

TRACE ELEMENTS IN CRETACEOUS ROCKS
OF MANITOBA

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ABSTRACT

Trace quantities of copper, zinc, and molybdenum have been determined in the Cretaceous beds of Manitoba. The contents of the metals are in the ranges: copper, 2 to 78 p.p.m.; zinc 5 to over 400 p.p.m.; and molybdenum, less than 2.5 to 180 p.p.m. The results indicate an enrichment of molybdenum in the Cretaceous beds and it is suggested that adsorption of molybdenum from sea water by clay minerals and organic matter in the shales, and by clay minerals in the bentonites is responsible for the enrichment. In order for such extensive enrichment the sea water must have contained an abundance of available molybdenum and the likely source of the excessive molybdenum in the sea water is Precambrian rocks in the shield area to the east.

The Cretaceous beds contain normal concentrations of copper and zinc but the bentonite layers contain much lower concentrations of copper and zinc than the interbedded shales.

Molybdenum poisoning of cattle in Swan River Valley is the result of the abundance of molybdenum in the Favel beds from which the soils in the valley were derived.

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CHAPTER I

INTRODUCTION

This investigation of trace element content in the Cretaceous beds exposed in Manitoba is the first extensive trace element study of sedimentary rocks in Manitoba. Recently Tourtelot (31) examined trace elements in the Pierre shales of Late Cretaceous age in the Western Interior of the United States and his results are directly comparable to those of the present study. Only molybdenum, copper, and zinc were determined in the present investigation.

I. PRELIMINARY STUDY

In a preliminary study Dr. G. M. Brownell assembled some fifty-four samples from widely scattered outcrops in Manitoba and had them analysed for molybdenum, copper, zinc, and lead. The analyses were carried out by Dr. R. E. Delevault of the Geology Department at University of British Columbia using standard colorimetric procedures.

The analytical results of the preliminary study revealed a high content of molybdenum in certain Cretaceous shales. Two analyses of samples from the Favel Formation showed a molybdenum content of 140 parts per million (p.p.m.) and a sample from the underlying Ashville beds contained 110 p.p.m. Most of the other samples from Cretaceous beds had a molybdenum content somewhat above the average for shale, eleven of them varying from 4 to 70 p.p.m.

According to Krauskopf (14) the average concentration of molybdenum in shales is 1 p.p.m. Kuroda and Sandell (16) stated that, "The probable average molybdenum content of all sedimentary material does not exceed 5 p.p.m. and could be considerably less."

In contrast, there were twenty-six samples from Paleozoic rocks of Manitoba in the preliminary collection and all of these samples contained less than 0.3 p.p.m. of molybdenum.

The high molybdenum concentrations discovered in Cretaceous samples suggested the source of excessive molybdenum content of the soils in the Swan River Valley. Studies of these soils made by Smith (29) showed that the average level of molybdenum in the soils is considerably higher than the average level of 2.5 p.p.m. for soils throughout the United States, as shown by Robinson and Alexander (26). Smith outlined some forty square miles where molybdenum in amounts up to 11.5 p.p.m. in the soil was detected. It was concluded that the above average molybdenum content in the soils is responsible, in part, for the molybdenum poisoning of cattle which has existed in the Swan River Valley for over forty years, according to Cunningham, Brown and Edie (4).

The results of the preliminary study led Dr. Brownell to begin a larger scale project to investigate further the molybdenum content of the Cretaceous beds. Samples from Early to Late Cretaceous beds were collected from several localities along the escarpment. It was at this stage that the author of the present study began working on the project.

II. PURPOSE OF THE STUDY

The aim of this study was to examine further the trace element content of Cretaceous rocks of Manitoba with particular emphasis on the molybdenum content and to discover factors responsible for the apparently high concentration of that metal. Copper and zinc were determined so that the relative enrichment of these elements could be compared with that of molybdenum.

Since, to the author's knowledge, no extensive study of trace elements in bentonite has ever been published and because many samples in the study collection are bentonite, this investigation furnishes some of the first analyses for trace elements in bentonites. At the same time it was of interest to compare the trace element composition of the bentonites with that of the interbedded shales.

CHAPTER II

TRACE ELEMENTS IN SEDIMENTARY ROCKS

I. DATA ON COPPER, ZINC, AND MOLYBDENUM

IN SEDIMENTARY ROCKS

Analytical data on copper, zinc, and molybdenum in sedimentary rocks as given in reports of Kuroda and Sandell (16), Krauskopf (14), LeRiche (17), and Tourtelot (31) are summarized in Table I.

Molybdenum analyses of shales and clays, carbonates, sandstones, and cherts from the United States and of some Permian shales in Germany as reported by Kuroda and Sandell (16) are given in Table I. Copper, zinc, and molybdenum concentrations of some Japanese and European Paleozoic and Mesozoic shales are also indicated. Kuroda and Sandell suggested that shales which are poor in organic matter contain about 1 or 2 p.p.m. molybdenum but there is, however, a definite concentration of molybdenum in carbonaceous shales. The Permian shales in Germany, which are rich in organic matter, averaged 150 p.p.m. molybdenum. Some coals, petroleum ash, phosphate rocks, bauxites, and manganese rich sediments are also enriched in molybdenum according to Kuroda and Sandell. On the other hand, as indicated by the figures shown in Table I, carbonates, sandstones, and cherts generally contain lower quantities of molybdenum than do shales.

TABLE I
 REVIEW OF ANALYTICAL DATA ON COPPER, ZINC, AND
 MOLYBDENUM IN SEDIMENTARY ROCKS

	p. p. m.		
	COPPER	ZINC	MOLYBDENUM
KURODA and SANDELL (1954)			
U.S. shales and clays	-	-	0.2-87
U.S. carbonates	-	-	0.1-1.2
U.S. sandstones	-	-	0.0-1.6
U.S. cherts	-	-	0.0-0.9
German Permian shales	-	-	150
14 Japanese Paleozoic shales	40	100	0.5
10 Japanese Mesozoic shales	55	100	2.9
36 European Paleozoic shales	65	130	4.5
KRAUSKOPF (1955)			
Shales	30-150	50-300	1
Black shales	20-300	100-1000	10-300
Sandstones	10-40	5-20	0.1-1
Carbonates	5-20	4-20	0.1-0.5
LERICHE (1959)			
Lower Lias shales	7-95	-	<3-320
TOURTELOT (1964)			
Pierre shales of western U.S.			
Non-marine, non-carbonaceous			
range	16-75	32-120	<1-3
median	25	81	1
Marine; nearshore			
range	7-40	80-150	<1-20
median	28	100	1.5
Marine, offshore			
range	18-150	37-380	<1-350
median	43	130	1

They concluded that it is difficult to arrive at an average value for molybdenum in sedimentary rocks because of the variable amounts in shale and that the average molybdenum content of all sedimentary material probably does not exceed 5 p.p.m.

The common ranges of copper, zinc, and molybdenum in shales, black shales, sandstones, and carbonates, as reported by Krauskopf (14), are given in Table I. He showed that nearly all trace metals are concentrated more in shales than in carbonates and sandstones. The enrichment of trace metals in carbonate sediments, evaporites, and silica sediments is generally slight.

The greatest enrichment is in the organic sediments. Sediments enriched in trace metals include black shales, coal ash, asphalt, phosphorites, iron oxide sediments, bauxite, and manganese oxide sediments. Molybdenum is enriched in all types of carbonaceous sediments, particularly asphalt and petroleum ash, and in manganese oxide sediments. Copper is widely disseminated and seldom markedly enriched in sedimentary rocks. Zinc, which is also generally widely disseminated in sediments, is only locally enriched in carbonaceous sediments.

Krauskopf's conclusions regarding the distribution and concentration of rare metals in sedimentary material are in close agreement with those of Kuroda and Sandell.

LeRiche (17) studied the distribution of copper and molybdenum in the Lower Lias shales of England which contain high concentrations of molybdenum (see Table I).

The soils formed from them contain a corresponding high level of molybdenum which is likely responsible for the molybdenum poisoning of cattle in Somerset County. This situation is analagous to that in the Swan River Valley of Manitoba, as described by Smith (28). LeRiche found that the high concentrations of molybdenum were always in shales containing appreciable quantities of organic carbon. He concluded that the sea water in which the organic shales were deposited must have contained an abnormally high concentration of molybdenum and that the molybdenum was adsorbed by the organic material or precipitated as sulphide in a reducing environment. He suggested that the source of the molybdenum may have been ore bodies that were eroded.

Trace elements of Pierre Shales were studied by Tourtelot (30) and the ranges and median values for copper, zinc, and molybdenum in non-marine and marine shales are given in Table I. Copper is concentrated more in the offshore marine shales than in the non-marine or nearshore marine shales. The nearshore marine shales contain larger quantities of zinc than do the non-marine shales and the offshore marine shales contain even larger amounts. The results indicate that there is an insignificant difference in molybdenum content between non-marine and marine shales although a few of the offshore marine shales contain much larger, up to 350 ppm. concentrations of molybdenum. In general copper, zinc, and molybdenum are concentrated in the offshore marine samples having the largest amounts of organic carbon and therefore, according to Tourtelot, marine organic material played an important role in the concentration of these metals.

Tourtelot's study of the Pierre shales is of particular importance in relationship to the present study because some of the Upper Cretaceous sediments of Manitoba are the stratigraphic equivalent of the Pierre shales and were deposited in the same sedimentary basin at approximately the same time.

Certain generalizations can be made from the foregoing review of literature on trace elements in sedimentary rocks and are as follows:

1. Shales generally contain larger amounts of trace metals than do sandstones and carbonates.
2. Trace metals are generally enriched in the carbonaceous sediments (black shales, coal, and asphalt) and in certain other sediments (phosphorites, bauxites, iron-oxide, and manganese oxide sediments).
3. Common ranges for molybdenum, copper, and zinc in shales as listed in Table I are presented and discussed below.

	Shales (p.p.m.)	Black Shales (p.p.m.)
Molybdenum	<1 - 5	10 - 350
Copper	7 - 150	20 - 300
Zinc	30 - 300	100 - 1000

- (a) Molybdenum concentration in shales is variable and large enrichments are common in carbonaceous shales.
- (b) Copper is widely disseminated and not as markedly enriched in carbonaceous shales as is molybdenum.
- (c) Zinc is also widely disseminated and is generally enriched in carbonaceous shales.

4. All three metals are generally more abundant in marine shales than non-marine shales.

II. PROCESSES CONTROLLING THE CONCENTRATION OF TRACE ELEMENTS IN SEDIMENTS

Krauskopf (15) presented an analysis of the factors controlling the concentration of rare metals in sea water. Rankama and Sahama (25), Goldschmidt (10), Kuroda and Sandell (16), Mason (18), LeRiche (17), Hirst (12), and Tourtelot (31), have discussed to some extent, the processes that contribute to concentrating trace elements in sediments. Rankama and Sahama (25) showed that for nearly all metals the amount added to the sea during geologic time far exceeds the quantity now present in sea water. Sea water is thought to be the source of the metals that are concentrated in the marine sedimentary rocks. The most important processes of concentrating the metals from the sea water are chemical precipitation, adsorption processes and organic processes.

Chemical Precipitation

Sea water is greatly undersaturated with respect to nearly all the trace metals and any direct chemical precipitation of insoluble compounds of the metals cannot be a major factor in concentrating the metals from sea water. However, under reducing conditions and in the presence of sulphide ion the precipitation of sulphides of certain metals may account for their enrichment in the sediments.

Adsorption Processes

Natural colloids are particularly effective adsorbing agents and substances, such as clay minerals, hydroxide minerals, and organic matter, that commonly show colloidal properties can effectively remove metal ions from sea water. The amount of adsorption is proportional to the concentration of metal ions and adsorbent in very dilute solutions such as sea water. Adsorption by organic matter and clay minerals has likely played an important part in concentrating some of the trace elements from sea water. Colloidal organic matter is an effective adsorbing agent and montmorillonite has the greatest adsorbing capacity of the ordinary clay minerals.

Adsorption is probably more important than direct precipitation in concentrating the rare metals.

Organic Processes

Molybdenum, copper and zinc are essential to the life processes of many present day plants and animals and the ability of living organisms to concentrate certain rare metals is well known and it is probable that such conditions occurred throughout geologic time. Organic processes, according to Krauskopf (14), are apparently responsible for the greatest enrichment of trace metals in sedimentary rocks.

Molybdenum, copper and zinc owe their enrichment in sediments probably in part to organic processes, in part to adsorption by clay minerals and organic matter, and in part to precipitation as sulphides.

CHAPTER III

GEOLOGIC SETTING AND SAMPLE LOCATIONS

Cretaceous beds in Manitoba are exposed along an eastward facing escarpment that trends south-easterly from the Porcupine Mountains, north of Swan River, to the Pembina Mountains in south-central Manitoba. The stratigraphy of the Mesozoic beds in Manitoba has been described by Tovell (32) and Wickenden (34) and more recently, although in less detail, by Davies, et al. (5). Only a brief description is given here.

I. CRETACEOUS STRATIGRAPHY

Table II presents a summarized stratigraphic section of the Cretaceous strata in Manitoba.

The Swan River Formation consists of unconsolidated sands, sandstone, grey shale, clay, and minor carbonaceous shale and coal. Swan River beds are exposed only in a few places north of Vermilion River. In Swan River Valley the formation is entirely non-marine.

Overlying the Swan River are dark grey to black, carbonaceous shales and sands of the Ashville Formation. It is thought that the Ashville includes beds of both Early and Late Cretaceous age. Exposures of Ashville are found in the valleys of streams that cut across the northern part of the escarpment. Ashville beds are not exposed along the southern portion of the escarpment.

TABLE II

TABLE II

CRETACEOUS FORMATIONS OF MANITOBA

	GROUP		FORMATION	MEMBER	MAX. THICKNESS	BASIC LITHOLOGY
UPPER CRETACEOUS	MONTANA GROUP	PIERRE SHALE	Riding Mountain		1100'	hard grey siliceous shale
			VERMILION RIVER	Pembina	80'	non-calcareous shale, bentonite beds
	Boyne	150'		calcareous speckled shale		
	Morden	200'		carbonaceous shale		
	Favel	125'		calcareous speckled shale, limestone and bentonite		
	LOWER CRETACEOUS	COLORADO GROUP		Ashville		375'
UPPER MANVILLE		Swan River		300'	sand, sandstone, shale, clay	

Range of sample collection

The Favel Formation, above the Ashville, is divided into two members, the Keld and Assiniboine, and is composed mainly of grey shale speckled with white calcareous material, with some limestone and thin bentonite layers. Favel beds are exposed in many stream valleys along the northern part of the escarpment. No exposures of the formation are found south of the Assiniboine River.

Overlying the Favel is the Vermilion River Formation which has been divided into the Morden, Boyne, and Pembina Members. The three Members are well exposed in valleys that cut into the escarpment of the Pembina Mountains. The Morden Member consists of mostly dark grey, non-calcareous shale with a few thin beds of bentonite. The uppermost Pembina Member consists of a series of dark grey to black non-calcareous shales with numerous thin beds of bentonite (see Table V on page 24, for thicknesses). The bentonite has been formed by the alteration of volcanic ash, which is believed to be the product of volcanic activity associated with mountain building to the west. Good exposures of Pembina Member occur along the Pembina River and in bentonite pits a few miles northwest of Morden.

Soft, greenish grey shales and hard, grey, siliceous shales of the Riding Mountain Formation overlie the Vermilion River Formation. No samples from the Riding Mountain Formation were included in the study collection.

The Riding Mountain Formation and the Pembina Member of the Vermilion River Formation are stratigraphic equivalents of the Pierre Shale of the western interior of North America. These Upper Cretaceous sediments were deposited in an extensive epeiric sea which covered much of the central part of the present continent. The bulk of the sediment was derived from the Mesocordilleran geanticline to the west, but it is likely that some of the sediments along the eastern side of the sea were derived from the Precambrian shield to the east.

II. SAMPLE LOCATIONS

Samples were collected from beds of the upper portion of the Swan River, Ashville, and Favel Formations and from the Morden and

Pembina Members of the Vermilion River Formation. The stratigraphic range of the samples is shown in Table II. They consist essentially of dark grey shales with a few harder calcareous layers. Interstratified, at irregular intervals, are beds of white to light yellow bentonite; samples from these layers were collected wherever they were thick enough to be separated from the enclosing shales. The bentonite bands are most predominant in the Pembina Member of the Vermilion River Formation and in the Favel Formation. There are also a few layers of limonitic material which were included in the sample collection. The sample locations are shown in Figure 1 and Table III summarizes the distribution of the samples. In Table V, on page 24, the samples are listed in stratigraphic order and a brief description of each sample is given.

Location 1, on the Swan River, is seven miles downstream from the Swan River townsite. Samples 140 to 149 are shales from the upper part of Swan River and the lower part of the Ashville. These localities were described by Wickenden (37).

Location 2 on the Vermilion River, is twelve miles southwest of Dauphin and includes two separate sections -- the type sections of the Keld and Assiniboine Members of the Favel Formation, which were described in detail by Wickenden (37). Samples 1 to 47 and 153 to 157, which were obtained from this locality, include shales of the Ashville Formation, and shales and bentonites of the Keld and Assiniboine Members.

A producing bentonite pit in the south-west quarter of Sec. 18, tp. 14, R.6, ten miles northwest of Morden, is the site of locality 3. Samples 70 to 84 are shales and bentonites from the lower part of Pembina Member of the Vermilion River Formation that were collected from this location. Pits in the area have been described by Bannatyne (1).

Location 4 on the Pembina River, is five miles directly south of Kaleida. This locality was described by Tovell (32) and is locality 16 on his map. Shales and bentonites from the middle of the Pembina Member, samples 107 to 114, were obtained at this location.

Location 5, also on the Pembina River is thirteen miles southwest of Morden. Samples 100 to 106, which are shales from the Morden Member, were collected from this locality. This site was also described by Tovell (32) and is locality 37 on his map.

Samples 83 and 84 are shales from the lower part of the Morden Member and are from a small valley one and a half miles southwest of Morden.

The samples described above were collected by Dr. G. M. Brownell and B. B. Bannatyne of the Manitoba Mines Branch.

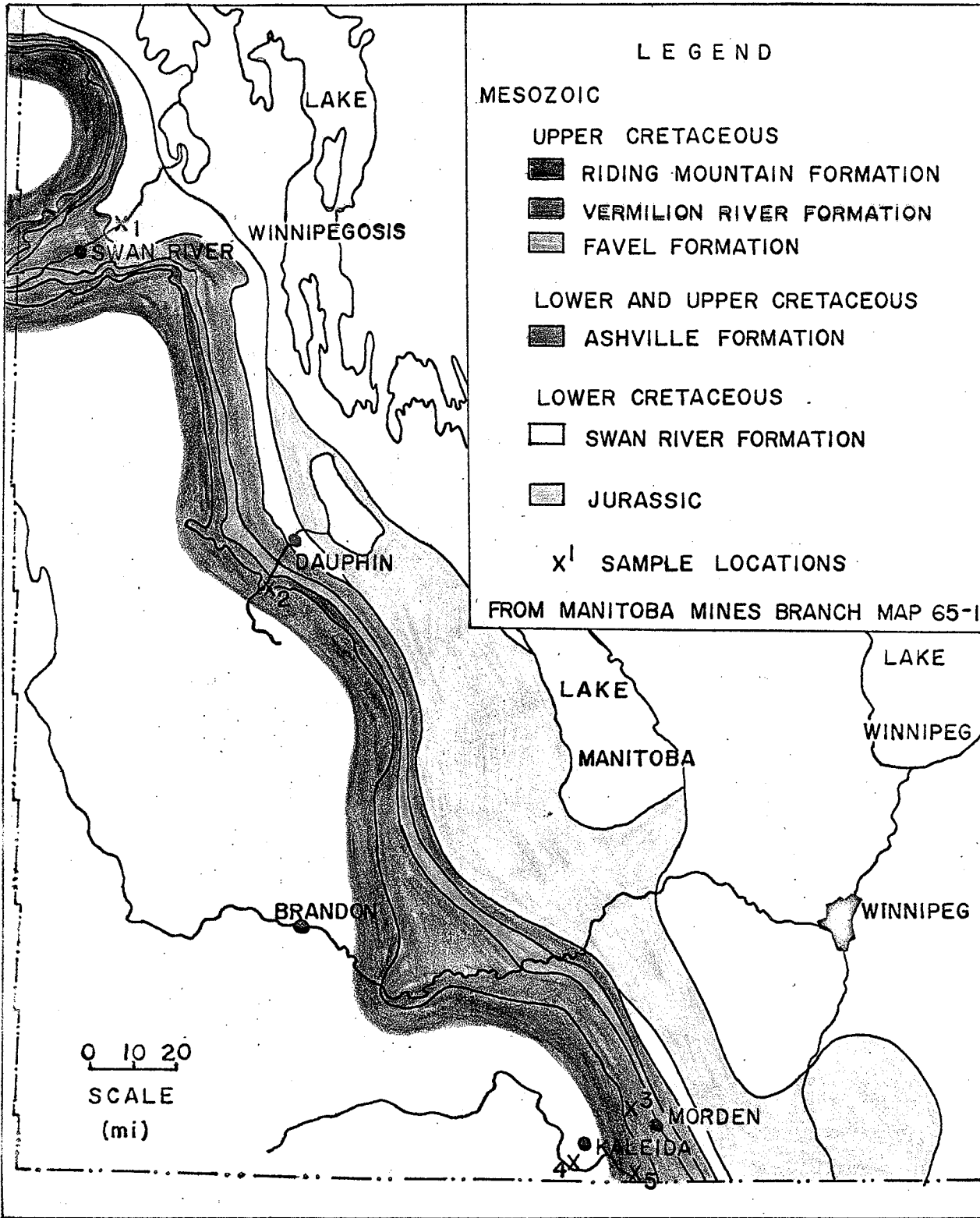


FIGURE 1.

SAMPLE LOCALITIES AND GEOLOGY OF SOUTHWESTERN MANITOBA

TABLE III
DISTRIBUTION OF SAMPLES

FORMATION AND MEMBER	SHALES	CLAYS	BENTONITES	LIMESTONES	SANDSTONES	LIMONITES	TOTAL
<u>VERMILION RIVER FORMATION</u>							
Pembina Member	13	1	6	-	-	-	20
Morden Member	7	1	-	-	-	-	8
<u>FAVEL FORMATION</u>							
Assiniboine Member	8	-	3	1	-	-	12
Keld Member	15	-	9	3	-	2	29
<u>ASHVILLE FORMATION</u>	10	1	1	-	-	1	13
<u>SWAN RIVER FORMATION</u>	6	-	-	-	1	-	7
TOTALS	59	3	19	4	1	3	89

CHAPTER IV

ANALYTICAL METHODS

I. SAMPLE PREPARATION

The samples were prepared by first pulverizing and drying at 110°C., then grinding to 200 mesh. A 1.0 gram portion of each sample was then subjected to a hydrofluoric acid attack, decomposed and brought into solution in 1:1 hydrochloric acid.

The digestion procedure used is a modification of that given by Sandell (27) for molybdenum analyses in silicate rocks and is as follows:

1. Weigh 1.00 gram of 200-mesh rock powder into a platinum crucible.
2. Add 4 ml. of water, 1.0 ml. of perchloric acid and 6 ml. of concentrated hydrofluoric acid.
3. Evaporate to dryness, add 4 ml. of hydrofluoric acid and repeat evaporation.
4. Add 4 ml. of water and 1.0 ml. of perchloric acid, evaporate to dryness and heat to expel the perchloric acid.
5. Add 4 ml. of 1:1 hydrochloric acid and 6 ml. of water to the residue and warm to bring all soluble material into solution.
6. Make solution up to 25 ml. with 1:1 hydrochloric acid.

The solutions were used for both the atomic absorption and colorimetric analyses and are referred to as the test solutions.

II. ANALYSES BY ATOMIC ABSORPTION SPECTROSCOPY

The Atomic Absorption Spectrophotometer consists essentially of a hollow-cathode discharge lamp of the element to be analysed, an atomizer burner for the production of oxyacetylene flame, a monochromator,