TRACE ELEMENTS IN CRETACEOUS ROCKS
OF MANITOBA

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Richard William Oddy
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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 Japenese 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, particularily 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 particularilly 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 montmorillionite 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

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'	←Range of sample collection→	non-calcareous shale, bentonite beds
	COLORADO GROUP			Boyne	150'		calcareous speckled shale
				Morden	200'		carbonaceous shale
			Favel		125'		calcareous speckled shale, limestone and bentonite
LOWER CRETACEOUS			Ashville		375'		non-calcareous silty shale, sand
	UPPER MANVILLE		Swan River		300'		sand, sandstone, shale, clay

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.

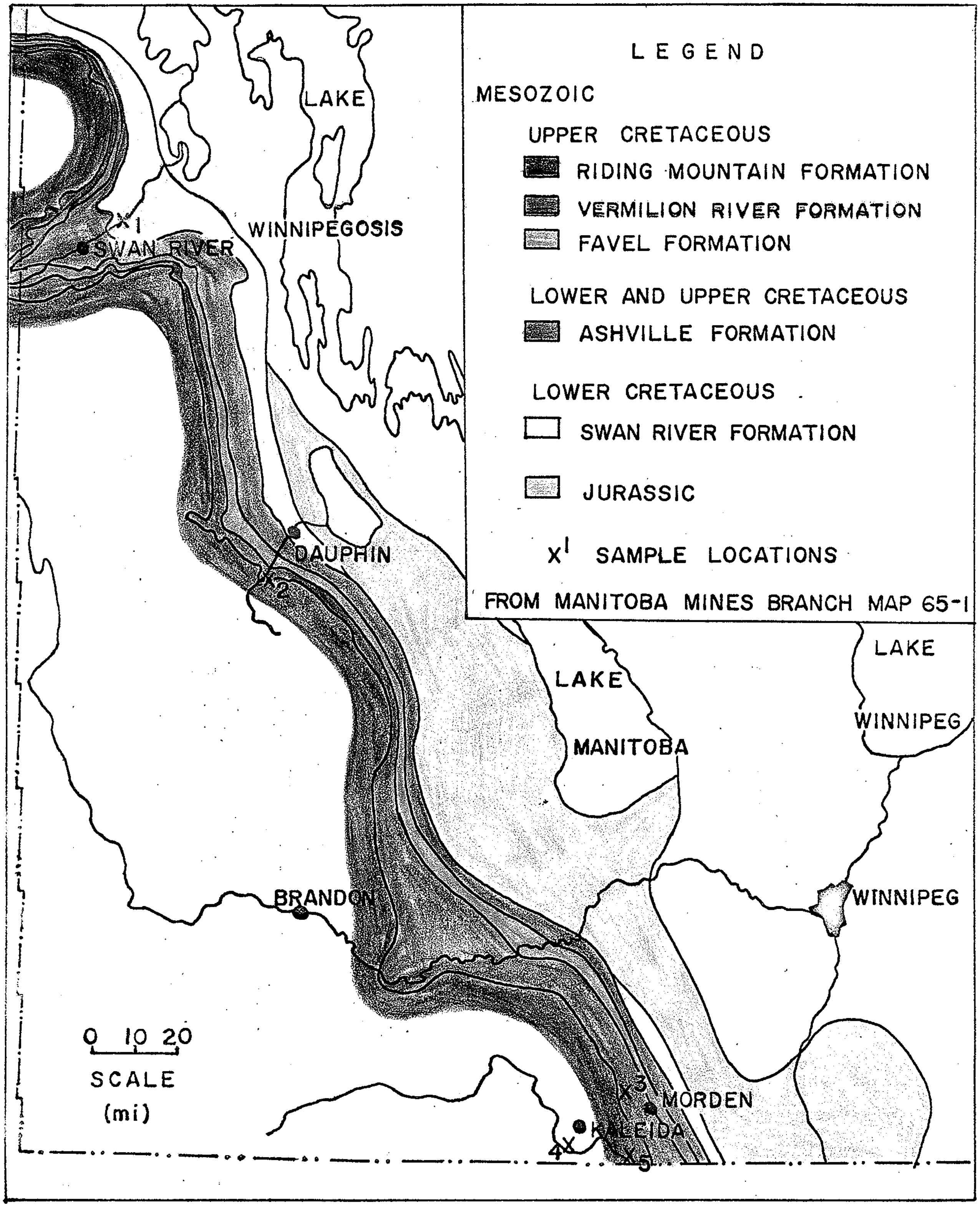

FIGURE I.

SAMPLE LOCALITIES AND GEOLOGY OF SOUTHWESTERN MANITOBA

TABLE III

DISTRIBUTION OF SAMPLES

FORMATION AND MEMBER	SHALES	CLAYS	BENTONITES	LIMESTONES	SANDSTONES	LIMONITES	TOTAL
VERMILION RIVER FORMATION							
Pembina Member	13	1	6	-	-	-	20
Morden Member	7	1	-	-	-	-	8
FAVEL FORMATION							
Assiniboine Member	8	-	3	1	-	-	12
Keld Member	15	-	9	3	-	2	29
ASHVILLE FORMATION	10	1	1	-	-	1	13
SWAN RIVER FORMATION	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, and a photomultiplier tube for detection. Light from the hollow cathode discharge lamp, which consists of the atomic spectral lines of the element to be analysed, travels through the flame and then into a monochromator, which separates out one line, and finally into a photomultiplier tube for detection and read-out.

A solution to be analysed is aspirated into the flame where atomization takes place. Any atoms of the element of interest in the flame will absorb light from the lamp and thereby cause a decrease of intensity at the detector.

Standards of copper and zinc covering the anticipated ranges in the test solutions were prepared and the absorption of each measured. Working curves for copper and zinc were prepared by converting the absorption measurements to absorbance, and then plotting absorbances of the standards against concentration. The absorbances of the test solutions were determined and compared with the appropriate working curve to obtain the copper and zinc concentrations. The test solutions are of 1 gram dissolved in 25 ml. Thus the dilution factor is twenty-five and the measured concentrations were multiplied by twenty-five to arrive at the concentration in the original sample. Copper standards were prepared from pure copper wire and zinc standards from 40-mesh reagent grade zinc. Copper was measured at 3246 Angstroms and zinc at 2148 Angstroms.

For copper the limit of sensitivity is 0.1 p.p.m. and the uncertainity, based on the replicate analyses listed in Table IV, is ±19 per cent (relative) or ± 12 p.p.m. (absolute, for the range investigated). The limit of sensitivity for zinc is also 0.1 p.p.m. and

TABLE IV

COMPARISON OF REPLICATE ANALYTICAL RESULTS

ELEMENT	SAMPLE NO.	ATOMIC ABSORPTION	COLOR.	GEOL. SURVEY OF CANADA		
				EM. SPECT.	COLOR.	
					(a)	(b)
Copper	5	n.d.	-	10	24	28
	103	52	-	57	76	68
Zinc	5	17	-	10*	20	20
	103	196	-	80*	120	110
Molybdenum	5	n.d.	55	9	18	14
	103	n.d.	15	5	14	12

All values in p.p.m. n.d.- not detected
(a)- direct determination
(b)- with preliminary extraction
* Estimates only, quantitative zinc curve was not finished. Therefore not used in calculating uncertainity.

the uncertainity is ± 28 per cent (relative) or ± 43 p.p.m. (absolute, for the range investigated). The limit of sensitivity for molybdenum is about 250 p.p.m., but because all the samples contain less than 250 p.p.m. the analyses could not be achieved by the atomic absorption method.

III. ANALYSES BY COLORIMETRIC TECHNIQUE

Molybdenum analyses were obtained using a modification of the stannous chloride-ammonium thiocyanate method described by Sandell (27). Standards containing 0, 0.2, 0.5, 1, 1.5, 2, 3, 4, 5, 10, 15 and 20 micrograms of molybdenum were prepared from a standard solution containing 100 micrograms per milliliter. The stock standard was prepared by dissolving pure molybdenum trioxide in a weakly acid solvent. To the standards and a 5 ml. portion of each of the test solutions were added 2 ml. of 1:1 hydrochloric acid, 1.5 ml. of 5 per cent ammonium thiocyanate solution and 0.5 ml. of 10 per cent stannous chloride solution. In some instances, to ensure that the unknown solution was completely free of ferric thiocyanate, another 0.5 ml. of stannous chloride was added. To extract the molybdenum thiocyanate complex, 0.5 ml. of isopropyl ether was added and the mixture shaken for 30 seconds. The colors of the ether layers of the unknown test solutions and the standards were compared and the molybdenum concentration determined. For example, if the test solution was determined, by comparison with the standards, to contain 4.0 micrograms of molybdenum then by multiplying by five the amount of molybdenum in the complete 25 ml. test solution is known, in this case 20 micrograms.

Since 1 gram of sample was dissolved in the 25 ml. test solution and because micrograms per gram is equivalent to parts per million the sample contained 20 p.p.m. For those test solutions that contained over 20 micrograms of molybdenum in 5 ml. the test was repeated using a 1 ml. portion of the test solution.

In this simplified method interference from tungsten is neglected although if tungsten did interfere the hue of the isopropyl ether layer would not match the standards and for all the samples it appeared as if tungsten interference was negligible.

The limit of sensitivity for molybdenum by the colorimetric method is 3 ± 2 p.p.m. The uncertainity, based on the replicate analyses (Table IV), is ± 72 per cent (relative) or ± 23 p.p.m. (absolute, for the range investigated).

CHAPTER V

RESULTS

The analytical results for each of the eighty-nine samples are listed in Table V and a summary of the analyses for copper, zinc, and molybdenum in Cretaceous beds of Manitoba is given in Table VI. For purposes of discussion the samples were divided into four groups - shales and clays, bentonites, limestones and limonites and within each group the range, average and median for the three metals are given. In Figure 2 the median values for each metal in shales and in bentonites are compared.

In general the Cretaceous beds of Manitoba contain concentrations of copper and zinc that are within the common ranges for similar rocks but they are enriched in molybdenum. Copper content ranges from 2 to 78 p.p.m. zinc from 5 to over 400 p.p.m. and molybdenum from less than 2.5 to 180 p.p.m. The quantities of molybdenum that were found correspond with concentrations that would be expected in black shales, as discussed on page 8. The Cretaceous rocks of Manitoba that are enriched in molybdenum include calcareous shales and bentonites as well as black, carbonaceous shales (see samples 46, 47, 70, and 71 in Table V).

I. MOLYBDENUM

Most shales normally contain only a few p.p.m. of molybdenum. Tourtelot (31) showed that Pierre shales averaged only 1 p.p.m. molybdenum, with the exception of a few marine shales that contained up to 350 p.p.m.

TABLE V

COPPER, ZINC, AND MOLYBDENUM IN CRETACEOUS ROCKS OF MANITOBA

Sample No.	Thick. Ft.	Description of sample	p. p. m.		
			Cu	Zn	Mo
VERMILION RIVER FORMATION					
Pembina Member					
107	2.0	Shale-bentonite mixture	75	202	25
108	2.0	Shale-bentonite mixture	69	400	50
109	3.0	Black shale with bentonite layers	55	377	30
110	3.0	Black shale with bentonite layers	66	326	30
111	3.0	Black shale	65	400	25
112	3.0	Black shale	64	400	40
113	3.0	Black shale	56	400	30
114	3.0	Black shale	54	400	50
70	0.8	Black clay	67	302	130
71	0.25	Bentonite, yellow	10	28	180(135)
72	0.25	Black shale	78	98	75
73	0.3	lost			
74	0.3	Bentonite	4	5	25
75	0.2	Black shale	37	100	25
76	0.5	Bentonite	8	13	15
77	0.2	Bentonite, yellow	8	12	13
78	0.1	Black shale	47	125	9(8)
79	0.3	Bentonite, yellow	8	19	14
80	0.2	Shale-bentonite mixture	43	84	15
81	0.3	Bentonite	6	18	15
82	0.3	Shale-bentonite mixture	66	71	35
Morden Member					
106	1.0	Black shale	37	154	13
105	4.0	Black shale	47	198	20
104	3.0	Grey shale	58	400	120
103	4.0	Grey shale	52	196	15
101	1.0	Clay with bentonite layers	21	90	5
100	4.0	Grey shale	18	86	3
83	2.0	Black shale	21	112	4
84	2.0	Black shale	26	110	8
FAVEL FORMATION					
Assiniboine Member					
44	2.5	Brown shale	53	400	120
43	0.2	Limestone	4	39	18

TABLE V (continued)

Sample No.	Thick. Ft.	Description of sample	p. p. m.		
			Cu	Zn	Mo
42	0.9	Brown shale	37	400	100
37	4.0	Limestone (lost)			
38	2.3	Grey shale	26	202	55
39	0.05	Bentonite	6	59	40
40	1.3	Grey shale	26	280	70
41	0.2	Bentonite	2.	24	23
47	1.0	Calcareous shale	40	250	140
46	4.0	Calcareous shale	31	225	100
45	5.5	Shale	34	124	70
1	0.2	Bentonite	8	84	70
2	1.0	Grey shale	26	132	48
<u>Keld Member</u>					
3	0.9	Limestone	2	35	23(16)
4	6.0	Grey shale	21	172	36
5	0.1	Bentonite	n.d.	17	55
6	2.0	Black shale	22	148	40(40)
7	0.6	Limestone	4	27	15
8	0.8	Grey shale	18	94	30(56)
9	0.05	Bentonite	8	55	50
10	4.5	Calcareous shale	18	92	25(32)
11	0.5	Limestone	3	22	13
12	0.05	Bentonite, yellow	5	75	75
13	5.0	Grey shale	18	119	38(32)
14	3.0	Calcareous shale	21	130	45(48)
15	0.25	Bentonite	n.d.	46	70(90)
16	3.8	Grey shale, calcareous	26	101	13
17	0.1	Bentonite, yellow	2	39	21
18	0.1	Grey shale	16	121	55(56)
19	0.01	Limonitic layer	14	75	55
20	2.8	Grey shale	17	106	63(52)
21	0.01	Limonitic layer	4	64	50
22	4.5	Grey shale	17	192	25
23	0.01	Calcareous shale	9	107	25
24	2.75	Grey shale	21	160	55
25	0.01	Bentonite	7	305	175
26	0.75	Grey shale	24	189	55
27	0.05	Bentonite	3	233	150(150)
28	2.75	Grey shale	21	211	45(88)
29	0.05	Bentonite	7	317	140
30	3.6	Grey shale	23	227	58(88)
31	0.5	Bentonite	3	55	25
<u>ASHVILLE FORMATION</u>					
32	1.6	Grey shale	37	221	75(56)

TABLE V (continued)

Sample No.	Thick. Ft.	Description of sample	p. p. m. Cu	p. p. m. Zn	p. p. m. Mo
33	0.1	Limonitic layer	5	82	50(35)
34	5.5	Black shale	19	168	25(48)
35	0.1	Kaolin layer	4	74	20
36	2.0	Black shale	29	135	23
153	3.0	Black shale	26	105	13
154	3.0	Black shale	19	144	4
155	0.4	Bentonite	5	103	10
156	3.0	Black shale	24	109	3
157	3.0	Black shale	19	146	4
140	2.0	Black shale with bentonite layers	18	162	2.5
141	2.0	Black shale with bentonite layers	11	78	5
142	2.0	Black shale	12	104	4
SWAN RIVER FORMATION					
143	0.1	Sand lens	3	13	2.5
144	1.5	Black shale	11	80	2.5
145	1.0	Black shale	7	93	2.5
146	1.5	Black shale	7	75	2.5
147	1.3	Calcareous shale	6	52	2.5
148	1.0	Shale	6	43	2.5
149	1.5	Black sandy shale	8	38	2.5

n.d. - not detected

Results given in brackets are repeated determinations.

TABLE VI

SUMMARY OF COPPER, ZINC, AND MOLYBDENUM IN CRETACEOUS BEDS OF MANITOBA

SAMPLE GROUP	TRACE ELEMENT CONTENT IN P.P.M.		
	COPPER	ZINC	MOLYBDENUM
89 samples			
range	2-78	5->400	<2.5-180
average	24	145	41
median	19	107	25
62 shales and clays			
range	4-78	38->400	<2.5-140
average	31	178	36
median	24	135	25
19 bentonites			
range	2-10	5-317	10-180
average	6	79	61
median	6	46	40
4 limestones			
range	2-4	23-39	13-23
average	3	31	17
median	3	31	17
3 limonites			
range	4-14	64-82	50-55
average	8	77	52
median	5	75	50

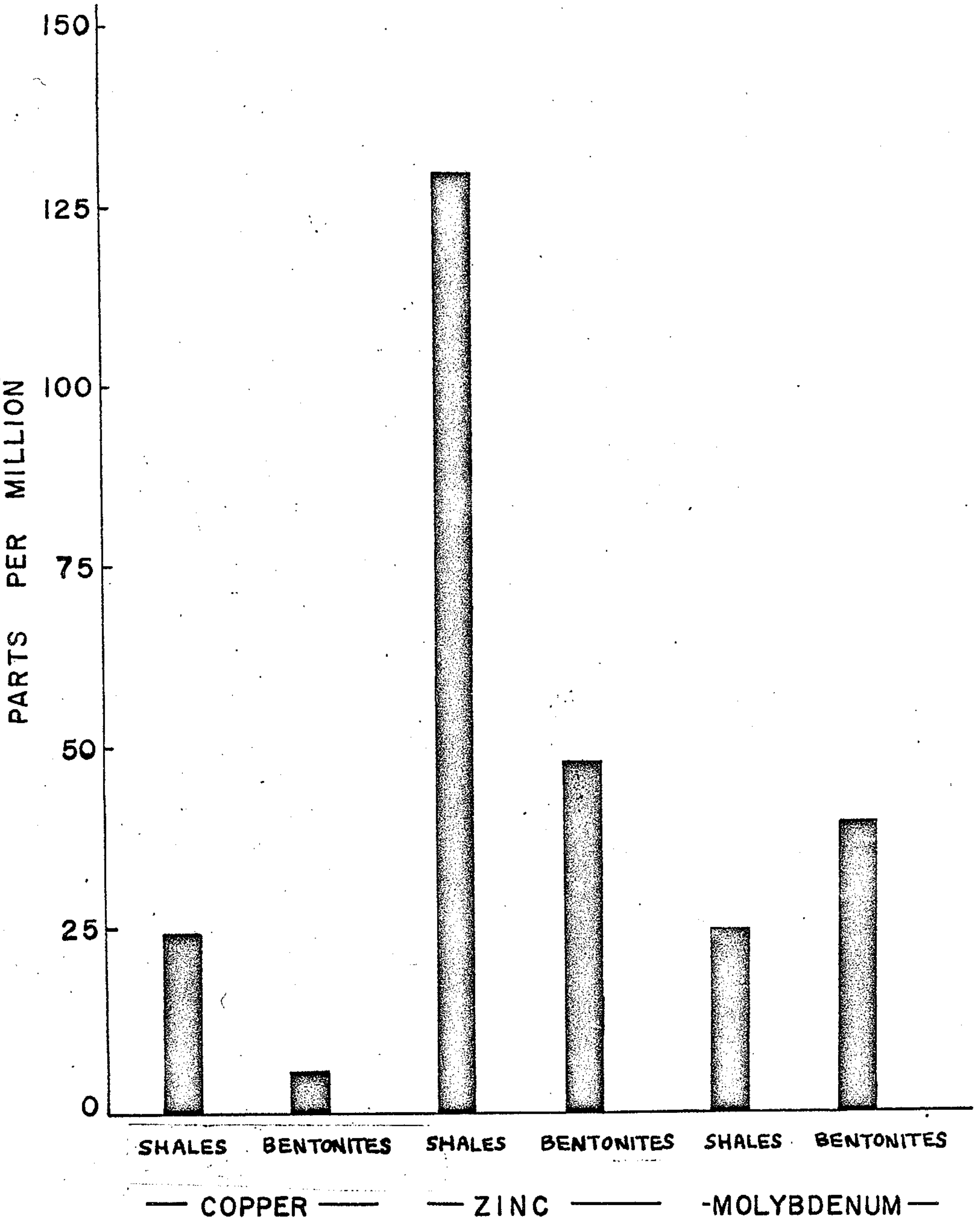

FIGURE 2.

HISTOGRAM OF MEDIAN VALUES OF COPPER, ZINC AND MOLYBDENUM IN CRETACEOUS SHALES AND BENTONITES OF MANITOBA

The Cretaceous sediments of Manitoba contain significantly greater quantities of molybdenum than most shales. The concentrations found in the Manitoba Cretaceous sediments are within ranges reported by Krauskopf (14) for carbonaceous shales and by LeRiche (17) for the organic rich Lower Lias shales (see Table I).

Molybdenum is abundant in all the Cretaceous sediments of Manitoba except in the shales of the Swan River Formation and the lowermost part of the Ashville Formation. The average content of molybdenum in the eighty-nine samples tested is 41 p.p.m. In shales and clays the average is 36 p.p.m., in bentonites, 61 p.p.m., in limestones, 17 p.p.m., and in limonites, 52 p.p.m., so that it is not only the shales that are enriched in molybdenum. Normally high molybdenum content is associated with carbonaceous or sulphide bearing sediments, but the bentonites, even though they contain very little carbonaceous material, have the highest average content of molybdenum.

Although there appears to be no correspondence between the molybdenum content and the zinc and copper content of the samples, there are three bentonites which contain, relative to the other bentonites large concentrations of zinc and which also have high concentrations of molybdenum, all above 100 p.p.m. (see samples 25,27, and 29 in Table V).

Organic material and clay minerals in the shales, the montmorillonite of the bentonites and limonite are materials that would be capable of adsorbing molybdenum from sea water. An abundance of molybdenum in the sea water in which the sediments were deposited has probably contributed to the abnormally high quantities of molybdenum in the Cretaceous sediments of Manitoba.

The presence of bentonite layers in the Cretaceous beds of Manitoba is an indication of ash from volcanic activity. Kuroda and Sandell (16) reported analyses of twelve volcanic glasses with an average molybdenum content of 3.2 p.p.m., and thirty-two basalts and diabases averaging only 1p.p.m. of molybdenum. Therefore it is not likely that volcanic activity is responsible for the abundance of molybdenum in either the bentonites, which formed by alteration of volcanic ash, or volcanic gases, which may have contaminated the sea water.

The concentration of trace metals in sedimentary rocks in different areas may vary considerably because of difference in the trace metal content of the rocks in the source areas. Before Jurassic and Cretaceous sediments were deposited in Manitoba there was a period of extensive erosion and rocks of Precambrian age were probably exposed during that time. If the Precambrian rocks of the shield to the east were exposed and being eroded during the time of deposition of the Cretaceous sediments then it seems likely that these Precambrian rocks, which are known to contain local concentrations of molybdenum, were the source of the molybdenum in the Cretaceous sediments.

II. COPPER AND ZINC

The Cretaceous shales and clays of Manitoba contain quantities of copper and zinc that closely correspond to the concentrations for most shales as given on page 8. Copper in the Cretaceous shales and clays of Manitoba ranges from 4 to 78 p.p.m. and zinc from 38 to over 400 p.p.m. In comparing the range for copper in the Manitoba Cretaceous shales with the common range for most shales it is evident that there is a slight scarcity of copper in the Manitoba shales. On the other hand several of the Manitoba shales contain over 400 p.p.m. of zinc. This value is somewhat above the common range for zinc in most shales and falls within the common range for zinc in black shales (see page 8).

The range and median values for copper in the Manitoba shales are similar to those found in non-marine and marine Pierre shales (see Table I). The zinc content of the Manitoba shales is similar to that found in the offshore marine Pierre shales.

There is a general increase in both copper and zinc concentrations in the younger Cretaceous formations of Manitoba and the greatest concentration of both metals occurs in the Pembina Member. Carbonaceous shales generally contain greater quantities of copper and zinc than do non-calcareous shales and the shales of the Pembina Member are more carbonaceous than the other Cretaceous shales that were analysed. These trace metals are generally more abundant in marine shales than non-marine shales (see page 8). The Swan River Formation is non-marine in origin in the area from which the samples were obtained and it seems likely that the low copper, zinc, and molybdenum concentrations of the samples from Swan River beds can be attributed to the non-marine origin.

The bentonites contain significantly lower quantities of copper and zinc than do the shales. Copper is consistently low in the bentonites, ranging from 2 to 10 p.p.m. and averaging 6 p.p.m. compared to 31 p.p.m. in the shales.

The bentonites are generally low in zinc with the exception of a few samples which contained over 200 p.p.m. Zinc in the bentonites ranges from 5 to 317 p.p.m. and averages 79 p.p.m. The average is misleadingly high due to the few high values and the median value of 46 p.p.m. is more meaningful. The bentonites contain from one-eighth to one-half as much copper and zinc as the shales (see Figure 2).

Limestones are low in copper and zinc. Limonites are also low in copper; they contain about twice as much zinc as the limestones. There were so few limestones and limonites among the samples analysed that the values obtained can not be considered very significant.

III. MOLYBDENUM POISONING

LeRiche (17) outlined several factors which contributed to molybdenum poisoning of cattle - a high level of molybdenum in the soils, the presence of limestone to provide alkaline soils, imperfect drainage conditions and an absence of copper which would act as an antidote. The Favel beds, from which the soils in the Swan River Valley were derived, are not only enriched in molybdenum but are also low in copper. It appears likely that the Favel beds are responsible both for the abundance of molybdenum and a deficiency of copper in the soils of the valley. The calcareous nature of the Favel shales and the occurrence of limestone beds account for the alkalinity of the soils derived from the Favel Formation. These factors along with poor drainage in certain areas of the valley are responsible for the molybdenum poisoning conditions.

CHAPTER VI

CONCLUSIONS

The Cretaceous beds of Manitoba, with the exception of the Swan River Formation, are enriched in molybdenum. The probable source of the excessive molybdenum is the sea water in which the sediments were deposited and the sea water must have been greatly enriched in molybdenum during the time when the sediments were being deposited. It is not likely that the enrichment of molybdenum in the sea water was associated with volcanic activity to the west. However, it does seem probable that Precambrian rocks to the east were the source of the molybdenum.

The Favel beds, from which the soils of Swan River Valley have been formed, are most certainly the source of the high level of molybdenum in the soils which has contributed to molybdenum poisoning of cattle in the valley.

There is no enrichment of copper and zinc in the Cretaceous shales and only normal concentrations of the two metals are present.

The Cretaceous bentonites contain significantly lower concentrations of copper and zinc than the interbedded shales. The bentonites are enriched in molybdenum, as are the shales, and contain concentrations nearly equivalent to those in the shales.

In order to understand the factors and processes that led to the enrichment of molybdenum in the Cretaceous beds a detailed study of the distribution of molybdenum in the various components of the samples would be necessary. A study of the quantity of molybdenum attributable to the organic material, clay minerals and sulphides would likely provide much valuable information. Other trace elements could be studied in an effort to locate other elements, beside molybdenum, that may be enriched in the Cretaceous beds and also to find if trace elements other than copper and zinc are present in the bentonites in lower quantities than in the shales.

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