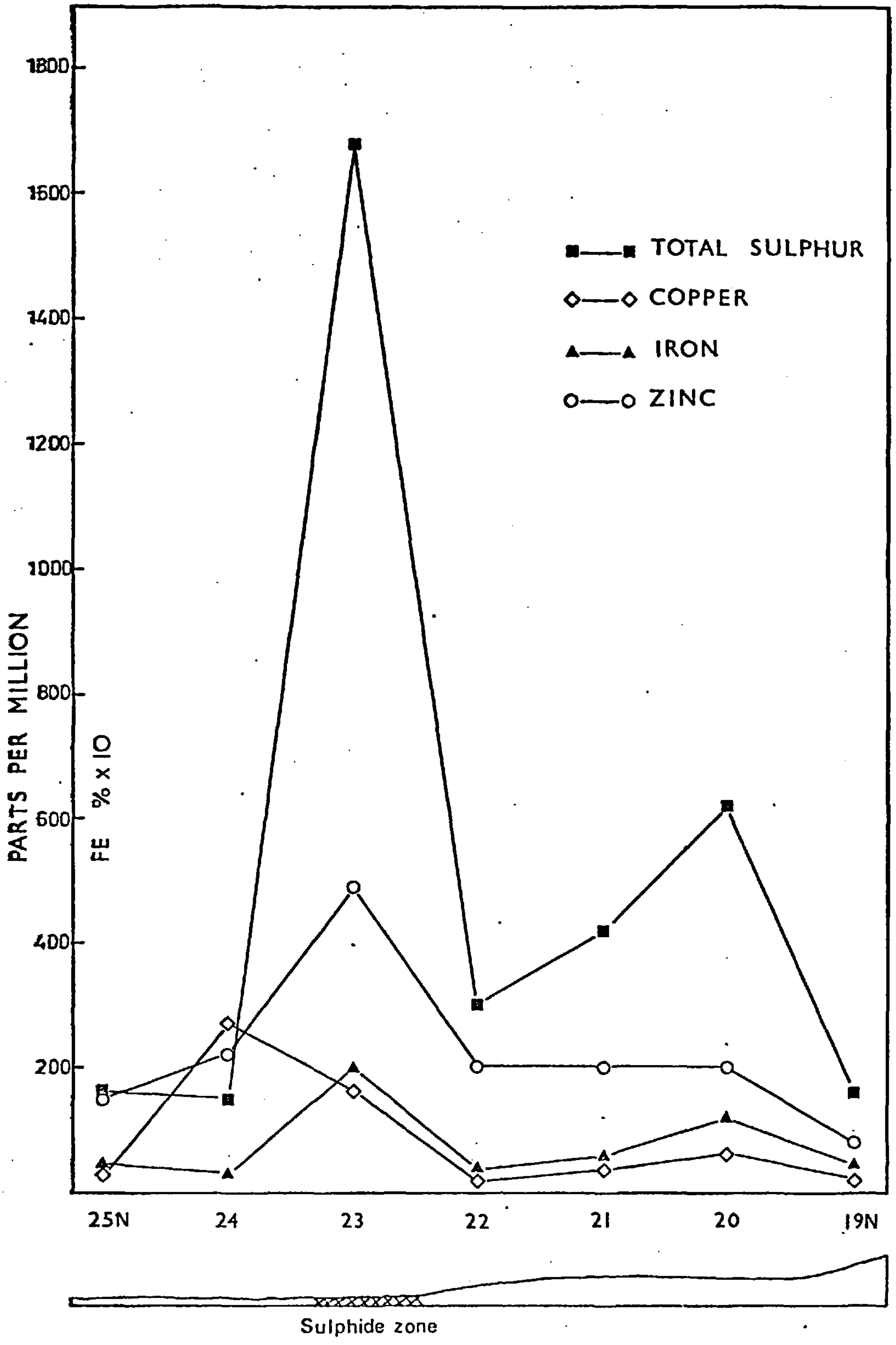


Figure 34. Total sulphur, copper, and zinc in B horizon soils collected across Dawes Pond showing (Line 20W).

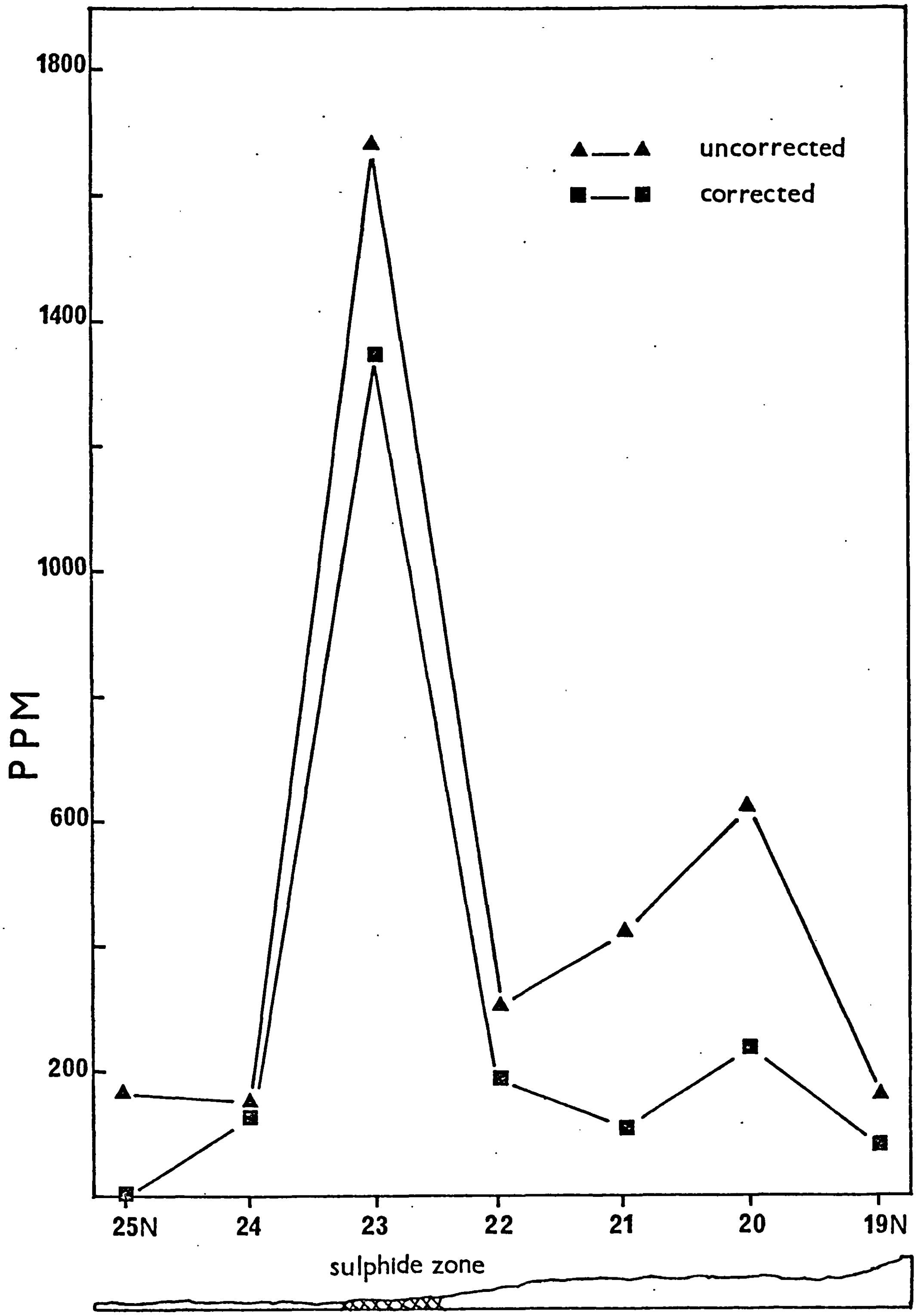


Figure 35. Effect of correction for organic content on total sulphur in soils, traverse of L20W, Dawes Pond area.

(620 ppm.) is indicated at grid location 20N by slight increase in Cu, Fe, and Zn as well as S.

Calculation of residual sulphur content after correction for organic content, using the regression ppm. S = 16.73 (% L.O.I.) - 26.14, showed that both the anomaly over the known sulphides at 23N and the subsidiary one at 20N are related to this source and not to the organic content of the samples.

4.4.3 A and B Horizon Sampling

Samples were collected from the A_1 humus layer and the B horizon at intervals of 100 feet along line 24W to compare the sulphur response to mineralization shown by the two layers. The distribution of sulphur in the B horizon coincides to some extent with the pattern shown by copper, lead and zinc, with peaks that reflect the irregular occurrence of disseminated sulphides in the bedrock (Figure 36). Sulphur in the humus provides a broad response to mineralization but the significance of the pattern is placed in doubt by the presence of high erratic values in an unmineralized area at the north end of the traverse. This supports the observations on the Sterling area that the B horizon sulphur is more closely related to underlying geology than the A_1 sulphur. It should be noted that high metal values in relation to sulphur may reflect an increase in chalcopyrite and sphalerite and a reduction in the amount of disseminated pyrite at this locality.

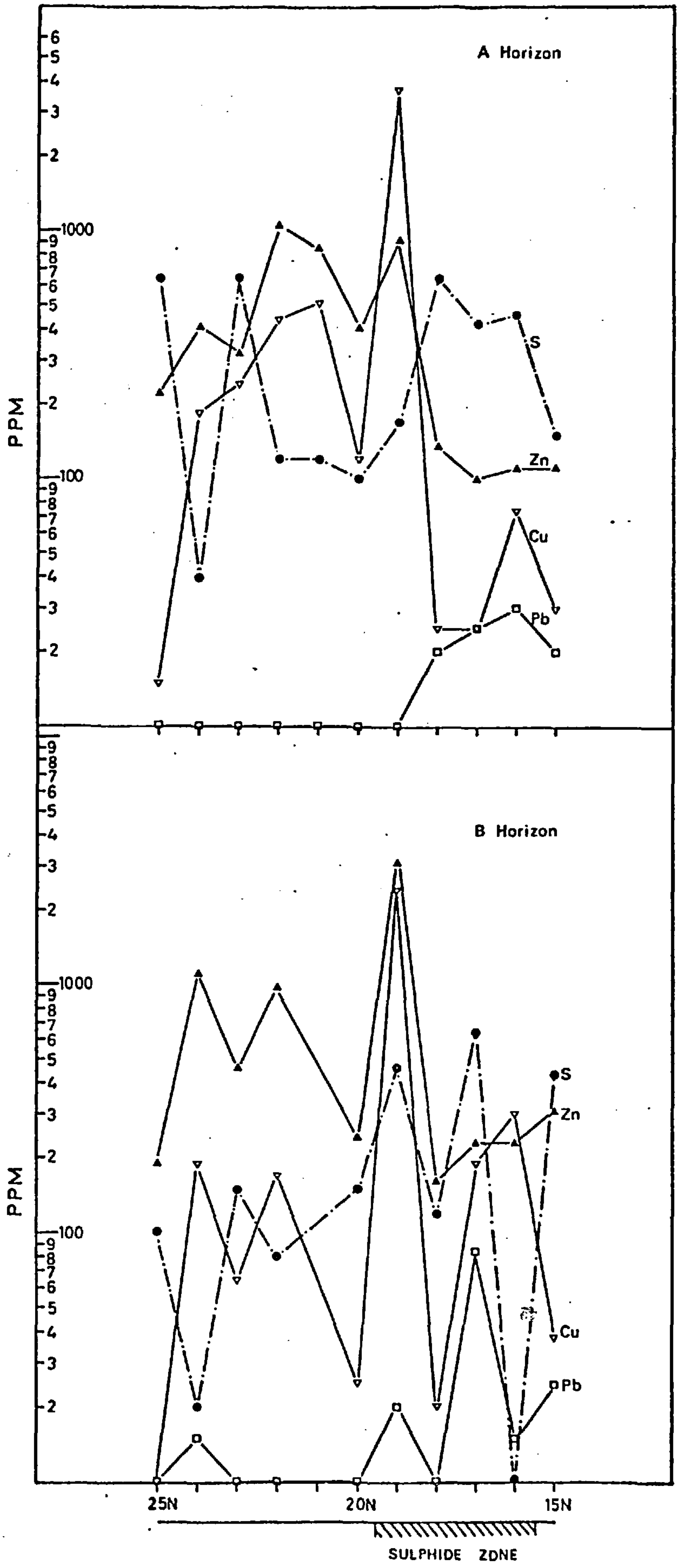


Figure 36. Total sulphur, copper, lead and zinc in A and B horizon soils collected on traverse across Dawes Pond showing, L24W.

4.4.4 The Vertical Profile

Examination of the soil in this area in a vertical profile on line 24W showed that the surface 2 feet is developed into good podzol A_1, A_2 and B horizons overlying 2 - 4 feet grey-brown till with a clay-sand matrix containing frequent small boulders from pebble size to more than 3 feet in diameter. The slope is about 30° NW and the till increases in thickness downslope. North of 20N the bedrock slopes under more than 10 feet of till underlying about 2 ft. of black humus in a semi-bog. No podzol is developed in this semi-bog area at the base of the slope.

The analysis of samples taken from the profile at 16 + 50 N is given in Table 20 and shows that sulphur decreases with depth and that the till contains only a small amount of sulphur. Copper and lead increase with depth even into the till, whereas iron and zinc reach maximum concentrations in the red, illuvial B horizon.

4.4.5 Analysis of Glacial Till at Dawes Pond

A bulk sample of the glacial till taken from the line 24W area was divided into ten size fractions and analyzed for five metals, total sulphur and loss-on ignition. The results indicate that some sulphide mineralization is included in the coarse rock fragments giving rise to higher sulphur, copper, lead and zinc in two coarser fractions (Table 21). The sample is taken from till overlying the schist zone containing disseminated sulphides and the high results probably arise from the inclusion of fragments of this schist in the till.

Table 20: Distribution of elements in a vertical profile, L24W, Dawes Pond area.

Depth	Hor.	Description	pH	Cu ppm.	Pb ppm.	Fe %	Zn ppm.	S ppm.
0-5 in.	A_1	Brown/black, humus, fresh.	4.30	12	10	0.75	50	510
5-7 in.	A_2	Grey-white, leached, clay and org.	4.72	8	10	2.40	30	150
7-24 in.	B	Red-brown, coarse sand-clay, stones.	5.72	38	15	4.30	225	80
24-48 in.	Till	Light grey-brown glacial till, clay-sand plus frequent small stones ½"-2" diam.	5.90	95	15	2.60	120	80

Table 21: Concentration of elements in various size fractions in glacial till, Dawes Pond area.

Sample	Size mm.	Wt. % in Fraction	L.O.I. %	Cu ppm.	Pb ppm.	Zn ppm.	Mn ppm.	Fe %	S ppm.
3A	>11.2	40.8	0.51	114	100	270	763	2.91	1120
3B	11.1 -4.76	20.8	0.28	121	48	170	588	3.75	1860
3C	4.75 -2.38	5.4	0.12	86	21	93	563	3.95	480
3D	2.37 -1.0	7.0	0.33	70	9	63	490	3.35	275
3E	0.9 -0.5	6.3	0.15	80	15	65	483	3.25	200
3F	0.49 -0.25	7.2	0.47	84	19	71	425	2.75	190
3G	0.24 -0.177	2.3	0.44	76	14	65	390	2.55	110
3H	0.176-0.125	2.9	0.32	70	9	43	325	2.04	<100
3I	0.124-0.063	2.9	1.21	60	6	35	300	1.94	<100
3J	<0.063	4.3	1.70	99	16	43	358	2.73	<100

It is also noted that more than 61% of the weight of the sample is contained in the two fractions coarser than 4.76 mm. diameter and that there is very little loss-on-ignition. The small loss of weight observed is probably the result of water loss from clays instead of organic material decomposition.

4.5 PILLEY'S ISLAND

4.5.1 Geology

The Pilley's Island deposit (Figure 1) of massive pyrite and chalcopyrite, with some sphalerite and galena, occurs as lenses in a rhyolite member of the Silurian (?) Roberts Arm volcanic rocks (Peters, 1967). Other rocks in the sequence include autobreccias, tuffs, agglomerates and greywackes, all of which have been hydrothermally altered. Sphalerite and galena are more abundant in a third zone located in chloritic basalts stratigraphically below the acid volcanic sequence containing most of the ore. Grades of 2 - 3% copper are typical of the ore lenses. The deposit has not been mined since 1908, but exploration has indicated reserves of between 500,000 and 700,000 tons of pyrite-chalcopyrite ore (Peters, op. cit.).

4.5.2 Distribution of Elements in Soil on a Traverse northwest of Head's Pond

The distribution of sulphur in relation to other elements in the soils of the area was briefly considered by examining samples taken on a traverse across a zone of the massive sulphide ore which had been located in the area north of Head's Pond (Figure 37). The samples were taken at 50 ft. intervals. The sample from 6S was not included because the soils had been disturbed during trenching operations. The values for total sulphur plus thirteen other elements determined by atomic absorption are given for this traverse in Figure 38.

It is observed that eleven of the fourteen elements show maxima over the mineralization, but Mg, Li and Mn are not distinctly higher close to the sulphides. Good contrast is noted for Cu, Pb, Zn, Ca, Cr, Hg, As and total S, but on such a small traverse it cannot be said that sulphur is any better indicator of the presence of the sulphides than either of the other elements.

4.6 SUMMARY: SOIL SULPHUR IN MINERAL EXPLORATION

The study of the distribution of sulphur in the soils of the Notre Dame Bay area has shown that in unmineralized areas the total sulphur content of the soil is almost completely a function of the organic content

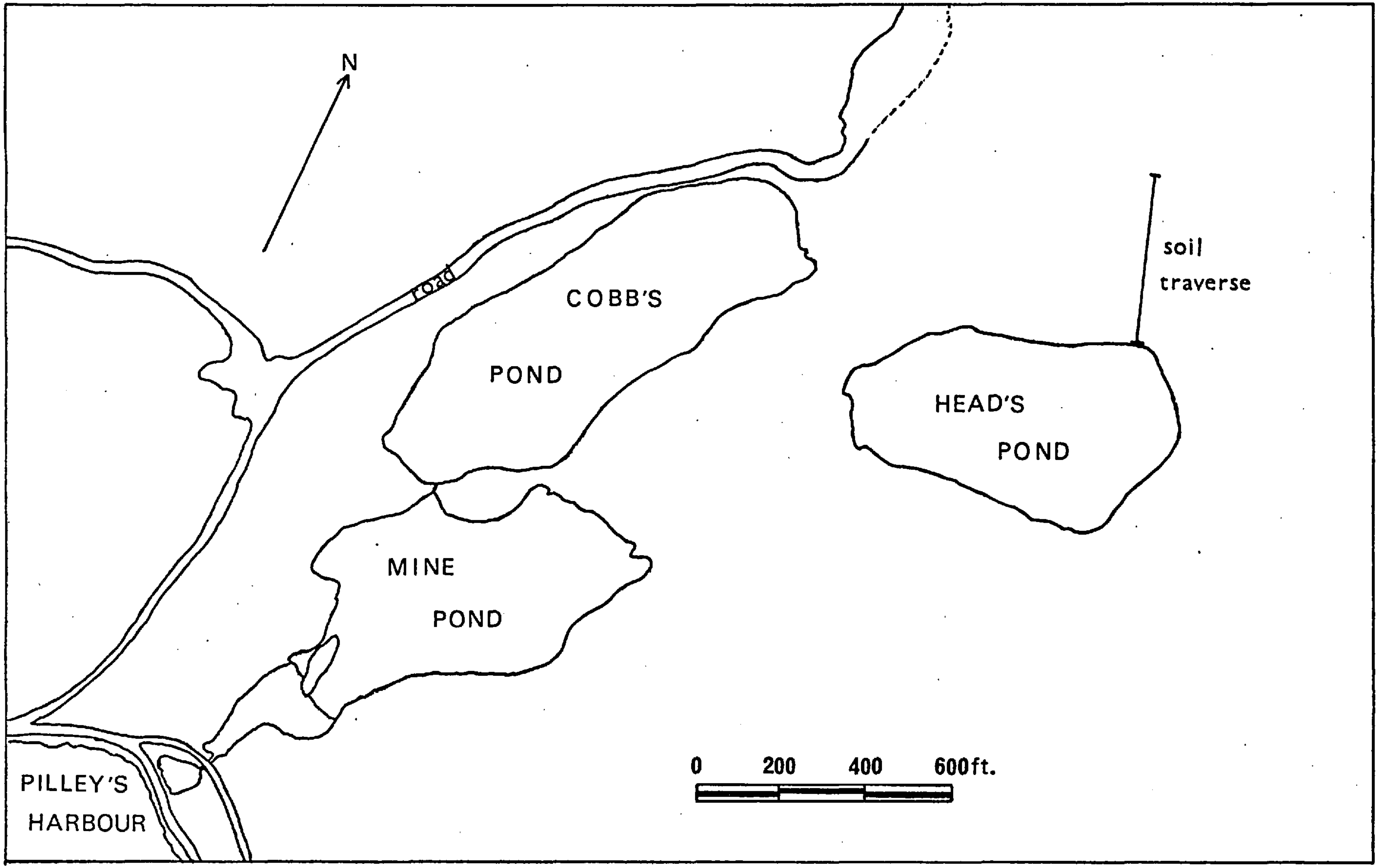


Figure 37. Location of soil traverse near Head's Pond, Pilley's Island.

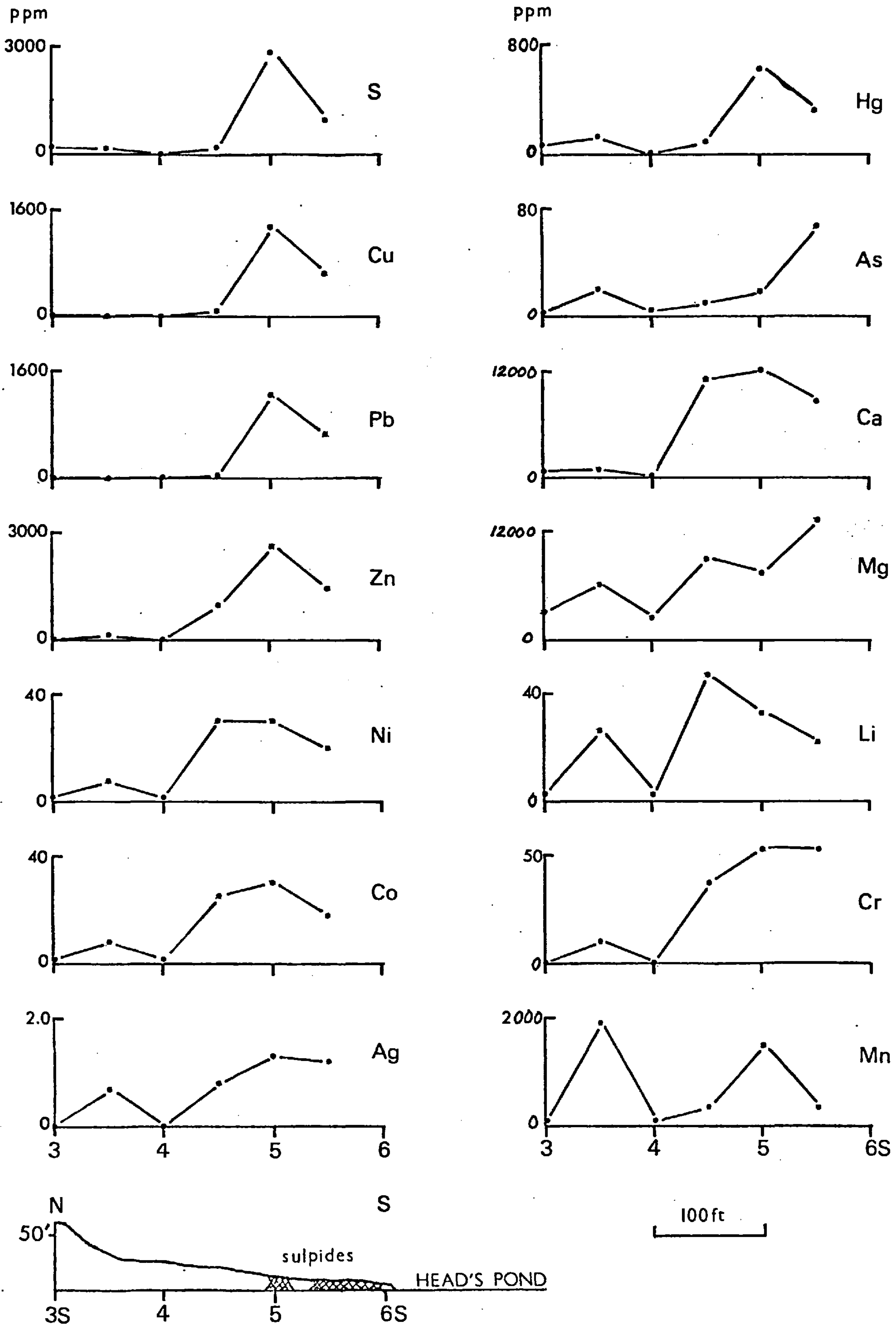


Figure 38. Distribution of elements in a soil traverse north of Head's Pond, Pilley's Island.

of the sample. Data from a large scale survey of the Rendell Jackman area showed that the organic sulphur compounds of the surface horizons contributed to greatly increased total sulphur content in those horizons relative to the lower parts of the profile. In this survey high organic content also gave rise to total sulphur anomalies over areas of peat bog.

In the vicinity of sulphide deposits, however, total sulphur anomalies occurred which were related to the sulphides and not to organic content. Discrimination was made possible by the derivation of an expression relating the total sulphur and organic matter contents of the soils by an analysis of the variance of total sulphur in terms of twelve other element variables plus loss-on-ignition in soils from the Rendell Jackman survey. Application of this correction for organic content in selected detailed surveys in the vicinity of sulphide occurrences showed that the residual sulphur patterns after correction were in most cases similar to the original patterns, indicating that in these cases the sulphur highs were related to the mineralization rather than to organic content. Limited data from unmineralized areas prevented comprehensive testing of the applicability of this discriminating technique, but data from the Sterling area suggests an approach of this nature could be successfully applied to the interpretation of total sulphur data from geochemical soil surveys.

In a few cases total sulphur showed improved contrast relative to copper, lead, zinc or iron over pyrite-chalcopyrite mineralization but the size and amplitude of any total sulphur anomaly is dependent partly on mineralogy and is expected to be better for pyritic than for non-pyritic ores. Consequently, in other cases, the metal anomaly may be more easily distinguished. Total sulphur in soils could perhaps be used in conjunction with the other variables to delineate sulphide zones more effectively.

CHAPTER 5

SULPHUR IN STREAM SEDIMENTS

5.1 FACTORS INFLUENCING THE SULPHUR CONTENT OF STREAM SEDIMENT

Sulphur in stream sediment derives from several sources, as follows:

1. grains of sulphide (and/or sulphate) minerals (or precipitates) mechanically carried in the sediment.

2. sulphur contained in organic material in the sediment.

3. sulphate adsorbed onto clay minerals and hydroxides.

The total sulphur content of stream sediment is influenced to a minor extent perhaps by the amount of dissolved sulphate in the stream water in that the amount precipitated or sorbed onto the sediment would depend on that concentration and local Eh-pH conditions. Turekian and Scott (1967) found, however, that for cations the trace element content of dissolved ions is not reflected in the trace element composition of the detrital load.

The concentration of total sulphur in the stream sediment at a particular location is expected to fluctuate seasonally by a small amount because of the influence of the suspended load. For instance, a sample taken after subsidence of a peak spring or fall flooding may contain more sulphur than one taken prior to the run-off because the suspended load of the flood period would then have settled, containing organic material and adsorbed sulphate ions particularly. Allan (1971) found this to be the case for copper and other trace elements in rivers of the Canadian Shield.

5.2 DISPERSION IN THE OVALS BROOK AREA STREAM SEDIMENT

5.2.1 Description of the Area and Geology

The Ovals Brook system drains the area to the south and west of the Rendell Jackman deposit, situated about 6 miles NW of the town of Springdale (see Figures 1 and 39). The area contains several ponds draining into Ovals Brook, namely, Spar Pond and Ovals Ponds on the main west tributary and Mining Pond, Bean Pond and others on the east. Drainage from the sulphide deposit at Rendell Jackman enters the system in Mining Brook. The drainage flows north into Southwest Arm, situated at the northwestern corner of Notre Dame Bay.

The area is underlain by basic volcanics of the Ordovician Lush's Bight Group, consisting of pillow lavas, pillow breccias, and aquagene tuffs (De Grace, 1971), and is largely covered with ground moraine.

5.2.2 Total Sulphur and Metal Content of the Stream Sediment

Samples were taken from all tributaries flowing into Ovals Brook and at intervals of about 1,000 feet on the main stream. The total sulphur and copper contents of these samples are given in Figure 39, and show that both sulphur and copper show anomalous concentrations in the sediment downstream from the Rendell Jackman deposit. Total sulphur concentrations of 1.2 and 1.3% occur on Mining Brook compared to values in the 700 - 1800 ppm. range for non-mineralized areas. Some samples from smaller streams contain higher than average sulphur because of high organic content, which accounts for most background fluctuations in the sulphur value.

Copper also shows good contrast and the anomaly persists further downstream than that of total sulphur. Zinc concentrations were in the 100 - 700 ppm. range for non-mineralized areas and 1000 - 1200 ppm. on Mining Brook, showing lower contrast than either copper or sulphur.

The more widespread copper anomaly probably indicates that the dispersion of copper is related to aqueous transport, adsorption and in organic complexes whereas the total sulphur anomaly arises from sulphide grains, which are not carried as far from the source mineralization. Vostroknutov (1968) found widespread water dispersion haloes of Cu in neutral waters around sulphide deposits in the Urals resulting from finely dispersed Cu hydroxide which was not precipitated in the sediment but transported for considerable distances. Because it showed better contrast and wider dispersion than sulphur in the stream sediment, copper is considered a more useful indicator of pyrite/chalcopyrite mineralization in this aspect of mineral exploration.

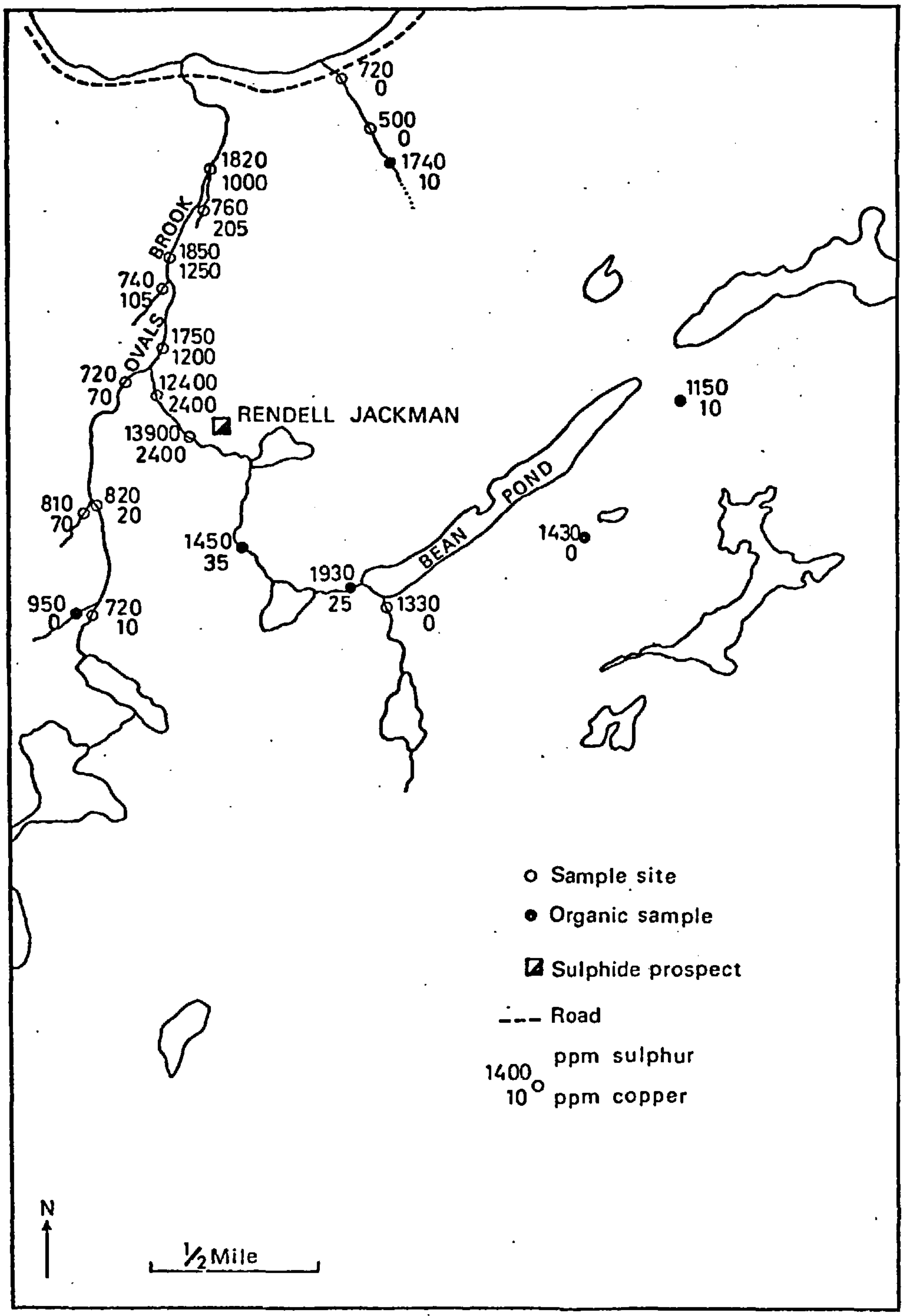


Figure 39: Total sulphur and copper in stream sediments from Ovals Brook drainage system, Rendell Jackman area.

5.3 SIZE FRACTION ANALYSIS

5.3.1 Comparison of Results from Mineralized and Non-Mineralized Areas

Bulk samples were taken from streams in non-mineralized and mineralized areas and each divided into ten size fractions and analyzed for six elements by atomic absorption as well as for total sulphur and loss on ignition (Table 22).

In the samples from non-mineralized areas, average values for Cu, Zn, Mn, total sulphur and organic content (L.O.I.) were lower than in mineralized areas (Figures 40 and 41). Comparison of the element distributions in the fractions shown in Figure 40 for non-mineralized areas shows that although the bulk of the sample weight is contained in the coarser fractions, the highest concentrations of Cu, Pb, Zn, Mn, Fe and S tend to occur in the finer fractions H, I and J, associated with the increase in organic matter content of those fractions. Even for mineralized areas Cu, Zn and Mn particularly show this tendency for association with organic matter.

It is evident in case 1 (Figure 41) that grains of galena-sphalerite mineralization occur in the coarsest fraction, shown by very high Pb, Zn and S values. The sulphide mineralization in the area from which the sample was taken is mainly pyrite and chalcopyrite, with lesser amounts of sphalerite and galena. The incidental occurrence of these grains illustrates, however, that the coarse fractions may sometimes indicate the presence of mineralization better than the fine, but, as this was not the case in other samples from mineralized areas, the finding of grains of sulphides in the coarse fraction is a matter of chance, and the finer fractions appear to be

Table 22: Sizes of fractions and locations of samples used for size fraction analysis.

Size Fraction	Diam. mm.	Tyler Mesh No.	Sample Number	Location	Character of Area
A	+11.2	+ 2	1	Wells Brook	Mineralized
B	11.1 -4.76	+ 4			
C	4.75 -2.38	+ 8			
D	2.37 -1.00	+ 16	2	Wells Brook	Mineralized
E	0.99 -0.50	+ 32			
F	0.49 -0.25	+ 60			
G	0.24 -0.177	+ 80	5	Harry's Brook	Unmineralized
H	0.176-0.125	+115			
I	0.124-0.063	+250			
J	-0.063	-250	6	Park Brook	Unmineralized

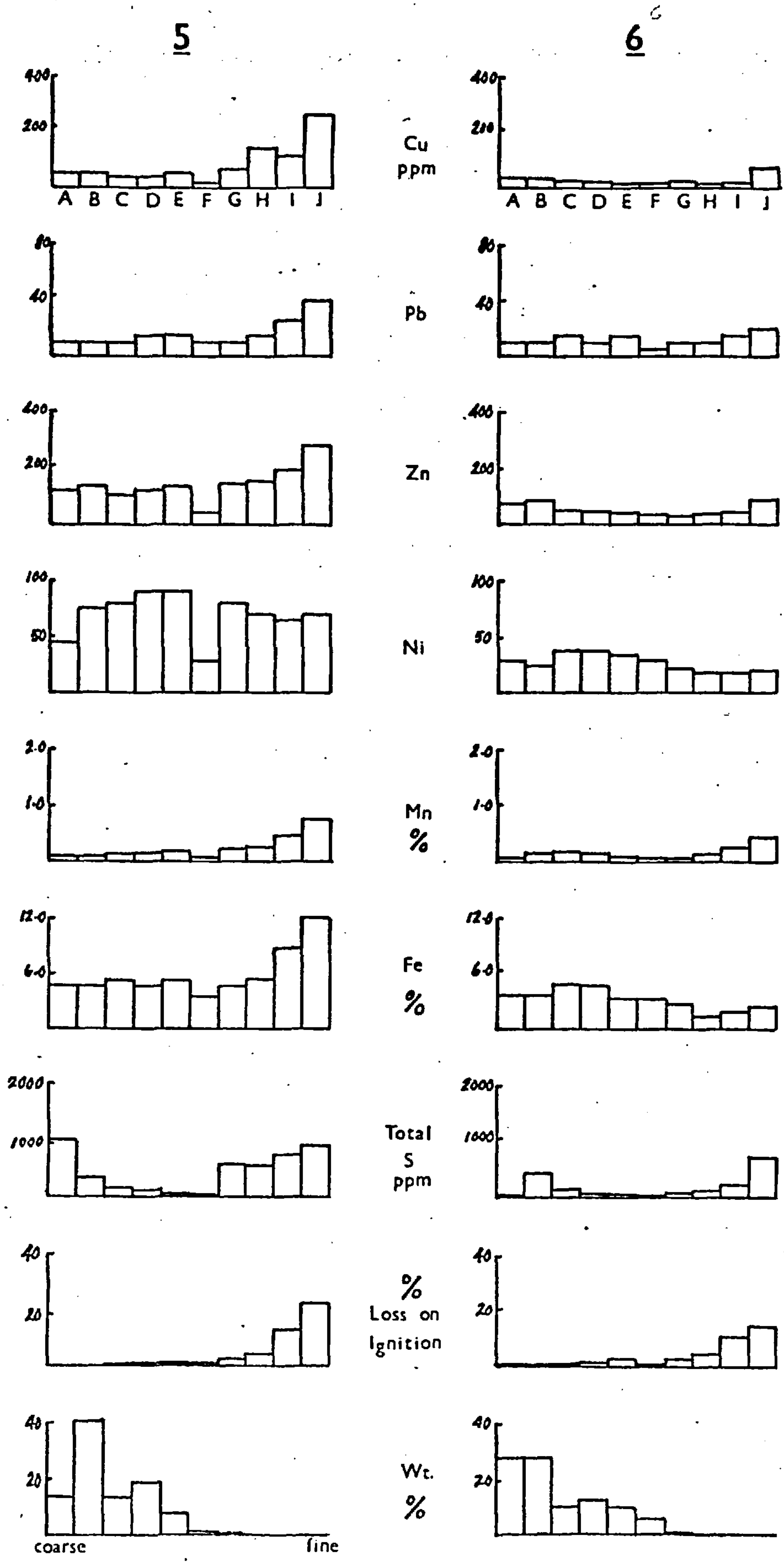


Figure 40: Concentration of elements in size fractions of non-mineralized area stream sediment.

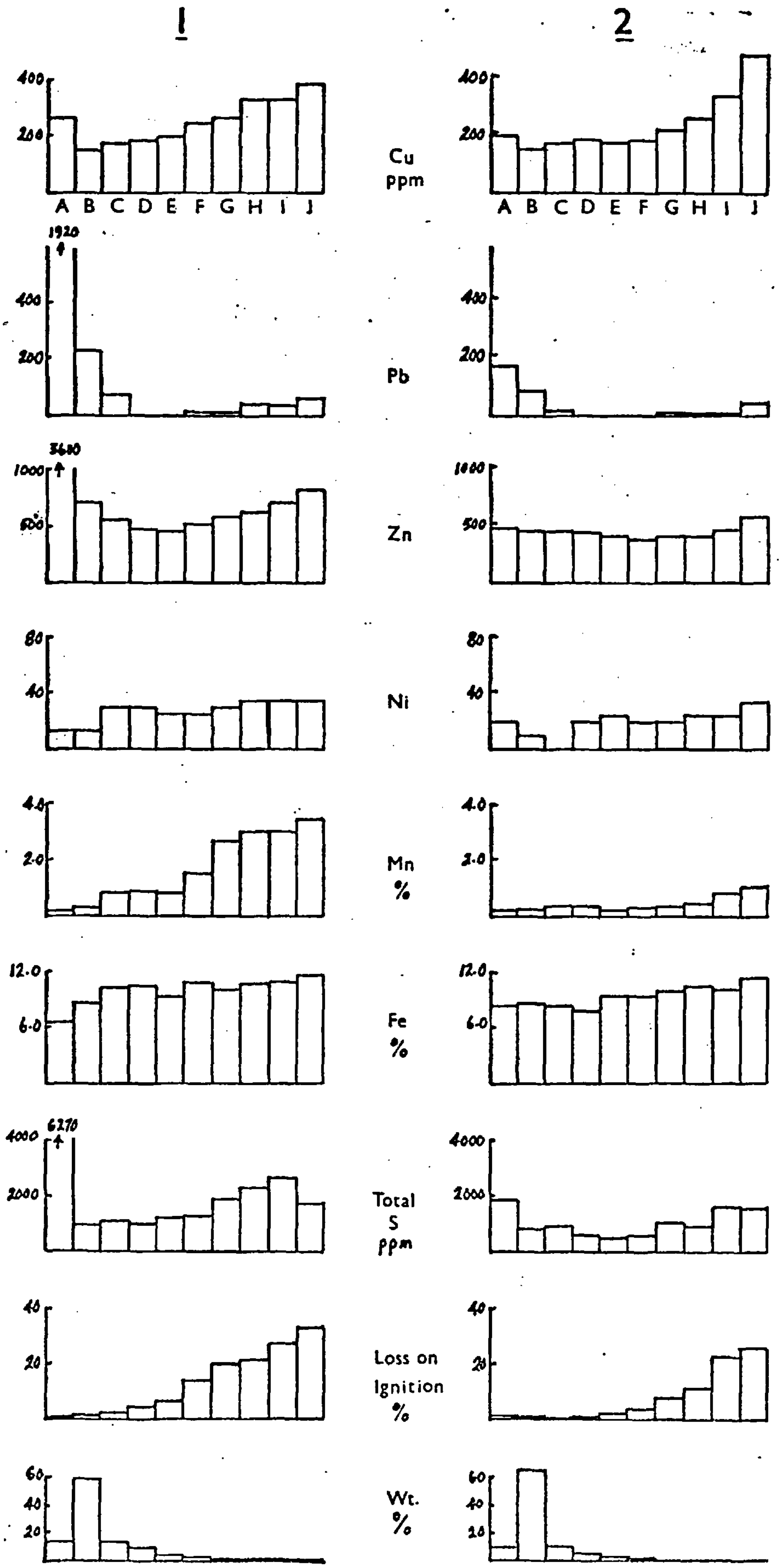


Figure 41: Concentration of elements in size fractions of mineralized area stream sediment.

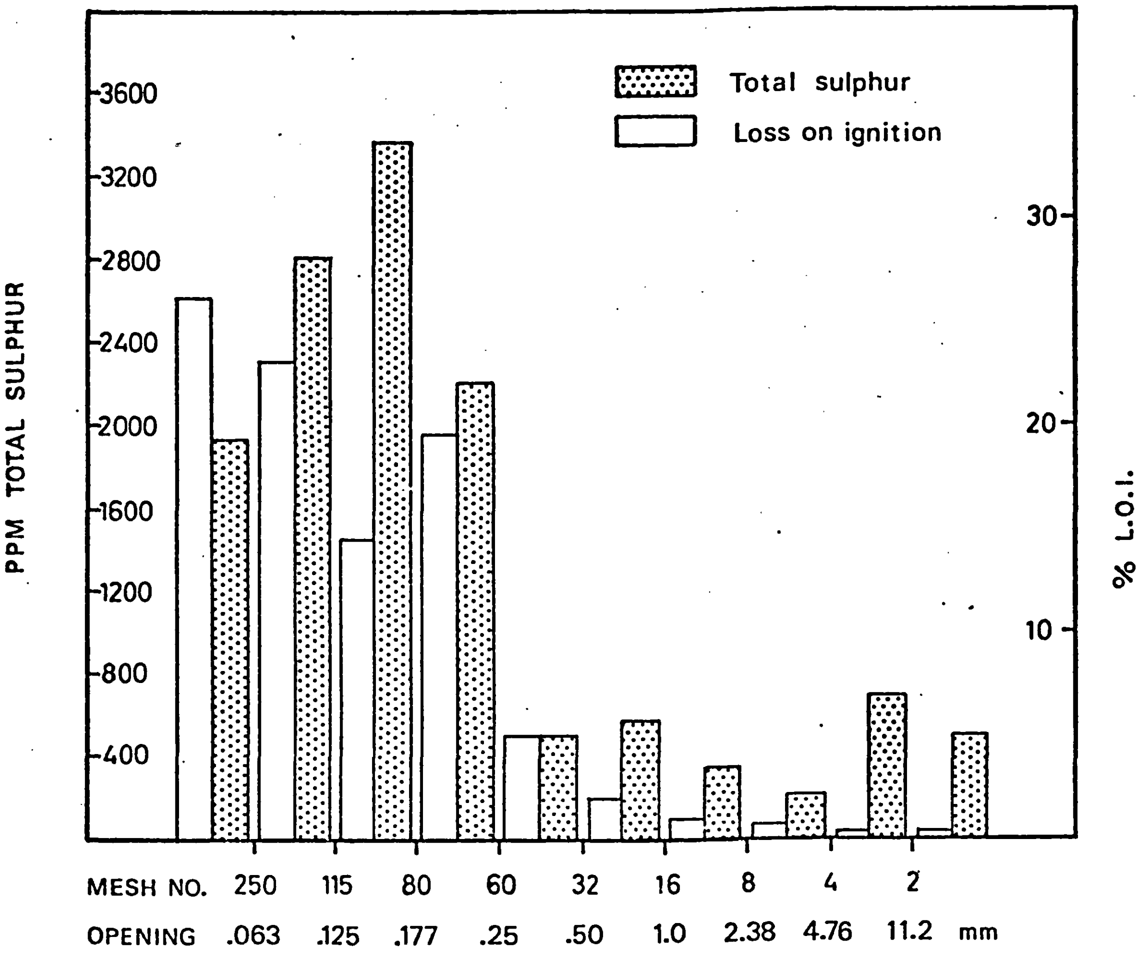


Figure 42: Total sulphur and L.O.I. in various size fractions, sample O, a bulk sample from Ovals Brook.

more representative of the geology of the drainage area.

A feature of the total sulphur distribution in the size fractions shown by case 1 of Figure 41 and in the fractions of a bulk sediment from the Ovals Brook area (Figure 42) is that total sulphur tends to increase in the finer fractions with increasing organic content, but may show a maximum in the 0.1 to 0.2 mm. region, whereas organic content continues to increase with decreasing particle size.

5.3.2 Sulphide Sulphur (as H_2S) and HCL - extractable Sulphate

Determination of sulphide sulphur as H_2S semi-quantitatively by the Pb - acetate paper method described in section 3.2.4 and of HCL - extractable sulphate was carried out on the size fractions of several of the bulk stream sediment samples (Table 23). The Pb - acetate technique works on inorganic samples and did indicate the presence of sulphide grains in sample 1A but the technique fails on the organic-rich fraction because of foaming, which traps the H_2S produced in bubbles and bleaches the stain if it reaches the Pb - acetate paper.

HCL - extractable sulphate is an estimate of the easily soluble fraction, mainly inorganic sulphate and absorbed sulphate. This easily soluble fraction is a very small proportion of the total sulphur content of the stream sediments (Table 24).

Sample Number	Size Fraction										
	11.2	4.76	2.38	1.0	0.50	0.25	0.177	0.125	0.063	mm	
	A	B	C	D	E	F	G	H	I	J	
0	170	50	20	200	Tr.	ND	Tr.	20	F	F	ppm S (as H_2S)
	480	690	200	350	570	480	2200	3350	2800	1920	Total S, ppm.
	0.59	0.58	0.91	1.18	1.93	4.66	19.91	14.30	22.81	25.95	L.O.I. %
1	300	20	Tr.	ND	ND	Tr.	Tr.	ND	F	F	ppm S (as H_2S)
	6270	950	1080	980	1160	1290	1850	2250	2650	1700	Total S, ppm.
	0.79	1.71	2.41	4.74	6.47	13.84	20.08	21.14	27.68	33.66	L.O.I. %
2	100	Tr.	ND	Tr.	Tr.	ND	ND	ND	F	F	ppm S (as H_2S)
	1880	830	920	600	540	600	1020	960	1630	1600	Total S, ppm.
	1.35	1.15	0.94	1.85	2.32	4.00	9.01	11.34	22.64	26.09	L.O.I. %
6	140	150	100	160	130	170	160	Tr.	ND	ND	ppm (as H_2S)
	60	440	120	60	40	20	100	120	220	720	Total S, ppm
	0.88	0.92	1.74	2.00	2.82	1.58	3.12	4.92	10.76	14.56	L.O.I. %

Tr. - Trace
ND - None Detected
F - Undetermined because of foaming

Table 23. Reducible sulphur (as H_2S) in various size fractions of some stream sediments.

Sample	ppm S (as H_2S)	HCL-extractable SO_4, ppm.	Total Sulphur ppm.	Loss-On-Ignition %
1A	300	75	6270	0.79
1B	20	15	950	1.71
1C	Tr.	<10	1080	2.41
1D	ND	<10	980	4.74
1E	ND	<10	1160	6.47
1F	Tr.	<10	1290	13.84
1G	Tr.	<10	1850	20.08
1H	ND	<10	2250	21.14
1I	F	<10	2650	27.68
1J	F	<10	1700	33.66

Tr - Trace

ND - None Detected

F - Undetermined because of foaming

Table 24. Reducible sulphur and HCL-extractable sulphur in various size fractions of stream sediment number 1 in relation to total sulphur and L.O.I.

5.4 SUMMARY

Analysis of stream sediment from the Notre Dame Bay area indicated that anomalous concentrations of total sulphur can be distinguished in the sediment of streams draining sulphide mineralization. It was noted in the Ovals Brook area, however, that the sulphur anomaly was fairly local and that the copper anomaly was wider and showed better contrast than the sulphur. Some samples have high total sulphur content because they contain a large proportion of organic matter.

Size fraction analysis showed that in both non-mineralized and mineralized areas the total sulphur content of the stream sediment tends to increase in the finer fractions with increasing organic content. In the vicinity of sulphide mineralization, the occurrence of sulphide grains may produce high total sulphur in the coarser fractions.

Dispersion appears to be accomplished mainly as sulphide particles as only a small proportion of the total sulphur is contained as inorganic sulphate. If adsorption or aqueous transport of ions were contributing largely to the total sulphur content of the sediment, one would also expect enhanced sulphur levels to persist for considerably greater distances downstream from the mineralization than is observed. The contribution of organic sulphur forms to the total sulphur value should always be considered in the interpretation of total sulphur data on stream sediment surveys.

CHAPTER 6

SULPHUR IN LAKE SEDIMENTS

6.1 LAKE SEDIMENT SAMPLING IN EXPLORATION GEOCHEMISTRY

Regional geochemical surveys have to the present largely relied on analysis of stream sediments but some surveys have been conducted in areas of the Canadian Shield by the Geological Survey of Canada which indicate that lake sediment sampling can be used as a low-cost but effective exploration tool in areas with numerous small lakes, such as the north of Canada (Allan, 1971). It has been shown by Allan (op.cit), that sampling densities as low as one per 10 sq. mile can effectively outline regional copper and zinc anomalies. Smaller scale lake sediment surveys have been successfully carried out in British Columbia and Newfoundland by Rio Algom and Brinex respectively (Allan, op. cit).

Reports of mineral exploration surveys using lake sediments from areas other than Canada are very few but limnological studies of lakes in the English Lake District by Mackereth (1966) and in a number of localities by Hutchinson (1957) have produced some information on the distribution of major and trace elements in lakes. Many lakes in the southern Shield and across much of the remainder of the non-Shield areas of Canada contain 1-6m. of organic gel/sediment above any inorganic sediment and research is continuing at the G.S.C. into the possible application of these sub-aquatic gels as a medium for the exploration of these areas.

6.1.1 Representivity of the Sample Medium

Studies in the Coppermine area of the Northwest Territories of Canada showed that a lake sediment sample does represent a good composite of the material in the drainage system and with a sample density of less than one per 5 sq. miles, sampling reflects underlying geology fairly well (Allan, et al., 1973; Dyck, 1971). A close relationship between the composition of lake sediment samples and the major geological units in the area was also observed by the author during lake surveys conducted by Brinex in Newfoundland in 1972.

A lake sediment sample represents not only the elemental composition of the rock in the drainage area, of course, but also the composition of any surficial materials. If the sediment is organic, as it frequently is in the Newfoundland field area, the contribution of vegetation and aquatic organisms is also represented. It is thus perhaps the best single representation of the bulk composition of materials in any single drainage area. If one is attempting to represent only geology, the contribution of the other environmental factors to the total composition of the sediment must be taken into account.

6.1.2 Dispersion of Elements in Lake Sediment

The trace element content of lake sediment is a function of the concentrations occurring as mineral grains in the sediment or included in the lattices of other minerals, of the amounts sorbed onto the sediment (by adsorption, absorption or cation exchange), of the amounts contained in or held by organic material, and of the trace element concentration of the surrounding waters. The trace element content of the sediment may vary seasonally with the amounts added to the sediment by suspended loads transported to the lake (Allan, 1971).

The cation exchange capacity (CEC) of lake sediment is one of the major influences on the amounts of trace elements held by the sediment and this has been shown by Toth and Ott (1970) to depend on clay content, clay mineralogy and organic content, with organic content being responsible for about 80% of the total CEC. It was also found that samples containing large amounts of organic matter or exchangeable H ions contained large amounts of Cu, Zn and Ni in exchangeable forms.

Exchange of trace elements constituents between the sediment and waters is influenced by coprecipitation mechanisms, as Co, Ni and P, for example, tend to be scavenged by precipitating Mn and Fe hydroxides (Mackereth, 1966). It has been found that the bulk of the constituents are held on the sediment at fixed sites and only to a minor extent in interestitial waters (Sugawara, et al., 1953; and Mackereth, 1966). In some cases the gross composition of the sediment may also be influenced by biological processes, as in the case of phosphorus enrichment in the skeletons of the diatom Asterionella in some English lakes (Mackereth, op. cit.) Living organisms (plants, animals and bacteria) are influential in the movement of material throughout the lake system and must be considered along with purely chemical processes in any conception of the distribution of elements in that environment.

6.1.3 Dispersion of Sulphur in Lake Sediment

The sulphur content of lake sediments is dependent largely on organic matter content, as organic sulphur compounds are included in virtually all plant remains, which are derived from the forests, peat bogs and soils of the region draining into the lake. In English lakes Mackereth (1966) found a good correlation between the carbon and sulphur contents of sediments (Figure 43) and this was substantiated by data from Big Deer Pond in the Notre Dame Bay field area, Newfoundland, presented in Figure 44.

Allan (1971) has shown from regional surveys in the Coppermine area, N.W.T., Canada, that sorption (adsorption, absorption, chemisorption) is the principal mechanism for transport of trace elements such as copper in lake sediments. However, it was suggested that if sulphide particles exist, they would be expected to be present close to sulphide showings. This was found to be the case in Three Corner Pond, in the Notre Dame Bay field area (see section 6.2). However, in areas not adjacent to sulphide showings the influence of the biosphere, i.e. the distribution of organic matter, and processes of adsorption onto clay minerals are considered important in the dispersion of both sulphur and various trace elements.

Sugawara, et al. (1953) found on examination of lake, river and sea muds in Japan that sulphur existed in these sediments largely as sulphide or pyritic sulphur (approx. 1.5% of dried weight), with 0.22% occurring as free sulphur and a small proportion, .04%,as sulphate contained mainly in pore water. No sulphite or thiosulphate was detected. The sediments

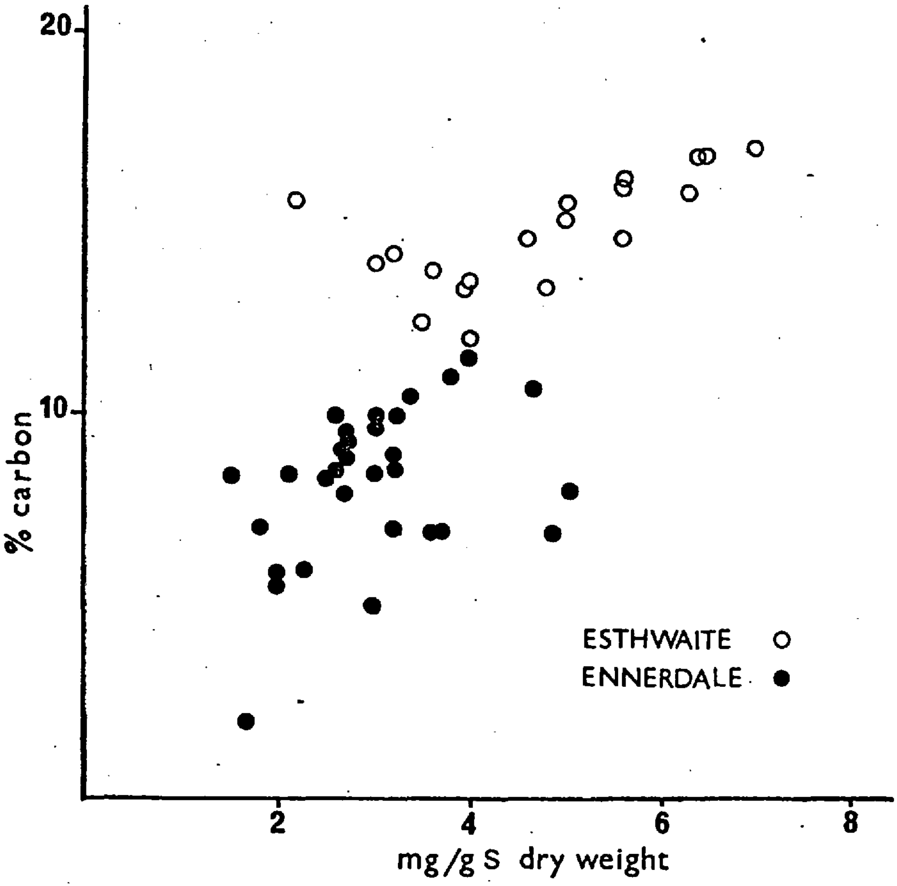


Figure 43: Relationship of Carbon and Sulphur in Lake Sediments of English Lake District (after Mackereth, 1965).

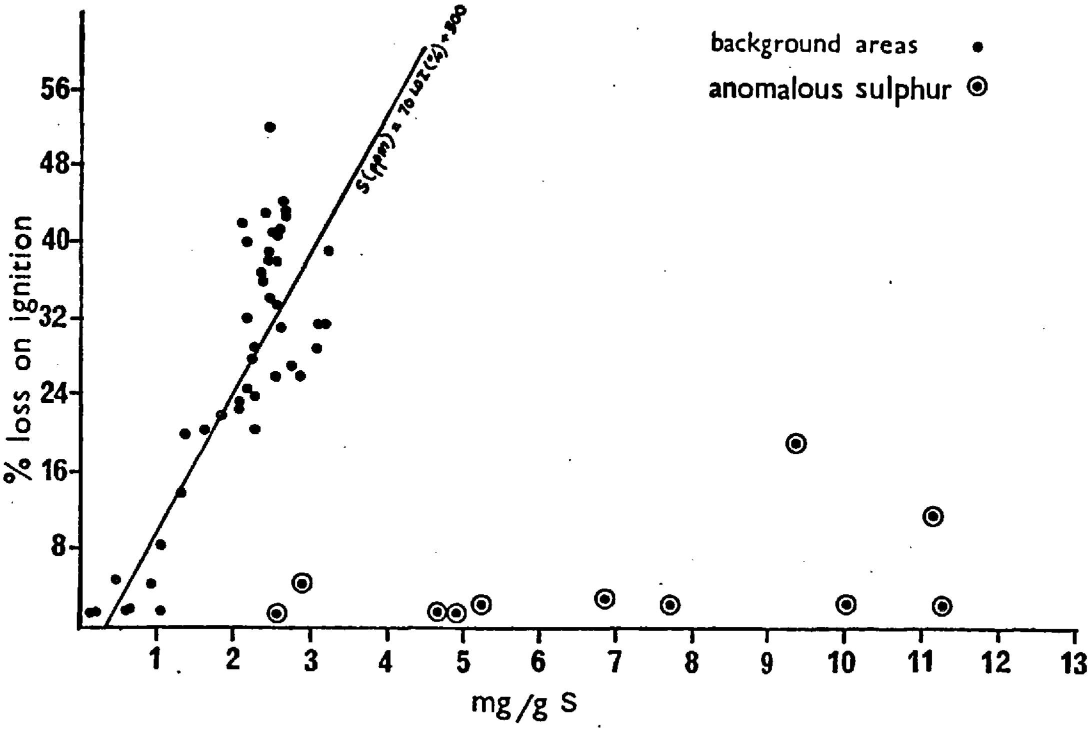


Figure 44: Relationship of organic matter and sulphur in Lake Sediments of Big Deer Pond, Notre Dame Bay area.

are assumed to be fairly inorganic as no mention is made of the organic sulphur fractions, though some of the free sulphur may possibly be soluble organic forms. Kaplan, et al., (1963) found a similar distribution of sulphur forms in marine sediments off California and points out that considerable quantities of organic sulphhydryl groups may be extracted with the sulphide fraction and partial extraction of other organic forms is expected in the other determinations. Both authors mentioned found significant quantities of pyrite sulphur in the sediments and this was considered as having been formed authigenically in the sediment at the sea water/sediment interface where abundant sulphate is reduced to sulphide apparently by anaerobic bacteria.

The formation of sulphides, in particular ferrous sulphides, pyrite and H_2S, by these bacteria in the upper layers of sediment is an important process in reduced lake sediments as well as in marine muds and evidence of this was found in the Newfoundland field area (see section 6.2.4). Similar observations have been made by various other workers in different areas (Hutchinson, 1957; Deevey and Nakai, 1962; Jensen, 1962).

6.2 THREE CORNER POND

6.2.1 Setting

Three Corner Pond is a small lake situated about 5 miles northeast of the Rendell Jackman property (Figure 1). The bottom sediments of this lake had been shown during a regional lake survey by Brinex in 1971 to have anomalous copper and molybdenum concentrations and these were followed up by covering the lake with detailed sampling at 100 feet intervals on lines 200 feet apart. The samples from the detailed coverage were subsequently analyzed in the course of this project to determine whether the sulphur content of the sediments could be related to the Cu and Mo anomalies and to sulphide mineralization in the area.

The pond is fairly deep, reaching depths of over fifty feet in four depressions in the bottom. The sediment consists of 6-24 inches of brown, organic gyttja over fine silt and grey clay. In shallower waters of the slopes small fragments of weathered or broken bedrock are also found in the sediment.

6.2.2 Total Sulphur, Organic and Metal Content of the Sediments

The total sulphur content of the 52 lake bottom sediments from Three Corner Pond covered a range from 930 to 55700 ppm., with seven of the samples greater than 1 per cent. Background levels in the 3000-5000 ppm. range reflect the high organic content of the sediments (30-50% L.O.I.), but are fairly uniform throughout most of the lake (Figure 45).

The area of high sulphur indicated in the central portion of the lake at grid lines 14E and 16E near the baseline is developed on the slope and in the depression immediately adjacent to the area where some sulphide mineralization is known and probably reflects the presence of this mineralization. Maximum copper and molybdenum values also occur in this area (Figure 46), with copper reaching 1000-1250 ppm. and molybdenum 680 ppm. Isolated high values of Mn, Ni, Co and Ag occur at several localities but are not considered significant with respect to mineralization. The Fe content of the sediment is fairly low, ranging from 0.2 to 8% and averaging about 1%, which again indicates the more organic nature of the sediment.

6.2.3 Relationship to Mineralization

Narrow veins of chalcopyrite with some disseminated pyrite are found in exposures on the shore of this lake and the enhanced sulphur and copper on the slope below appears to reflect the presence of this mineralization and/or extensions of the mineralization in the rock beneath the lake. That the sulphur highs are caused by the mechanical dispersion of sulphide grains by gravity and water movement over the area immediately adjacent to the mineralization thus appears probable. The mineralization exposed on the shore is not extensive, however, and if the case is similar underwater a large train of sulphide grains would be unlikely. Away from any mineralization, sorption and biogeochemical processes remain as the important influences on sulphur dispersion.

Microscopic examination of some detailed samples taken from various localities in this lake in the summer of 1972 showed no visible sulphide

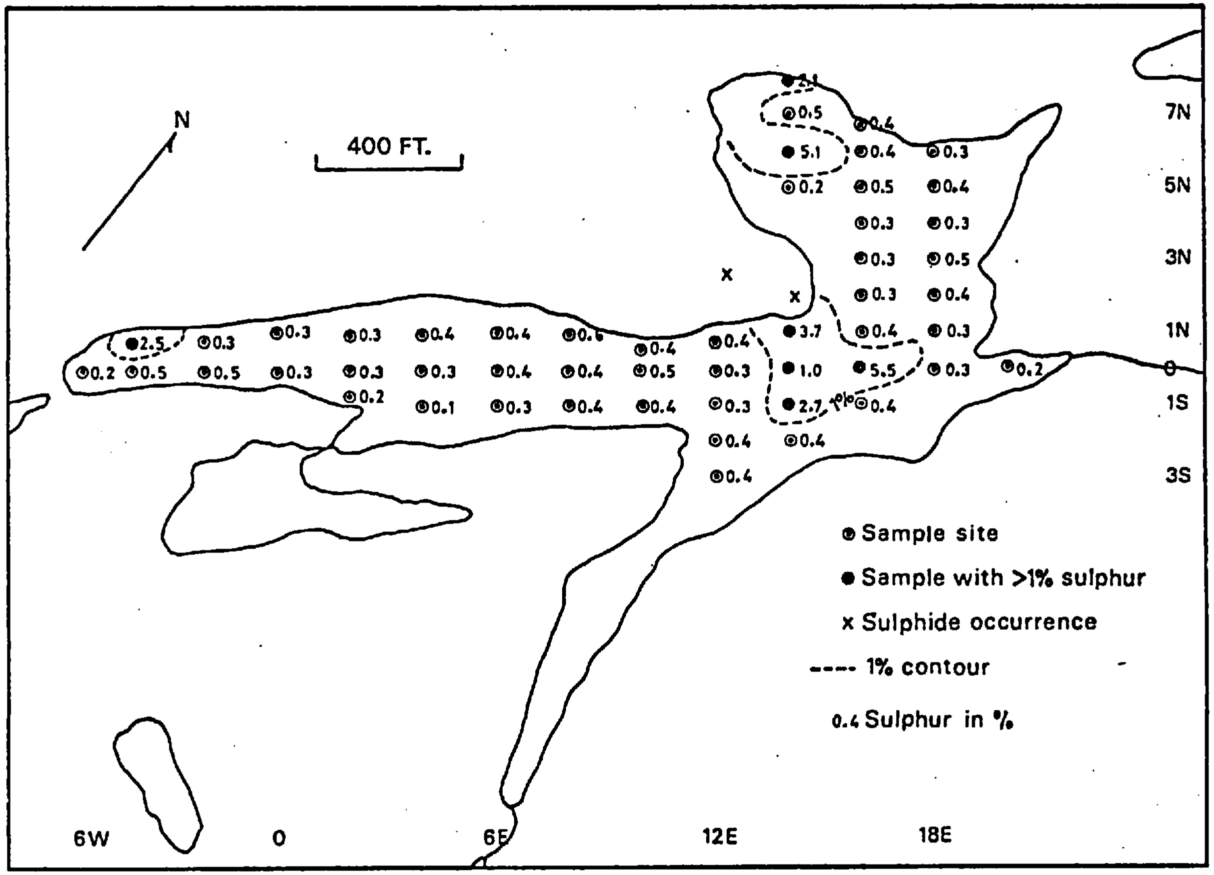


Figure 45: Total sulphur in lake sediments, Three Corner Pond.

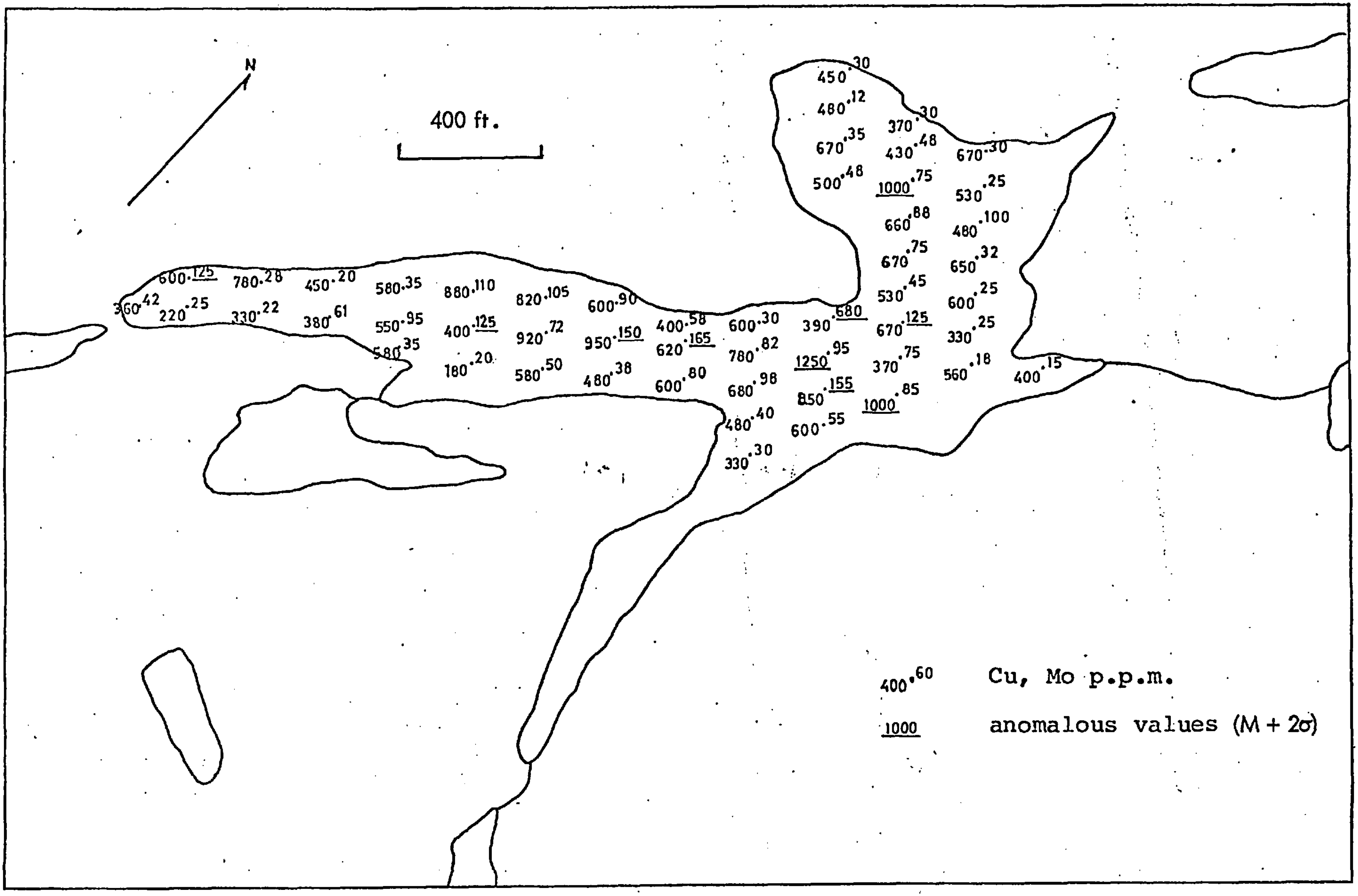


FIGURE 46: Copper and Molybdenum in Lake Sediments, Three Corner Pond, 1971

grains in the sample taken from this slope and only in one sample of grey clay from the northwest corner of the lake was any sulphide distinguished. This occurred as tiny pyrite grains a few microns in diameter which in one instance formed a loose aggregate of grains. The aggregate suggested a clastic derivation as opposed to formation by in situ precipitation or by a biochemical process. The occurrence of these sulphide grains accounts for the enhanced total sulphur in the sediments of this locality.

The bottom sediments of Three Corner Pond and of Mine Pond, situated $\frac{3}{4}$ mile east of Three Corner Pond, contain high concentrations of Mo which may derive from MoS_2 mineralization associated with small aplite dykes, known to occur in the Three Corner Pond area. Analysis of the aplite, chloritic shist and basaltic rocks from the west side of Three Corner Pond revealed no significant Mo concentrations but this remains as the only likely original source of Mo in the area.

6.2.4 Other Characteristics of Lake Sediments from this Region

6.2.4.1 Drying Effects

Ten of the samples collected from Three Corner Pond in 1972 for detailed study were split and one portion air dried at 15°C-20°C and the other oven-dried at 70°C. Both portions were subsequently analyzed for total sulphur by LECO combustion to determine whether oven drying produced any loss of sulphur from the sample compared to air-drying

(Table 25). Although the results on these ten samples showed an average decrease of -5.9% in the total sulphur content of the oven-dried portions, the differences between the two sets of values are such that they are not considered to be indicative of any sulphur loss by drying at temperatures up to 70°C.

It may be noted that these organic sediments, usually brown in colour, dry to a brittle, dense cake which is quite difficult to crush and sieve. Also, there is considerable water loss and subsequent volume decrease on drying, making it necessary to take fairly large quantities of the sediment (several hundred grams) to ensure sufficient dry material for analysis.

Another characteristic of the sediments from Three Corner Pond which became evident on drying was that in two cases spots of red FeO/Fe_2O_3 were formed, presumably by the oxidation of FeS produced in the sediment by the reaction of ferrous iron and the H_2S produced by the bacterial reduction of sulphate. The sediments in which this was observed were blacker than most of the other sediments because of the FeS and were taken from depths greater than 30 feet, where anaerobic bacterial activity is likely greater than in shallower parts of the lake.

6.2.4.2 H_2S, Sulphide, and HCL-extractable SO_4

The production of H_2S in the lake sediments from Three Corner Pond by bacterial reduction of sulphate in the lake water or by bacterial decomposition of organic matter was evident by the smell of H_2S from some of the samples. Of the twenty-two samples taken for detailed study in 1972,

Table 25: Total Sulphur Content of Oven-Dried and Air-Dried Portions of Lake Sediments from Three Corner Pond.

Sample Number	Total Sulphur, ppm. Oven-Dried 70°C	Air-Dried 15°-20°C	% Change (of Air-Dried)	Loss-On-Ignition %
PB-72-12	12,500	14,050	- 11.3	45.63
13	5,000	6,450	- 22.4	33.04
14	1,690	4,050	- 58.5	16.00
15	3,260	4,850	- 32.8	43.84
16	4,250	5,140	- 17.3	36.80
17	6,840	6,920	- 1.1	32.77
18	2,780	2,650	+ 5.0	32.34
19	2,850	2,550	+ 11.9	47.25
20	2,430	2,230	+ 9.0	34.67
21	3,450	2,670	+ 28.5	24.88
		Average	- 5.9%	

only the four samples which were found to contain greater than 1% total sulphur had been recorded in the field notes as smelling of H_2S. It is concluded that bacterial activity is greater in the brown organic sediments of these localities than elsewhere in the lake, with the possibility existing of an additional source of sulphate from oxidizing sulphides at these localities, as one of the samples (4C) came from the northwest corner of the lake, where the organic sediment overlies the grey clay (4BC) in which microscopic sulphide grains were found. As Sandqvist (1964) and Kanwisher (1962) indicate, gaseous H_2S may be released where insufficient concentrations of ferrous compounds occur to hold the H_2S in the sediment by the production of insoluble FeS.

Semi-quantitative estimates of the sulphide content of the sediments were made using the Pb-acetate technique and the results are presented with the other analytical data on these samples in Table 26. The semi-quantitative nature of the analysis is indicated by the difference between the results on the duplicate sets, in which the results on series A are somewhat higher than for series C. Sample 12 clearly contains more sulphide than any other sample and also has high Mo and S contents. The possibility of MoS_2 occurring is thus suspected, though no grains were distinguishable microscopically. In most samples the sulphide estimated by this technique constitutes only 0-10% of the total sulphur content.

Six samples were selected and analyzed for sulphate content by hot HCl leach and turbidimetric estimation as $BaSO_4$ (see section 3.2.3). The results are shown in Table26 and indicate that several hundred ppm.

Table 26: Analytical Data on Detailed Lake Sediments from Three Corner Pond, taken in 1972.

Sample Number	Odour of H_2S	Depth feet	% L.O.I.	Total S ppm.	Cu	Pb	Zn	Mo	ppm. S^1 as H_2S	ppm. S^2 as H_2S	ppm. SO_4
PB-72-1C		30	41.29	1,330	410	8	120	30	0	150	120
" 2C		50	55.78	4,000	500	7	80	15	100	220	...^{3}
" 3C	x	52	50.16	10,430	560	8	100	35	0	220	700
" 4C	x	39	34.47	11,460	540	7	105	58	50	80	...
" 4BC		39	0.00	7,590	130	18	110	90	150	250	...
" 5C		21	33.13	3,800	470	7	120	28	0	100	300
" 6C	x	15	35.65	13,300	480	8	130	75	150	220	...
" 7C		20	33.81	3,050	410	6	120	30	0	20	...
" 8C		21	33.68	2,020	440	8	105	25	100	200	...
" 9C		18	9.15	4,900	300	8	70	48	200	200	...
" 10C		33	37.71	2,820	510	6	150	12	300	100	300
" 11C		45	37.72	1,970	630	7	130	28	0	80	...
" 12C	x	10	45.63	14,050	690	8	265	210	1250	1800	...
" 13C		12	33.04	6,450	680	7	160	42	80	80	...
" 14C		8	16.00	4,050	380	6	40	3	0	120	300
" 15C		18	43.84	4,850	200	7	80	3	30	50	...
" 16C		12	36.80	5,140	320	7	110	15	120	20	...
" 17C		35	32.77	6,920	420	7	115	10	50	80	...
" 18C		27	32.34	2,650	510	7	125	15	100	20	...
" 19C		53	47.25	2,550	540	12	150	72	80	200	...
" 20C		30	34.67	2,230	780	8	280	70	400	350	...
" 21C		20	24.88	2,670	470	8	120	18	30	100	...
" 15B		4	15.00	1,870	330	10	40	0	...	150	200

[1] Series C; [2] Series A, duplicate set of Series C; [3] ... not determined

sulphate may be held in these sediments as adsorbed or soluble sulphates, approximately 5-10% of the total sulphur content. Some soluble organic sulphur compounds may be included in this estimate and any sulphide minerals present would also be partially attacked by the HCl leach to release some sulphate. It is probable that some sulphate may have been loosely held in the pore water of the sediment and became fixed on drying (Toth and Ott, 1970).

6.2.4.3 Diatoms

Sediments from the shallow water areas on the south side of Three Corner Pond (Figure 47) were found to consist of several inches of light brown to white organic material overlying a dark brown organic sediment. Microscopic examination of this light coloured material showed it to be largely composed of the remains of silicious diatoms. These phytoplankton varied from several microns to 0.2 mm. in length and a few microns in width, having a single nucleus and rectangular shape. Silicious diatoms are known to occur in many fresh water lakes and as these are long and rectangular in shape, they are thought to be of the species Chaetoceras, of the genus Diatomacea.

Some fresh water micro-organisms are capable of carrying considerable quantities of some elements in their structures. Mackereth (1966) found that Asterionella, a phytoplankton type, concentrated considerable amounts of phosphorus in sediments of some English lakes, but the samples from Three Corner Pond which contained large amounts of diatoms showed

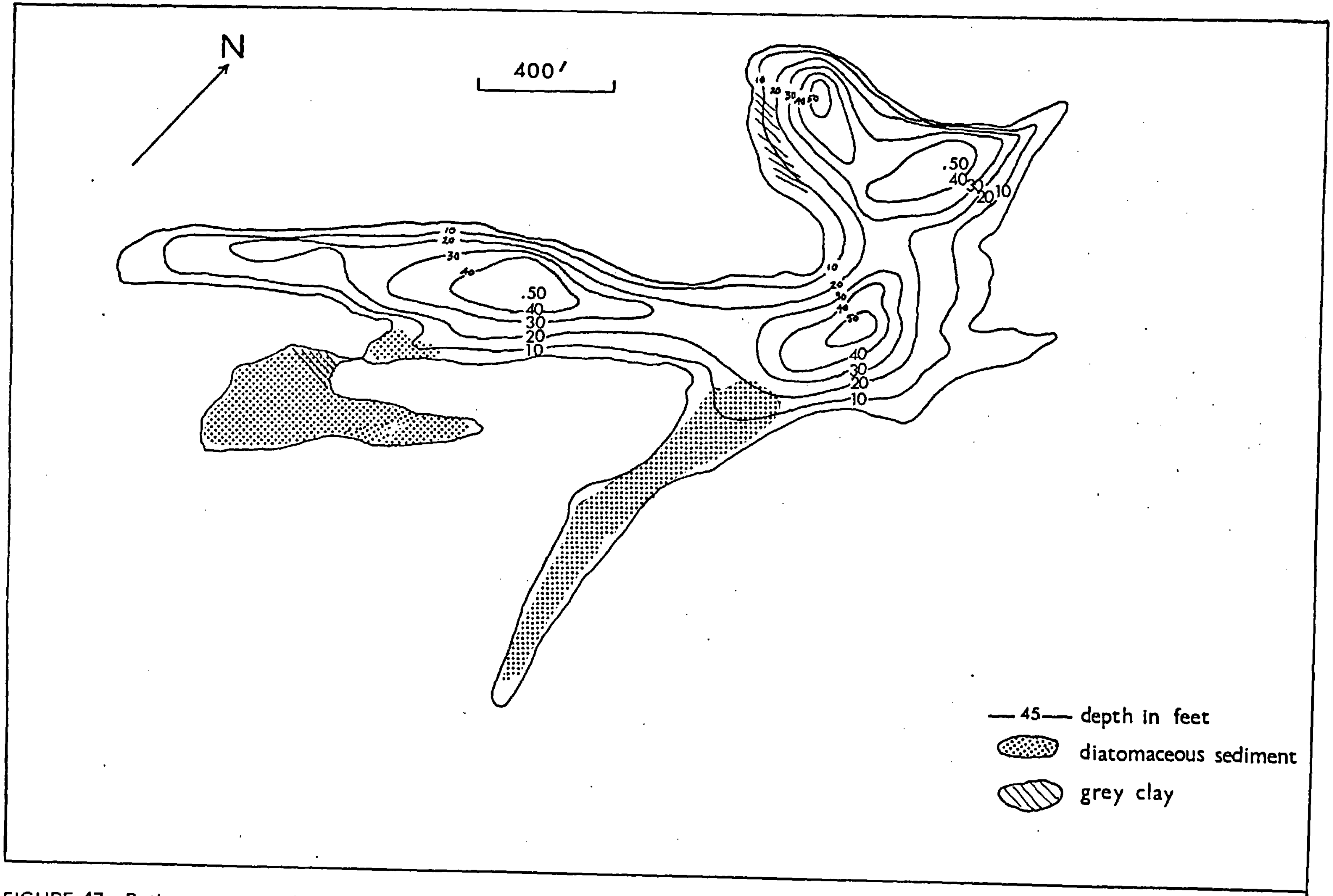


FIGURE 47. Bathymetry and location of sediments, THREE CORNER POND

no enrichment in sulphur, Cu, Pb, Zn, or Mo over other sediment in the lake. In fact, those samples differ only in somewhat lower carbon (L.O.I.) and Mo contents than most of the others.

6.3 BIG DEER POND

6.3.1 Description of Area

6.3.1.1 Geological Setting

Big Deer Pond is situated about 1 mile west of the Whalesback mine (Figure 1) and the geology of the area has been described by Brinex geologists as consisting of andesite and dacite flows, with pyrite and chalcopyrite mineralization, plus some associated gold and silver, occurring in chloritic shist zones in these volcanics (Figure 48).

Two northeastward trending zones of mineralization were indicated by geological and geochemical soil surveys by Brinex in 1962-63. The larger zone outcrops in the southwest near Mine Pond and had been explored by a single shaft at this site by an earlier mining venture. Lake sediment surveys of Big Deer Pond in 1963 and again in 1964-65 indicated that these zones extended some distance under the lake. The copper anomalies found in the vicinity of the mineralization in both soil and lake sediment surveys are shown in Figure 49. Diamond drilling by Brinex in

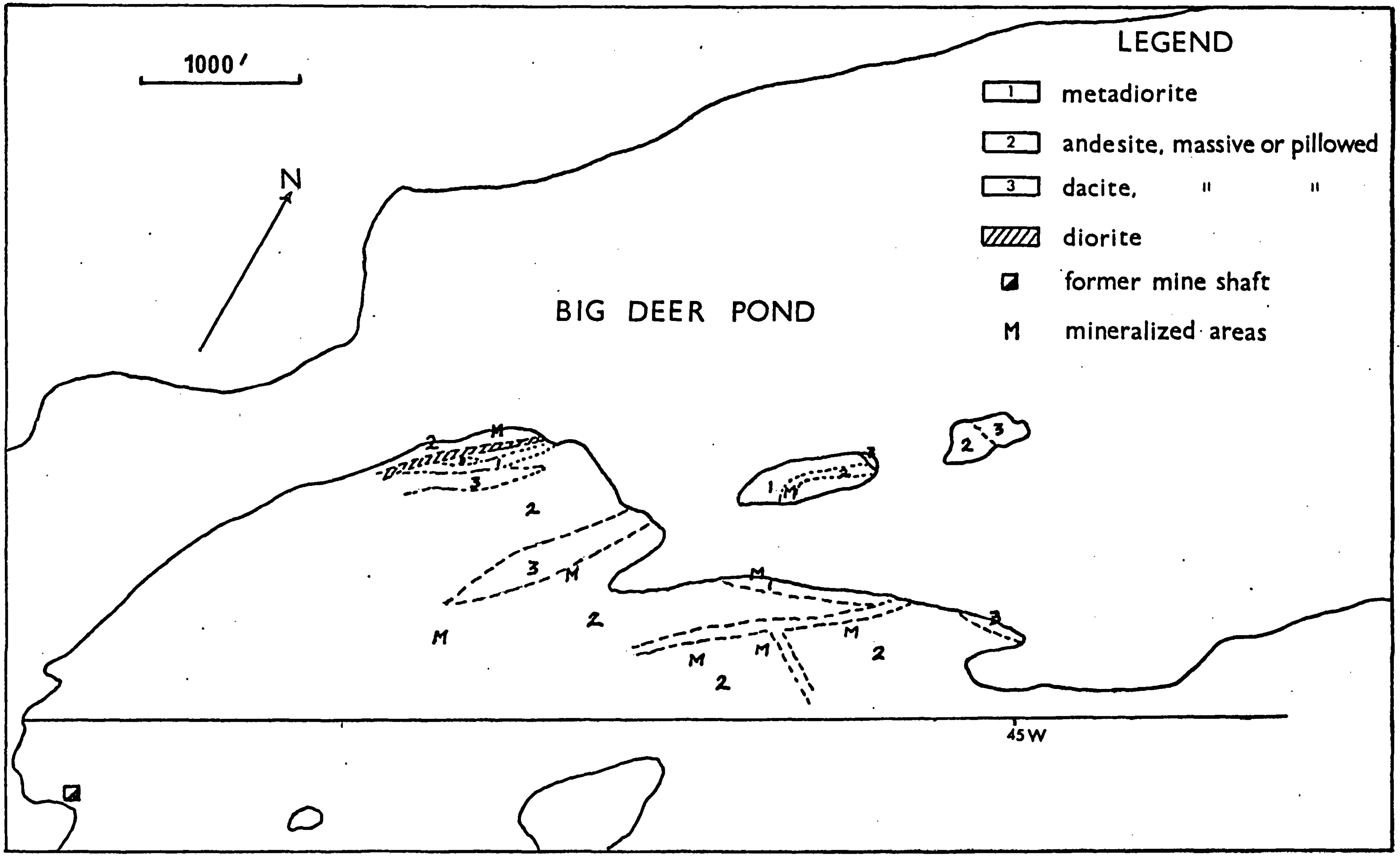


Figure 48: Generalized geology of southwest BIG DEER POND area (after Moghul and Bedford, Brinex 1963).

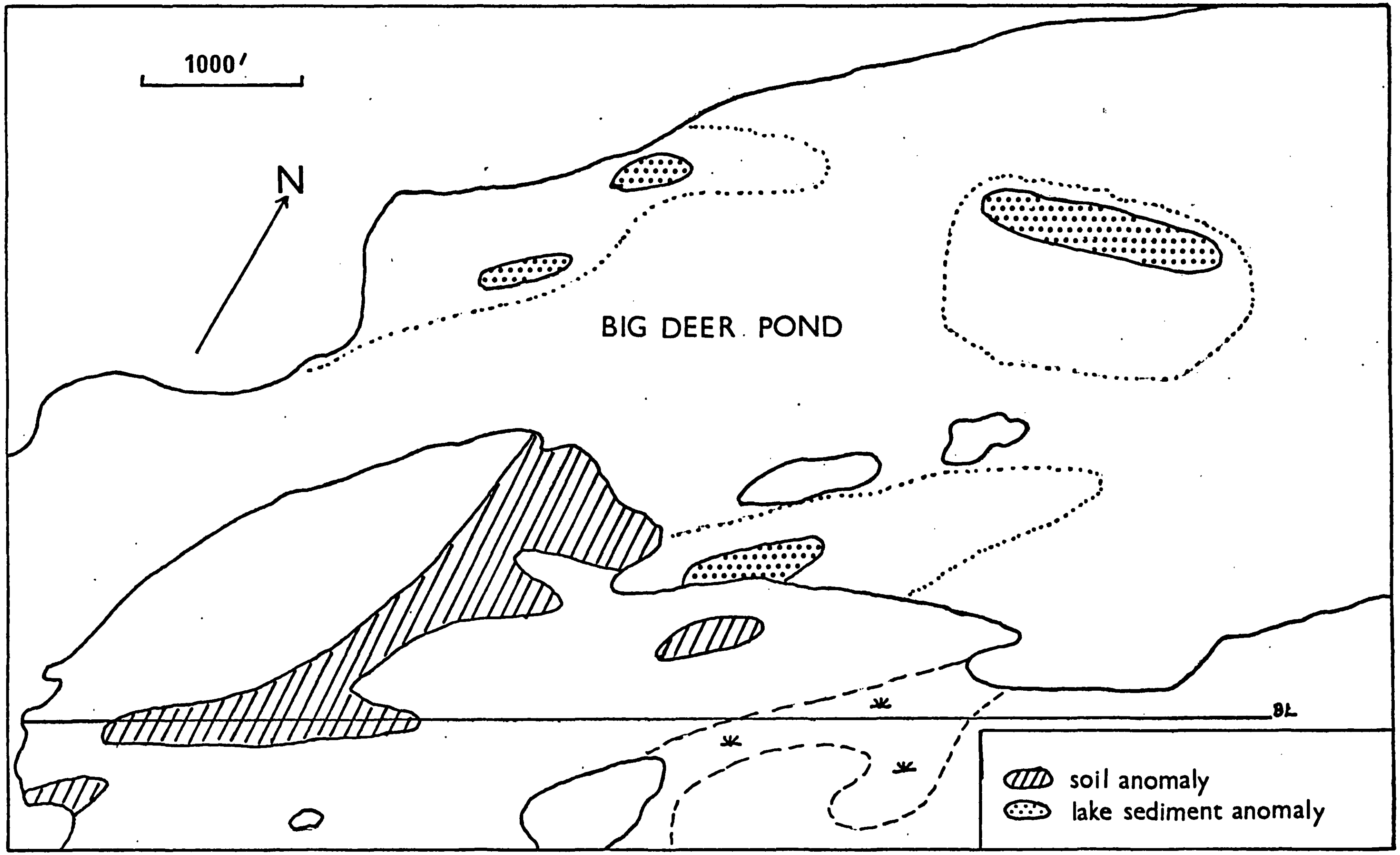


Figure 49: Copper anomalies in soils and lake sediments of the Big Deer area. (1962,1963 surveys)

the off-shore extensions of the mineralization zones as indicated by the lake sediment surveys intersected good sections of chalcopyrite-pyrite ore, confirming expectations, although the amounts defined remain sub-economic.

6.3.1.2 Eh-pH Characteristics of Sediment in Big Deer Pond

The variation of Eh and pH in the lake sediments in Big Deer Pond has been examined by Meyer (1963) during Brinex geochemical surveys in the area. It was found that Eh values ranged from 0.24 volts in oxidized shallow sediments to -0.06 volts in reduced deep-water muds. The Eh was stable in the region of -0.01 volts below 40 feet depth, representing the relatively undisturbed hypolimnion, but generally became increasingly oxidized as the surface was approached (Figure 50). The pH extremes were 5.8 and 7.6 but no pH-depth correlation was observed. Figure 51 shows the Eh variations in the part of the lake examined.

6.3.2 Total Sulphur in Relation to other Variables on Selected Traverses

Samples from the 1964-65 lake sediment survey by Brinex were selected for three lines 200 feet apart traversing the lake in a NNW-SSE direction. Samples were taken at 50 feet intervals on each line using a short steel tube sampler dropped through a hole cut in the lake ice. Depths of over 90 feet were recorded from the depression north of the two small islands and of up to 40 feet south of the islands. The sediment obtained was largely

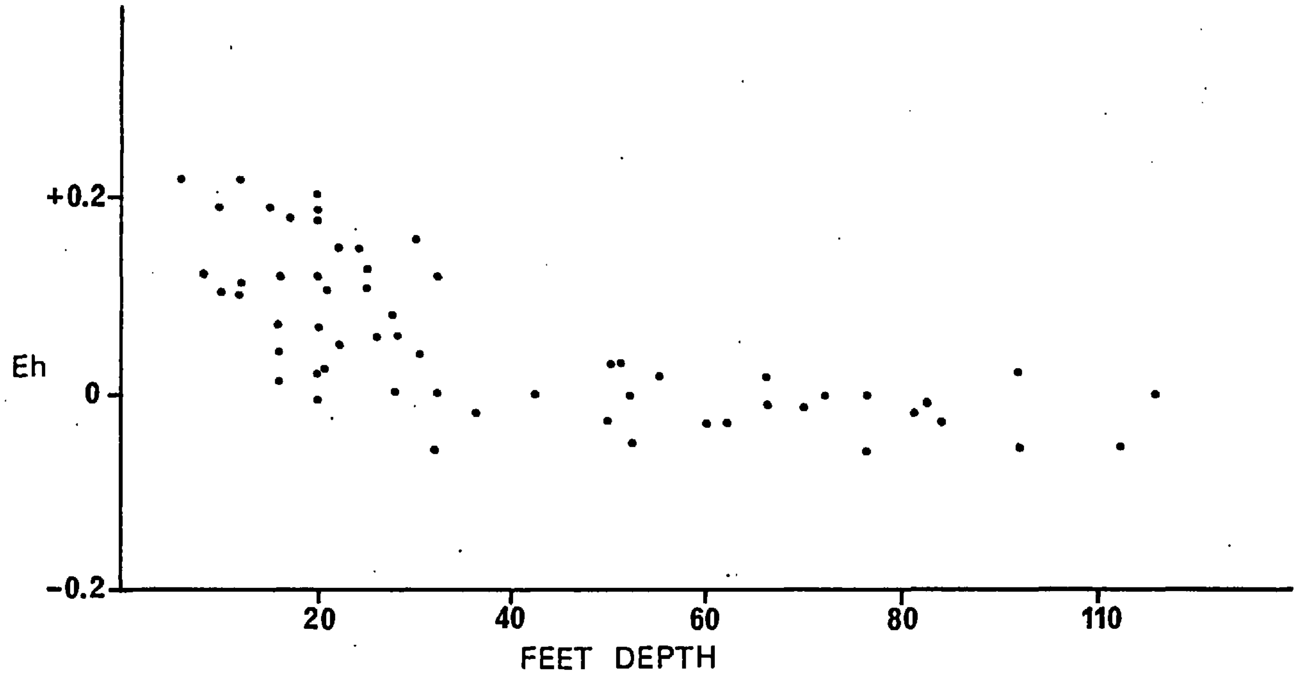


Figure 50: Variation of Eh with depth in Big Deer Pond sediments (after Meyer, 1963).

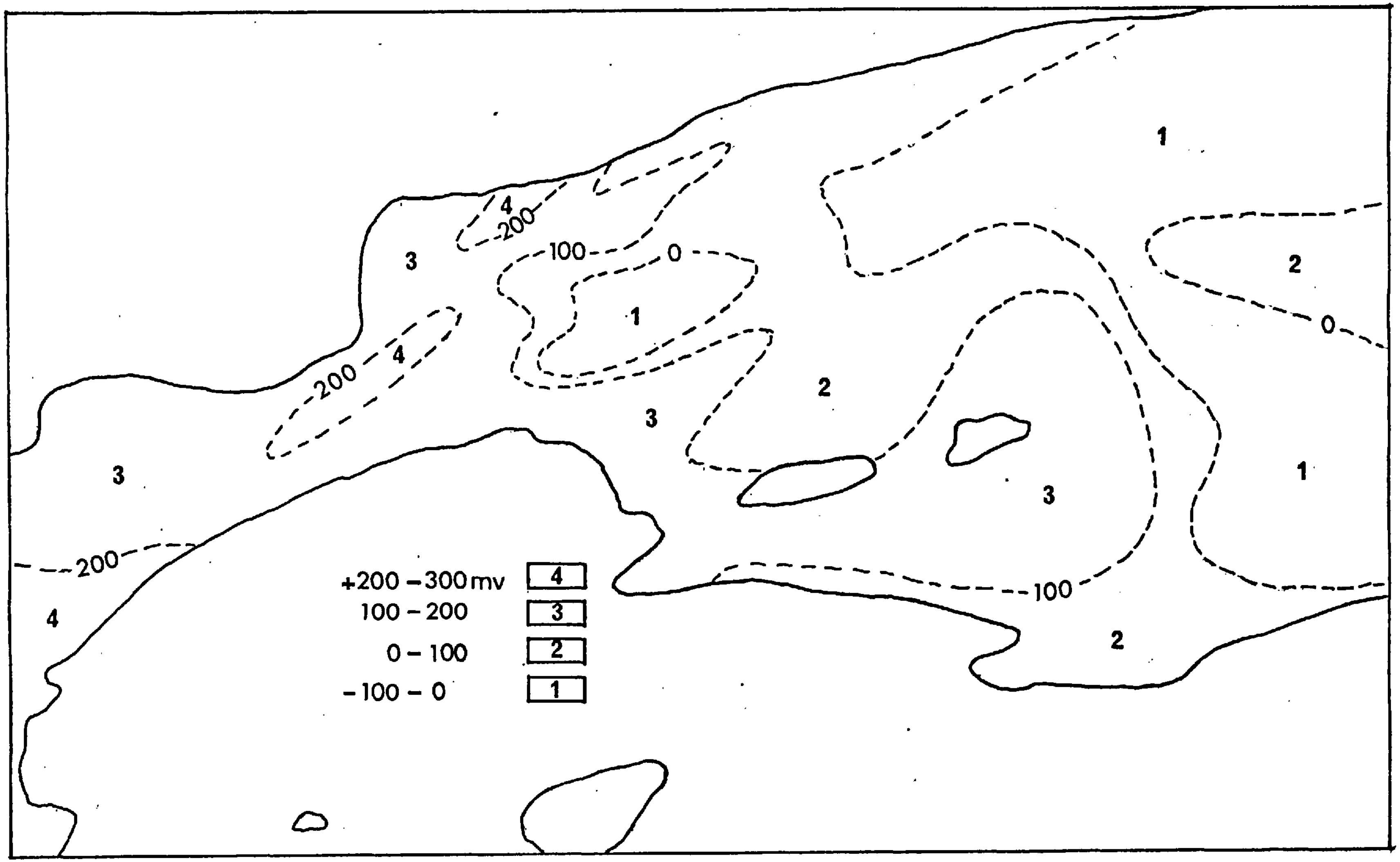


Figure 51: Eh of lake sediments, Big Deer Pond (after Meyer, 1963).

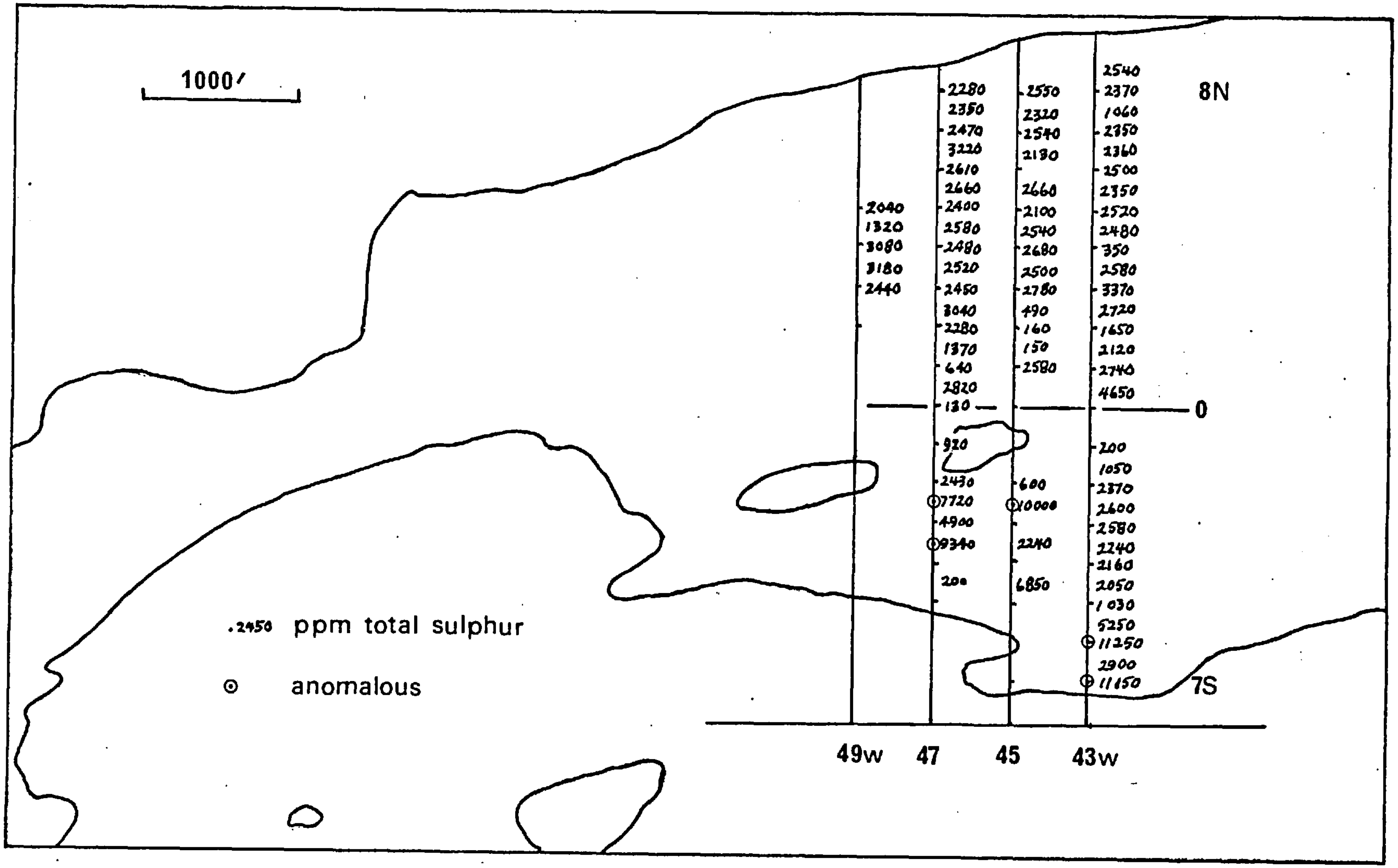


Figure 52: Total sulphur in lake sediments of Big Deer Pond.

brown organic ooze or gyttja, with some deposits of clay and silt occurring in shallower waters around the islands and near the shore. Steep talus slopes form the shoreline on some sections of the lake and in some cases it was impossible to obtain sediment from the rocky bottom near such slopes.

The total sulphur content of the selected samples was determined using LECO combustion and the results are plotted in Figure 52. At least two areas of high sulphur values occur south of the islands whereas to the north the sulphur content is fairly uniform around 2000-3000 ppm. The high values on grid lines 45W and 47W immediately south of the smaller island probably indicate an extension of the zone of mineralization outcropping on shore to the SW and evidenced by Cu anomalies in the soil and lake sediment adjacent to it. The two sulphur values greater than 1.1% near the south shore of the lake on line 43W, however, are not related to known mineralization but may indicate a pyritic zone not distinguished on shore because of peat bog cover in the area immediately to the SW. No copper anomaly occurs in the vicinity and the possibility of the sulphur deriving from the peat bog drainage appears unlikely in this case as the sediments are quite inorganic in this area.

A fairly positive relationship exists in these lake sediments between total sulphur and organic matter content as determined by loss-on-ignition, as already illustrated in Figure 44. Samples with exceptionally high S : C ratios, occurring on the southern part of the traverses, are related to the occurrence of sulphide mineralization.

Cu, Pb, Zn and Ni was determined by atomic absorption and the variation of these elements plus sulphur and organic content is illustrated

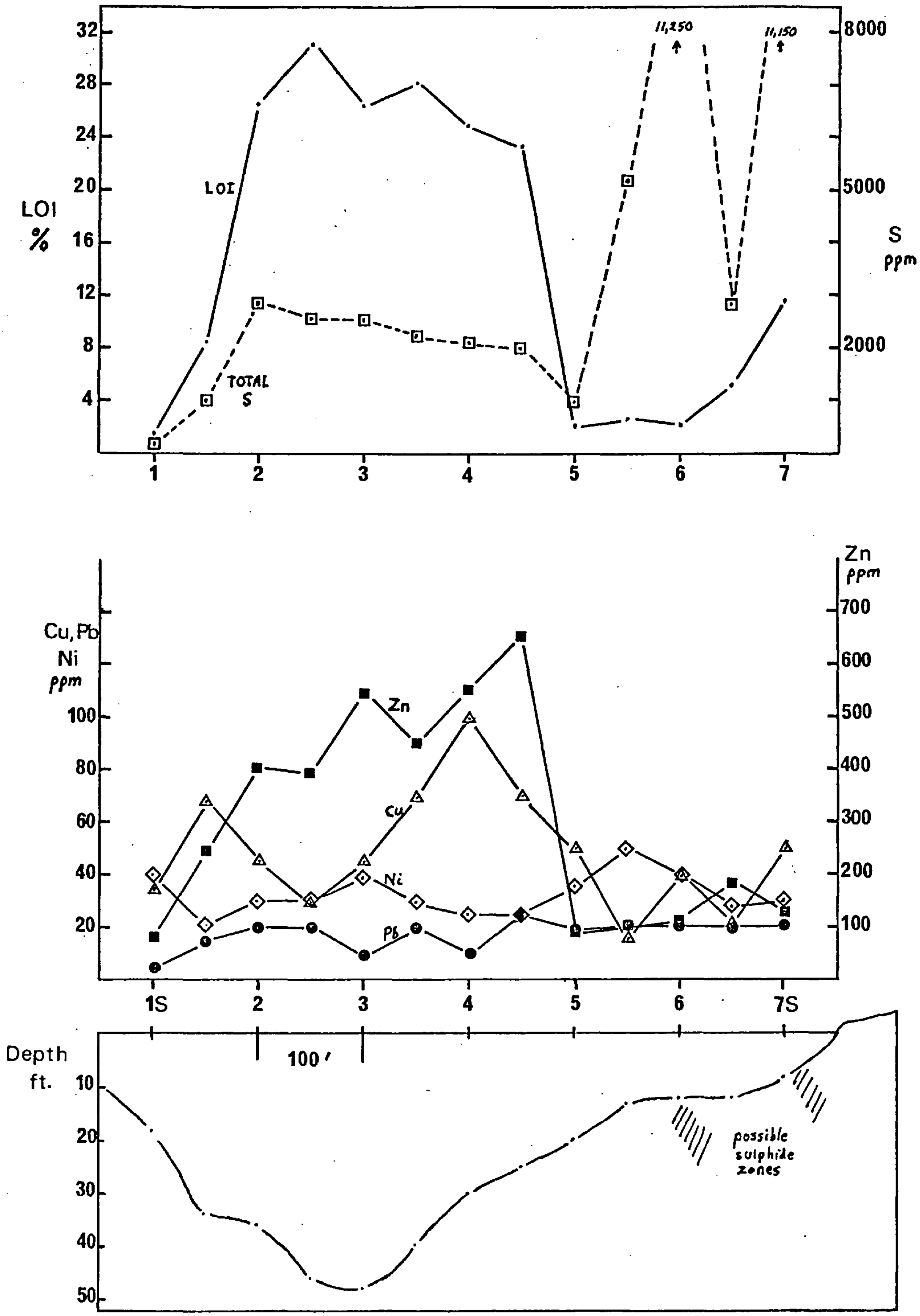


Figure 53: Variation of S, Zn, Cu, Pb, Ni, and loss-on-ignition on a profile in lake sediments on L43W, Big Deer Pond.

in Figure 53 for the southern part of line 43W traverse. In the deeper part of the lake between 200 and 500 feet south, the sediments are quite organic (24-30% L.O.I.), with zinc and sulphur accumulating in this organic material. Sulphur shows very high concentrations between 500 and 700 feet south which are not related to organic content but to possible mineralization. Pb and Ni show little relationship to the other variables and Cu reaches a maximum of 100 ppm. at 400 feet south but has no associated sulphur, which might be expected if the source of the copper were chalcopyrite.

6.4 SUMMARY

It is concluded from the study of lake sediments in the Three Corner Pond and Big Deer Pond areas that sulphur may be used effectively in detailed surveys to delineate extensions of zones of known sulphide mineralization and also mineralization outcropping beneath lakes but not on shore. Whether determination of sulphur would be useful on regional lake surveys as an indicator of sulphide mineralization is yet to be investigated but the indications are that sulphur anomalies which can be discriminated as related to sulphides and not to organic matter are limited to within a few tens of feet of the mineralization and not widely distributed in the bottom sediment of the lake. On smaller scale surveys it may be just as effective as copper, lead, zinc or nickel but it would be a useful data supplement in any regional survey as well.

It is important to note that any interpretation of sulphur data should be made on the basis of organic matter or carbon content because of the extremely biophile nature of the element. Without an estimate of the organic contribution to the total sulphur value it would be very difficult to interpret sulphur highs as due to a source such as sulphide mineralization.

CHAPTER 7

SULPHATE IN SURFACE WATERS

7.1 INTRODUCTION

Hydrogeochemical exploration techniques using sulphate analysis have been applied in the U.S.S.R. in the search both for oil and gas deposits (Gutsalo and Krivosheya, 1967) and for sulphide ore deposits (Vostroknutov, 1968; Yushkov, 1968). Ivanov (1969) has proposed examination of salt aureoles as an exploration method for permafrost areas. More recently, Dall'Aglio and Tonani (1973) have shown from study in the Tuscany region of Italy that this technique can be successfully applied in low-density reconnaissance surveys for sulphide deposits provided fairly complete hydrogeochemical data is obtained. Discrimination of sulphate anomalies related to sulphide ores from others caused by marine sulphate or the leaching of evaporite formations was made on the basis of a regression of SO_4 against Ca and Cl constituents. Sulphate from thermal springs could be differentiated on the basis of boron content, as the spring waters tended to contain more than the waters from sulphide deposits.

A brief detailed study of sulphate in surface waters was carried out in the Rendell Jackman area (Figure 1) by sampling the ponds and streams of the Ovals Brook drainage system, to determine the extent of any existing sulphate aureole and the influential variables in this aspect of the dispersion of sulphur compounds from sulphide deposits. The region is underlain by basaltic pillow lavas, pillow breccias and aquagene tuffs, covered by a moderate amount of glacial till (which is thicker toward the northwest), with podzol and peat bog development in different parts of the area.

7.2 RESULTS FROM THE OVALS BROOK DRAINAGE SYSTEM

The location of the sites from which water samples were taken on the Ovals Brook system is shown in Figure 54. The samples were analyzed for sulphate content using the indirect method of Rose and Boltz (1969) and the pH determined using a Fisher Acumet 210 pH meter with glass/calomel electrodes. The results are discussed below with respect to variations in these factors relative to the sulphide deposit at Rendell Jackman as well as in unmineralized areas.

7.2.1 Unmineralized and Mineralized Areas

The region was sampled on five occasions from the summer of 1971 to the autumn of 1972, and the best contrast in sulphate levels between unmineralized and mineralized parts of the area was obtained in the autumn, 1972, when sulphate concentrations of 0-9 mg/l were observed in unmineralized areas compared to 12-24 mg/l on the stream into which drainage from the Rendell Jackman sulphide deposit flows. An increase

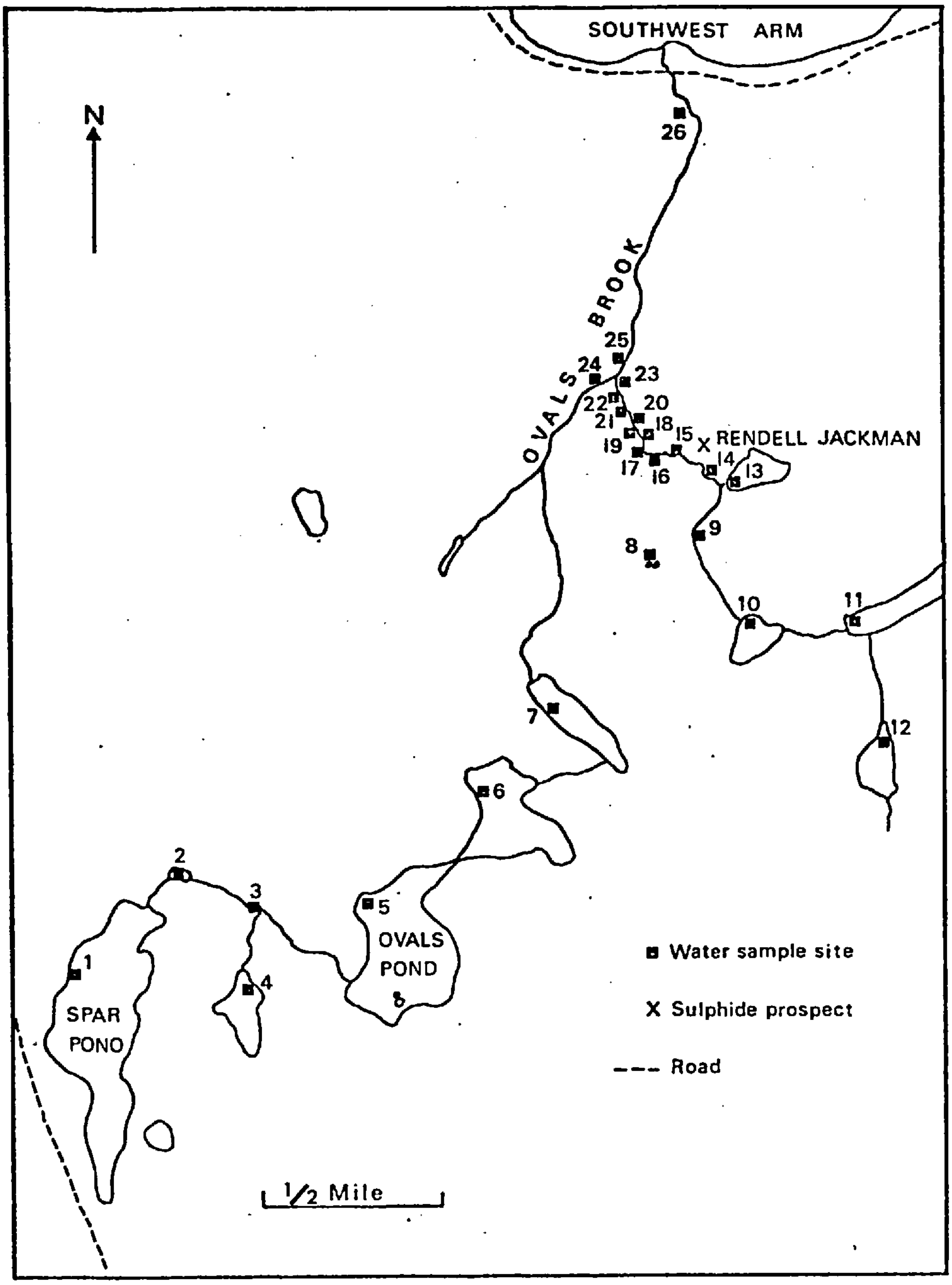


Figure 54: Location of water sampling sites used in studying seasonal changes in sulphate concentration, Rendell Jackman area.

from less than 5 mg/l upstream to 24 mg/l immediately below the mineralization occurs. The values are given in Figure 55.

The enhanced sulphate levels persist for only a few hundred feet downstream from the mineralization and on every sampling occasion decreased to background levels of less than 10 mg/l upon entering the main stream. This is considered due to dilution by the increased volume of the main stream flow.

The range of values observed (0-30 mg/l) is consistent with data produced by Hutchinson (1957) for fresh water lakes and rivers in areas underlain by volcanic rocks and containing no evaporite deposits. It is noted, however, that the contrast even under optimum sampling conditions is not very great, i.e., the Rendell Jackman pyrite/chalcopyrite deposit is not releasing very large amounts of sulphate to the surrounding drainage waters. Since pyrite tends to release more sulphate than any of the other common sulphides (Dall'Aglio and Tonani, 1973), it is concluded that unless the deposits are larger than those occurring in the Notre Dame Bay area the prospects of detection using this technique are somewhat reduced.

7.2.2 Seasonal Variations

The seasonal variations in the sulphate content of the waters of the Ovals Brook drainage system was studied by resampling on five seasons (Figure 56). During this period the volume of water flowing varies from flooding during the run-off from melting snow in the spring to minimum flow in later summer and restricted flow during the winter when the surface

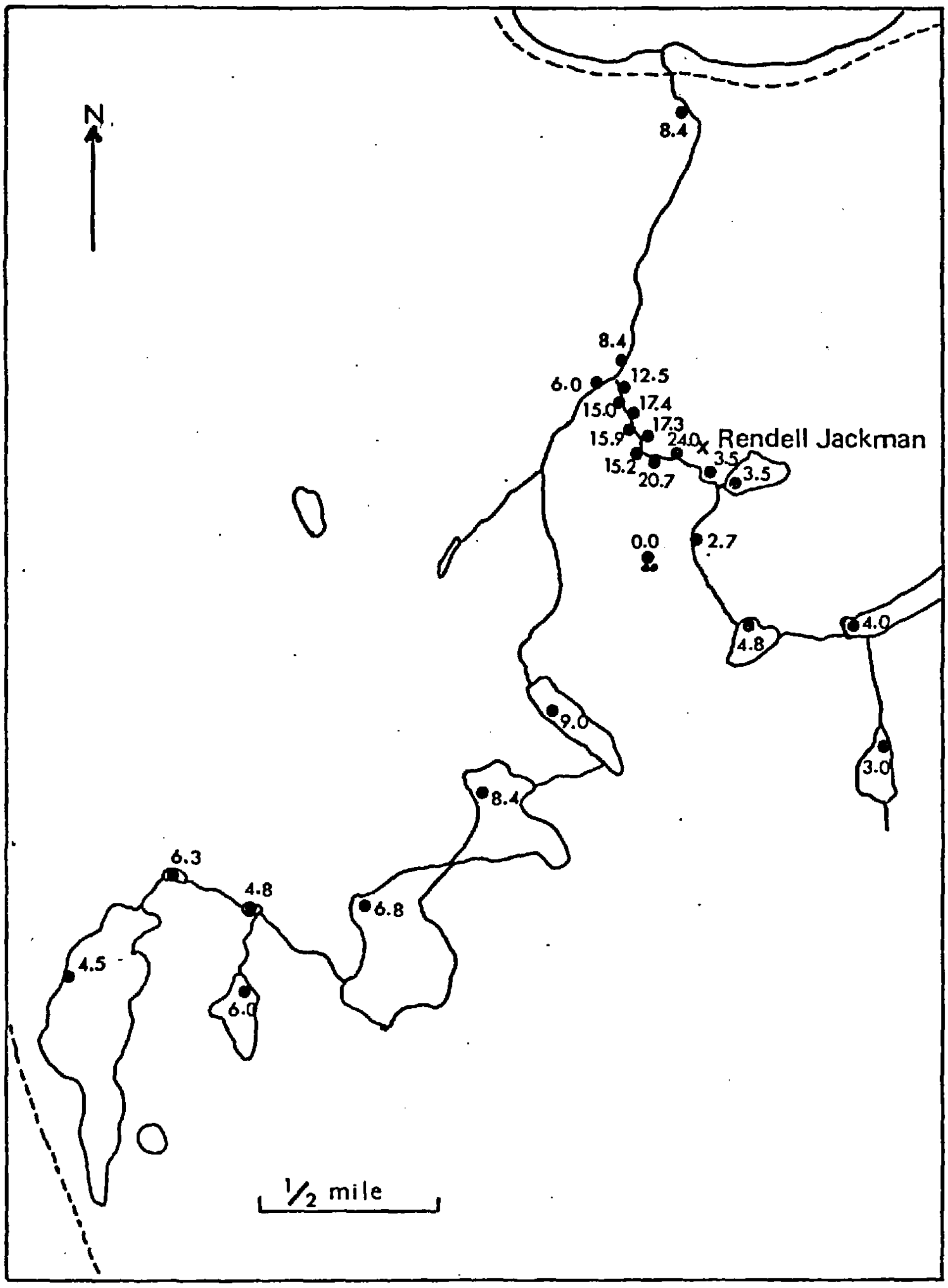


Figure 55: Sulphate content of lake and stream waters, Rendell Jackman area, 1972.

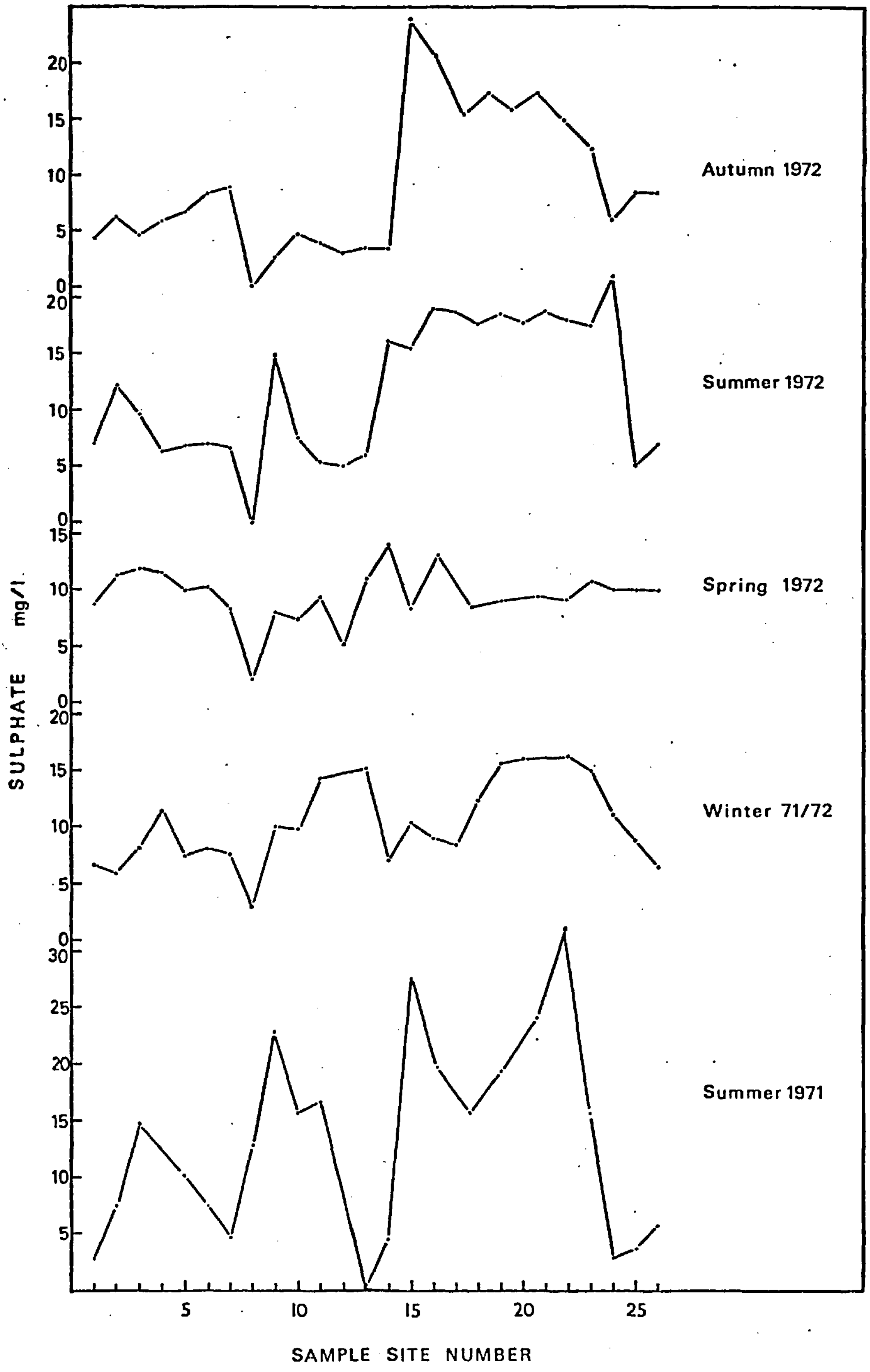


Figure 56: Seasonal changes in sulphate concentration of surface waters, Rendell Jackman area.

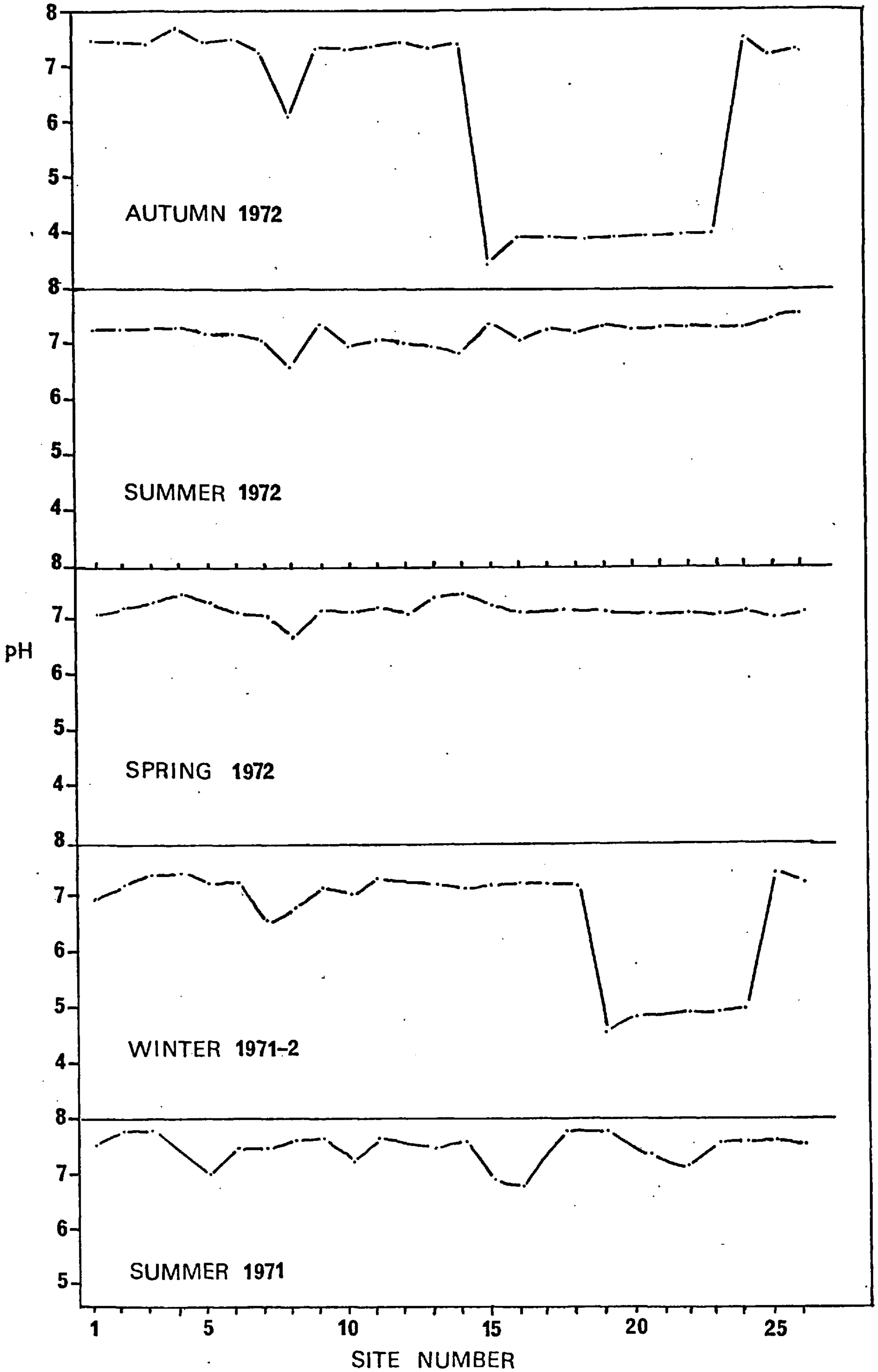


Figure 57: Seasonal variation of pH in surface waters, Rendell Jackman area.

of the streams is frozen. Summer and autumn samples provide a better contrast than those collected in mid-winter, but samples collected during the period of peak run-off in the spring did not show any discernible build-up of sulphate downstream from the mineralization.

The seasonal variations in pH were also monitored (Figure 57) and show a decrease in the pH of the stream below the mineralization in the autumn and winter, whereas in the spring and summer periods little pH change is observed. The waters of the region are fairly neutral, varying from pH 6.5 to 7.5, except in small ponds in peat bogs where the water is very slightly acid, with pH about 6.0.

7.2.3 Factors Influencing Sulphate Dispersion in the Area

The amount of sulphate released in surface waters from an oxidizing pyritic deposit is dependent firstly on the size of the deposit and it was observed that the Rendell Jackman prospect, being fairly small, contributes only about 10-20 mg/l sulphate to the nearby stream. The rate and amount of sulphate production is related to the amount of ore above the groundwater table i.e. the amount being oxidized. Greatest decomposition of the sulphides seems to occur where conditions are fairly moist and the exposed or oxidizing sulphides are subject to alternating wet and dry periods, as this tends to permit an optimum combination of oxygen supply, bacterial activity and removal of the oxidation products.

Examination of field and analytical data from the area, particularly the seasonal variation plots in Figures 56 and 57, showed that four variables appear to be related. These are sulphate concentration, pH, volume of water flow and precipitation of ferric hydroxides. It had been observed that red Fe $(OH)_3$ precipitates were found in the stream in fair quantities in the autumn sampling.

The processes contributing to the seasonal variations in sulphate concentration and pH are suggested to be as follows:

In the spring the run-off waters wash sulphates from the oxidizing sulphide deposit into the stream in the form of ferrous and ferric sulphates and H_2SO_4 but the large volume of water flowing dilutes these to such an extent that no sulphate or pH effect is observed in the stream. At all seasons the increased volume of the main stream (Ovals Brook) compared to the tributary draining the sulphide deposit reduces the sulphate and pH effects so that no increased sulphate or reduced pH is observed below the junction of the two. Similar results were observed in mountain streams by Korven and Wilcox (1964).

In the summer, as the volume of flow decreases, the dilution is lessened and an increase in the sulphate level below the mineralization, relative to above, is observed. The amount of H_2SO_4 produced must be small compared to ferrous and ferric sulphates as no pH decrease is detected whereas an increase in the sulphate content of the stream water is observed.

As the volume of flow reaches a minimum in late summer and early autumn, considerable amounts of ferric iron, sulphate, and H_2O are combining to produce Fe $(OH)_3$ precipitates by the following reaction:

$$Fe_2(SO_4)_3 + 6H_2O \longrightarrow 2\,Fe(OH)_3 + H_2SO_4$$

The production of H_2SO_4 by this reaction decreases the pH so that the combination of high sulphate content, low pH and Fe $(OH)_3$ precipitation is observed.

In the winter the freezing of the surface waters restricts the amount of water flowing in the small streams and whether any surface drainage occurs in the area at all depends on the weather. Some increased sulphate and low pH is noted in the samples obtained from the area in the winter of 1971-72 but patterns are not as good as in the summer or autumn, and sampling conditions are far from optimal.

Undoubtedly the processes contributing to the seasonal variations in sulphate and pH are more complex than has been outlined above and what is observed is a net effect of a large number of reactions or variables. Periods of maximum production of sulphate, H_2SO_4, or Fe^{3+}, for example, are likely related to the activity cycles of the various bacteria. It appears, for instance, that the bacterial production of ferric iron from ferrous and of H_2SO_4 may be greater in the autumn than earlier in the summer.

7.3 SULPHATE IN THREE CORNER POND WATER

During the course of detailed lake sediment study in the Three Corner Pond area, five water samples were taken at various depths from the central section of the lake and subsequently analyzed for sulphate content to determine whether significant variation with depth existed. The production of H_2S and FeS in the sediments at various localities had indicated that some bacterial reduction of sulphate may have been occurring and that this might be reflected by a decrease in the sulphate content of the deeper waters.

The results presented in Table 27 show, however, a very slight increase in sulphate content with depth, which is consistent with data from Linsley Pond and Wisconsin lakes reviewed by Hutchinson (1957). It was concluded by Hutchinson that in these lakes sulphate reduction could not be observed to significantly affect the sulphate concentration of the lake waters. It is possible that a decrease may occur very close to the sediment/water interface near the end of the summer, as was found by Mortimer (1941-42) in English lakes, but this was not observed in Three Corner Pond as the samples were taken in mid-July and the deepest sample (45 ft.) was taken some 3 feet above the bottom sediment.

The sulphate concentration in the lake water appears to bear no relation to the total sulphur content of the sediment, which is almost entirely a function of organic matter content and/or sulphide mineralization. No relationship between sulphate content and pH was detected.

Table 27: Analytical data for Water Samples from Three Corner Pond.

Sample Number	Depth (ft.)	mg/l SO_4	pH
PL-72-2	1	9.8	7.07
3	15	9.6	6.91
4	25	10.3	7.04
5	35	10.1	7.15
6	45	10.6	7.10

7.4 SUMMARY

Studies by various workers, notably Dall'Aglio and Tonani (1973), have shown that hydrogeochemical surveys for sulphide deposits using sulphate analysis may be successfully applied provided fairly complete data is obtained to permit discrimination between sulphate from sulphide deposits and that from other sources. Sulphate determinations in the waters of the Rendell Jackman region of the Notre Dame Bay field area successfully detected the sulphide deposit but contrast was low and seasonal variation studies indicate that sulphate aureoles may be completely obscured in these northern climates during periods of spring run-off. Late summer or autumn is the optimum sampling time.

Drawbacks to the application of sulphate determinations in surface waters as a mineral exploration technique are the difficult analytical chemistry of sulphate in natural waters, and of the various cations in which one might be interested. An advantage in northern regions is that lakes are a most accessible and feasible medium for exploration. In any region, water samples are generally easier and more feasible to collect than sediments, rocks or soils.

CHAPTER 8

SULPHUR DIOXIDE IN SOIL GAS AND THE ATMOSPHERE

8.1 INTRODUCTION

In view of recent trends in geochemical exploration in the area of vapour geochemistry, it was considered important to include in the study of secondary sulphur dispersion some investigations on the dispersion of gaseous sulphur compounds from sulphide deposits. Rouse and Stevens (1971) have reported detectable sulphur dioxide anomalies in the atmosphere and soil air over a variety of sulphide deposits in the U.S.A. and in British Columbia, but little other work has been carried out in this respect elsewhere. Their sampling was conducted under warm, sunny conditions with a surface air temperature of 75°F (23.9°C), not often encountered in the cool, maritime climate of the Notre Dame Bay area. One aspect of these investigations was to determine whether detectable sulphur dioxide concentrations could be measured over smaller sulphide deposits and under poorer climatic conditions.

A survey of the literature (section 2.3) indicated that SO_2 values in the low ppb. range could be expected, so a review of the available analytical techniques for the measurement of such low concentrations led to the adoption of the colorimetric West and Gaeke procedure for the determination of sulphur dioxide concentrations in air. The method has been described in section 3.2.9, and with minor modifications proved to be quite reliable.

As low concentrations of SO_2 were expected under Newfoundland conditions, initial studies were particularly concentrated on sampling the atmosphere in the vicinity of surface accumulations of sulphides derived from mining activity to determine the influence of various factors on the dispersion of SO_2. Detailed sampling was also carried out of both soil air and the atmosphere in the vicinity of sulphide mineralization at several localities.

8.1.1 Previous Work on Factors Influencing the Movement of Gases between Soil Air and the Atmosphere, and Discussion of Gaseous Dispersion from Sulphide Deposits.

Baver (1956), Khonke (1968) and Currie (1970) have discussed the effects of physical variables on the movement of gases in soils and between the soil and the atmosphere. Two main mechanisms of transport of gases are recognized: (1) mass flow in response to a pressure gradient, and (2) diffusion, which is in response to a partial pressure or concentration gradient. In the soil air/atmosphere context, diffusion is the more important of these mechanisms (Currie, op. cit.).

The amount of mass flow is influenced by the soil permeability and external factors such as change in atmospheric pressure. An increase in pressure compresses the air in the soil and some atmospheric air is taken in at the surface and vice versa. On a soil uniformly permeable for 1 m. an increase in pressure of 33 mbar would admit fresh air to the surface 3 cm. or so of the soil (Currie, op. cit.). In practice, soils are not uniformly permeable and in the Nfld. field area the maximum pressure changes over a 24 hr. period are about 25 mbar (Gander weather office reports), so the exchange due to pressure changes usually involves the top 1 cm. or so of soil air. Wind, and air turbulence associated with it, sometimes causes pressure differences which could also induce mass flow.

The effect of temperature change on mass flow of soil air is even less than pressure influences. The effect of increased soil temperature is to raise the pressure of air in the pores and flow is induced on the pressure gradient. Temperature changes affect the surface layers most, however, and do not significantly influence air movements below the surface few centimeters. The net effect on gas exchange is minor (Baver, 1956). Rainfall is also said to influence air exchange by the displacement of air from the soil pores by the water but Currie (1970) considers the net effect of little importance.

The diffusion of gases from the soil to the atmosphere and vice versa is the principal mechanism resulting in net flow. Amounts of gas exchanged and rates of diffusion appear to be dependent on the porosity and permeability of the soil, the diffusion constant (which relates partial pressures or concentrations and cross sectional area), the diffusion coefficient (relating temperature and pressure effects), and soil moisture content (Baver, 1956). Compaction of a soil reduces pore space and restricts diffusion as well. Several works reviewed by Baver (op. cit.) indicated that in soils which retained a lot of water in the pore spaces diffusion was greatly reduced. In one instance it was observed that diffusion was practically stopped at a saturation of 80 per cent.

In view of this information it is concluded that sulphur dioxide gas released from an oxidizing sulphide deposit under considerable thickness of soil or glacial till would be transported upwards by diffusion to the surface and into the atmosphere. Near the surface, wind and pressure-temperature changes may induce a small amount of mass flow but the net affect on gaseous exchange to the atmosphere would be small. Diffusion through the overburden would be severely restricted if the moisture content is high or if compact, impervious horizons occur.

In the Newfoundland field area, the glacial till is mostly loose, poorly sorted material which is fairly permeable but where layers of clay occur in the till, which is often moist and less porous, diffusion of gases is undoubtedly impeded. Soils of the area tend to be fairly permeable where developed on sandy till but in many other areas the moisture content is high and in areas where drainage is restricted, such as peat bogs, it would be extremely difficult for gaseous diffusion to occur. Where drainage is restricted, of course, as in peat bogs, any deposits underneath would tend to be very slowly oxidizing (if at all), so very little sulphur dioxide would be produced.

Moisture content is critical with respect to sulphur dioxide dispersion (the case in point) for the additional reason that SO_2 is fairly soluble in water. A wet soil could therefore absorb large amounts of SO_2 or H_2S gas as well as restricting diffusion.

It appears possible, on the other hand, that dissolved SO_2 or H_2S released from sulphides at depth may be transported in groundwaters to the surface where drying would permit their release to the soil air and the atmosphere. Whether this occurs to any great extent under natural conditions has not been investigated. It is likely that in the presence of considerable amounts of oxygen near the surface most of the dissolved SO_2

or H_2S would tend to be oxidized to sulphate, so a fairly large source of the dissolved species would have to be envisaged in order for significant quantities of the gaseous forms to reach the atmosphere by this process.

Meteorological factors influence gaseous dispersion in the atmosphere considerably and these are discussed in the relevant sections on the investigations carried out in the Notre Dame Bay area.

8.2 WHALESBACK TAILINGS POND

Tailings, with a high concentration of sulphur in the form of fine grains of pyrite, have filled a small lake adjacent to the Whalesback copper mine (Figure 1) which closed in 1972. Several samples taken from the tailings contained an average of 11.7% and 1.9% sulphur in the -80 and +80 mesh fractions respectively and just over 0.1% copper (Table 28). As the samples came from near the surface, where pyrite is slightly enriched, a reasonable estimate of the average sulphur content of the tailings is 5-6%.

Sampling of air pumped from the tailings, and from the near surface atmosphere, took place on a warm day (20°C) in July, 1972. Gas pumped from a 20-inch auger hole in the tailings contained 49.7 ppb. SO_2 with the temperature of the tailings at 33°C, measured by a steel probe resistance thermometer. Gas evolved from a mud crack in the tailings contained 45.5 ppb. SO_2 while a sample collected 2 inches above the surface showed a slight reduction to 37.5 ppb. By contrast, simultaneous sampling at 2'6" above ground level indicated a seven-fold decline in sulphur dioxide concentration to 5.1 ppb.

Table 28: Composition of tailings in Whalesback tailings pond.

Sample Number	Grain Size	Total Sulphur %	Cu ppm.	Pb ppm.	Zn ppm.
PA-72-1001	-80 mesh	6.1	1150	10	600
1002	+80 mesh	0.8	1050	15	370
1003	-80 mesh	5.6	900	20	550
1004	+80 mesh	1.9	950	15	440
1005	-80 mesh	22.6	1550	30	710
1006	+80 mesh	1.2	1500	15	500
1007	-80 mesh	11.0	1550	30	550
1008	+80 mesh	2.8	1600	10	300
1009	-80 mesh	13.4	1200	...	...
1010	+80 mesh	2.8	1800	...	...
	Average (-80)	11.7	1270	22	602
	Average (+80)	1.9	1380	14	402

... not determined.

It is concluded from these observations that on such a warm day, when the temperature of the tailings was over 30°C, higher than the air temperature, significant amounts of SO_2 are produced in the tailings. The temperature and partial pressure gradients may induce some flow so that the SO_2- rich soil air is emitted from the surface few cm., accounting for the high concentration in the air close to the surface, whereas above this the wind rapidly disperses the gas and dilutes the concentration.

Further investigations of the effect of temperature, barometric pressure, and height above ground level on the amount of sulphur dioxide in the atmosphere were made in September, 1972. By use of the wooden framework supporting the former tailings inflow channel, samples were collected at regular intervals to a height of 12 feet above the surface of the tailings with simultaneous sampling at a base station at the foot of the framework. Sampling took place on a cool (10°C), calm day with 100 per cent cloud cover. The effect of lower temperature was observed in that sulphur dioxide levels in the tailings and surface air were considerably lower than those found on the warm day in July, with only 1.9 ppb. detected in gases pumped from an auger hole at the base station, and 7.6 ppb. at the site which contained 49.7 ppb. on the previous occasion.

The sulphur dioxide content of surface air collected at ground level at various times over the day reached a broad maximum of 3.5 ppb. which coincided with the peak air temperature recorded between 11.30 a.m. and 12.00 noon (Figure 58). As the sampling configuration only permitted the simultaneous collection of two samples, the effect of height above ground has been recorded as the ratio between the sulphur dioxide concentration

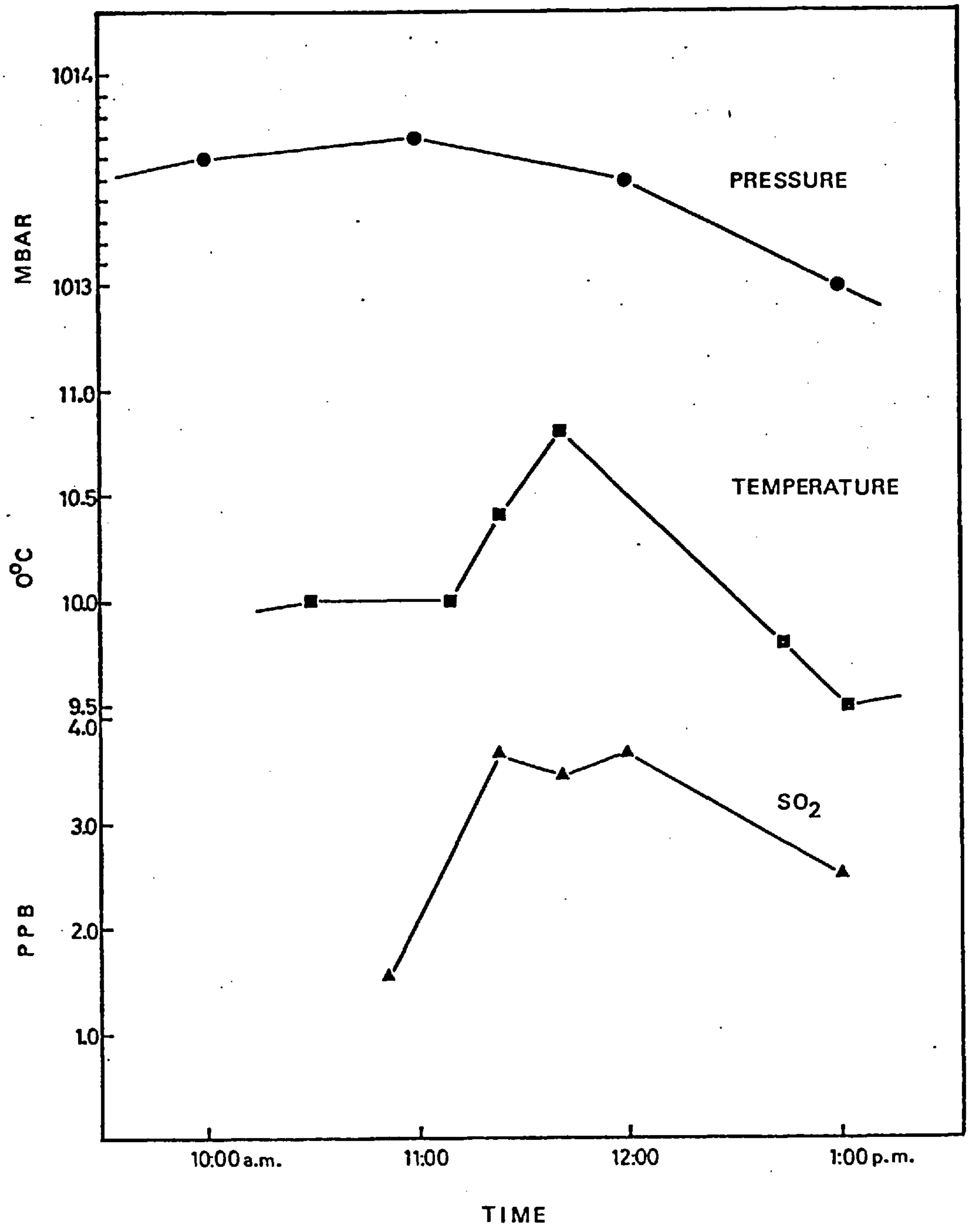


Figure 58: Variation in SO_2 concentration of air at ground level with temperature and pressure, Whalesback tailings pond.

at the sampling point and the value recorded at the base station at the same time (Figure 59). The concentration of sulphur dioxide was reduced to 25 per cent of the value at ground level at a height of 8 feet, but showed an increase in the ratio at 12 feet. This increase at 12 feet seems to reflect a delay in the temperature effect, as the maximum concentration of SO_2 at ground level was recorded one hour before the sample was collected (Table 29). A sampling configuration permitting simultaneous sampling at each of the different heights is necessary to measure the true variation with height, as a pulse of SO_2 is released at the surface with maximum daily temperature. No conclusion could be reached on the effect of changes in atmospheric pressure because of the relatively short time period covered by the sampling.

8.3 PILLEY'S ISLAND

The sulphur dioxide content of air samples collected at ground level was measured across an oxidized dump at Pilley's Island. This dump differed from the Whalesback tailings dump in that the material had stabilized during the sixty year period since mining took place. Conditions during sampling were cloudy with a light wind and recorded air temperatures in the shade spanned the range of 15 to 19°C. The maximum concentration of sulphur dioxide was not found directly over the dump, but in the flanking forested areas not so much affected by the light breeze which swept over the oxidized material (Figure 60). Sulphur dioxide levels may also be influenced by forest fires,

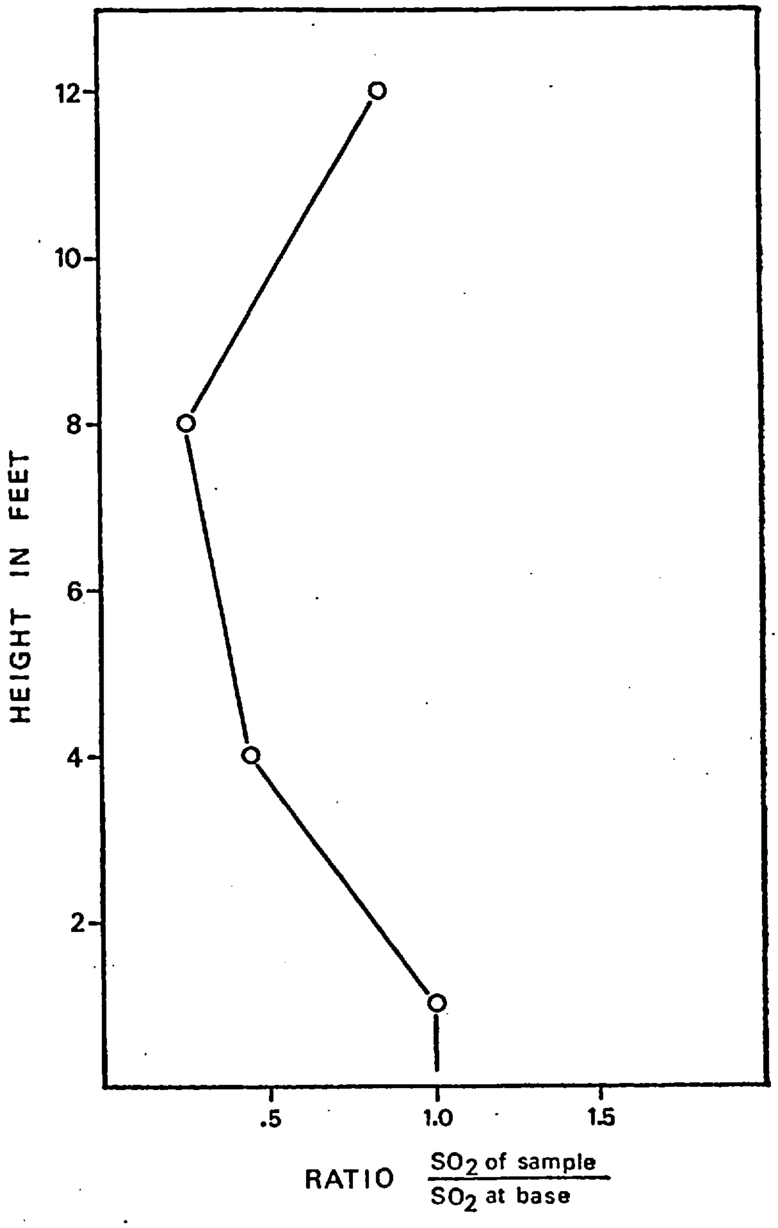


Figure 59: Variation in SO_2 concentration with height above ground, Whalesback tailings pond, 1972.

Table 29: Concentration of sulphur dioxide and air temperature determined during sampling at different heights above Whalesback tailings pond, 1972.

Height (feet)	Air Temperature (°C)	Sulphur Dioxide (ppb.)	Time
Base (ground level)	10.4	3.63	11:00 a.m.
1	10.4	3.63	
Base	10.8	3.44	
4	10.8	1.53	
Base	10.4	3.63	
8	10.4	0.96	
Base	9.7	2.48	
12	9.7	2.10	1:00 p.m.

as the highest concentration (13.4 ppb.) occurred in an area that had suffered from a minor fire not long before sampling took place. Samples collected on the surface of the dump exposed to the wind gave values of 5.7 and 6.6 ppb., while the sheltered side recorded 11.1 ppb. SO_2. A base station established at the western end of the traverse showed an increase from 1.2 to 3.6 ppb. during the 3 hours required to carry out the sampling, coinciding with a change in air temperature from 15 to 22°C.

Soil air samples were also collected at regular intervals along a road on the northwest side of Cobb's Pond (Figure 60). Encouraging variations from 0 to 7.4 ppb. SO_2 were found, with some indication of a coincidence of high SO_2 and metal values in the soil. Only a weak relationship, if any, can be observed between the SO_2 content of the soil air and the total sulphur content of the soil along this traverse (Figure 61).

8.4 RENDELL JACKMAN

A series of soil gas and surface air samples was collected across the zone of mineralization at the Rendell Jackman prospect, at sites corresponding to the detailed soil sampling discussed in section 4.2.3.1. Sulphur dioxide values in soil gas show a consistent increase to a peak of 1.9 ppb. on the axis of the sulphur anomaly in the B horizon soil, but the significance of this pattern is placed in doubt by the presence of an erratic

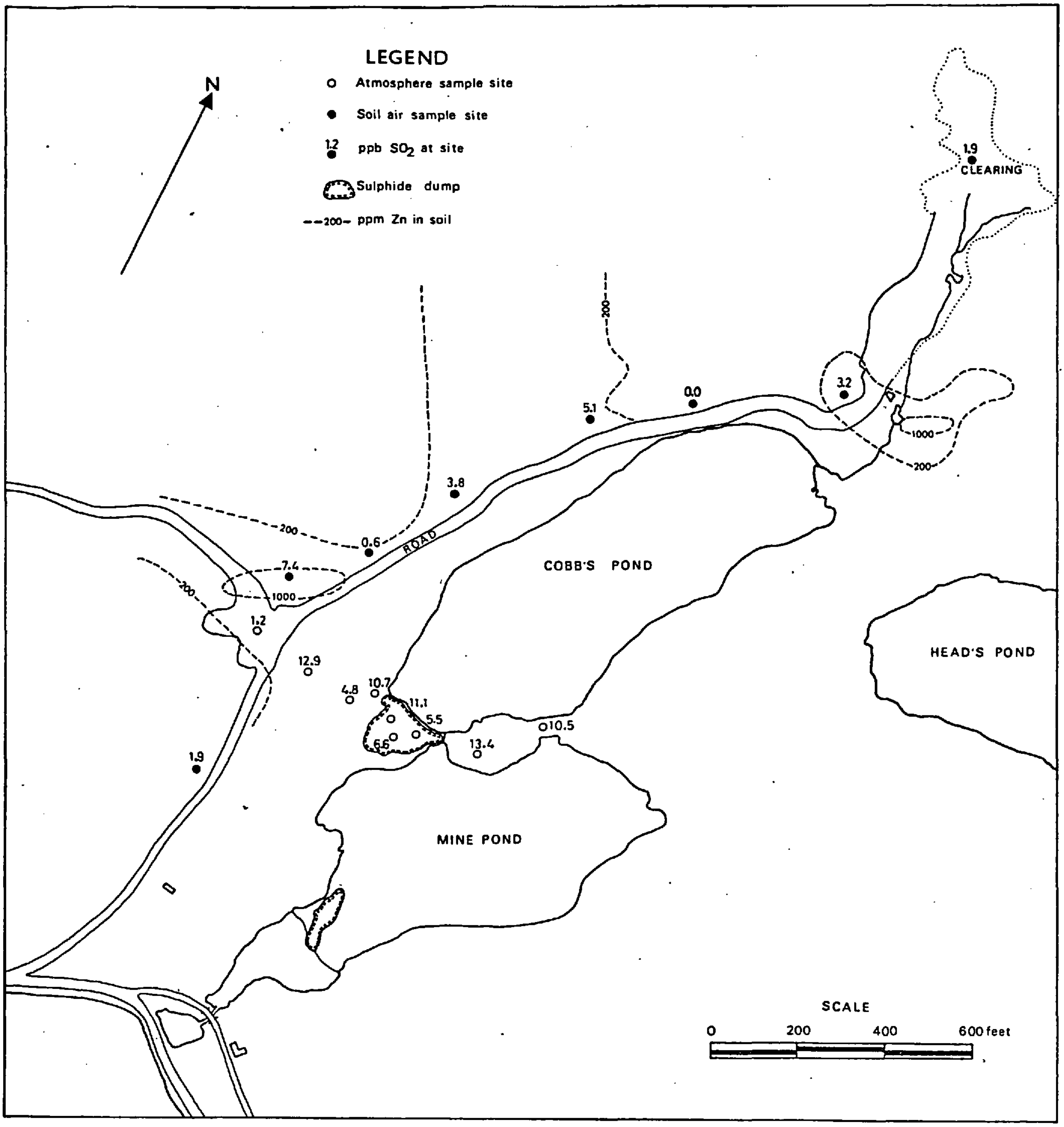


Fig. 60 Concentration of sulphur dioxide in soil gas and atmosphere, Pilley's Island area

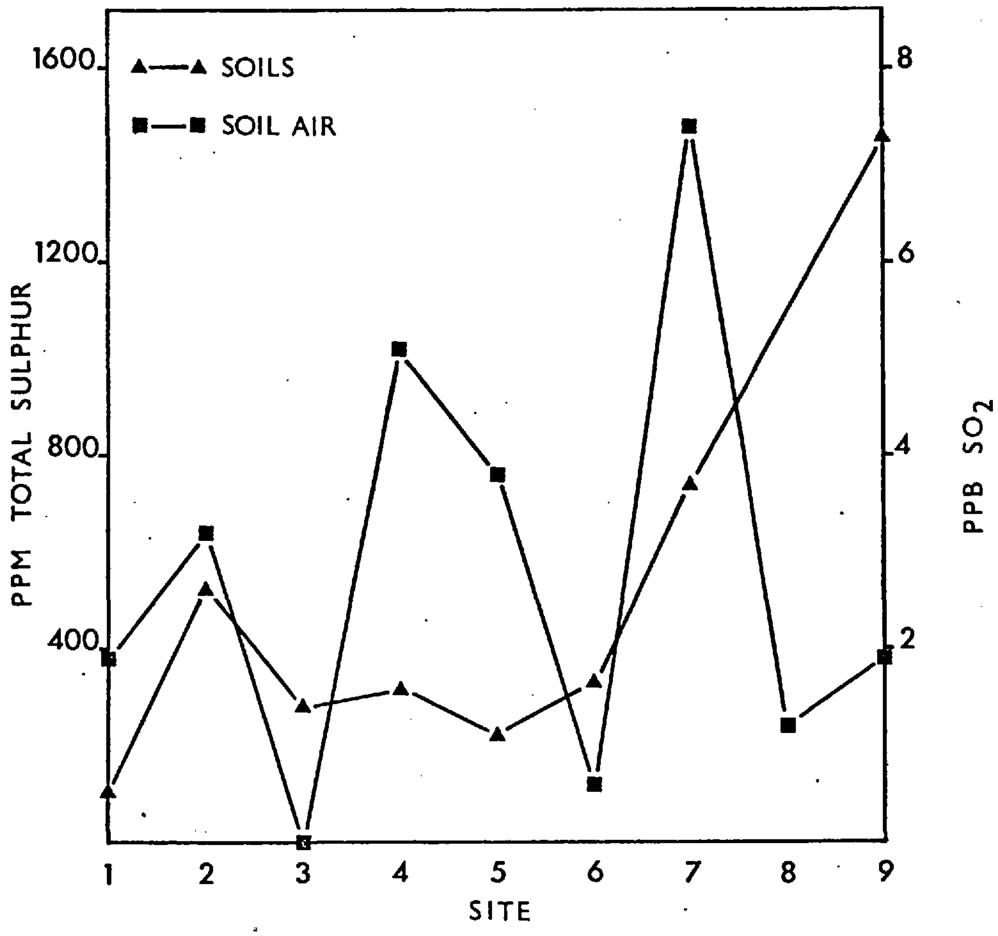


Figure: 61: Relationship between SO_2 in soil air and total sulphur in soils, Cobb's Pond traverse, Pilley's Island.

value of 2.5 ppb. 300 feet south of the soil anomaly (Figure 62). The pattern of SO_2 dispersion on the south side of the mineralization was reflected by the surface samples, but the soil gas and surface air patterns do not correspond to the north of the anomaly. Surface air sampling cannot be said to reflect the presence of sulphides in this area as SO_2 values reached a maximum 200 feet north of the soil sulphur anomaly, with the concentration fluctuating in the range of 0.5 to 1.2 ppb., near the detection limit of the system. This may be related to the fact that the peak of the sulphur soil anomaly coincided with open ground while the surface air maximum occurred in a forested area. Also it is noted that during the soil air traverse, conducted N-S, air temperature increased from 12°C to 18.5°C and towards the end of the traverse the light wind that has been blowing had died out. During the surface air traverse temperature increased from 10°C to 21°C under calm conditions. The soil air concentrations were more promising, but disappointing in view of the strong total sulphur anomaly in the B horizon, and the relatively shallow depth of till cover (less than 5 feet) in this area.

8.5 DAWES POND

Soil air samples collected in the vicinity of the soil anomaly over disseminated sulphide mineralization at Dawes Pond (see section 4.4) on a cool day in August, 1972, did not exceed the 0.25 ppb. detection limit of the system, possibly due to the low soil temperatures (10 to 12°C) at the time of sampling. However, on a sunny day in September, investigation of an induced polarization anomaly not reflected by high metal values in the soil indicated a positive response coincident with maximum charge-

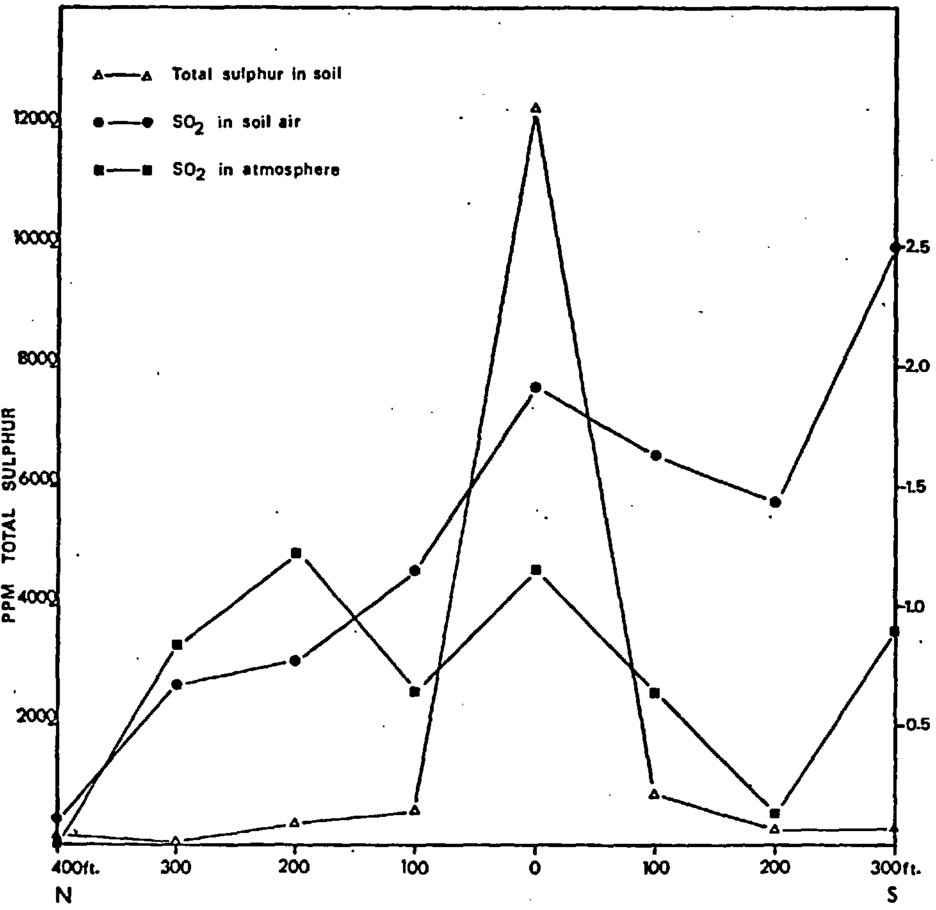


Figure 62: SO_2 in soil gas and atmosphere over sulphide zone in Rendell Jackman area compared with B Horizon total sulphur.

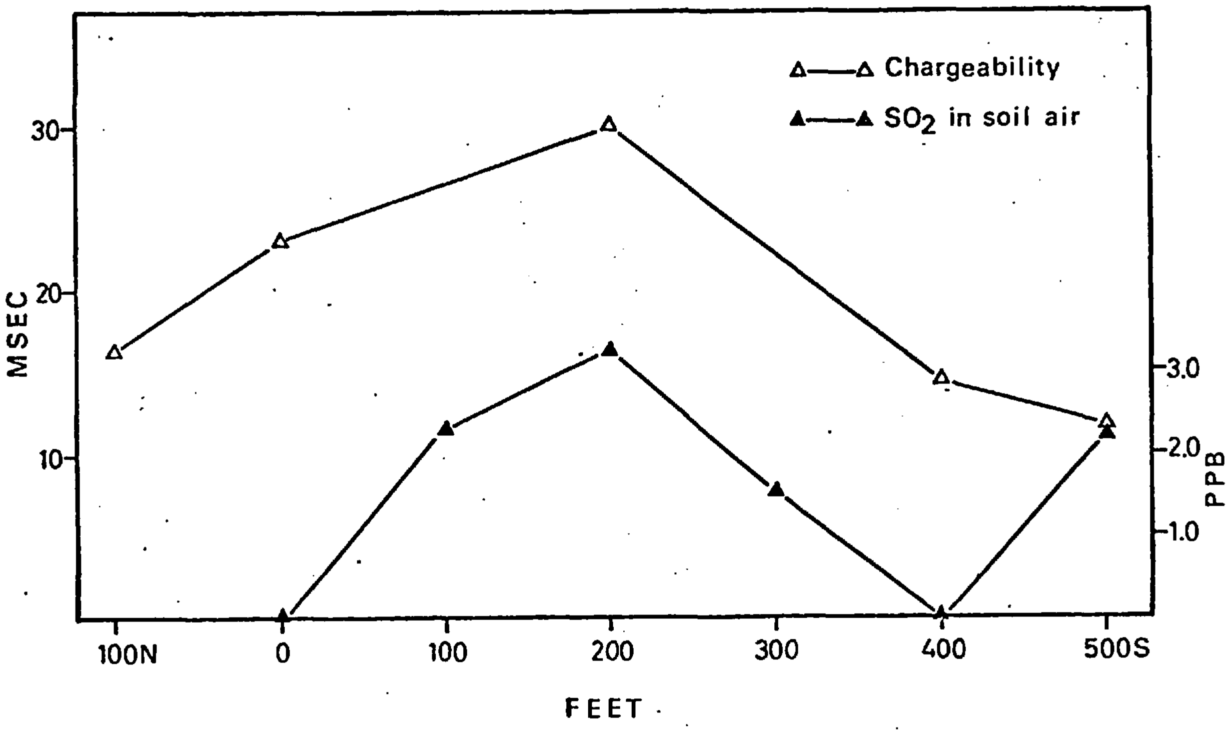


Figure 63: Sulphur dioxide in soil gas across induced polarization anomaly, Dawes Pond area.

ability (Figure 63). The level of sulphur dioxide in soil air reached a peak of 3.2 ppb. in this case.

8.6 LABORATORY INVESTIGATIONS

In the laboratory, tests were conducted to determine whether temperature had any effect on the amount of sulphur dioxide absorbed by the tetrachloromercurate absorbing solution used in the West and Gaeke procedure for the determination of SO_2 in air. Apparatus was assembled as in Figure 64 and a small amount of sulphur dioxide generated in the flask. The air stream carrying the SO_2 was split so that 2 l/min. was bubbled through each impinger containing the absorbent. One impinger was cooled in a water/ice bath to the desired temperature and the other maintained at room temperature. Samples were run in duplicate pairs with the impingers reversed in one case so that any differences between the calibration of the flow meters or between the two impingers could be negated.

Determination of the concentration of SO_2 absorbed was made colorimetrically using HCL-bleached p-rosaniline, with absorbance measured at 540 mu. using a Unicam spectrometer after 30 minutes colour development. Tests were made at temperatures ranging from 4°C to 31°C and temperature differences between the two impingers of 0 to 15°C. The conclusion made from the plot of per cent variation between the two impingers versus temperature difference (Figure 65) is that even for temperatures as low as 4°C no significant effect on the amount of sulphur dioxide absorbed by the

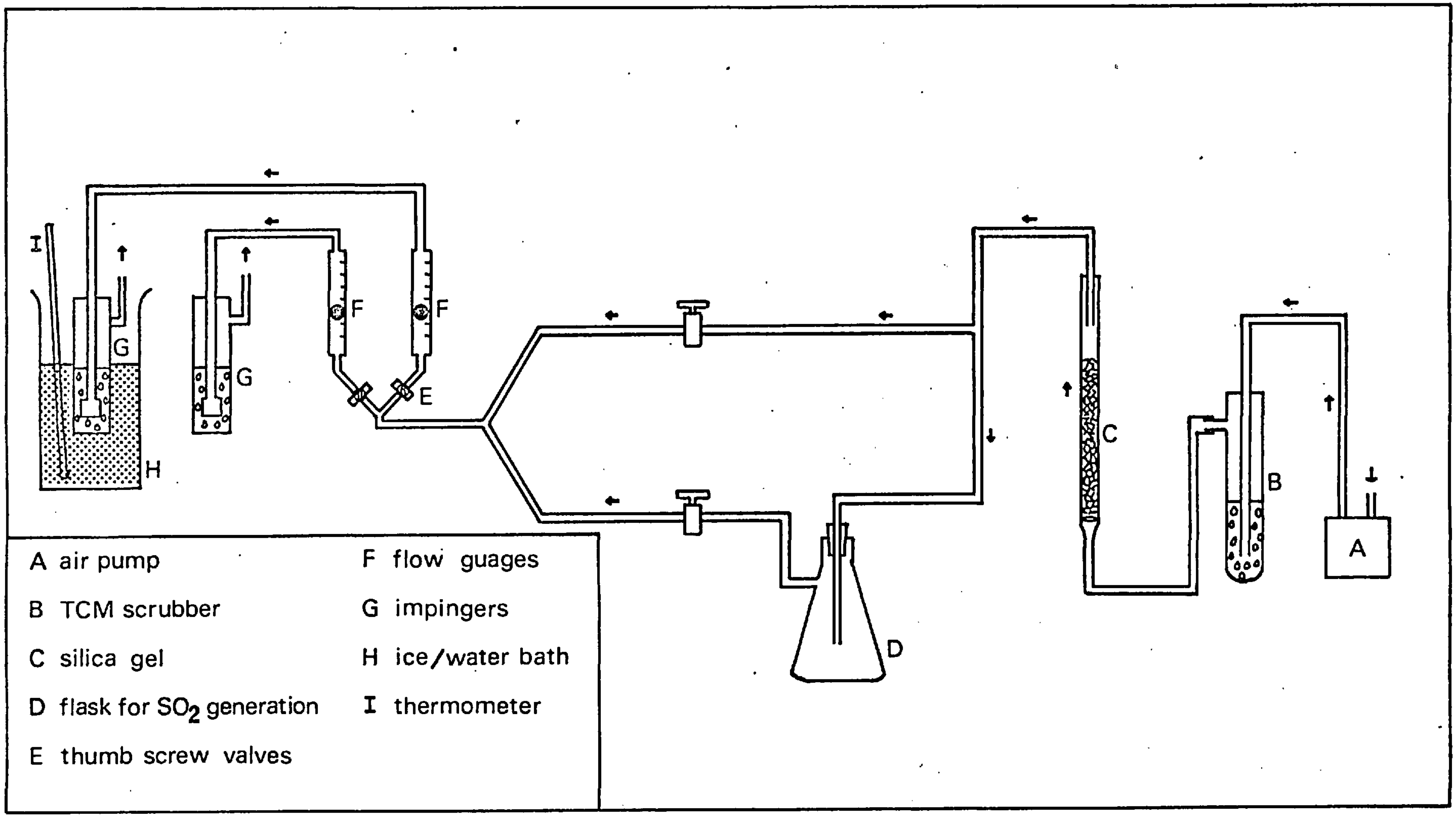


Figure 64: Diagram of apparatus used to determine temperature effects on absorption of SO_2 by tetrachloromercurate.

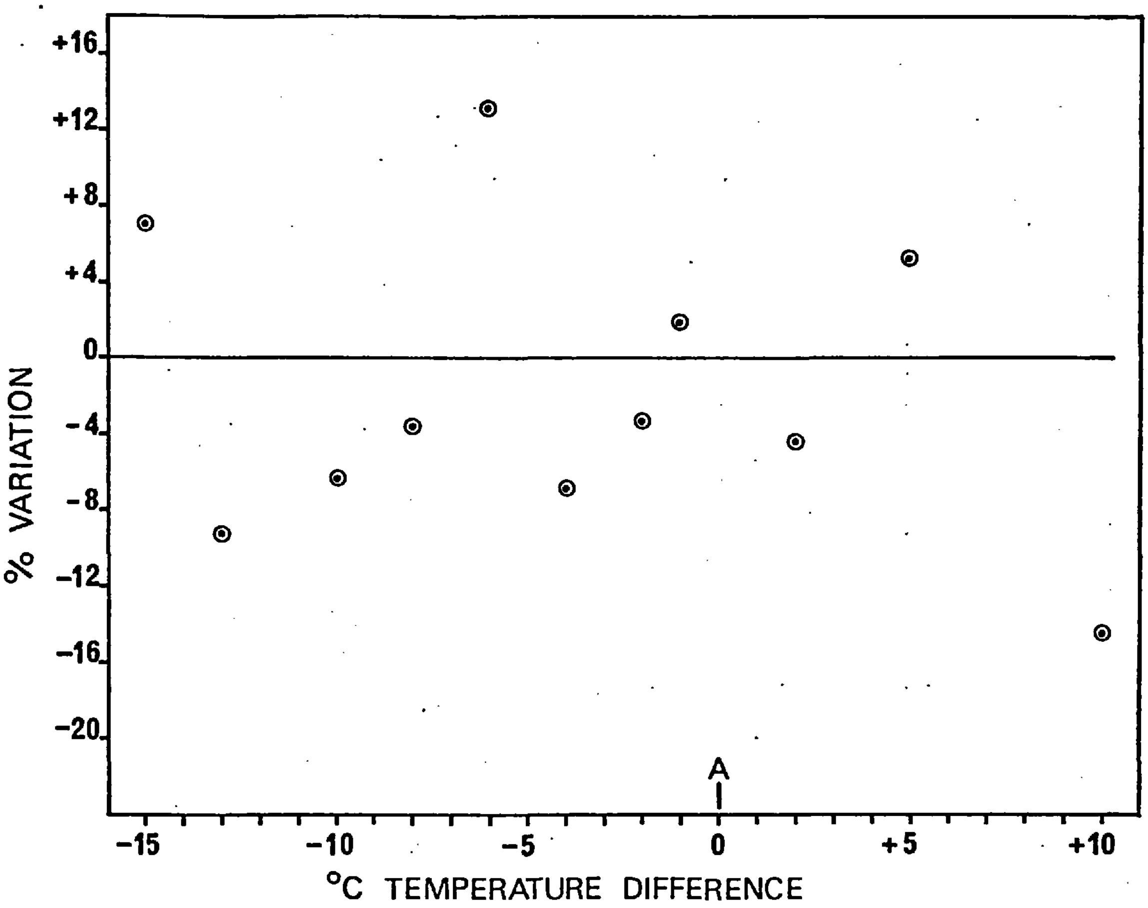


Figure 65: Effect of temperature on absorption of SO_2 by tetrachloromercurate. Temperature difference is between one impinger at ambient temperature (A), 19°-21°C and another at a different temperature.

tetrachloromercurate can be observed. The scatter of points in Figure 65 is a reflection of analytical variability only.

Investigations were also attempted to determine whether significant amounts of sulphur dioxide is held in soils by adsorption but these were unsuccessful because of the difficulty in extracting only the adsorbed SO_2 and not generating SO_2 from other sulphur compounds in the soil. However, Fuhr et al., (1948) found that soil adsorbed quantities of SO_2 added to it (up to 5-10 mg/l) fairly quickly. It is suspected therefore that soils above oxidizing sulphides may retain some gaseous SO_2 by adsorption and this may be an important factor in gaseous dispersion through soils as well as such factors as moisture content and permeability.

8.7 SUMMARY AND CONCLUSIONS

Measurement of sulphur dioxide levels in the atmosphere in the vicinity of surface concentrations of sulphides has shown a strong dependence on warm, sunny days for the production of detectable SO_2 concentrations (preferably above $20^\circ C$). The concentration of SO_2 was found to decrease with height above ground, and wind played an important role in lowering SO_2 levels. Increased levels of SO_2 were found in densely forested areas and hollows where wind action was restricted. Sulphur dioxide surveys carried out by sampling surface air should be interpreted with reference to a base station in the field area, monitored at regular intervals throughout the day for background SO_2 fluctuations and temperature changes.

Soil gas was more effective than surface air sampling in indicating mineralization in the Rendell Jackman area, but the pattern could not be completely interpreted in terms of soil geochemistry and known mineralization. Encouraging coincidence of patterns of sulphur dioxide in soil air and metal values in the soil were observed at Pilley's Island but little relation was discerned between SO_2 in soil air and the total sulphur content of the soil either at Pilley's Island or Rendell Jackman prospects.

The climate of Newfoundland does not favour the conditions required for successful application of sulphur dioxide sampling, and this was confirmed by the failure of the system in the Dawes Pond area during cool weather. The part per billion range of the analytical technique is clearly inadequate under unfavourable weather conditions and routine application of SO_2 analysis under these conditions will depend on the satisfactory development of instrumentation suitable for measuring low background values. The fact that detectable levels of SO_2 were recorded in soil gas using the current technique lends encouragement for the future application of sulphur dioxide analysis in areas of transported overburden.

It is recommended that the distribution of hydrogen sulphide gas in the soil air and atmosphere could also be examined if suitably sensitive methods for H_2S analysis are developed.

CHAPTER 9

THE ANALYSIS OF SULPHUR COMPOUNDS USING THE ARGON PLASMA EMISSION SYSTEM

9.1 INTRODUCTION

A sensitive technique for the analysis of geochemical samples by fractional volatile analysis and the production of thermal-evolution profiles using a microwave-induced argon plasma emission system has been developed by Meyer and Lam Shang Leen (1973) at the Applied Geochemistry Research Group, Imperial College. The development and application of the technique in exploration geochemistry is the subject of a Ph.D. thesis by Meyer (1973), from which much of the specification and descriptive data on the system are obtained.

The analysis of several elements has been investigated, including Hg, Cd, S, Pb, Zn, Cu, I, and Se. Emphasis has been placed on the development of Hg and Cd analysis and has been successfully applied to a variety of sample types, both solid and solution. Analysis of sulphur in geochemical samples from the Notre Dame Bay area using this technique is discussed in later sections of this chapter.

9.2 DESCRIPTION OF METHOD

9.2.1 Apparatus and General Procedure

A schematic outline of the system is given in Figure 66. A LECO induction furance (Laboratory Equipment Corp., Michigan, U.S.A.) operating at a frequency of 14.6 MHz with an output of 1500W was used to heat 10 mg. samples of soil or rock powder in an argon stream in a cavity in carbon crucibles within the quartz combustion tube (35 mm. in diameter), which had been modified by the addition of a 5-cm. length of transparent quartz tubing(with a 2 mm. diameter)at the top. The argon flow was regulated using a needle valve, pressure regulator and flow meter. Temperatures in excess of 800°C could be obtained using this induction furnace and carbon crucibles of 3 mm. diameter x 27 mm. length.

Excitation of argon atoms in the gas stream and vapours evolved from heated samples was achieved by microwave-induction at 2450 MHz produced by a Microton 200 microwave generator (Electro-Medical Supplies, Wantage, Berkshire) operating on a stabilized line voltage, with coupling through an Evanson one-quarter wavelength resonant cavity (214L). The plasma thus formed was about 1 mm. in diameter and 25 mm. in length situated at the top of and partly inside the 2 mm. diameter quartz tubing at the outlet of the furnace.

Emission from the plasma was dispersed and lines selected using a plane grating, symmetrical Czerny-Turner 0.3 m. monochromator (Hilger and Watts D 330 single), with bilaterally adjustable slits. The vertical entrance

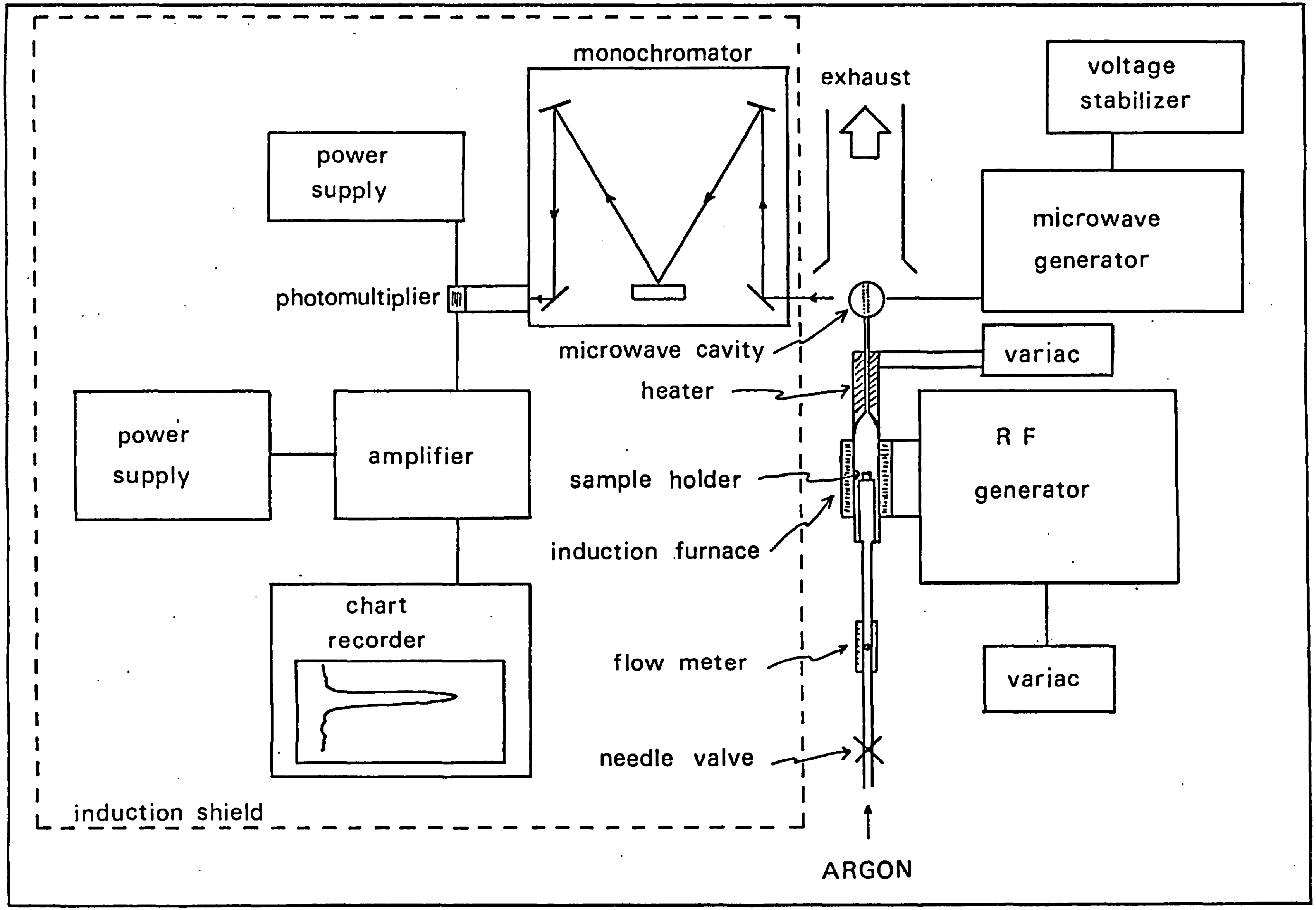


Figure 66. Schematic diagram of the microwave-induced argon plasma emission system (after Meyer, 1973).

slit was aligned with the plasma at the point of maximum emission on a suitable argon line with the slit about 5 cm. from the plasma. The emission signal from the monochromator was detected using a photomultiplier (EMI 9601 B), amplified, and displayed on a Servoscribe chart recorder.

The general procedure for soils, rocks, or sediments was to loosely pack the cavity of the carbon crucible to obtain a volumetric estimate of the 10 mg. sample weight required and raising the crucible on the furnace pedestal into the combustion tube at the center of the induction coil. An argon flow of 1.7 l/min. was set and after flushing air from the system, the plasma was started by a spark from a 'Tesla' coil vacuum tester. The spectral line of interest was selected prior to sample introduction by use of the emission from the appropriate electrodeless discharge lamp activated within the microwave cavity, or, in the case of sulphur, by reference to the spectral tables of Mass. Inst. of Technology (1960) for selection of a sensitive line and location of the line using emission from a volatilized pure sulphur compound.

Heating of the sample was accomplished using a variable transformer to control the voltage to the induction coil. The maximum temperature obtained using carbon crucibles heated to full power on the induction coil was 1100°C but the normal working range was 0-800°C because at near maximum power a radio-frequency discharge was formed immediately above the carbon crucible which affected both the volatilization of the sample and the emission intensity of the argon plasma. Heating was controlled by increasing the voltage to the induction furnace at a fixed rate and using the second channel of the chart recorder to mark the chart at regular intervals over the voltage range, which could be directly related to calibrated temperature.

9.2.2 Different Heating Methods Used

9.2.2.1 Induction Furnace

The general procedure described above applies to the heating of samples in the LECO induction furnace, used for more rapid, less precise analysis of the thermal evolution of sulphur compounds from soils and sediments. A heating rate of 20% of the voltage/min. was usually used which corresponded to an average temperature increase of 240°C per minute and permitted the analysis of four samples per hour. The cooling of the induction coil required only a few seconds, but about two minutes was required to cool the ceramic pedestal supporting the crucibles. Sample interchange was accomplished over about three minutes in all. The additional elapsed time was required for air flushing, tuning of the plasma, adjustment of the chart recorder response, and so on.

9.2.2.2 Resistance Furnace

More precise thermal evolution profiles were obtained by using a low-mass nichrome-wound vertical tube resistance furnace (Stanton Redcroft VB 100) instead of the induction furnace. A temperature range of 0 to 1100°C was attainable using this furnace, but 950°C was the maximum reached in routine applications because higher temperatures at the heating rates used put too much strain on the electrical system. Heating of the furnace was controlled by an automatic linear variable temperature programmer (Stanton Redcroft LVP/CA 40) with pre-set heating rates of 2 to 40°C per minute.

Samples were heated in a small ceramic cup fixed to the top of the thermocouple support within a 35 mm-diameter mullite sheath and the evolved volatiles passed upward in the argon stream through the removable quartz plasma tube at the top. The tip of the chromel-alumel thermocouple projected into the sample so that an accurate measurement of the sample temperature was obtained. The temperature was recorded simultaneously with the emission intensity by using the second recorder channel, calibrated at 1 inch to 100°C, so that at any point the sample temperature could be read to within 2°C.

A heating rate of 30°C per minute was most frequently applied and using this rate about four samples per day could be analyzed, heating to 900°C. Considerable time was required for cooling the furnace between runs, which was aided slightly by using a fan to blow air through it.

The slow technique using the resistance furnace is not as suitable as the fast (LECO) technique for routine analysis of geochemical samples, but the temperature calibration is much more accurate and the heating rate is controlled far more precisely than is attainable using the manual voltage control of the induction furnace. The control of the heating rate and accurate monitoring of temperature permits accurate location of peaks on the thermal evolution profiles using the slow technique. An example in application is that some emissions which are recorded as composite peaks in the fast method may be resolved into two or more single peaks using the slow technique, representing possibly two or more different compounds instead of one. More specific results for sulphur determinations particularly are given in later sections.

9.2.3 Advantages of Argon Plasma Emission Analysis

The application of microwave-induced argon plasma emission analysis in geochemistry is attractive for the determination of those elements which are not particularly suited to routine determination using conventional techniques such as atomic absorption but which may occur in significant concentrations over ore deposits. For example, the technique may be used for the determination of Hg and Cd in soils and rocks in the low ppb. range and in solutions at less than 0.2 ppb. (Meyer, 1973). A large number of elements have been determined using microwave plasmas, including antimony, arsenic, boron, beryllium (Aldous, et al., 1971); aluminium, calcium, molybdenum, tellurium, tungsten, platinum, and bismuth (Murayama, et al., 1968). Meyer (1973) has investigated Hg, Cd, S and C in solid samples and Cu, Pb, Zn, Se and I in solutions.

The advantage of this technique for the analysis of geochemical samples is that no sample preparation is required, only a small amount of sample is needed (10-20 mg.), and it is extremely sensitive on elements such as Cd and Hg and is as sensitive as existing techniques on many other elements. In addition, the analysis of the volatile emissions under controlled heating permits diagnosis of the forms in which particular elements are occurring in the sample. In the case of sulphur in soils, for example, the fractions associated with organic carbon may be distinguished from the higher temperature inorganic forms.

9.3 ANALYTICAL PARAMETERS

9.3.1 Calibration and Standardization

The analysis of sulphur using the argon plasma emission system was investigated using both the induction furnace and the resistance furnace. Most soils were analyzed using the fast method of heating and the slow technique was used for temperature calibration and for accurate location of peaks on evolution profiles in experiments on the identification of particular sulphur compounds.

In order to calibrate the system to cover the range of sulphur concentrations expected in soils, standards were prepared by adsorbing solutions of $(NH_4)_2 SO_4$ onto rock base, drying, pulverizing and homogenizing the powders and heating in the induction furnace. A 10 mg. portion was used in each case and the emission detected using the 469.6 nm sulphur line. The resulting calibration curve (Figure 67) shows that over the 0-800 ppm. range the concentration is proportional to the log of the peak height or intensity.

Temperature calibration of the induction furnace was difficult because the induction heating coil interferes with any thermocouple measurement of sample temperature within the coil. Calibration was therefore achieved

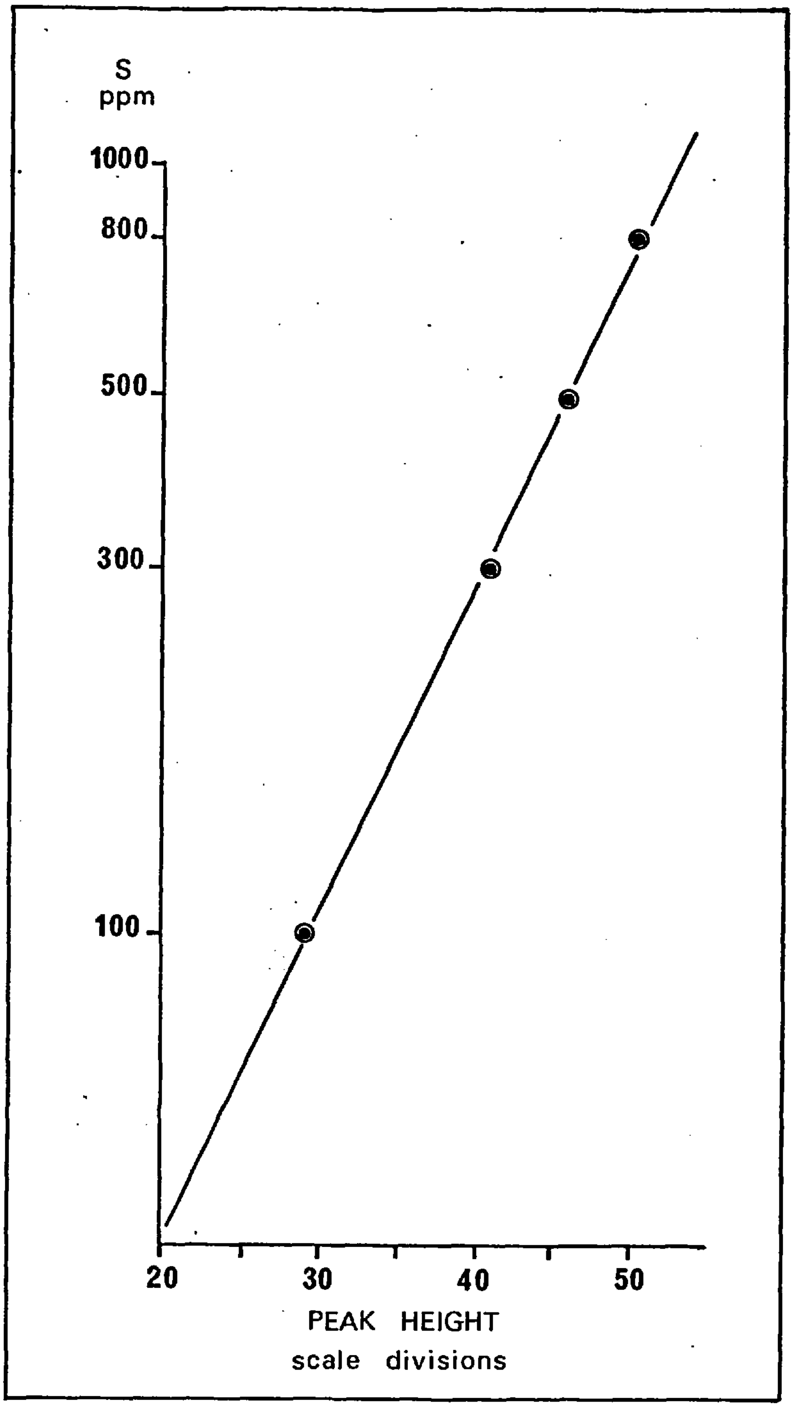


Figure 67: Calibration curve for sulphur.

indirectly by use of the temperature-programmed resistance furnace. Known peak temperatures determined on the resistance furnace for standards prepared from $HgCL_2$, HgS, natural mercury-containing samples and artificial sulphur compounds were used to fix points on the temperature curve for the fast furnace. The accuracy of the temperature curve at any point is only about ± 10°C because of the variability of the heating using the manual rheostat control. The calibration curve, relating temperature and power to the furnace, is given in Figure 68.

9.3.2 Interferences and Other Problems

9.3.2.1 Carbon and Organic Materials

Initial studies of sulphur emission were made using a fairly sensitive sulphur line at 469.6 nm but it was found that molecular band emission from carbon (C_2-Swann bands) could cause interference problems in this region, so subsequent determinations were made using a less sensitive line at 190.0 nm in order to avoid this interference.

Samples containing high organic carbon concentrations were also found to create problems by flooding of the system with the products of the combustion of the organic substances, often resulting in the extinguishing of the plasma. This could be avoided to some extent by slowing the heating rate to produce a more even evolution of the volatiles or by increasing the power applied to the microwave cavity by about 5-10W to provide a stronger plasma. The frequent analysis of organic substances

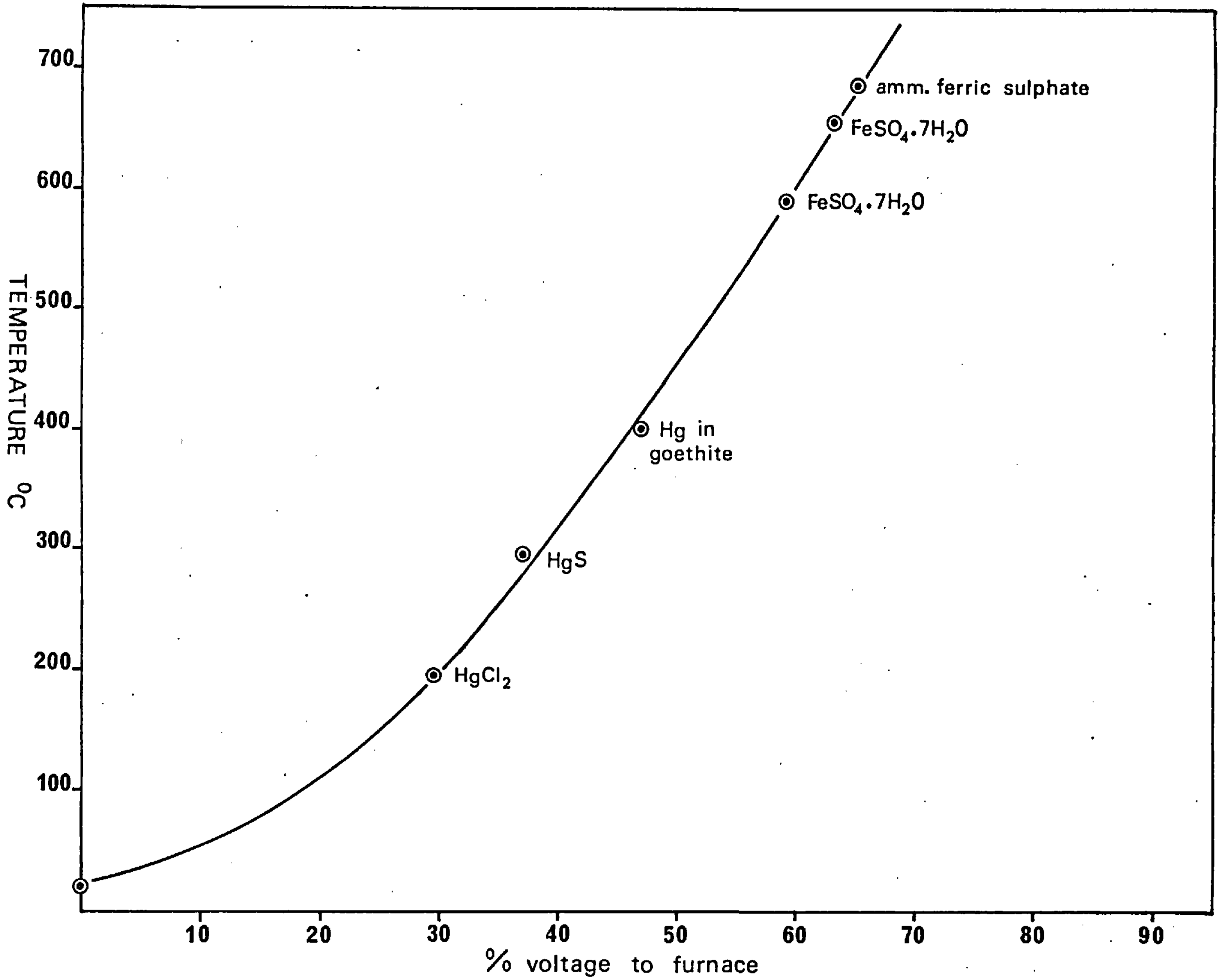


Figure 68: Temperature calibration for induction furnace.

also tended to produce deposits of carbon on the quartz combustion tube, necessitating cleaning of the apparatus more often than is necessary when analyzing inorganic samples.

9.3.2.2 Condensation

In using both the induction furnace and the resistance furnace the tubing between the sample combustion area and the quartz plasma jet was wound with heating wire connected to a variable transformer to provide temperatures up to 550°C, to minimize any condensation of volatiles onto the walls of the tubing. In preliminary investigations using pure sulphur, low results were found to be caused by this problem and the use of the heating wire was necessary in order to overcome this difficulty.

9.3.3 Factors Involved in Sample Heating

Meyer (1973) has reviewed the different processes which may result from heating samples to fairly high temperatures (Table 30), and has indicated that most of these processes may be involved in the evolution of trace elements from geochemical samples, whereas vaporization, desorption, and decomposition processes are most important ones producing gases. Without expansion on the physics of each of these processes involved in the destruction of samples by heating, it may be said that, on the basis of investigations made to date on the evolution of sulphur from

Process	Thermal Response	Gas Evolution	
		Major	Trace
Vaporization	Endothermic	Yes	Possible
Sublimation	Endothermic	Yes	"
Desorption	Endothermic	Yes	"
Dehydration	Endothermic	Yes	"
Decomposition	Endo- or Exothermic	Yes	"
Crystal transition	Endo- or Exothermic	No	"
Melting	Endothermic	No	"
Solid-state reaction	Endo- or Exothermic	Possible	"
Solid-gas reaction	Endo- or Exothermic	No	"

Table 30: Thermal response of processes induced by sample heating, and the possible evolution of gaseous products and volatile trace components (after Meyer, 1973).

soil and sediment samples, the processes of vaporization, desorption and decomposition seem to be responsible for most of the sulphur evolved, whereas small amounts may be produced at high temperature by the melting or crystal transition of various minerals.

The heating rate may influence the pattern of sulphur evolution detected for any sample. For example, at high rates emissions due to desorption may be overlapped and included in the much larger response due to decomposition, whereas the emission due to each process may be distinguished at a slower heating rate.

The heating of samples in an inert argon atmosphere is quite different from combustion in an oxygen stream, and as well as causing the evolution of more reduced compounds than would be formed in an oxygen atmosphere, some importance is placed on the composition of the sample matrix. For example, it was noted that red iron oxides were present in the residues of pyrite plus organic soil, which were not formed in the heating of pyrite alone. The composition of the sample is known to influence heating by induction in the use of the LECO furnace for total sulphur determinations, as those samples containing fairly large amounts of metals are more easily heated than samples composed say of organic material. In the procedure used in these investigations, however, heating was relatively independent of sample materials as the carbon crucibles themselves heated quite readily.

9.4 RESULTS

9.4.1 Soils

Typical evolution profiles for sulphur from soils are illustrated in Figure 69, which shows that in most soils two peak emissions occur, the lower temperature one corresponding to sulphur related to organic material and a higher temperature one related to inorganic sulphates and oxidation products associated with the presence of sulphides. The interpretation of the peaks is discussed in section 9.4.4. The relation of the lower temperature peak with carbon was confirmed using emissions on the atomic carbon line at 247.8 nm. That the higher temperature peak is related to the presence of sulphides was confirmed by the analysis of artificial compounds using both the induction and resistance furnaces (section 9.4.4) and by the enhancement of this peak for soils overlying sulphides, observed on several soil traverses. Figures 70, 71, and 72 shows evolution profiles on B horizon soils over the Rendell Jackman and Dawes Pond sulphide zones, in which the second peak emission is seen to increase over the sulphides whereas the lower temperature one may be just as high in background as in mineralized areas.

In addition, the association of the high temperature emission with the presence of sulphides in the soil was indicated by an increase in this emission when finely ground pyrite was added to a B horizon soil (Figure 73). However, this emission at just over 500°C is not considered due to decomposition of the pyrite but to partial oxidation products such as ferric

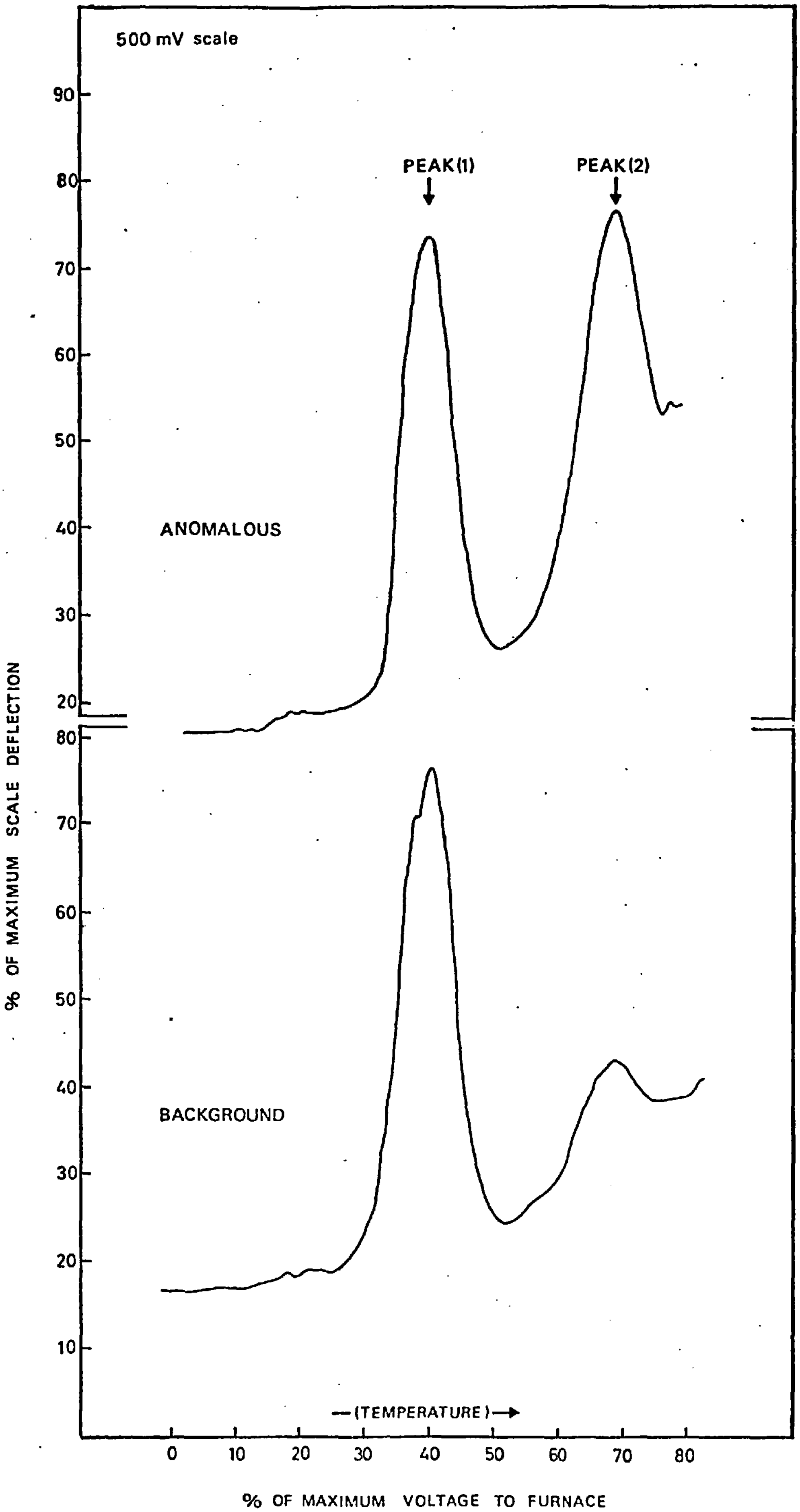


Figure 69: Evolution profiles for sulphur in B horizon soils from anomalous and background sample sites, detected using microwave-induced argon plasma emission system.

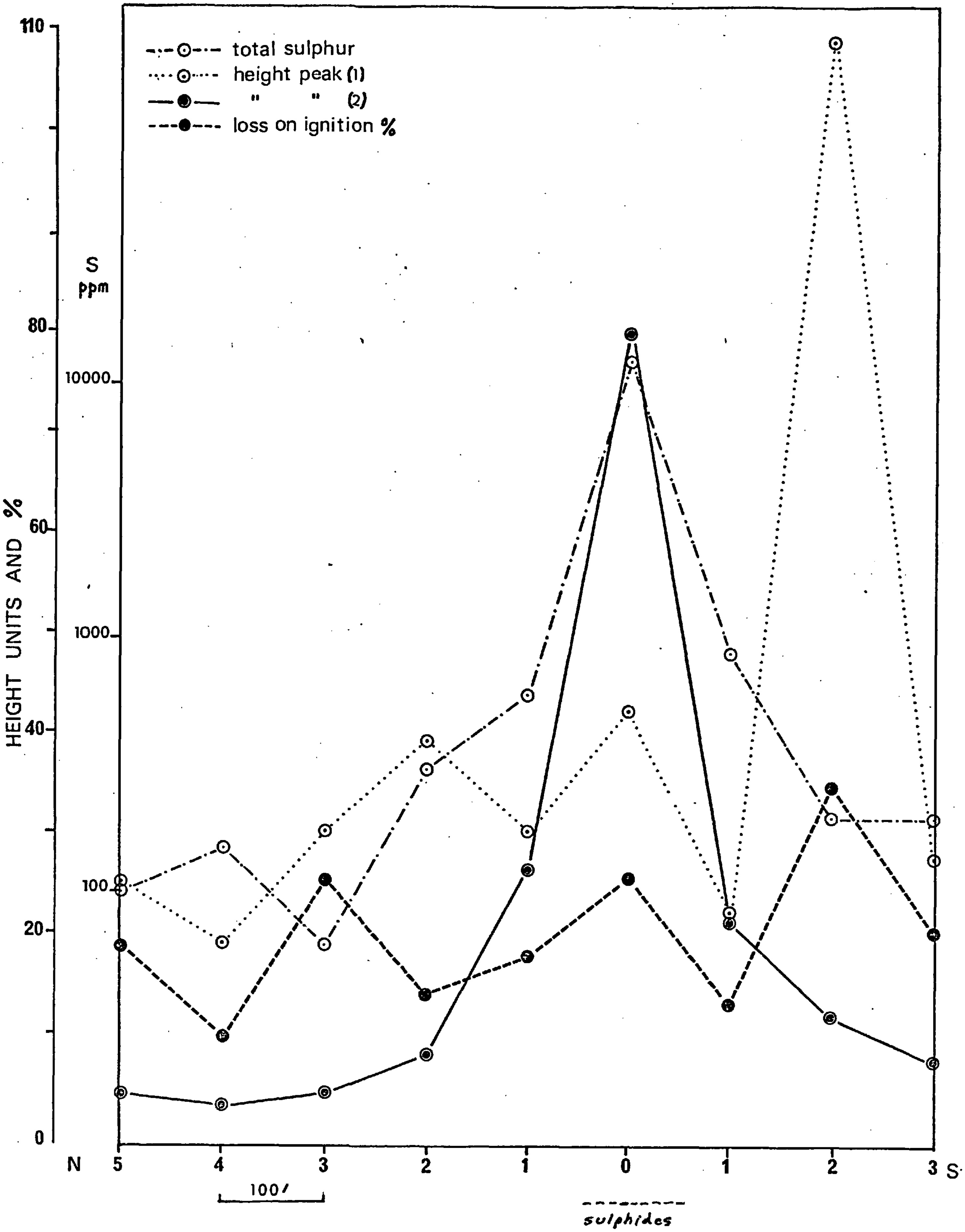


Figure 70: Comparison of low- and high-temperature peak heights for sulphur with total sulphur and loss-on-ignition, Rendell Jackman soil traverse.

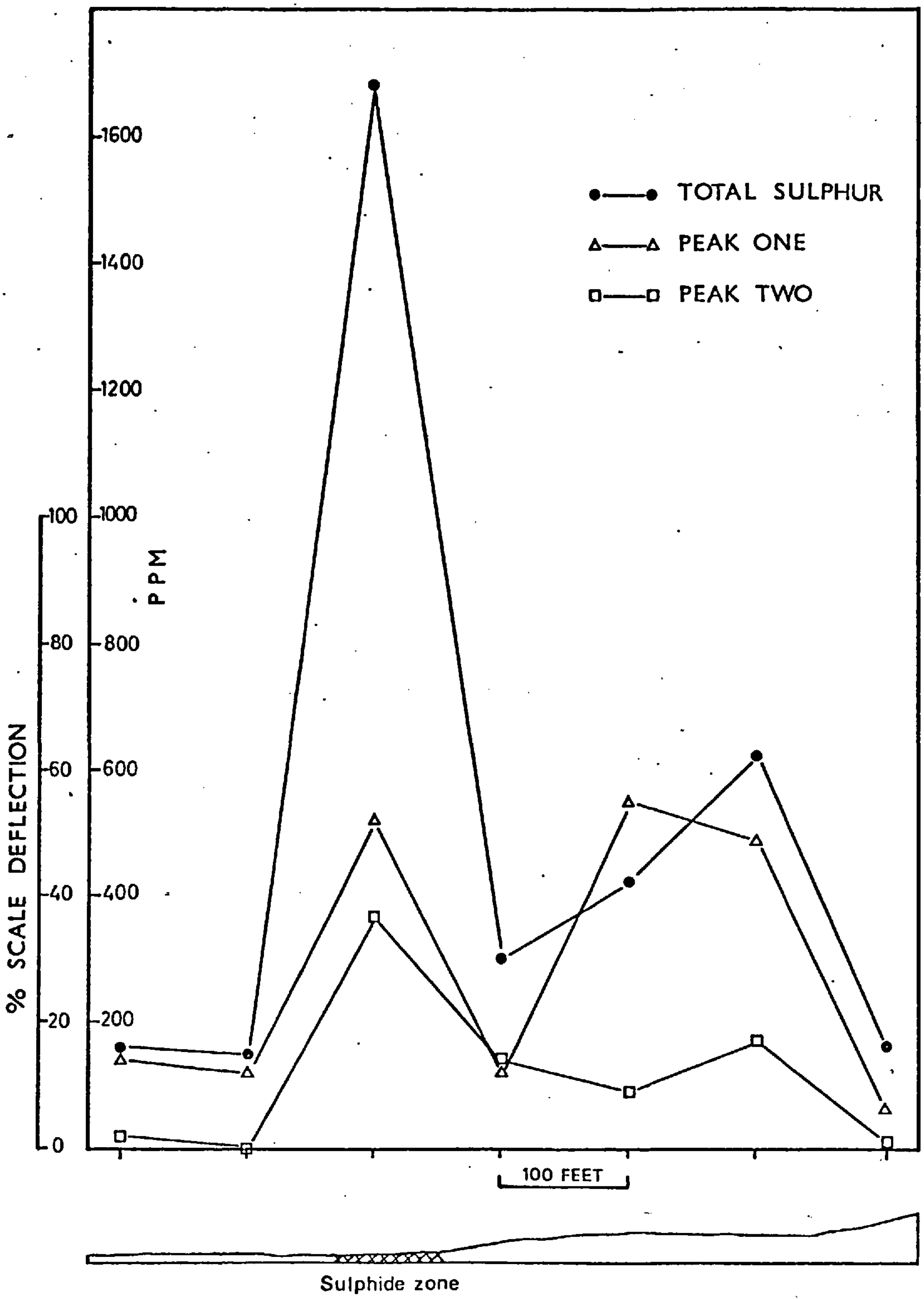


Figure 71: Comparison of low-and-high temperature peak heights for sulphur from evolution profiles on B horizon soils from line 20W, Dawes Pond area.

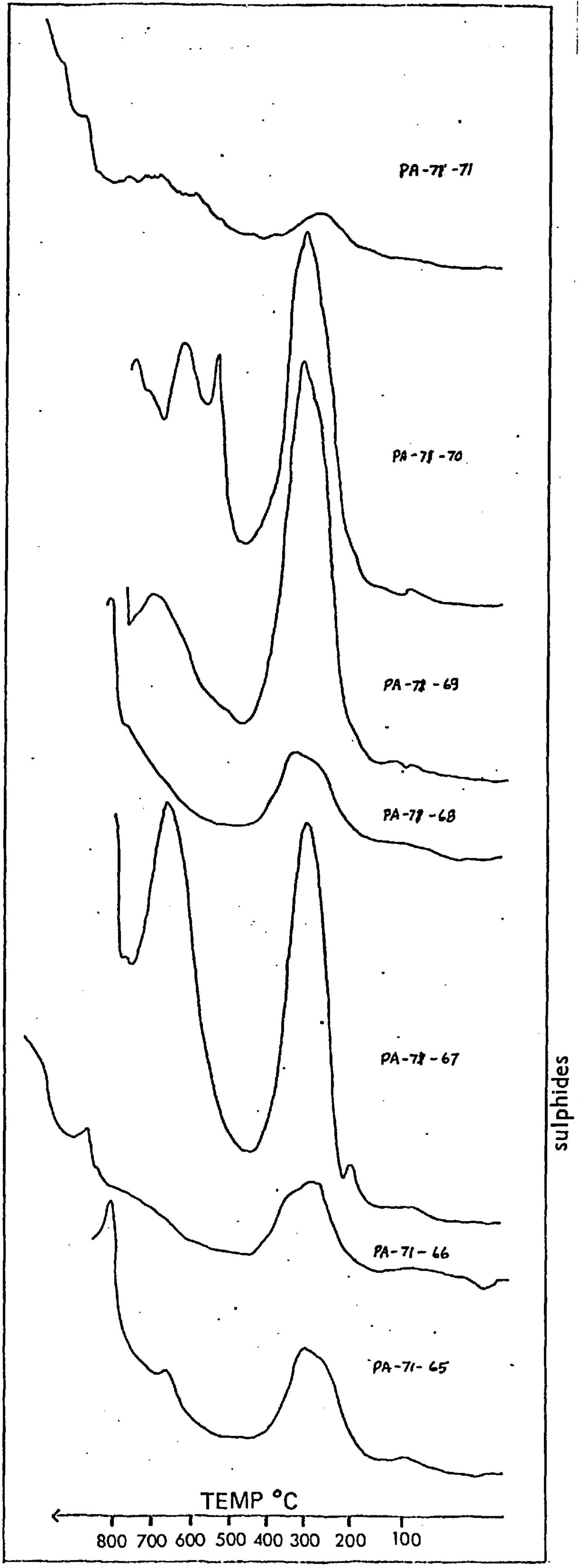


Figure 72: Sulphur evolution profiles for B horizon soils, traverse at Line 20W, Dawes Pond.

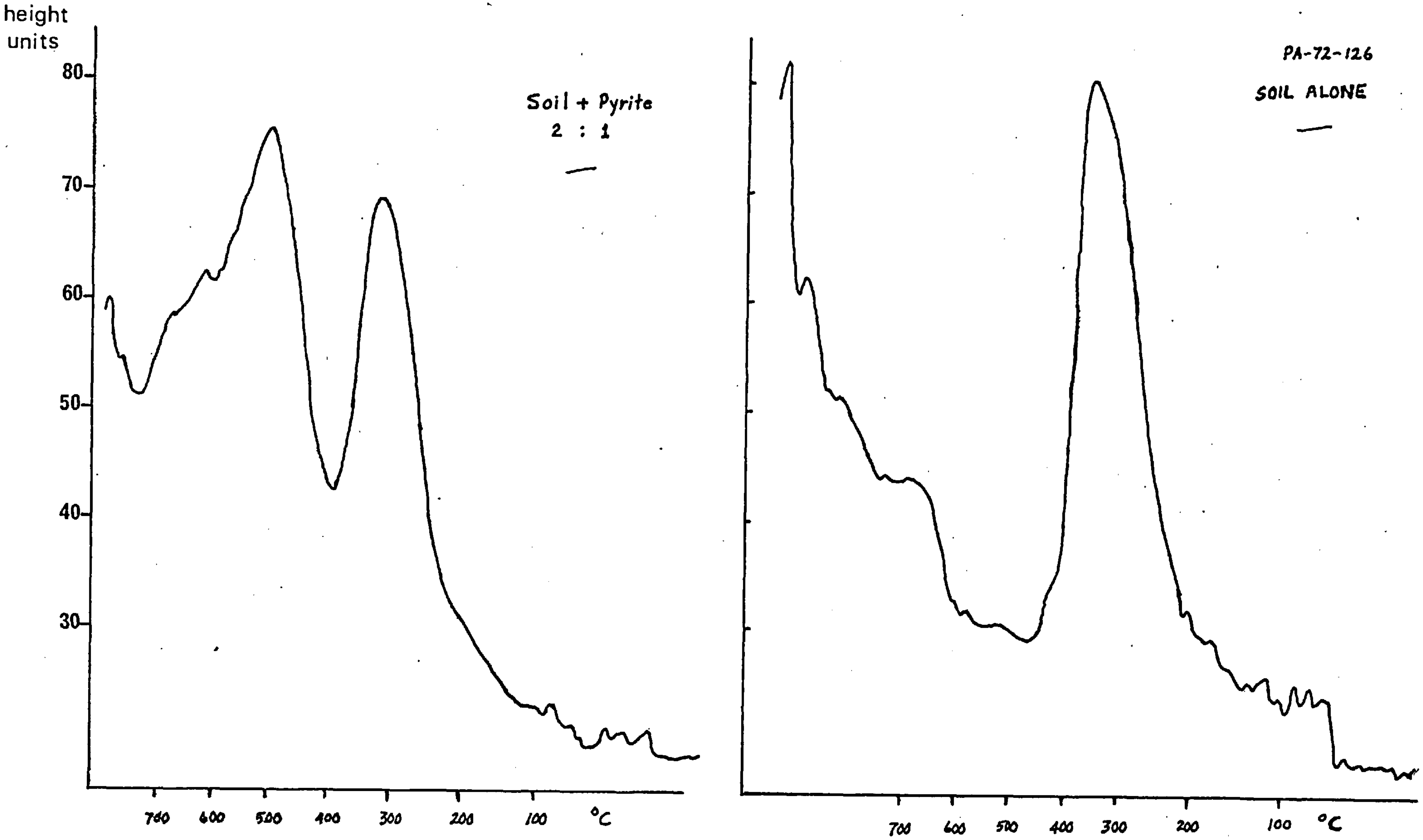


Figure 73: Sulphur evolution profiles for a B horizon soil sample and for the same sample plus pyrite.

sulphates and/or release by crystal transition or melting, as maximum emission from pyrite alone was observed at temperatures above 800°C, though emission in the 600°-650°C range did occur.

The emission profiles for sulphur evolved from soils taken from different horizons in a vertical profile at Dawes Pond showed that virtually all the sulphur is related to the organic material in the soils, being emitted at low temperature. The high content of sulphur in the humus compared to virtually none in the underlying till is clearly indicated (Figure 74).

An additional aspect of sulphur in soils was investigated using argon plasma emission analysis, which was to determine whether prior ignition of the sample at temperatures up to 450°C in a muffle furnace could be used effectively to eliminate the sulphur related to the organic material, i.e., the low-temperature emission, but retaining the higher temperature forms related to the presence of sulphides. The results (Figure 75) indicated that ignition of the samples in an oxygen atmosphere even for one hour caused the decomposition of the organic forms and oxidation of the higher temperature sulphur forms. The conclusion was obviously that ignition in oxygen could not be used for this purpose as loss of most of the sulphur content occurred.

9.4.2 Sediments

A number of selected lake and stream sediments from the Notre Dame Bay area were examined using microwave-induced argon plasma emission, to determine how the emissions from the sulphur compounds in these samples

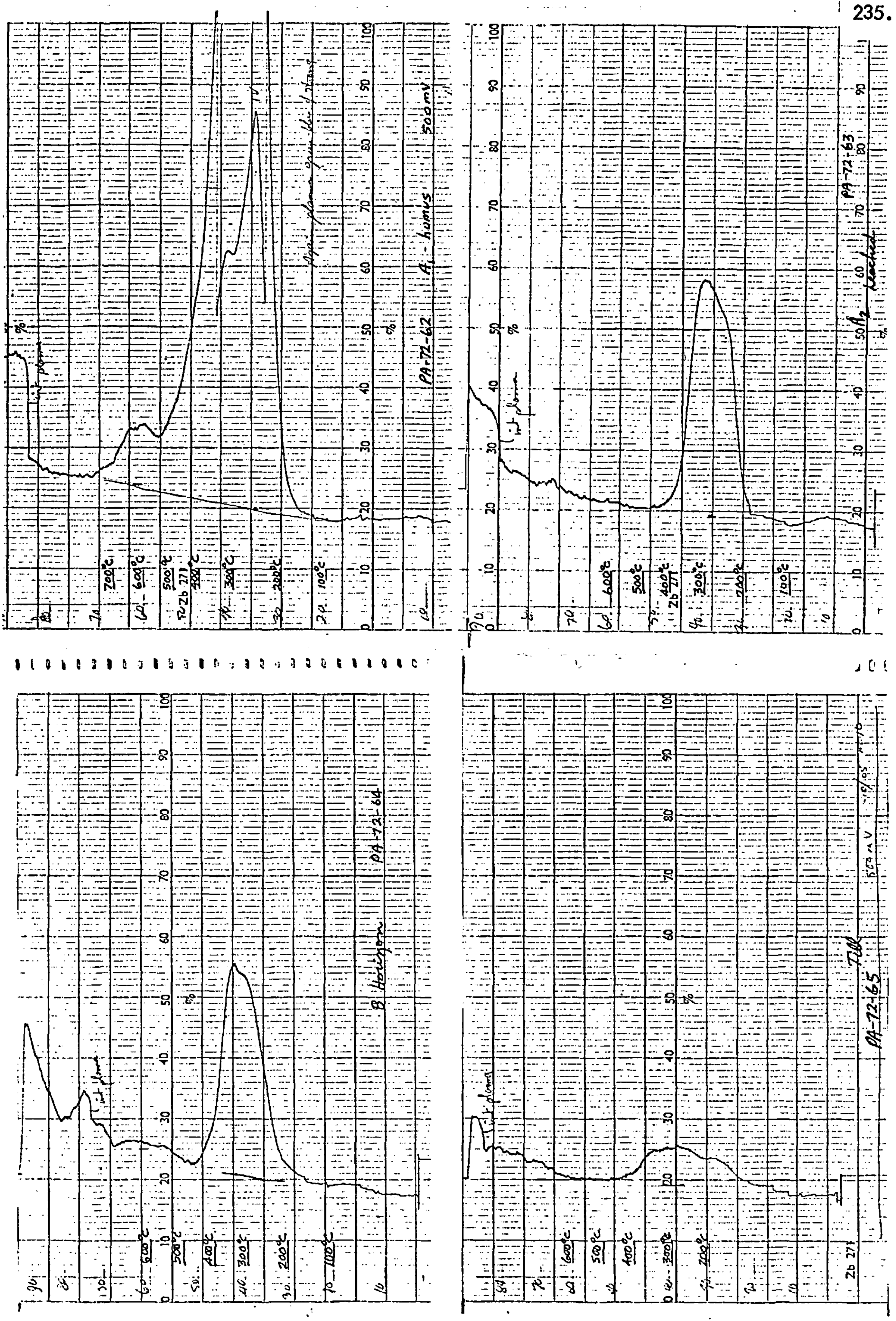


Figure 74: Sulphur evolution profiles for different horizons in a vertical profile, Dawes Pond area.

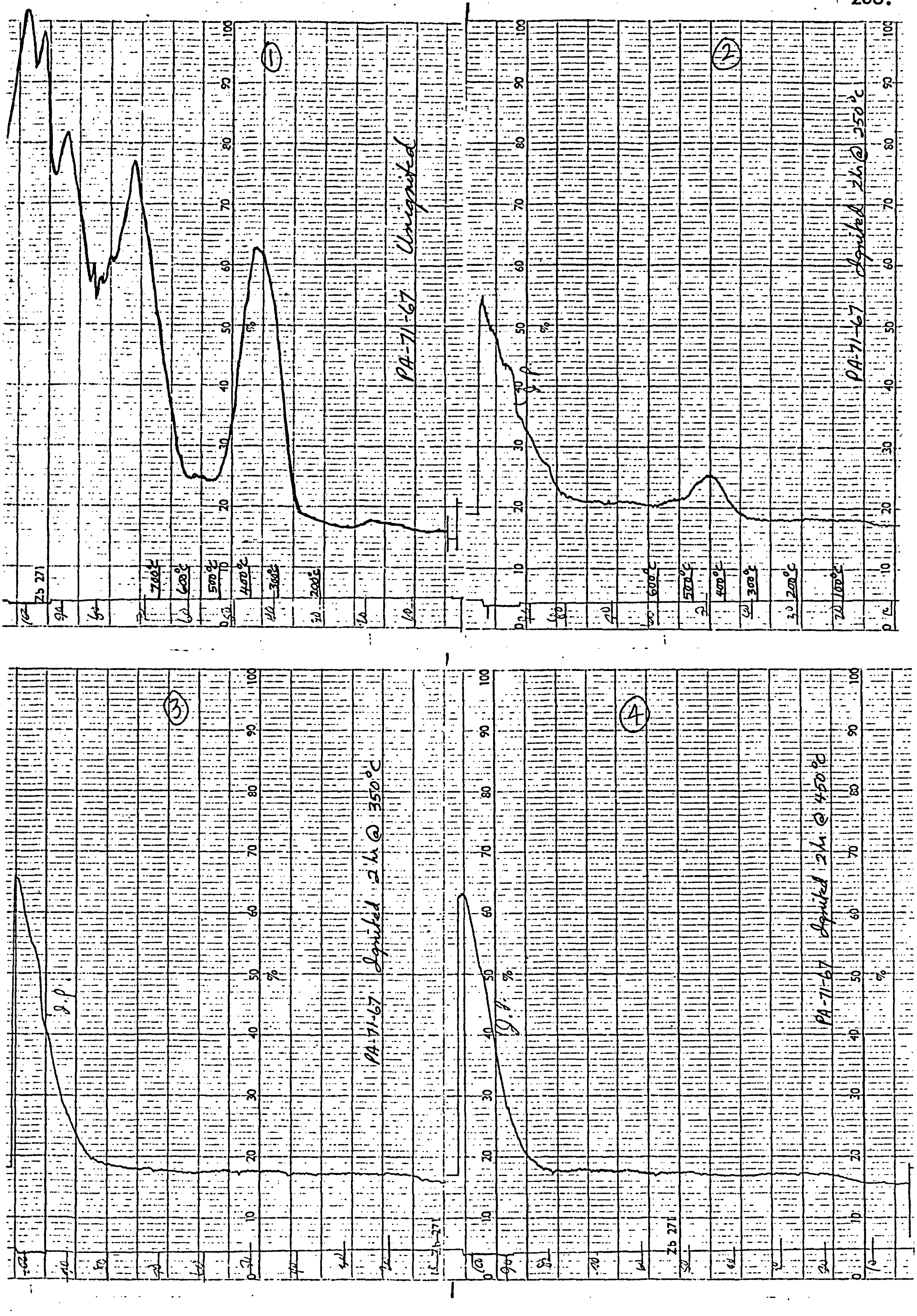


Figure 75: Effect of prior ignition at various temperatures on sulphur evolved from a soil sample.

compared with sulphur evolved from soils.

Sulphur evolution profiles for a number of lake sediments from Three Corner Pond produced using the induction furnace show that, as with the soils, most of the sulphur is emitted with the decomposition of the organic substances, at temperatures in the 280° - 440°C range (Figure 76). However, it is observed that the emission in this range forms a large asymmetrical peak in some cases and is resolved into two or more peaks in several other samples. That there are in fact often three emissions from sulphur associated with organic carbon in this area was confirmed using the slower, controlled-heating resistance furnace (see section 9.4.4). A small emission of sulphur is observed in the 650-790°C range believed related to inorganic forms (sulphates or sulphides). A comparison of typical sulphur evolution curves for a lake sediment and a soil sample are given in Figure 77.

Sulphur evolved from the various size fractions of a stream sediment sample heated in the induction furnace reached maxima in the 300-440°C and 680°-800°C ranges corresponding in many ways to emission from soil samples (Figure 78). Comparison of the peak heights with the total sulphur and organic matter contents (Figure 79) indicates that the grains of pyrite/chalcopyrite giving rise to the high total sulphur in fraction 1A are not decomposing during heating in the argon atmosphere but were decomposed with the aid of accelerators in combustion in an oxygen stream of the LECO total sulphur method. The variation of the peak heights in the remainder of the samples follows the organic content variation to a large

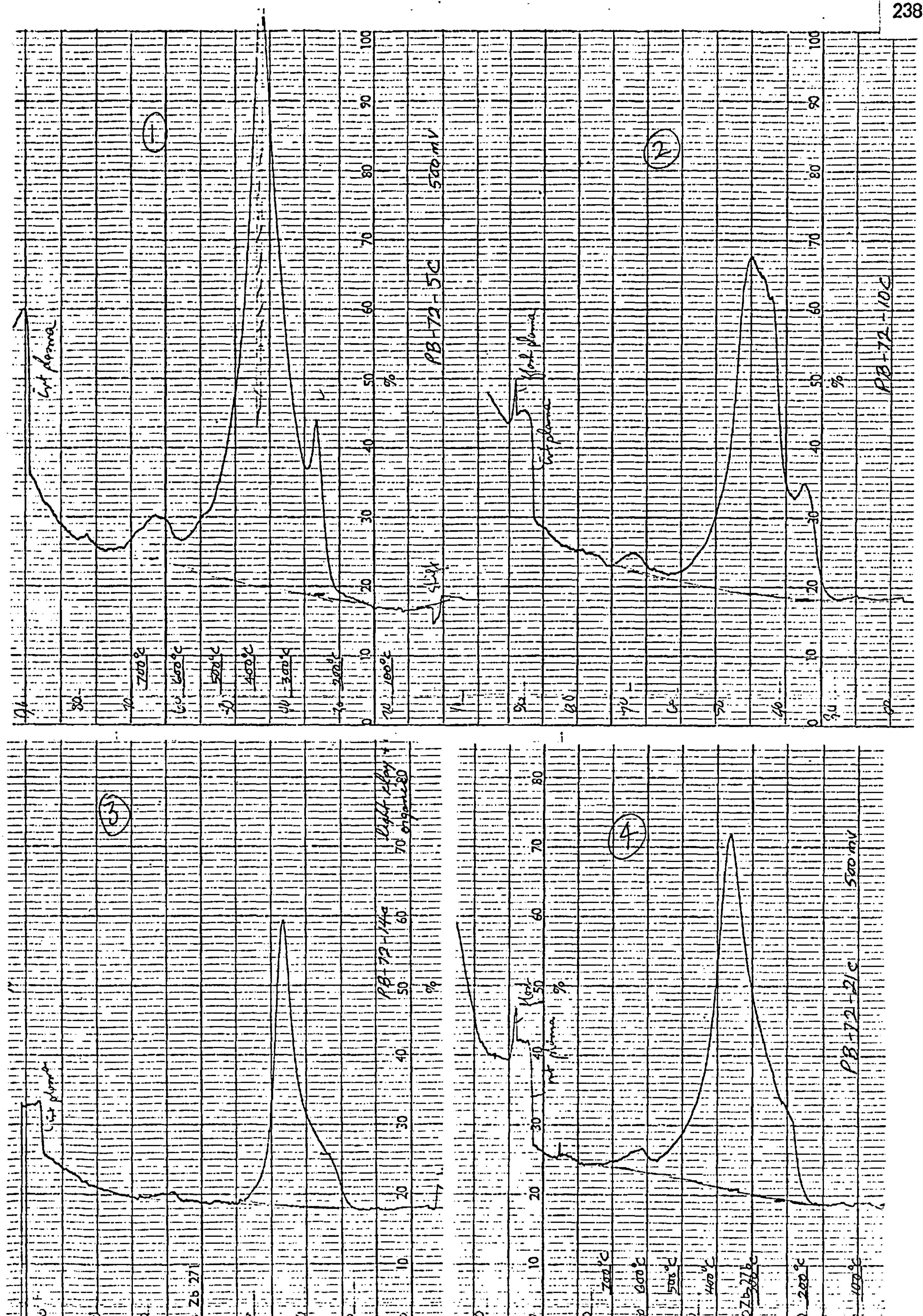


Figure 76: Sulphur evolution profiles for several selected lake sediment samples from Three Corner Pond.

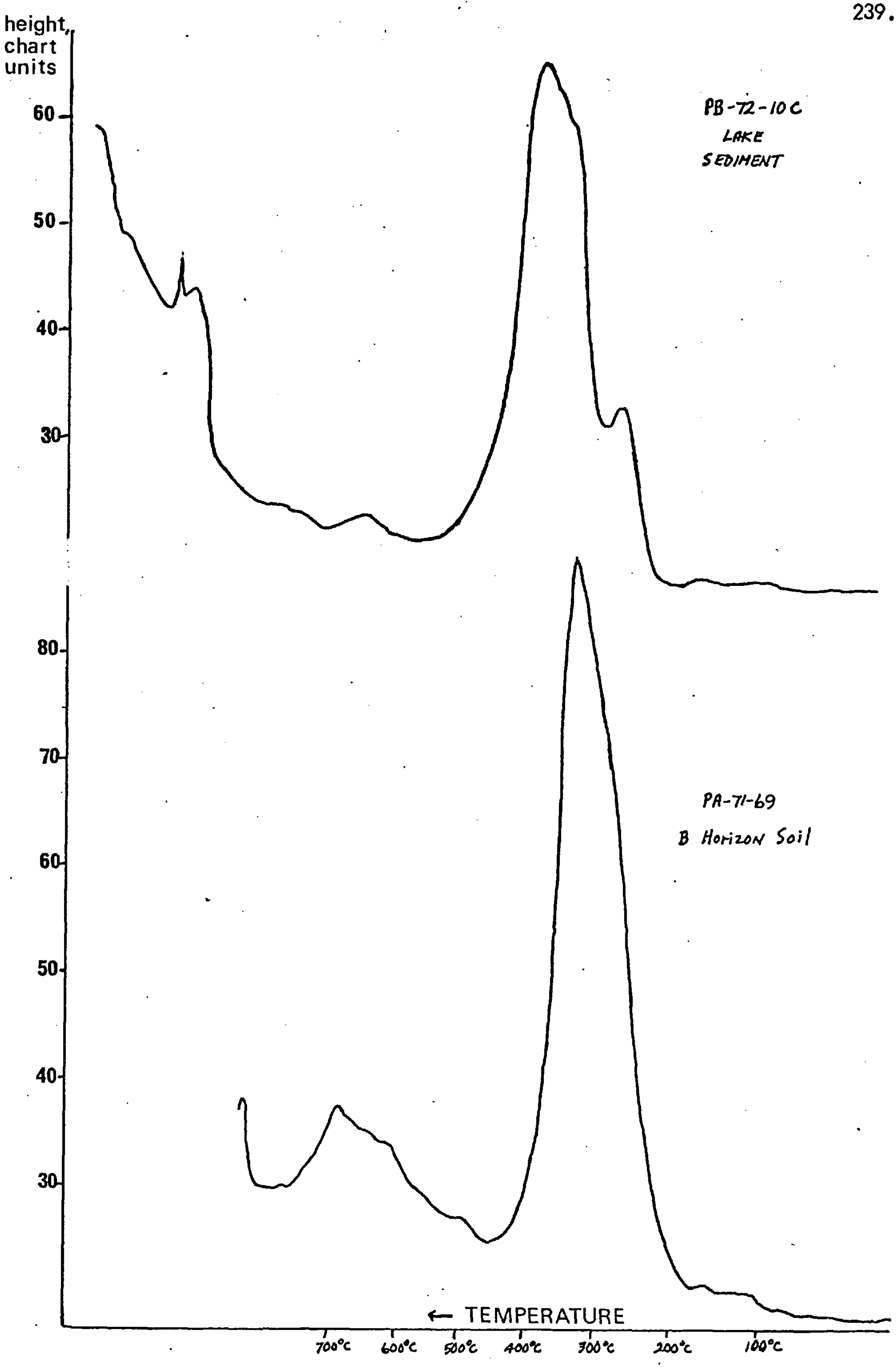


Figure 77: Comparison of typical lake sediment and soil evolution profiles for sulphur.

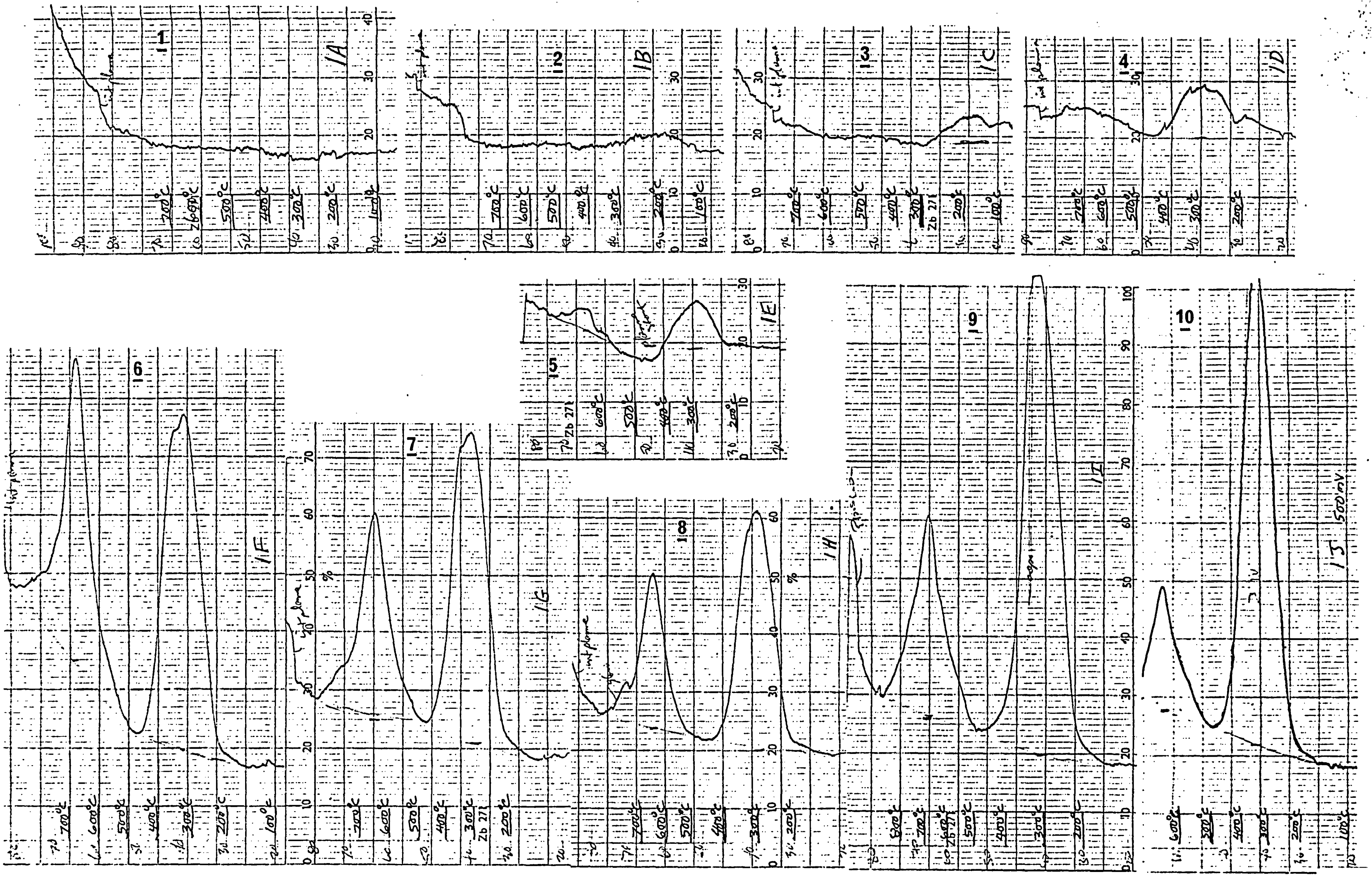


Figure 78: Sulphur evolution profiles for ten size fractions of a stream sediment sample draining a mineralized area.

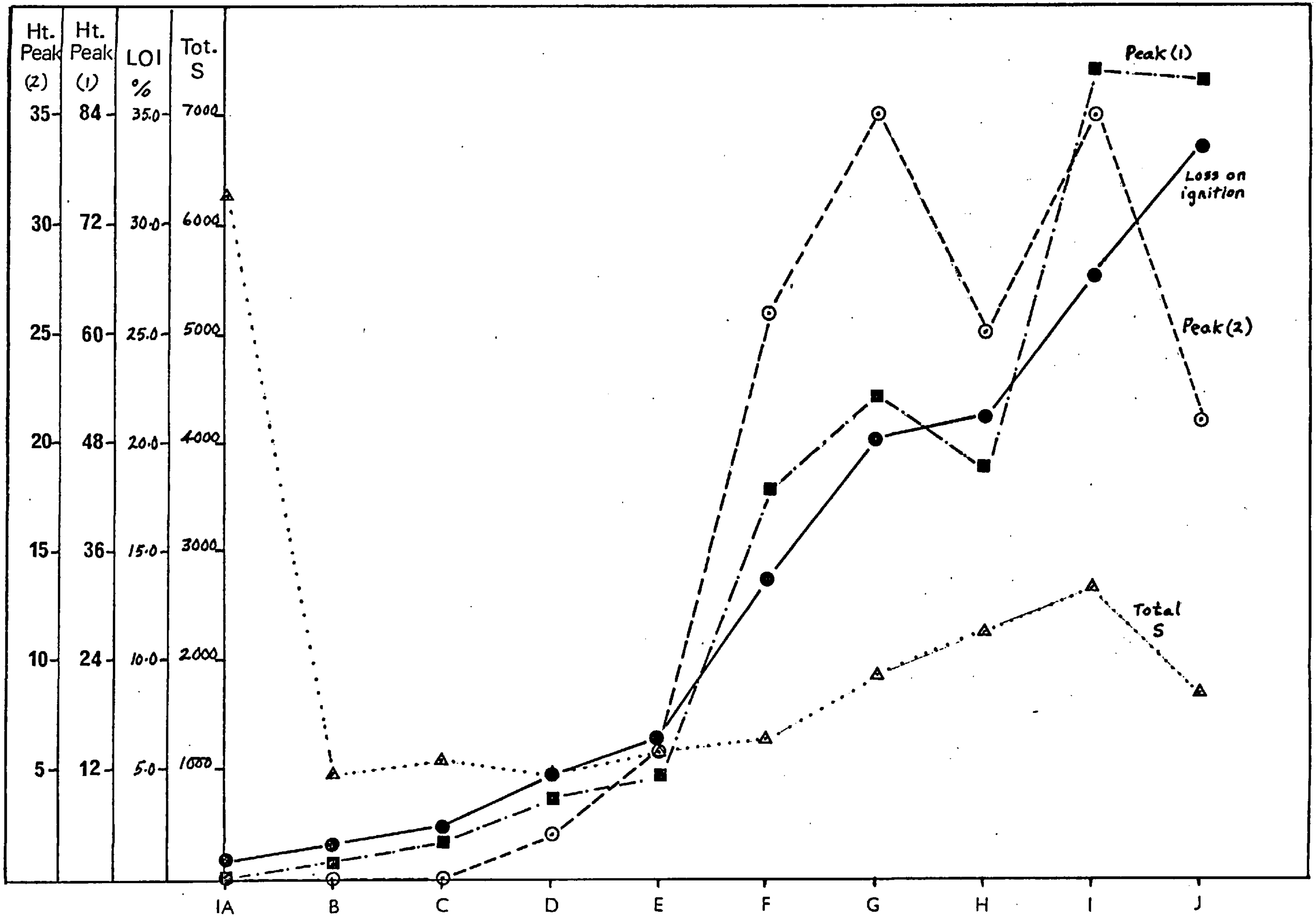


Figure 79: Comparison of low- and high-temperature peaks with total sulphur and loss-on-ignition for ten size fractions of a stream sediment sample.

extent, with the lower temperature peak more closely related from the higher temperature peak.

9.4.3 Other Samples

Several samples of materials other than soils and sediments were analyzed and show interesting features in the sulphur evolution profiles. A sample from the Whalesback tailings which contained very fine grained pyrite in a crushed chloritic basalt matrix (plus residues from the milling process), was analyzed by heating in the temperature-programmed resistance furnace and detection of the emission on the 190.0 nm sulphur line. The chart of the sulphur emission is given in Figure 80, and shows that two well-defined peak emissions occur at temperatures of 590°C and 735°C. Later determinations on artificial and natural compounds indicated that the lower temperature peak may be due to an oxidation product of the pyrite such as $FeSO_4$, and the higher temperature one to a release from the finely ground pyrite itself (see 9.4.4).

A sample of fine pyritic sulphides from the Pilley's Island dump gave an emission profile on heating in the resistance furnace to 950°C which shows strong responses at temperatures of 230°C and 505°C as well as several smaller emissions at higher temperatures (Figure 81). The peak at 230°C is suspected to be due to either native sulphur or loosely adsorbed sulphate but positive identification has not been made. It is mentioned as significant in that if this volatile component occurs in small quantities in soils or sediments containing organic matter, the emission due to this form

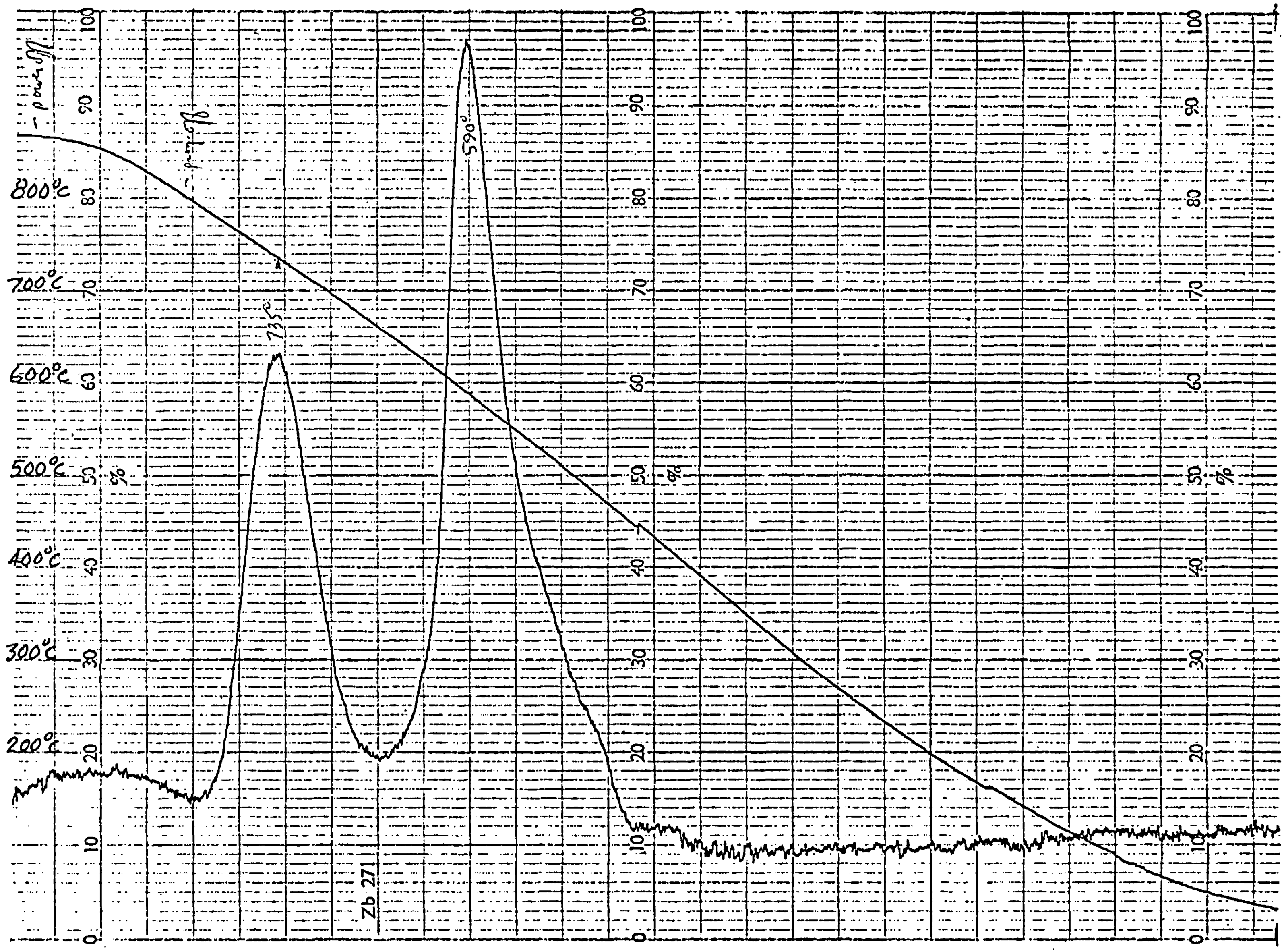


Figure 80: Sulphur evolution profile for a sample of tailings from Whalesback pond, heated in temperature-programmed resistance furnace.

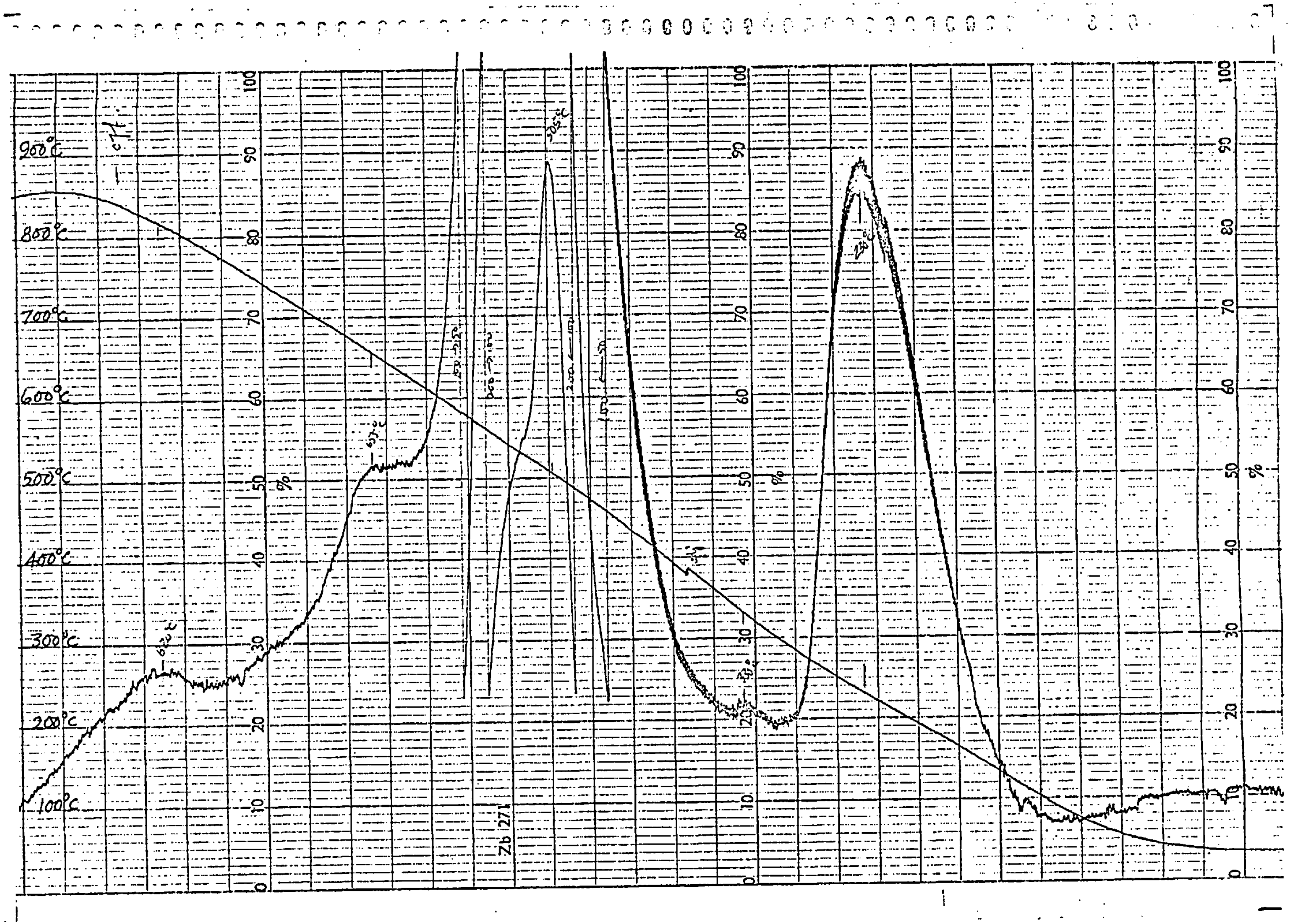


Figure 81: Sulphur evolution profile for a sample from oxidized Pilley's Island sulphide dump, heated using resistance furnace.

may well be masked in some cases by the emission from the organic sulphur forms. Emission at this temperature was also distinguished in the coarser fractions of two inorganic stream sediment samples but not in any other soil or sediment samples.

9.4.4 Interpretation of Sulphur Evolution Profiles - Identification of Emission Peaks.

In order to help interpret the variety of sulphur emissions observed by heating different types of geochemical samples, a number of artificial sulphur-containing compounds were analyzed in conjunction with natural samples, using the temperature-programmed resistance furnace and detection on the 190.0 nm atomic sulphur line. A diagram of the sulphur emissions from some of these artificial and natural samples at different temperatures is presented in Figure82.

The primary general conclusion to be derived from these investigations is that a great variety of sulphur forms are possible and do occur in geochemical samples of different materials. Under precisely similar heating conditions, the emission from each form can be reproduced, but the evolution pattern is a response to the net effects of the processes listed in Table 30 and the temperature at which the emission from a compound may occur by any one of these processes may be influenced by such things as heating rates and matrix effects. For example, the emission from desorption of sulphate in an inorganic sediment may occur at a slightly different temperature than emission from sulphate desorption in an organic soil.

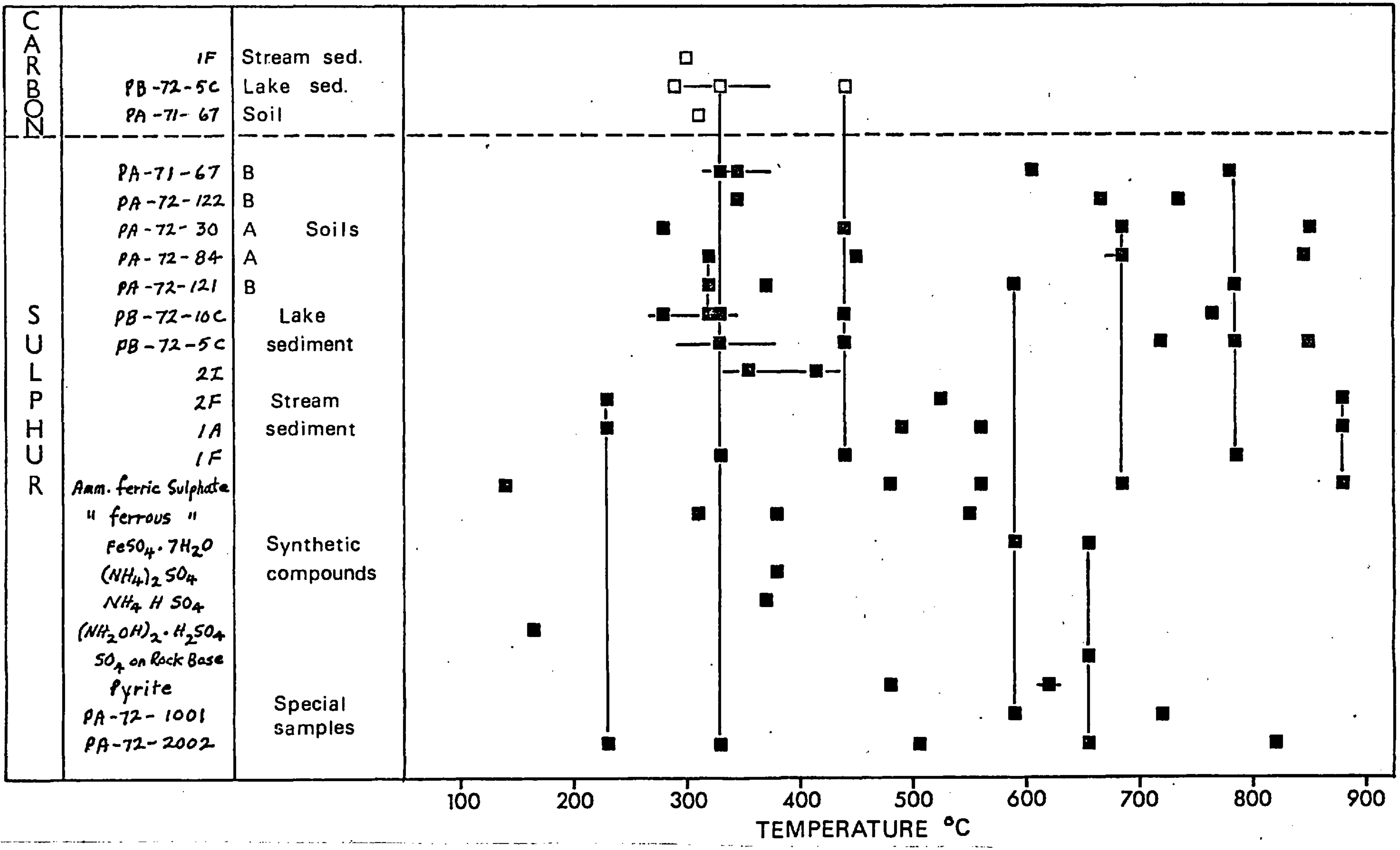


Figure 82: Sulphur emissions from various artificial and natural samples heated in the resistance furnace. Squares indicate temperatures at which peaks occur; horizontal lines broad emissions and vertical lines join peaks recurring in three or more different samples.

However, despite the number of variables involved, several observations can be made from Figure 82 which are significant in illustrating aspects of the distribution of sulphur compounds in geochemical samples. Firstly, two peak emissions at temperatures in the 290°-350°C and at 440°C recur in soil samples, lake sediments and stream sediments, and are directly related to carbon, confirmed by detection of carbon emission on the 247.8 nm carbon line at the same temperatures on several of the samples, as plotted at the top of the figure. Secondly, peaks at 590°C and 655°C produced by the volatilization of ferrous sulphate also occur in samples from sulphide dumps and in one case a soil over the sulphide zone at Rendell Jackman, which also contains pyrite grains, suggesting that oxidation of the pyrite has produced ferrous sulphate in the samples, from which the emissions at these temperatures occur. Thirdly, an emission from organic soil samples in the 680°-690°C region coincides with an emission from ammonium ferric sulphate, suggesting that in the heating of humus samples, compounds similar in volatility to ferric sulphate may be produced. Fourthly, sulphates of calcium and barium were heated on the slow furnace to greater than 950°C and were decomposed at temperatures estimated in the 1000-1100°C range, giving strong sulphur emissions. This suggests a possible means of discriminating between sulphur products derived from oxidizing sulphides, which do give emissions below 950°C and sulphur derived from gypsum or barite deposits, which do not, but the applicability of this discriminant needs further investigation. Fifthly, a large number of sulphur emissions occur above 480°C which are believed to be produced by various thermal reactions involving sulphate and sulphide minerals but have to date not been characterized.

9.5 SUMMARY

Sulphur emitted on heating of geochemical samples in an argon atmosphere has been investigated using the microwave-induced argon plasma emission system. Soils characteristically have two areas of peak sulphur emission, a lower temperature one (290°-440°C) related to organic carbon, and a higher temperature one (590°-790°C region) related to the presence of sulphides, as indicated by enhancement of this peak over sulphide zones during soil traverses across the mineralization. Stream and lake sediments evolved sulphur at several different temperatures, with organic lake sediments showing two or three low-temperature emissions associated with the organic material.

Subsequent attempts to identify the various sulphur emissions produced by several thermal processes from different sample types were carried out by using the temperature-programmed resistance furnace instead of the faster induction furnace, which is more suited to routine analysis. Some emissions related to organic carbon and to oxidation products of pyrite such as ferrous and ferric sulphates were identified, but further research is recommended to provide a more complete catalogueing of the large number of sulphur emissions observed.

With further development of the system and analytical procedures, microwave-induced argon plasma emission analysis may be used in exploration geochemistry to detect sulphur related specifically to oxidizing sulphide deposits. During investigations conducted to the present, there were indications that the sulphur evolution profiles alone could effectively discriminate between sulphur related to organic material, that related to the presence of sulphides, and that derived from gypsum or barite deposits. Expansion of the detection system by the addition of spectrographic and read-out channels in order to determine sulphur and carbon emissions simultaneously would be a very useful asset.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 SUMMARY OF THE RESULTS OF INVESTIGATIONS IN THE NOTRE DAME BAY AREA.

Investigations on the secondary dispersion of sulphur from sulphide deposits have been carried out in the vicinity of a number of disseminated to massive pyrite/chalcopyrite deposits in the Notre Dame Bay area, Newfoundland. Determination of total sulphur concentrations in soils indicated that in unmineralized areas the largest part of the sulphur is contained in the soil in organic forms and it is therefore enriched in the organic surface horizons relative to the mineral horizons of podzols, and in areas of peat bog relative to areas covered by forest soils. Adjacent to sulphide deposits, soils contained anomalous total sulphur concentrations related to the presence of sulphides and not to organic matter content. In a few cases total sulphur showed improved contrast relative to Cu, Pb, Zn or Fe, reflecting the high ratio of sulphur to the other elements in the ore, but in other areas determination of the specific ore metals would be more beneficial.

Because of the strong relationship between total sulphur and organic matter a regression relating the two was derived, from an analysis of the variance of sulphur in relation to other variables in soils from an unmineralized area, which could be used to correct for sulphur due to organic content. Calculation of residual sulphur contents can then be used to discriminate between sulphur anomalies related to organic content and those related to other sources such as sulphides.

Determination of total sulphur concentrations in lake sediments from Three Corner Pond and Big Deer Pond indicated that this could be used effectively in detailed surveys to locate off-shore extensions of known sulphide zones and, again,a strong correlation between the total sulphur value and organic content, as estimated by loss-on-ignition, is observed. It is evident, however, that a much greater sulphur : carbon ratio occurs in lake sediments than in soils, since the expression relating sulphur and organic content in the Big Deer sediments is S (ppm.) = 70 L.O.I. (%) + 300, whereas that for soils in the Rendell Jackman area is S (ppm.) = 16.73 L.O.I. (%) - 26.14.

Stream sediment analysis indicated that sulphur dispersion takes place mainly as discrete sulphide particles, but away from any sulphide deposit, the total sulphur value fluctuates with organic content. Size fraction analysis showed that in all areas total sulphur generally increases towards the finer grain sizes, with increasing organic content. In the vicinity of mineralization sulphide particles gave high sulphur and ore-metal values in the coarsest fractions of a few samples. The total sulphur anomaly in the sediments of the drainage from the Rendell Jackman deposit did not persist as far downstream or show as good contrast as the copper pattern in that area.

Oxidizing sulphides at the Rendell Jackman deposit were found to add several mg/l sulphate to the surrounding drainage waters, causing a detectable, but low-contrast aureole about the deposit. Season variations in the sulphate concentration and pH were observed to occur with variations in the amount of water flowing, and believed to be related to the seasonal productivity cycles of the sulphide oxidizing bacteria. Best contrast was observed in the autumn (the optimum sampling time) but no indication of sulphide mineralization could be observed during periods of flooding, such as during the spring run-off.

The dispersion of gaseous sulphur dioxide from oxidizing sulphides was examined in the vicinity of sulphide occurrences and sulphide dumps derived from former mining activity. Investigations over Whalesback tailings pond indicated a decrease in SO_2 concentration with height above ground, and wind is considered an important influence in rapid dispersion of SO_2 released to the atmosphere. An increase in the SO_2 released from the tailings was observed coincident with maximum daily temperatures. Investigations at Pilley's Island indicated similarly the importance of wind in atmospheric dispersion, as maximum concentrations were found in sheltered hollows where wind action was restricted.

Determination of sulphur dioxide concentrations in soil air on traverses in the Rendell Jackman, Pilley's Island, and Dawes Pond areas were partially successful in that detectable levels were found which, in the Pilley's Island traverse, showed fair correlation with metal values in the soil; in the Dawes Pond area showed a maximum coincident with an induced polarization anomaly, suggesting a possible application for interpretation of I.P. anomalies; and in the Rendell Jackman area showed a slight increase over the sulphide zone. However, in all areas values were in the low ppb. range, near the detection limit of the West and Gaeke procedure used, and in both soil air and atmospheric measurements a strong dependence on calm, warm, sunny days for the production of SO_2 is indicated. Pending the development of suitable techniques for the measurement of sulphur dioxide concentrations in the range of less than 1 ppb., the applicability of sulphur dioxide studies under climatic conditions similar to that of the Newfoundland field area is quite limited.

It may be noted that the principal mechanism for the dispersion of sulphur dioxide from oxidizing sulphides through overburden to the atmosphere is diffusion, as mass flow is known to influence gaseous exchange in only the surface few centimeters of soil air. The moisture content and permeability of the soil appear to be the most important parameters limiting gaseous diffusion through overburden.

The analysis of sulphur in soils and sediments using the microwave-induced argon plasma emission system, developed by Meyer and Leen (1973) in the AGRG, greatly aided interpretation of the distribution of sulphur compounds in these media. Study of the sulphur evolved at different temperatures when the samples were heated to temperatures up to 950°C showed that, in soils, two emissions occurred, one at low temperature related to organic carbon and the other at higher temperature which was related to the presence of sulphides. Evolution profiles for sulphur in lake sediments showed considerable amounts of the sulphur contained were evolved at lower temperatures in two or three separate emissions related to organic matter, with lesser emissions at higher temperatures related to inorganic sulphates. Identification of some of the emissions was aided by the analysis of artificial and natural compounds using the temperature-programmed resistance furnace.

analyzing samples from geochemical surveys. The indirect procedure for the determination of sulphate ion in surface waters worked reasonably well for the 0-30 mg/l range found in the Newfoundland field area, but difficulties with this procedure could be expected in analyzing waters from regions containing much higher concentrations of other dissolved ions than occurs in the waters of this area. It is not recommended as suitable for routine analysis of natural waters without further investigations on standardization and interferences. The procedures used for sulphide and sulphate fractions are semi-quantitative only and not generally applicable to a variety of sample materials.

The microwave-induced argon plasma emission system has potential as an analytical technique in geochemistry for the determination of low concentrations of Hg and Cd in solid and solution samples, and for the determination of the forms in which various elements are contained in the samples (Hg and S have so far been successfully investigated). The detection of volatile emissions under controlled heating conditions is a more convenient and useful procedure for the distinguishing of the forms occurring than are partial extraction procedures. Expansion of the system to permit simultaneous multi-element determinations is possible. The argon plasma emission procedure is still in the development stages and other than limited application remains to be investigated.

10.2 RECOMMENDATIONS ON THE APPLICATION OF SULPHUR STUDIES IN GEOCHEMICAL EXPLORATION.

Total sulphur determinations in soils can be used successfully to outline areas containing sulphide mineralization, preferably in conjunction with other elements which may be determined on a routine basis using standard analytical techniques. Around pyritic ore deposits, a disseminated pyrite aureole may give rise to a fairly large total sulphur anomaly in the overlying soils but only a small metal anomaly, in which case the exploration target is enlarged by the inclusion of total sulphur determinations. Interpretation of total sulphur data must be made on the basis of the variance in the sulphur value not accounted for by the organic content of the sample.

Lake sediment total sulphur can also be used on a detailed scale to locate off-shore sulphide zones, but, again, interpretation must allow for the organic contribution to the total sulphur content, and interpretation is aided by the inclusion of more analytical variables. The use of total sulphur determinations on low-density regional scale surveys has not been investigated, but theoretically, and on the results of the detailed surveys in the Notre Dame Bay area, it may at least be a very useful data supplement which may in fact indicate the presence of sulphide mineralization where other elements do not.

The limited dispersion of sulphur in stream sediments makes the application of total sulphur determinations on samples from other than very detailed surveys somewhat less beneficial than standard heavy metal determinations, which are also more specific.

It is recommended that exploration for sulphide deposits utilizing the determination of sulphate ion concentrations in surface waters be conducted in the autumn or late summer when water flow is low and release of oxidation products from sulphide deposits is expected to be greatest. In areas containing evaporite deposits or of unknown geology, interpretation of sulphate data could best be made on the basis of Ca and Cl constituents, as proposed by Dall'Aglio and Tonani (1973).

The determination of sulphur dioxide concentrations in soil air, as a guide to buried sulphide ores, appears to have slightly better potential than determination of atmospheric concentrations, as meteorological variables are more influential on sulphur dioxide dispersion there. Under climates which are warmer and drier than in the Newfoundland area, more favourable levels of sulphur dioxide likely occur in the air in the pore spaces of the overburden and in the surface air. The determination of SO_2 using the procedure of West and Gaeke is adequate for the ppb. range but successful application of sulphur dioxide in air measurements in areas with unfavourable climates depends on the development of a suitable technique for measuring reliably concentrations at less than 1 ppb. level. Atmospheric measurements should always be made with reference to a base station in the field area monitoring SO_2 and temperature changes. It is also recommended that soil temperature be recorded at each site during any soil gas survey.

Of the other analytical procedures used in these investigations on sulphur dispersion, the LECO combustion procedure followed by iodine titration for the determination of total sulphur in soils, sediments and rocks, is also recommended to be sufficiently fast and precise for routine application in

10.3 SUGGESTIONS FOR FURTHER RESEARCH

Some areas for further research have been indicated during the course of this research project relating to various aspects of the geochemical dispersion of sulphur and other elements from sulphide deposits. The use of sulphur determinations in regional lake sediment surveys warrants investigation as the use of lake sediments as a medium for the exploration of Shield areas of Canada, Scandinavia and the U.S.S.R. increases.

The possible applicability of sulphur dioxide measurements in soil air in areas with fairly warm climates is suggested, and the variables affecting the whole process of gaseous dispersion through overburden are not very well documented as yet. Further development of analytical methods for the determination of sulphur dioxide concentrations in the 10^{-10}g. range and hydrogen sulphide in the 10^{-9} to 10^{-10}g. range would permit more successful application of these determinations in gaseous prospecting.

It is also recommended that further research be conducted into the possible expansion of the microwave-induced argon plasma emission technique to include the simultaneous detection of sulphur and carbon emissions and on the development of procedures to permit routine diagnosis of the forms in which various elements such as Cd, Se, Cu and S occur in geochemical samples.

As well as research in developing analytical procedures, investigations on the dispersion of elements through or in consolidated overburden, as well as unconsolidated, and the possible mechanisms for such dispersion might be beneficial in the continuing search for means of detecting ore deposits concealed at depth.

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