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A survey of 24 elements in North Dakota lignite (Fort Union Group, Paleocene) and possible geologic implications

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A SURVEY OF 24 ELEMENTS IN NORTH DAKOTA LIGNITE (FORT UNION GROUP, PALEOCENE) AND POSSIBLE GEOLOGIC IMPLICATIONS

by

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This thesis submitted by Susan A. Zimmer-Dauphinee in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

(Chairman)

This thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

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Permission

TITLE A Survey of 24 Elements in North Dakota Lignite (Fort Union Group, Paleocene), and Possible Geologic Implications

DEPARTMENT Geology

DEGREE Masters of Science

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Signature Howard G. Zimmer-Dauphinee

Date November 5, 1982

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ABSTRACT

Claystone, carbonaceous shale, lignitic shale, and lignite samples were collected from western North Dakota for element analysis during May 1978, April 1979, and August 1979. Lignite was collected from the Sentinel Butte Formation--Hagel Bed (Oliver and McClean Counties), Beulah-Zap Bed (Mercer County), Lehigh Bed (Stark County)-- and from the Bullion Creek Formation--Harmon Bed (Bowman County). Claystone samples were also collected from clay partings present in the Hagel Bed and Harmon Bed. Control samples were collected from an outcrop of the marine lower middle Cannonball Formation (carbonaceous shale) south of Mandan, North Dakota and from an outcrop of the brackish oyster lignite and oyster bed (lignitic shale) of the Slope Formation north of Marmarth, North Dakota.

The samples were analyzed for 24 major, minor, and trace elements using an Inductively Coupled Argon Plasma (ICAP) Spectrometer. Generally Cd and high concentrations of Na occurred at the top of a seam. Concentrations of V and Zn were usually higher at the top and bottom of a seam, whereas other elements were equally dispersed throughout the seam. The position of high concentrations in a seam indicate that: Cd and Na may be deposited by groundwater; that V and Zn may be influenced by groundwater; and that most of the other elements occur as the result of primary deposition.

The five elements used to attempt to differentiate between the Beulah-Zap, Lehigh, Hagel, and Harmon Beds were As, Ba, Ca, Co, and Sr. Considering average values, it appears that the Beulah-Zap Bed may be generally characterized by high concentrations of Ba (630 ppm) and As (170 ppm), moderate concentrations of Sr

(660 ppm), and low concentrations of Ca (0.5%) and Co (5 ppm). The Lehigh Bed may be characterized by high concentrations of Sr (1170 ppm), Ba (620 ppm), and Ca (0.9%) and moderate concentrations of As (110 ppm) and Co (30 ppm). The Hagel Bed may be characterized by low concentrations of As (5 ppm), Ba (290 ppm), and Sr (340 ppm) and a high concentration of Ca (0.9%) and Co (170 ppm). The Harmon Bed is characterized by moderate concentrations of As (60 ppm), Ba (410 ppm), Ca (0.7%), and Co (40 ppm) and low concentrations of Sr (410 ppm).

Elemental concentration may indicate relative rate of basin subsidence. The higher the concentration the slower the rate of subsidence. A comparison of lignites from North Dakota (Williston Basin) and coals from the Powder River Basin indicate that North Dakota lignites have a higher inorganic element concentration. Therefore, the Williston Basin may have subsided at a slower rate than the Powder River Basin.

Cr, Ga, Ni, and V may be indicative of the salinity of the depositional environment of a lignite. The samples of the marine lower middle Cannonball Formation are higher in Cr, Ga, Ni, and V than are the samples of the brackish oyster bed (Slope Formation). The Harmon Bed (Bullion Creek Formation) is higher in Cr, Ga, Ni, and V than the oyster lignite (Slope Formation). Values for these elements for the Beulah-Zap and Hagel Bed lignites (Sentinel Butte Formation) are irregular.

A low K/Li ratio for noncoalified material is indicative of a higher salinity environment. The Beulah-Zap and Lehigh Beds had no clay partings, so K/Li ratios could not be determined for these beds. The Harmon Bed and oyster bed K/Li ratios are similar, whereas the Hagel Bed K/Li ratio is two orders of magnitude higher than the oyster bed, indicating lower salinity.

INTRODUCTION

Purpose

The present study was undertaken to determine if elemental chemistry can help in understanding the depositional environments of North Dakota Paleocene lignite-forming peat. A secondary purpose was to determine if trace elements can be used to differentiate between the sampled lignites. Since the lignites in the study area serve as aquifers, it was also deemed necessary to determine which elements are not mobilized by groundwater.

Previous work

Earlier coal researchers in North Dakota, such as Babcock (1899, 1914), Brant (1943), Densen (1950), Dove (1923), and Leonard (1906), were concerned primarily with coal rank, the areas of coal outcrop, and the extent of the coal reserves. Knowlton (1921) examined the plant material found in lignite and associated strata and identified it as poplar, oak, walnut, fig, elm, maple, birch, alder, dogwood, hickory, boxelder, buckhorn, viburnum, witch-hazel, horse chestnut, bittersweet, ginkgo, conifers, cypress, and arbor vitae.

Later, lignite was studied as a material for emplacement of uranium (Densen 1950 and Moore 1954). Since 1970, the depositional environments of North Dakota lignite and the Sentinel Butte and Bullion Creek Formations have become an area of major study.

Because of complexities and often unsatisfactory results associated with efforts to map the Cannonball and Tongue River Formations, Clayton and others (1977) named the Slope Formation for the sediments between the T Cross Bed of the Ludlow Formation and a white marker zone. They also gave a new name, the Bullion Creek Formation, to what had been previously described in whole or in part as the Tongue River Formation. This stratigraphic nomenclature seems appropriate for this study. Therefore, this nomenclature is used in the discussion which follows.

Roe (1949) said that Paleocene sediments were deposited cyclically. Royse (1967, 1970) stated that the Bullion Creek and Sentinel Butte Formations were deposited in a fluvial environment and several facies could be distinguished, including channel, floodplain, and backswamp. Jacob (1971) stated that the lignite sequences were deposited in a flood basin environment, whereas the remainder of the Bullion Creek was deposited on the lower subaerial portion of a high-constructive delta.

Johnson (1972) studied the sedimentology of the Sentinel Butte Formation along the north border of the North Unit of Theodore Roosevelt National Memorial Park, and stated that the silt and clay grade upward from natural levee and crevasse-splay deposits into highly bioturbated beds of clay and silt that are overlain by lignite. He interpreted these sediments as being flood basin deposits. Cherven (1975) studied the sedimentology of the Sentinel Butte Formation in and near the North Unit of the park, and suggested that the sediments were deposited in a deltaic environment. Kulland (1975) studied the Sentinel Butte Formation (Hagel Bed and Beulah-Zap intervals), and interpreted the sediments as being deposited in a high-constructive delta.

Rehbein (1978) studied the stratigraphy and sedimentology of the Ludlow, Bullion Creek, and Sentinel Butte Formations using SP, resistivity, gamma-ray, lithology, and other logs. He stated that the Ludlow was deposited in a fluvial-deltaic environment, whereas the

Sentinel Butte and Bullion Creek Formations were deposited in a fluvial environment.

In 1973, Cohen and Ting studied the petrology and palynology of North Dakota lignites and the peats of Okefenokee Swamp. They found that the two floras were similar and that North Dakota peats were deposited in an Okefenokee Swamp-type environment (backbarrier).

Most trace element studies of North Dakota lignite have been performed by coal companies. Presently, the Grand Forks Energy Technology Center (DOE) is studying the chemistry of North Dakota lignites in relation to ash fouling of boilers. Baria (1975) studied the trace elements of North Dakota coal ash. He determined the mean concentrations of 62 trace elements in North Dakota lignite, and discussed whether the elemental concentrations in the gases and ash were within the environmental limits of state and federal law.

Casagrande (1976) studied trace elements in the peats of Okefenokee Swamp to determine if trace element concentration varied from the top to the bottom of the swamp. He found no variation, but did find that peats formed at the edges of the basin were generally higher in trace elements than those formed in the center. He also found that the mean concentration of trace elements for peat was approximately the same as for coal.

Horne and others (1977) studied coals of the eastern United States and found that high sulfur concentration indicates marine-influenced depositional environments.

Frazier (1978) studied BTU values, ash content, specific gravity, and sulfur content of lignite from Texas and suggested that low ash (12.2%± 3.3%), moderate sulfur (1.4 ± 0.07%), and high BTU values (11,000-

12,000) indicate lignite deposited in a marine-influenced environment. A higher ash content (13.8% ± 5.6%), low sulfur (1.0% ± 0.4%), and low to moderate BTU values, and/or stumps in growth position indicate deposition in a freshwater environment.

Gluskoter and others (1977) studied 60 major, minor, and trace elements in coal to determine organic or inorganic affinities. They determined that in general, in Illinois coal Be, B, Sb, and Ge have organic affinities with Ge having the greatest affinity; Zn, Cd, Mn, As, Mo, and Fe have inorganic associations, and a number of metals, including Co, Cu, Cr, and Se, are associated with both the organic and inorganic fraction. When the tests were expanded to include coals in the western and southern coal regions Be, Ge, and B were found to still have organic affinities, but only As retained a strong association with the inorganic fraction.

Drever and others (1977) analyzed coal from Wyoming for As, Be Cd, Cu, Hg, Pb, and U. They found that As, Be, Cd, Cu, and U were enriched at the top and bottom of coal beds, as well as in the adjacent sediment. This enrichment led them to believe that these elements were deposited by groundwater.

Bonatti and others (1971) studied the post-depositional mobility of Mn, Ni, Co, and Cr in salt marshes. They concluded that redox reactions can account for metal mobility, and that Fe and Cu did not migrate because of sulfide in the reduced sediments.

Bhate (1972) analyzed samples for Fe, Mn, Zn, Ca, Co, Ni, and Hg from two salt marshes south of Savannah, Georgia. He found the Fe is tied up with the sulfide fraction, Mn is either adsorbed by the plants or deposited in the insoluble MnO form, the marsh acts as a sink for Zn, and that the Cu, Co, and Ni concentrations are due to sedimentation.

Nicholls (1968) studied trace element content in coal ash from throughout the world, and suggested that As, B, Cr, Cu, Ga, Ni, and V are concentrated in marine shales and marine coals.

Location

Most of the samples for this study were collected from the following surface mines in southwestern North Dakota (fig. 1): Center (Oliver County), Glenharold (Mercer County), Falkirk (McClean County), South Beulah (Mercer County), Husky Industries (Stark County), and Gascoyne (Bowman County). Control samples from the marine lower middle Cannonball Formation were taken from an outcrop overlooking the Missouri River south of Mandan (NE¼NW¼ sec. 13, T. 138 N., R. 81 W.) and from the brackish Slope Formation from an outcrop overlooking the Little Missouri River north of Marmarth (NW¼ sec. 15, SW¼ sec. 10, T. 105 N., R. 136 W.).

Geologic Setting

The stratigraphic sequence in the study area is shown in figure 2. The collection sites, with the exception of the Husky Industries and Gascoyne mines and the Marmarth and Mandan sites, are in the Knife River Basin of North Dakota. The stratigraphy of the Knife River Basin has been extensively studied and is well understood; the following description of the stratigraphic units in the Knife River Basin is from Groenewold and others (1979).

The Quarternary sediments in the Knife River Basin are within the thin (6-m) Holocene Oahe and Pleistocene Coleharbor Formations, consisting of clay, silt, sand, and gravel. At most of the study sites the

Figure 1. Location map of study area. x= sampled open pit mine, o= sampled outcrop.

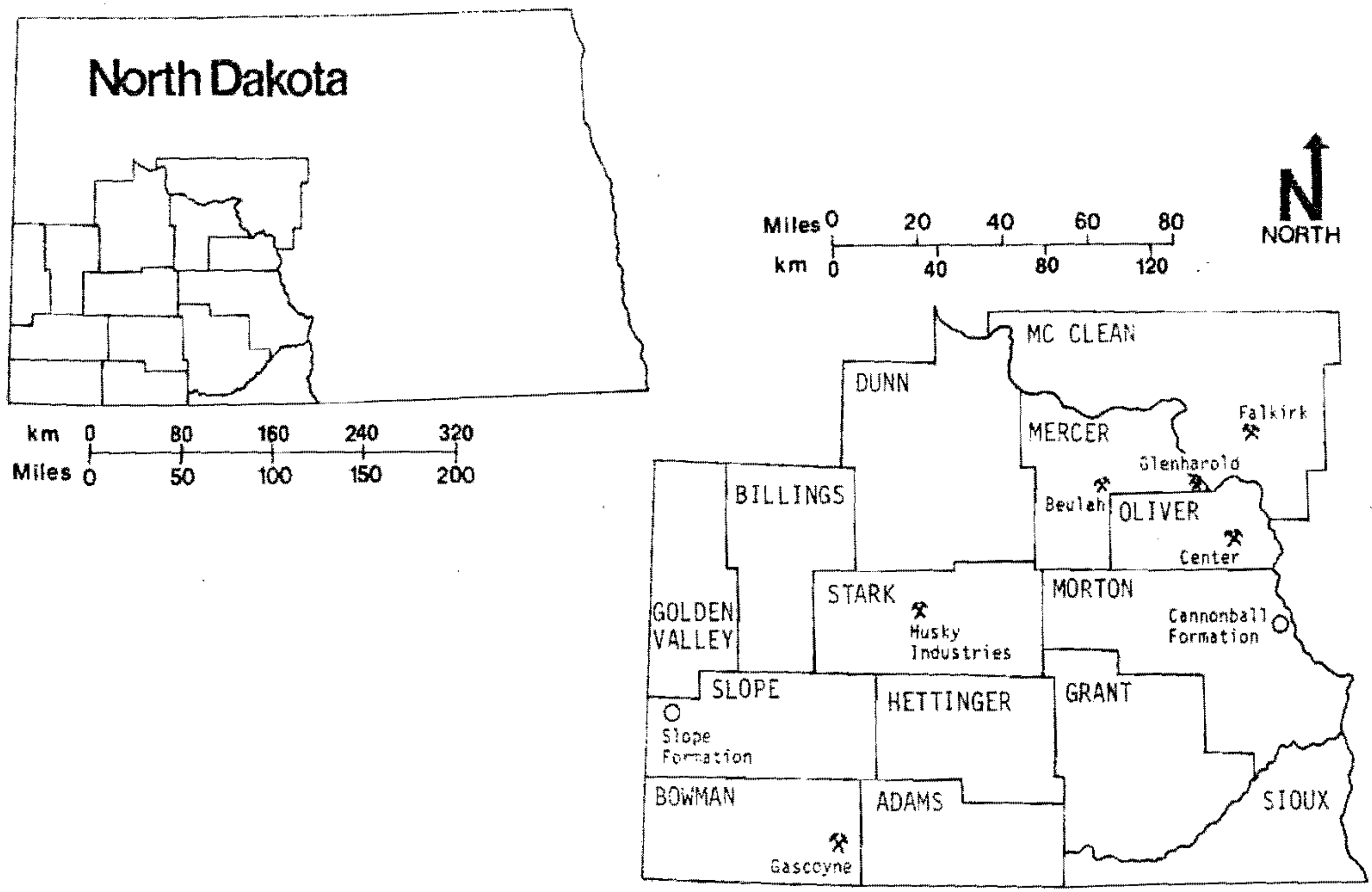

North Dakota
km 0 80 160 240 320
Miles 0 50 100 150 200
Miles 0 20 40 60 80
km 0 40 80 120
N
NORTH
MC CLEAN
DUNN
MERCER
Falkirk
Glenharold
Beulah
OLIVER
Center
BILLINGS
STARK
Husky Industries
MORTON
Cannonball Formation
GOLDEN VALLEY
SLOPE
Slope Formation
HETTINGER
GRANT
BOWMAN
Gascoyne
ADAMS
SIOUX

Figure 1

Figure 2. Generalized stratigraphic sequence of the bedrock of the study area (after Clayton and others 1977).

EOCENE		GOLDEN VALLEY FORMATION
PALEOCENE	FORT UNION GROUP	SENTINEL BUTTE FORMATION
		BULLION CREEK FORMATION
		SLOPE FORMATION
		CANNONBALL FORMATION
		LUDLOW FORMATION
UPPER CRETACEOUS		HELL CREEK FORMATION
		FOX HILLS FORMATION
		PIERRE FORMATION

Figure 2

glacial sediments either do not occur (Gascoyne, Husky Industries, and Marmarth) or are thin (South Beulah, Baukol-Noonan, and Glenharold). At the Falkirk Mine, thick glacial deposits overlie the lignite bearing sediments.

The Golden Valley Formation occurs as erosional remnants. It consists of the upper yellow brown Camels Butte Member and the lower, highly weathered grey to orange Bear Den Member. The Golden Valley is 69 m thick and consists of interbedded sand, silt, and clay with obvious crossbedding. Both members contain lignite.

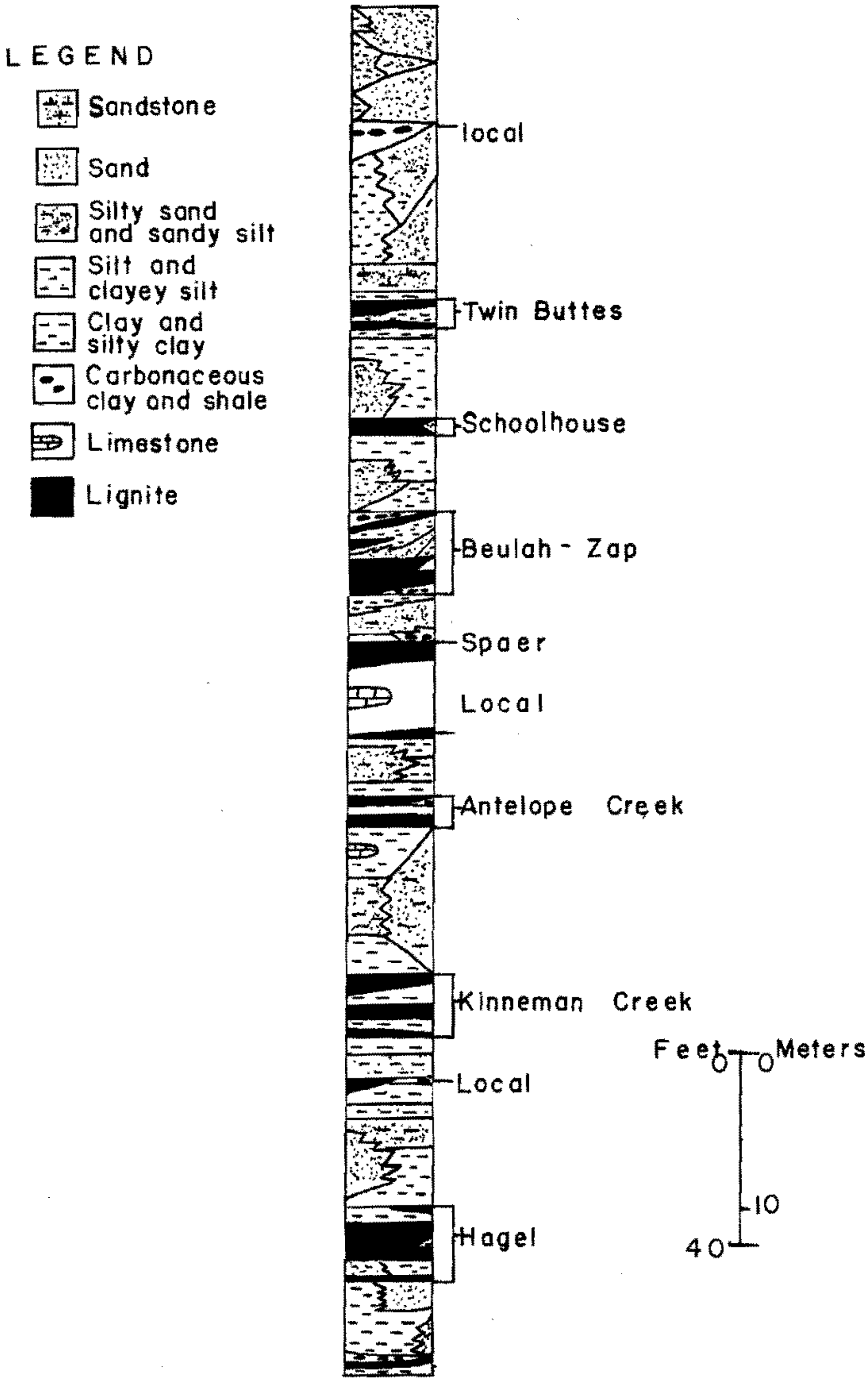
The Sentinel Butte Formation consists of interbedded, somber gray-brown silt, clay, sand, and lignite. It is 150-165 m thick. All the major lignites in the Sentinel Butte have been named (fig. 3).

The Bullion Creek Formation is 75 m thick in the eastern and 210 m thick in the western part of the Knife River Basin. The formation is differentiated from the overlying Sentinel Butte Formation by its yellowish color.

The drab brownish gray Slope Formation is 90 m thick in its type area and probably thins to 0 m in McClean County (Clayton and others, 1977). It consists of clay, silt, sand, and lignite. A portion of the Slope Formation north of Marmarth consists of the oyster lignite and oyster bed. The oyster bed is a carbonaceous to lignitic shale and is underlain by the oyster lignite. The following fossils have been identified by Van Alstine (1974) from the oyster bed: the bivalves *Corbicula berthoudi* White?, *Corbula subtrigonalis* (Meek and Hayden), and *Crassostrea glabra* (Meek and Hayden), and the trace fossil *Ophiomorpha*. The bivalves indicate deposition in a brackish environment.

The Cannonball Formation south of Mandan consists of sandstone,

Figure 3. Generalized stratigraphic sequence of the upper section of the Sentinel Butte Formation (after Groenewold and others 1979).



LEGEND
Sandstone
Sand
Silty sand and sandy silt
Silt and clayey silt
Clay and silty clay
Carbonaceous clay and shale
Limestone
Lignite
local
Twin Buttes
Schoolhouse
Beulah - Zap
Spaer
Local
Antelope Creek
Kinneman Creek
Local
Hagel
Feet
0
0
Meters
10
40

Figure 3

mudstone, and a lens of carbonaceous shale. From the Cannonball Formation Fenner (1976) described a foraminiferid fauna indicating a marine environment.

Methods

Samples were collected from the Hagel Bed (Sentinel Butte Formation) at the Center, Falkirk, and Glenharold Mines; the Beulah-Zap Bed (Sentinel Butte Formation) at the South Beulah mine; the Harmon Bed (Bullion Creek Formation) at the Gascoyne Mine; an outcrop of the oyster bed and oyster lignite (Slope Formation) north of Marmarth; and from an outcrop of the lower middle Cannonball Formation south of Mandan. Oxidized material was cleared away with a shovel and pick ax from the top, middle, and bottom of each seam, and if a clay parting was present samples were collected from the parting. Approximately 2 kg of unoxidized sample was collected, placed in a plastic bag and sealed with a twist-tie. At each mine this procedure was repeated laterally throughout the seam at 30 m intervals in the smaller mines and up to 100 m intervals at the larger mines. These samples were collected in a rigid grid system so that no one feature such as fractures, stumps, or differences in overlying sediments would be overrepresented.

Each of the Slope and Cannonball samples were collected at only one location. Each sample was placed in a plastic bag and frozen until it was prepared for analysis.

A representative portion of each sample was obtained by coning and quartering. This portion was weighed and dried at 120°C for eight hours to determine the moisture content. The sample was further subdivided; one subsample was ashed, another was used for trace element analysis, and the remainder was set aside for microfossil study.

For chemical analysis, each sample was ground to less than 150 mesh. A 0.1 g sample was digested in a Teflon Parr bomb using standard digestion methods as described by Harstein, Freedman, and Platter (1973) and used by the Grand Forks Energy Technology Center. To digest the lignite, the fuming nitric acid (90%) treatment was increased to 18 hours and the hydrofluoric acid (analytical grade) was increased to 10 hours. Boric acid was added to stabilize the solution. A control of fuming nitric acid, hydrofluoric acid, boric acid, and distilled water was also analyzed and used as a correction factor.

Each sample was analyzed for aluminum (Al), arsenic (As), barium (Ba), beryllium (Be), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), gallium (Ga), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), silicon (Si), strontium (Sr), tellurium (Te), uranium (U), vanadium (V), zinc (Zn), and phosphorous (P), using an Inductively Coupled Argon Plasma (ICAP) Spectrometer.

For the microfossil study, the samples were soaked in water and sieved through a 200 mesh sieve and allowed to dry. Representative lignite samples were searched for non-lignitized fossils using a binocular microscope at 350 power.

To further understand the elemental relationships several statistical programs were run using the Statistical Analysis System (SAS) Package Program. Symbol Mapping (SYMAP) was used to portray the distribution of trace elements in the highwall. The Student's t test was used to determine the statistical significance of the results.

RESULTS

The results of the chemical analyses of 102 lignite, lignitic shale, carbonaceous shale, and claystone samples are given in Tables 1 and 2. All lignite analyses are given on the "whole coal" basis and not as a percentage of ash. The complete chemical analyses for the major, minor, and trace elements of the samples can be found in Appendix 1.

The mean, maximum, and minimum values for a selected group of major, minor, and trace elements were plotted (figs. 4 and 5) so that four sampled beds might be differentiated.

From the tables and figures a number of observations can be made:

1. The tested Sentinel Butte lignites (Beulah-Zap, Lehigh, and Hagel Beds), the Bullion Creek lignite (Harmon Bed), and the samples from the Slope and Cannonball Formations have values below the Clarke value (Handbook of Chemistry and Physics, 1972-1973) for the major and minor elements Al, Fe, K, Mg, Na, and Si.

2. The aluminum content in the sampled Sentinel Butte lignites is 0.1 to 0.01 that of the Clarke value of 81300 ppm (average Al composition of earth's crust). The mean Al concentration of the Sentinel Butte is variable with the Lehigh Bed having the least Al (7560 ppm) and the Hagel Bed having the most (20530 ppm). The Harmon Bed (Bullion Creek Formation) is higher in Al than most of the overlying Sentinel Butte Formation lignites. The Al content appears to generally increase downward through the studied section as indicated by the analyses of the samples obtained from the Bullion Creek (13680 ppm), Slope (26810 ppm), and Cannonball (50280 ppm) Formations.

Table 1. Average, maximum, and minimum major and minor element content (ppm) of the sampled beds.

		Al	Ca	Fe	K	Mg	Na	Si
Sentinel Butte Formation								
Beulah-Zap (n=19)								
Mean		11530	5850	8570	160	4460	4470	6070
Maximum		114640	14380	77180	1320	7110	9480	26400
Minimum		630	0	0	–	750	1590	0
Lehigh (n=10)								
Mean		7560	9350	2800	220	4500	4110	16960
Maximum		18900	34720	11720	590	7670	7140	82700
Minimum		1680	190	120	–	2650	2810	240
Hagel (n=20)								
Mean[1]		20530	9370	16040	5320	4810	3840	72760
Maximum	lg[2]	32090	54410	74030	5970	5910	5510	>200000
	cy[3]	87300	21440	28910	20660	12980	7450	>200000
Minimum	lg[2]	870	1210	160	–	1630	300	–
	cy[3]	36650	0	5880	11850	1910	2920	>200000
Bullion Creek Formation								
Harmon (n=29)								
Mean[1]		13680	6780	4470	4610	4960	2290	85560
Maximum	lg[2]	15200	33570	30810	7100	7480	4470	170270
	cy[3]	48340	25000	12220	15910	9860	5500	>200000
Minimum	lg[2]	690	2820	0	0	50	30	0
	cy[3]	5010	20	0	0	110	560	1380
Slope Formation								
oyster lignite and oyster bed (n=6)								
Mean[4]		26810	40750	12950	6730	5820	3500	112950
Maximum	lg[2]	1550	50610	3820	470	3040	2010	4220
	cy[3]	55550	90240	30090	13050	11420	4930	193100
Minimum	lg[2]	1060	1280	1100	460	1640	1370	3090
	cy[3]	17350	1270	5640	7070	1900	3480	115300
Cannonball Formation								
Lower Middle Cannonball (n=2)								
Mean[4]		50280	35860	23380	10060	9170	5220	121550
Maximum		58870	44130	26960	10780	10580	7000	123200
Minimum		41680	27580	19800	9330	7760	3450	119900

[1] Clay partings used in determining mean

[2] lg = Lignite

[3] cy = Claystone

[4] Majority of samples are carbonaceous mudstones

Table 2. Average, maximum, and minimum trace element content (ppm) of the sampled beds.

	As	Ba	Be	Cd	Co	Cr	Cu	Ga	Li	Mn	Ni	Sr	Te	U	V	Zn	P
Beulah-Zap (n=19)																	
mean	170	630	-	10	5	70	190	-	20	160	3	660	-	-	100	120	-
maximum	450	1400	-	90	40	530	3050	-	10	1470	30	1170	-	-	950	1040	-
minimum	0	160	-	-	-	0	-	-	-	0	-	50	-	-	-	-	-
Lehigh (n=10)																	
mean	110	620	-	10	30	70	0	-	3	70	0	1170	5	-	50	300	-
maximum	250	1610	-	60	150	390	0	-	20	160	5	5810	50	-	510	650	-
minimum	0	20	-	-	-	0	0	-	0	0	-	390	-	-	-	110	-
Hagel (n=20)																	
mean*	5	290	0	10	170	80	10	-	20	40	20	340	-	0	30	130	1220
maximum lg	60	570	5	40	2140	170	50	-	80	80	180	810	-	5	40	730	5900
cy	0	760	-	40	110	450	50	-	30	180	20	200	-	-	220	210	-
minimum lg	-	20	-	-	-	0	0	-	0	0	-	5	-	-	-	0	-
cy	0	270	-	-	-	0	0	-	10	0	-	20	-	-	0	0	-
Harmon (n=29)																	
mean*	60	410	0	20	40	60	1	30	20	180	20	410	5	-	80	150	-
maximum lg	410	5520	20	130	460	470	5	80	90	2060	100	940	-	-	280	890	-
cy	300	380	-	80	190	270	20	410	110	900	370	910	120	-	700	800	-
minimum lg	-	-	-	-	-	0	0	-	0	0	-	310	-	-	-	-	-
cy	-	50	-	-	-	0	0	-	10	0	-	10	-	-	-	-	-
oyster lignite and oyster bed (n=5)																	
mean*	3	220	-	10	290	80	40	160	20	110	50	220	-	80	50	440	1700
maximum lg	10	10	-	10	100	40	20	-	10	50	10	820	-	-	10	70	4960
cy	-	440	-	40	650	120	80	290	40	280	190	280	-	380	100	1560	1060
minimum lg	10	10	-	-	40	40	20	-	10	40	-	10	-	-	10	20	3820
cy	-	170	-	-	130	50	40	160	20	20	10	40	-	-	30	150	-
Lower middle Cannonball (n=2)																	
mean*	-	780	-	5	520	140	40	240	40	220	60	2560	-	20	100	220	-
maximum	-	1130	-	10	600	180	40	260	40	250	90	4860	-	50	110	240	-
minimum	-	430	-	-	450	90	40	210	30	190	30	250	-	-	100	190	-

* Claystone analyses included in calculations

lg = Lignite

cy = Claystone

-Indicates concentration is below detection limit of ICAP

Figure 4. Representation of concentrations of Al, Ca, Fe, K, Mg, and Na, in percent for the four sampled lignites. The points represent the minimum, average, and maximum values.

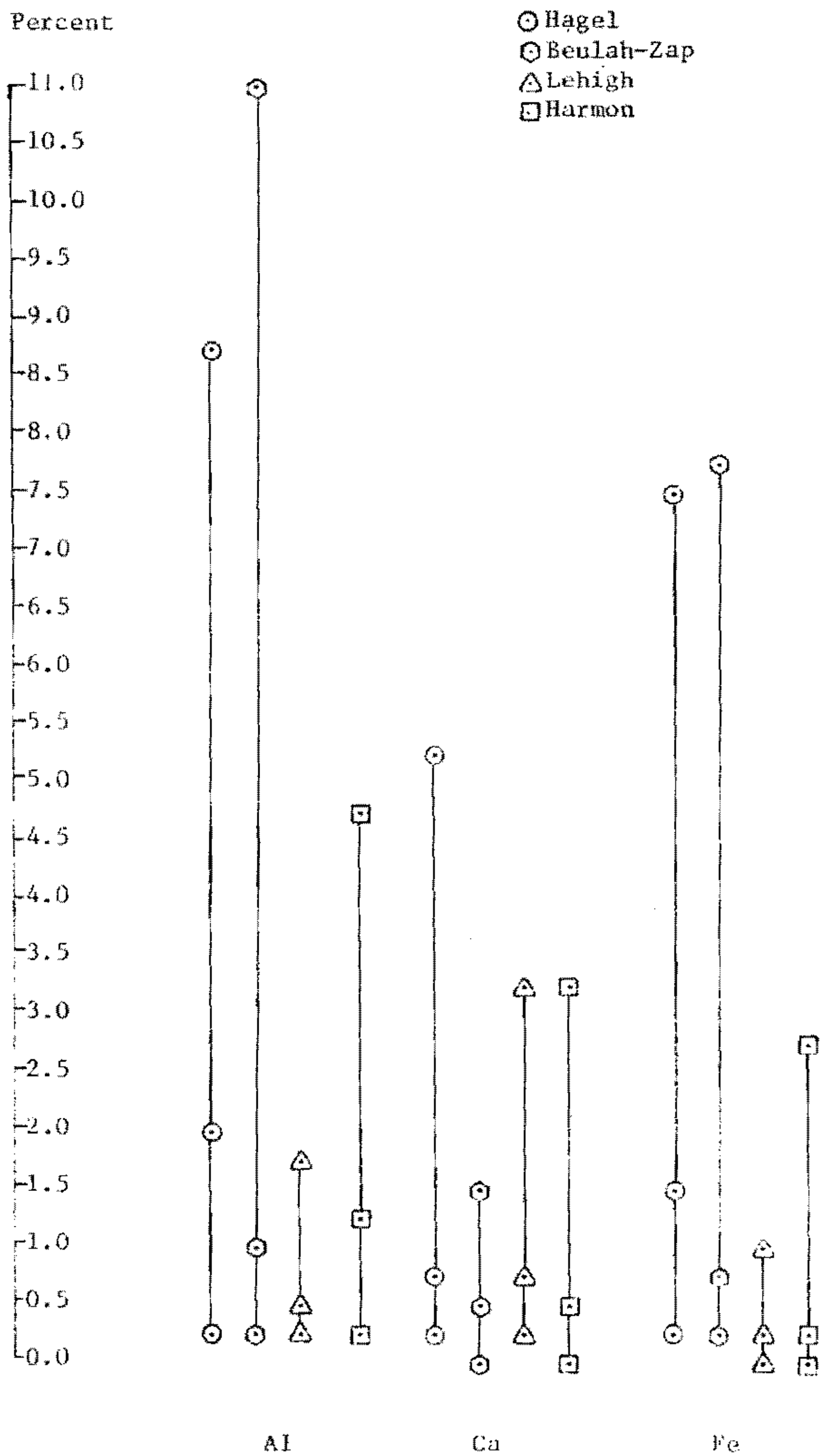

Percent
Hagel
Beulah-Zap
Lehigh
Harmon
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Al
Ca
Fe

Figure 4

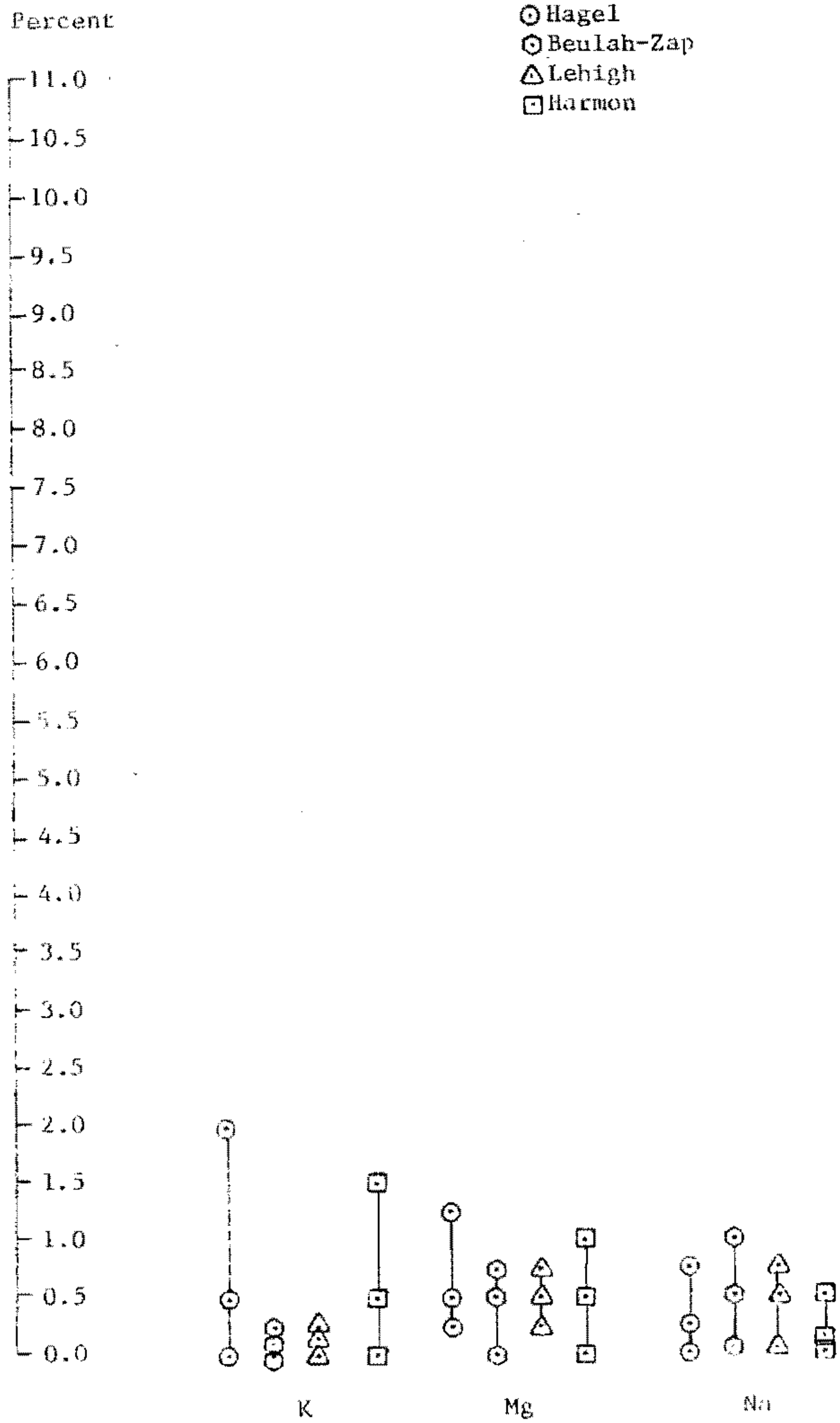


Figure 4 continued

Figure 5. Logarithmic representation of concentrations of As, Ba, Co, Mn, Sr, and Zn, in ppm, for the four sampled lignites.
The points represent the minimum, average, and maximum values.

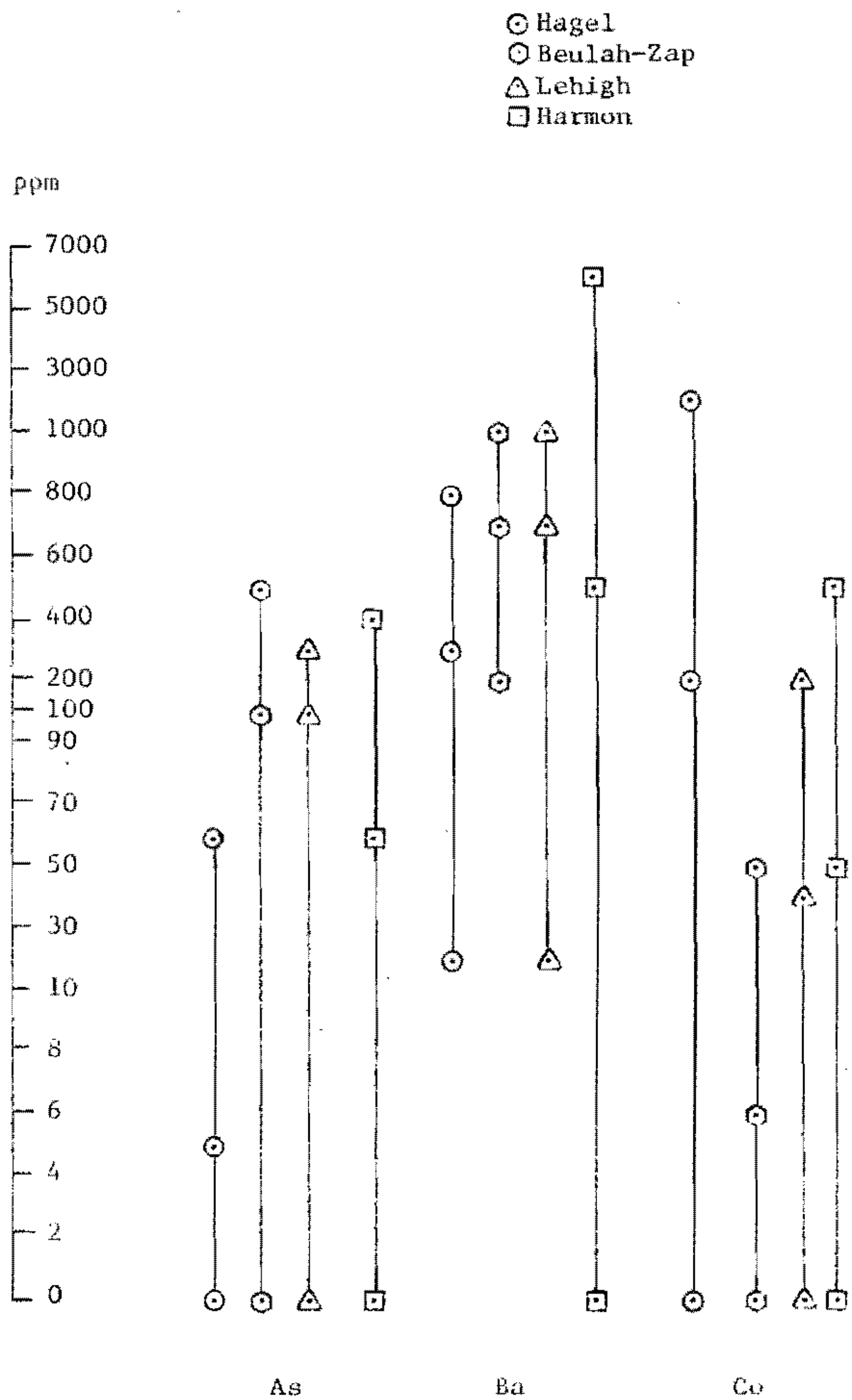

Hagel
Beulah-Zap
Lehigh
Harmon
ppm
7000
5000
3000
1000
800
600
400
200
100
90
70
50
30
10
8
6
4
2
0
As
Ba
Co

Figure 5

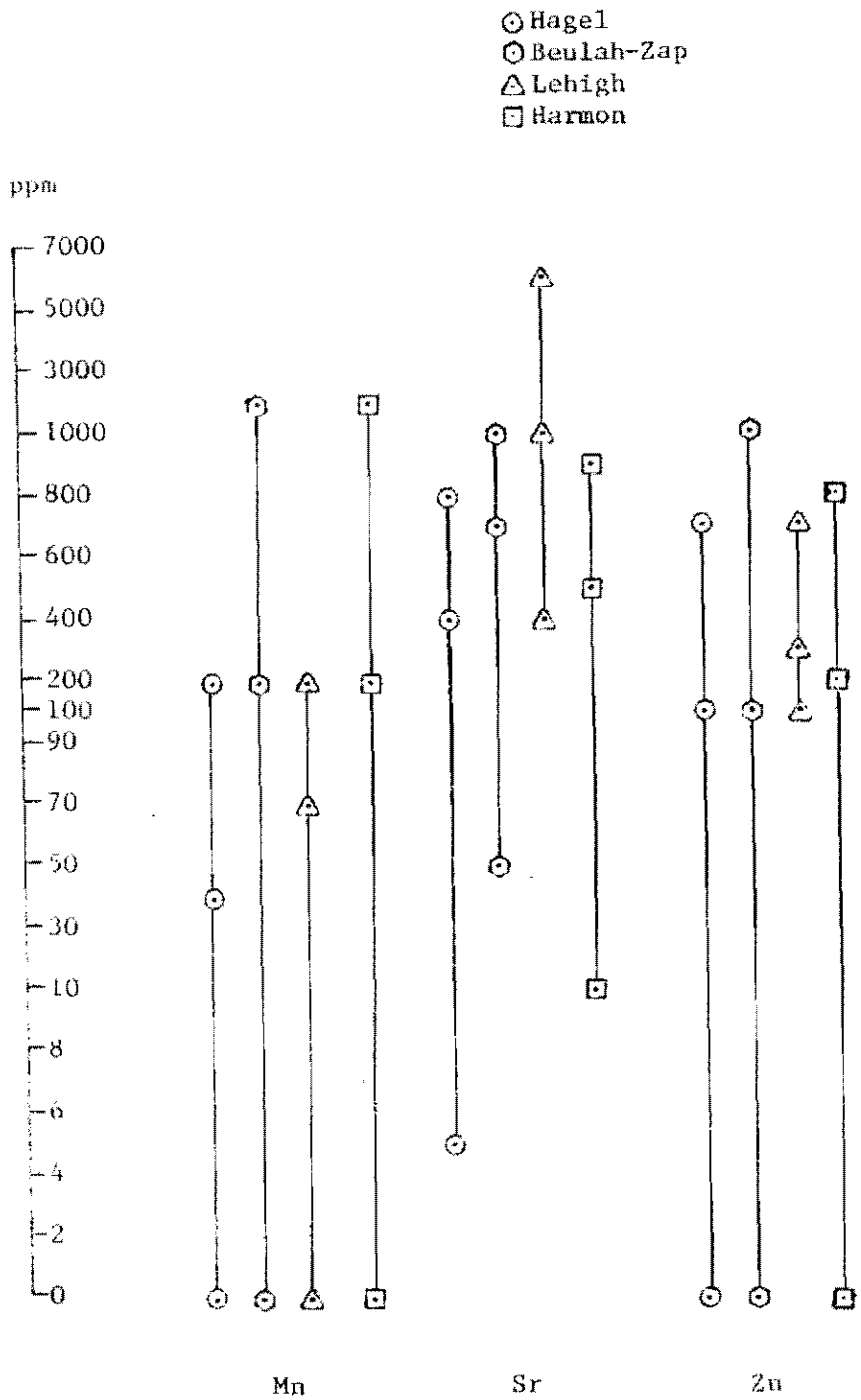


Figure 5 continued

3. K and Si generally increase downward through the section (Table 1) with the Beulah-Zap Bed being greatly depleted in K.

4. Ca content in the sampled Sentinel Butte shows a downward increase, with the Beulah-Zap Bed having 5850 ppm and the Hagel Bed having 9370 ppm. The Harmon Bed (Bullion Creek Formation) has less Ca than the Hagel and Lehigh Beds. The Slope and lower middle Cannonball Formations are highest in Ca.

5. A comparison between the sampled beds indicates that the average Na content is similar (Beulah-Zap 4470 ppm, Lehigh 4110 ppm, Hagel 3840 ppm, Harmon 2290 ppm, Slope Formation 3500 ppm, lower middle Cannonball 5220 ppm).

6. The average trace element content of the studied sections when compared with the earth crust's average trace element composition can be divided into four major groups: those at least one order of magnitude higher than the corresponding Clarke value, those similar to the corresponding Clarke value, those less than the corresponding Clarke valoe, and those that are variable.

6a. As and Cd content of the tested beds is generally at least one order of magnitude higher than their Clarke values. As, however, appears to be less concentrated as the clay content increases. The Clarke value of 0.15 ppm for Cd is 0.1 to 0.01 that of the concentration of Cd in the lignites. The Beulah-Zap Bed has the highest average As content (170 ppm), whereas none was detected in the lower middle Cannonball Formation. The Harmon Bed has the highest Cd content (20 ppm) and the lower middle Cannonball has the lowest (5 ppm).

6b. Cr, Ba, V, and Zn have approximately the same concentration in lignite as in the earth's crust. In general, the Slope Formation has the highest average Zn content and the Beulah-Zap and the Hagel beds have the lowest. The lower middle Cannonball Formation has the highest average Ba content and the Slope Formation has the lowest.

6c. The average Mn content of the studied lignite beds was at least one order of magnitude lower than the Clarke value.

6d. Co, Li, Ni, and Sr content in the studied lignite beds are either greater than or less than their Clarke values.

7. The clay partings found in the Hagel Bed, Harmon Bed, and sampled Slope Formation are generally higher in the major and minor elements as well as in Ba, Cu, Ga, Li, and V than the surrounding lignites (Tables 1 and 2). Cr, Mn, Ni, and Zn are usually higher in the clay partings.

8. Cd occurs at the top of a seam except where Cd is highly concentrated at the top, it also occurs lower in the seam (Fig. 6). Cd also occurs in the clay parting and in the lignite directly below a clay parting.

9. The highest concentrations of Na found in a seam also tend to occur at the top of a seam.

10. The highest concentrations of V and Zn generally tend to occur at the top, in clay partings, and at the bottom of a seam. In contrast Al, As, Ba, Ca, Co, Cr, Fe, K, Li, Mg, Mn, Ni, Si, and Sr are randomly dispersed throughout a seam (fig. 6).

11. Be, Ba, U, Te, and P were found only in a few samples so no conclusion can be drawn as to their occurrence in a seam.

12. No non-lignitized macrofossils or microfossils were found in representative samples from each studied section.

Figure 6. Concentration of Cd, V, and Sr within the Hagel Bed (Center Mine, locations 1 and 3), Beulah-Zap Bed (South Beulah Mine, locations 1 and 5), Harmon Bed (Gascoyne Mine, locations 1 and 3), and Lehigh Bed (Husky Industries Mine, locations 1 and 3). Each highwall is rotated clockwise to a horizontal position. The dots in each stratigraphic column represent sample positions in each bed. ▲ = V concentrations, ● = Cd concentrations, and ○ = Sr concentrations.

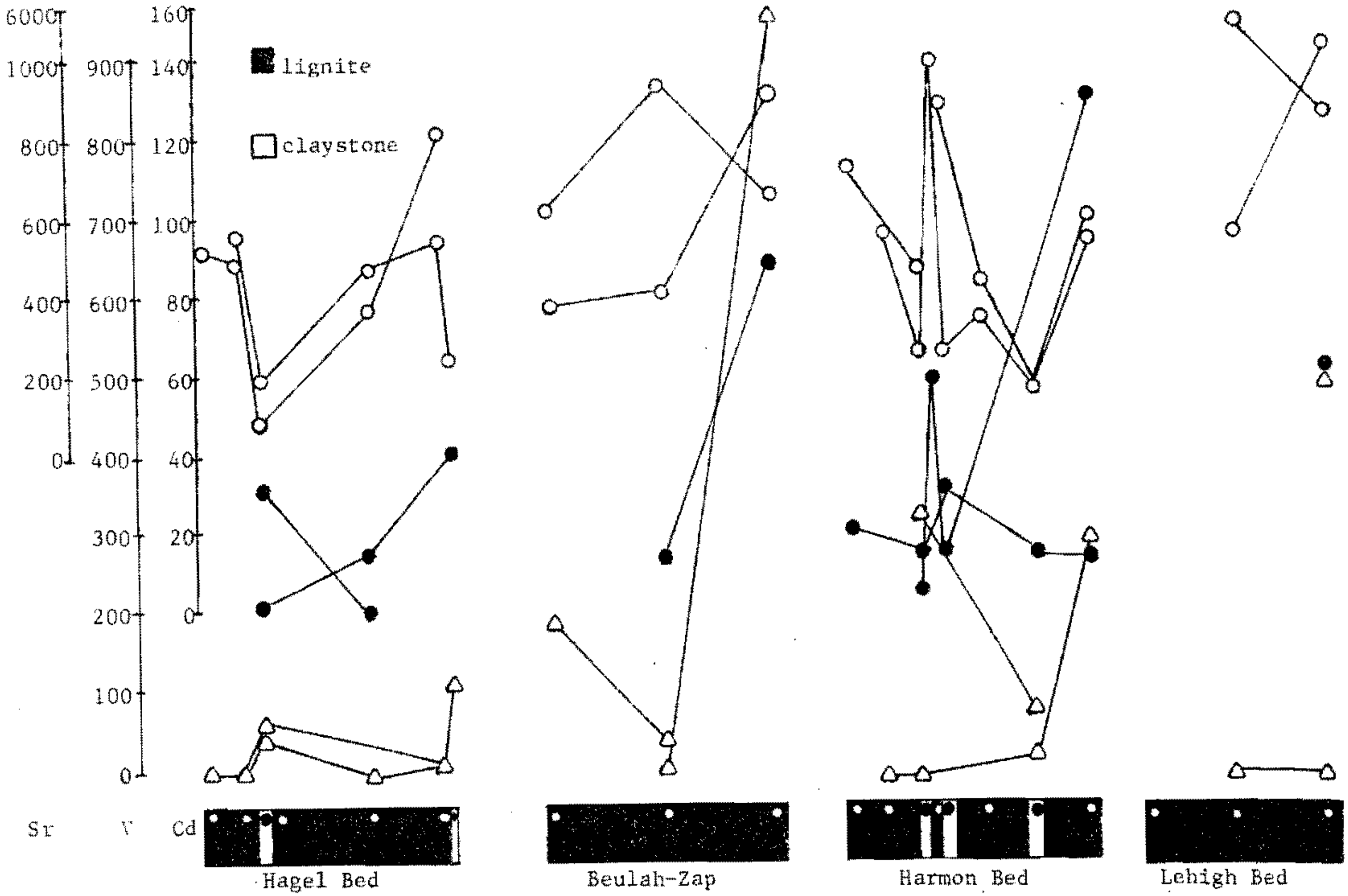

6000
1000
800
600
400
200
0
900
800
700
600
500
400
300
200
100
0
160
140
120
100
80
60
40
20
0
lignite
claystone
Sr
V
Cd
Hagel Bed
Beulah-Zap
Harmon Bed
Lehigh Bed

Figure 6

DISCUSSION

Zubovic and others (1961) suggested that As, Be, Sr, Ca, and Co may be useful in differentiating between the various lignite beds in the Sentinel Butte and Bullion Creek Formations. Working with the assumption that a group of elements was needed to differentiate between beds and the stratigraphic and chemical data from this study, it appears possible to differentiate between the Beulah-Zap, Lehigh, Hagel, and Harmon Beds using As, Ba, Sr, Ca, and Co. From figures 4 and 5 it appears that the Beulah-Zap Bed is characterized by high concentrations of Ba (630 ppm) and As (170 ppm), moderate concentrations of Sr (660 ppm) and low concentrations of Ca (0.5%) and Co (5 ppm). The Lehigh Bed is characterized by high concentrations of Sr (1170 ppm), Ba (620 ppm), and Ca (0.9%) and moderate concentrations of As (110 ppm) and Co (30 ppm). The Hagel Bed is characterized by low concentrations of As (5 ppm), Ba (290 ppm), and Sr (340 ppm) and a high concentration of Ca (0.9%) and Co (170 ppm). The Harmon Bed is characterized by a moderate concentration of As (60 ppm), Ba (410 ppm), Ca (0.7%), and Co (40 ppm) and low concentrations of Sr (410 ppm).

Coalification, groundwater movement, rate of subsidence of the Williston Basin, source area, and depositional environment are all factors contributing to the chemical composition of North Dakota lignites. Throughout the coalification process organic molecules (lignins or humic acids) were rearranged to form coal, and some elements (Na, K, Mg) were mobilized (Zubovic and others 1961). The mobilization of these elements make them undesirable for use in determining source area, or rate of subsidence of the basin. It may

Table 3. Comparison of the trace element content (%) of the ash of trees, peat, and coal

	Be	Co	Cr	Cu	Ni	V	Zn
Trees (USGS)[1]	0.1	0.7	7.5	12.3	7.1	15	37.4
Minnies Lake Peat[2]	-	8	18	19.5	4	-	130
Chesser Prairie Peat[3]	-	8	23	30.5	3	-	14.5
North Dakota Coal[4]	0.8	0.9	11.6	4.6	4.6	6.6	2.3
Wyoming Coal[4]	0.3	2.3	12.3	11.7	6.6	21.1	9.3
Montana Coal[4]	2.1	8.2	8.5	7.2	2.4	7.7	2.5

[1] Zubovic and others (1961).
[2] Okefenokee Swamp, Charlton County, Georgia; Casagrande and others (1976).
[3] Okefenokee Swamp, Ware County, Georgia; Casagrande and others (1976).
[4] Gluskoter and others (1977).

be possible to use these elements as indicators in non-lignitized sediments. A comparison of tree, peat, and lignite ash composition suggests, that in most cases, the composition of the tree ash is similar to the composition of peat, lignite, and coal ash (Table 3). The difference of two to three times between materials is of small consequence, and can be due somewhat to differences in accuracy of the instruments used. The data seem to suggest that Be, Co, Cr, Cu, Ni, V, and Zn are not released during coalification, thus these elements, if unaffected by groundwater, may be used as chemical indicators. The lignites in the Knife River Basin are highly fractured, allowing water to move through them faster than through the silty clays and clayey silts above and below the lignites. The water passing through the lignites can transport large quantities of dissolved solids making it necessary to determine if any of the elements analyzed are being affected by groundwater. In general, water enters the lignites from above and discharges into the sediments below.

In the mine pits the author visited, the overlying sediments, with the exception of the southern end of a South Beulah Mine pit, are usually silty clay or clayey silt. At South Beulah, a portion of the lignite was overlain by sandy gravel channel sediments. These sediments discharge more water into the lignite than the clayey silts and silty clays, and could cause concentration or depletion of elements affected by groundwater movement in the Beulah-Zap lignite. Cd and Mg appear to be more concentrated in the lignite directly underlying the sandy gravel (fig. 7) than in the lignite underlying the silty clays or clayey silts and the Student's t test suggests the difference is statistically significant at the 99% and 90% level, respectively.

Figure 7. Concentration of Cd in the highwall of the South Beulah Mine. Each dot represents a sampling site.

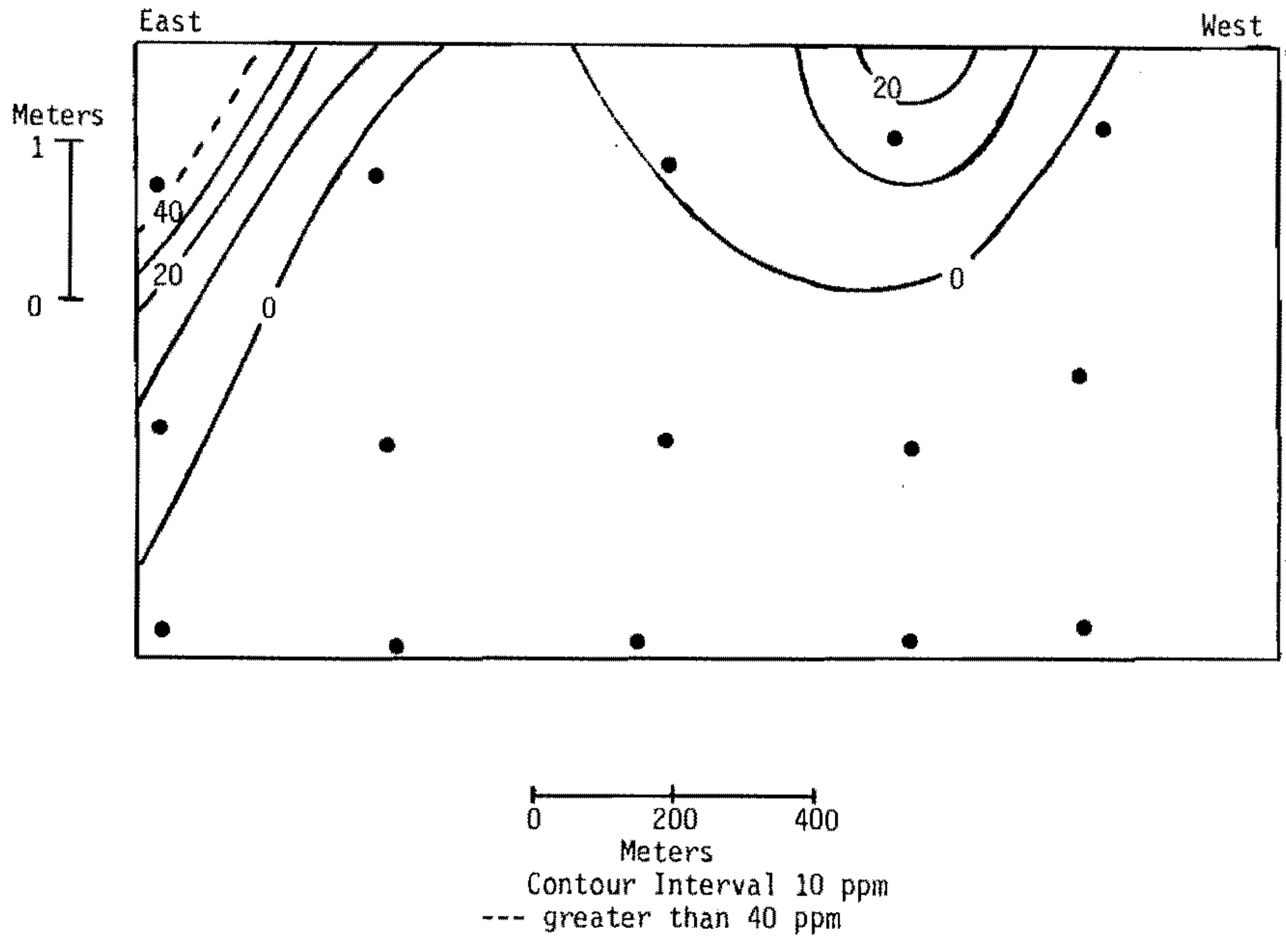

East
West
Meters
1
0
40
20
0
20
0
0
200
400
Meters
Contour Interval 10 ppm
--- greater than 40 ppm

Figure 7

Table 4. Average major, minor, and trace element content, in parts per million, of North Dakota lignites and Wyoming and Montana subbituminous coal.

	North Dakota				Wyoming[1]	Montana[1]
	Beulah-Zap[2]	Lehigh[2]	Hagel[2]	Harmon[3]		
Al	11530	7560	20530	13680	70	9860
As	170	110	5	60	1	2
Ba	630	620	620	410	840	340
Be	–	–	–	0	–	0.3
Ca	5850	9350	9370	6780	21750	2
Cd	10	10	10	20	–	–
Co	5	30	170	40	18280	2
Cr	70	70	80	60	10	10
Cu	190	0	10	1	10	10
Fe	8570	2800	16040	4470	4000	5560
Ga	–	–	–	30	1	2
K	160	220	5320	4470	100	790
Li	20	3	20	20	–	–
Mg	4460	4500	4810	49600	20	1340
Mn	160	70	40	180	60	70
Na	4470	4110	3840	2290	1420	1060
Ni	3	0	20	20	2	5
Si	6070	16960	72760	85560	8350	18680
Sr	660	1170	340	410	330	190
V	100	50	30	80	10	20
Zn	120	300	130	150	3	10

[1] Gluskoter and others (1977). Values are rounded.
[2] Sentinel Butte Formation.
[3] Bullion Creek Formation.

Using analyses of North Dakota water above and within a lignite (Appendix 2) it is possible to determine the activities of the dissolved solids using the following equations:

Activity ([ ]) is equal to the concentration multiplied by the activity coefficient (γ) ($A\gamma = [A]$). The activity coefficient is determined from the Davies equation (Krauskopf, 1967):

$$-\log \gamma = Az^2(I^{\frac{1}{2}}/I^{\frac{1}{2}}+1)-0.2I$$

where A depends on the dielectric constant and temperature (at 10°C, the temperature of North Dakota groundwater, A is 0.4979), z is the ionic charge, and I is the ionic strength and is equal to:

$$I = \tfrac{1}{2}\sum c_i z_i^2$$

where c_i = moles/liter.

Cd^{2+} decreased from an activity of 9.88×10^{-5} in the overburden to 9.79×10^{-7} in the lignite, indicating Cd may be precipitated in the lignite.

The process of Cd deposition may be explained by adsorption or precipitation. A radical change in Eh at the boundary between the lignite and overburden could cause the deposition of Cd and other groundwater-influenced elements. The change in Eh may create a Cd redox reaction, decreasing Cd solubility and causing precipitation. Cd^{2+} is the predominant ion in freshwater under most Eh-pH conditions (fig. 8) (Gong and others 1978). Only under reducing conditions does Cd^{2+} change to Cd or CdS. In natural waters of 18°C, Cd^{2+} is saturated (10^{-7}) and the CdS solubility product is 3.6×10^{-29}; therefore, Cd^{2+} is 22 times more soluble then CdS. CdS will precipitate in the lignite if there is enough S.

Gong and others (1978) also found that Cd is strongly adsorbed

Figure 8. Eh–pH diagram for Cd in freshwater. $P_{CO_3} = 10^{-3.5}$ atm., total sulfur = 10^{-4} moles/liter, and total $Cl^- = 10^{-3.54}$ moles/liter. After Gong and others 1977.

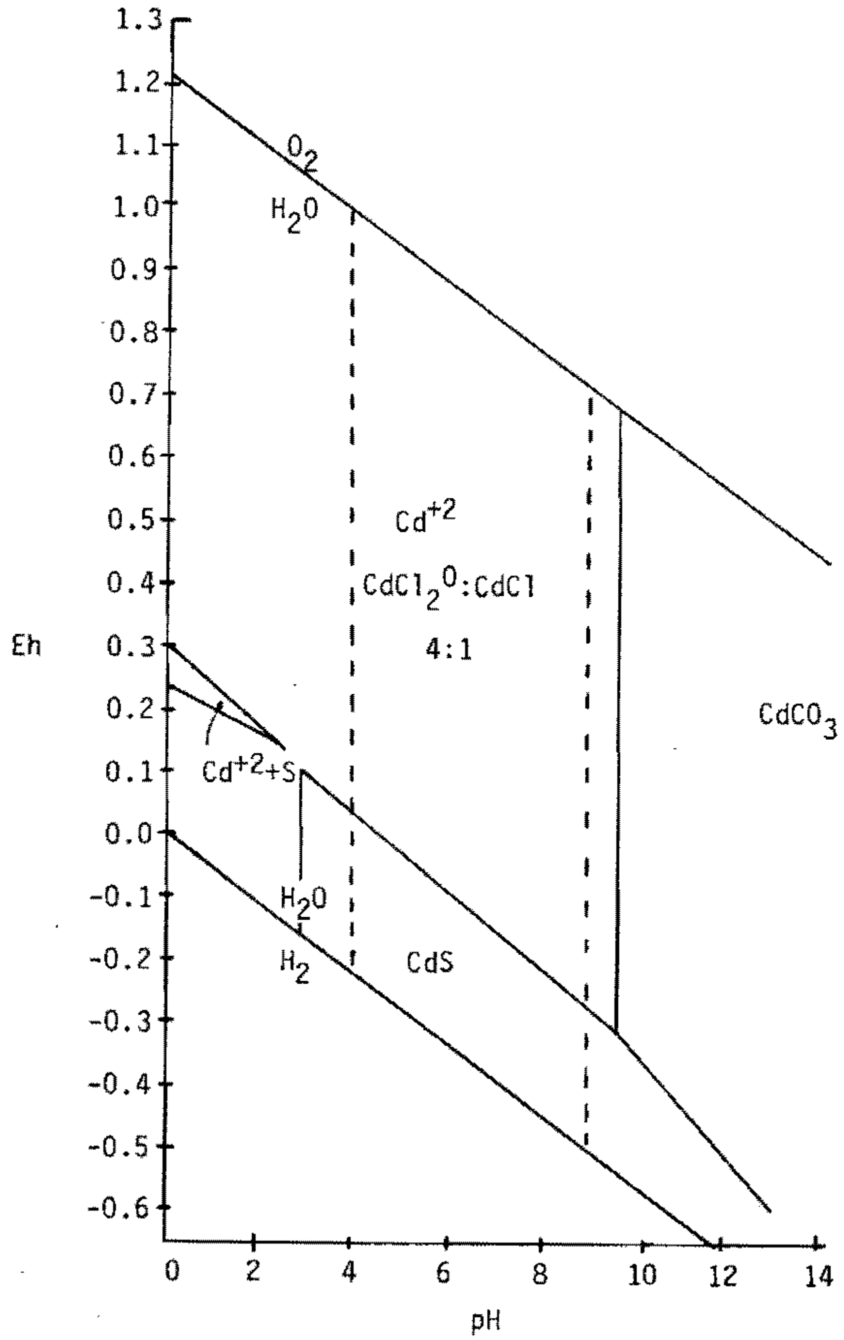

1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
Eh
O_2
H_2O
Cd^{+2}
$CdCl_2^0$:CdCl
4:1
$CdCO_3$
Cd^{+2}+S
H_2O
H_2
CdS
0
2
4
6
8
10
12
14
pH

Figure 8

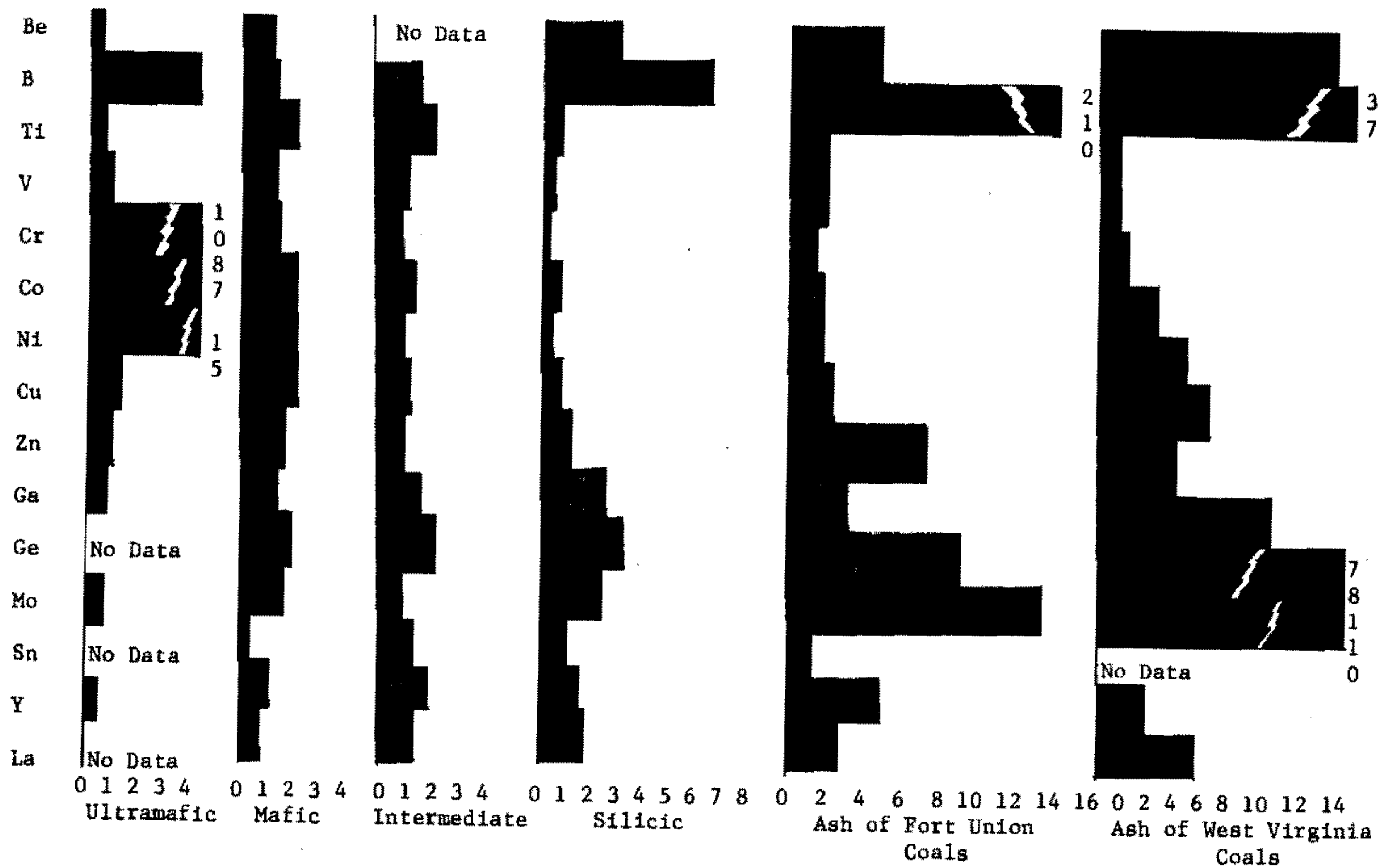
by carbon. A combination of adsorption and precipitation of Cd from the groundwater probably accounts for the Cd concentration at the top of the studied lignite beds.

Zubovic and others (1961) theorized that volcanics to the west served as the source area for Paleocene Fort Union sediments. The Antelope orogeny produced large quantities of andesitic, dacitic, and some rhyolitic magmas that later contributed sediments to the Fort Union. Zubovic and others (1961) believed that the chemistry of Fort Union sediments best resembled the chemistry of a silicic source area (fig. 9).

Horne and others (1977) and Casagrande and others (1976) have suggested that the concentrations of trace elements could indicate how rapidly a basin of accumulation subsided. A rapidly subsiding basin would be characterized by a lower trace element concentration than that of a slowly subsiding basin. The three sampled lignites from the Sentinel Butte Formation and the one sampled lignite from the Bullion Creek Formation generally have the same Al, Ba, Ca, Fe, K, Mg, Na, Ni, Si, Sr, and V content as the subbituminous coals from the Fort Union Group in Montana and Wyoming (Table 4). The sampled North Dakota lignites are significantly higher in As (99% level), Co (95% level), Cr (99% level), Ga (75% level), Mn (75-90% level), and Zn (99% level) than the coals from either Montana or Wyoming. This suggests that the Williston Basin may have subsided at a slower rate than the Powder River Basin.

The depositional environment during sedimentation affects the trace element chemistry of the sediments. Nicholls (1968) stated that Cr, Cu, Ga, Ni, and V may be more highly concentrated in marine rocks

Figure 9. Comparison of the minor-element content of coal ash with the minor element content of different rock types (numbers are the ratio of the element in the sample to the average abundance of the element in the earth's crust). After Zubovic and others 1961.



Be
B
Ti
V
Cr
Co
Ni
Cu
Zn
Ga
Ge
Mo
Sn
Y
La
No Data
No Data
No Data
No Data
No Data
1 0 8 7
1 5
2 1 0
3 7
7 8 1 1 0
0 1 2 3 4
Ultramafic
0 1 2 3 4
Mafic
0 1 2 3 4
Intermediate
0 1 2 3 4 5 6 7 8
Silicic
0 2 4 6 8 10 12 14 16
Ash of Fort Union Coals
0 2 4 6 8 10 12 14
Ash of West Virginia Coals

Figure 9

than in fresh water rocks. Using these elements as depositional environment indicators, it was found that the brackish mudstone of the Slope Formation is lower in Cr, Ga, Ni, and V than the marine mudstone of the lower middle Cannonball Formation and is statistically significant at the 60-95% level (low sample number may account for the somewhat low significance). The mudstone of the Slope Formation is significantly higher in Cr, Cu, and Ga (99% level) than either the mudstone from the Hagel Bed (Sentinel Butte Formation) or Harmon Bed (Bullion Creek Formation).

The brackish oyster lignite of the Slope Formation was selected as the standard. The values of Cr, Cu, Ga, Ni, and V can be found in Appendix 1. A comparison of the values of the Harmon Bed with those of the oyster lignite shows that the Harmon Bed is statistically higher in Cr, Ga, Ni, and V (70-99% level). The Hagel Bed is significantly (92-99% level) lower in Cr, Ga, Ni, and V than the brackish oyster lignite, suggesting that the Hagel Bed was deposited in a depositional environment different from the oyster lignite. The Harmon Bed was significantly (90-99% level) higher in Cr, Ga, and V than the Hagel Bed suggesting the Harmon Bed was deposited in water of higher salinity. The statistical data for Cr, Ga, Ni, and V was variable for the Beulah-Zap Bed and Lehigh Bed.

The K/Li ratio may be a salinity indicator (Yudina 1977); a low K/Li ratio indicates a higher salinity environment. Since K is given off during coalification, this test can only be applied to non-lignitized sediments. The K/Li ratio of the oyster bed (mudstone) (0.1-5.0) and the Harmon Bed (shale parting) (0.1-3.0) are similar, whereas the K/Li ratio of the Hagel Bed (600–2000 for a shale parting) is 2–3 orders of magnitude higher. These ratios suggest that the oyster bed and the Harmon Bed were deposited in environments of similar salinity, whereas the Hagel Bed was deposited in an environment of lower salinity. No conclusion can be drawn about the Beulah-Zap and Lehigh Beds since no clay partings were present.

The chemical evidence (Cr, Ga, Ni, and V) indicates that the Harmon Bed was deposited in a more saline environment than the oyster lignite, whereas the K/Li ratios indicate a salinity similar to that of the oyster bed. A number of possibilities could account for this apparent inconsistency. The control group, since they were only sampled at one site at each location, may not be entirely typical of that formation A larger sample number might indicate if this is a problem. The oyster bed (claystone) and oyster lignite are two different beds of the Slope Formation. It may be possible that the salinity of the formation varied. Possibly the oyster lignite was deposited in a less saline environment than the oyster bed.

Little is known about the non-lignitized fossils found in the lignites from the Sentinel Butte and Bullion Creek Formations. There have, however, been a considerable number of accounts of freshwater fauna found in the associated strata of the Sentinel Butte and Bullion Creek Formations. The Harmon Bed, if it is brackish, should have brackish fossils associated with it. To date, no brackish fossils have been found in the lower Bullion Creek Formation.

CONCLUSIONS

1. The local recharge and discharge areas of North Dakota cause the lignites to be recharged from the top. Evidence from South Beulah Mine, chemical analysis of North Dakota groundwater, and positions of chemical concentrations in a seam, indicate that Na and Cd are being deposited by groundwater. V and Zn concentrations may be influenced by groundwater, whereas Al, As, Ba, Ca, Co, Cr, Cu, Fe, Ga, Li, Mn, Ni, Si, and Sr are probably primarily deposited. Be, Te, U, and P were detected in only a few samples so no generalization as to their occurrence can be made.

2. It may be possible to distinguish between stratigraphic units using a number of elements. As, Ba, Sr, Ca, and Co appear to be the most useful elements in distinguishing between beds considering average values, it appears that the Beulah-Zap Bed is characterized by high concentrations of Ba (630 ppm) and As (170 ppm), moderate concentrations of Sr (660 ppm), and low concentrations of Ca (0.5%) and Co (5 ppm). The Lehigh Bed may be characterized by high concentrations of Sr (1170 ppm), Ba (620 ppm), and Ca (0.9%) and moderate concentrations of As (110 ppm), and Co (30 ppm). The Hagel Bed may be characterized by low concentrations of As (5 ppm), Ba (290 ppm), and Sr (340 ppm) and high concentrations of Ca (0.9%) and Co (170 ppm). The Harmon Bed may be characterized by a moderate concentration of As (60 ppm), Ba (410 ppm), Ca (0.7%), and Co (40 ppm) and low concentrations of Sr (410 ppm).

3. Elemental concentration may indicate relative rate of basin subsidence. The higher the concentration the slower the rate of subsidence. A comparison of lignites from North Dakota (Williston Basin) and coals from the Powder River Basin indicate that North

Dakota lignites have a higher element content. Therefore, the Williston Basin may have subsided at a slower rate than the Powder River Basin.

4. The marine lower middle Cannonball Formation has a higher concentration of Cr, Ga, Ni, and V than the brackish oyster bed (Slope Formation) indicating that these four trace elements can be used as indicators of the salinity of the depositional environment.

5. Cr, Ga, Ni, and V concentrations and K/Li ratios indicate that the Hagel Bed (Sentinel Butte Formation) may have been deposited in an environment of lower salinity than the oyster lignite (Slope Formation). The Harmon Bed (Bullion Creek Formation) may have been deposited in an environment similar in salinity to that of the oyster lignite (Slope Formation).

APPENDICES

Appendix 1. Elemental Analyses of North Dakota Lignite

SYMBOL EXPLANATION

* indicates claystone, lignitic shale, or carbonaceous shale.

- indicates elemental concentration was below detection limits of the ICAP.

0 indicates a 0 value after the control value was subtracted.

KRB Knife River Coal Company, Beulah Mine; collected from working face May 16, 1978.

KRG Knife River Coal Company, Gascoyne Mine; collected from working face September 4, 1978.

BNC Baukol-Noonan Coal Company, Center Mine; collected from working face May 14, 1978.

HI Husky Industries, Dickinson Mine; collected from working face May 18, 1978.

NAF North American Coal Company, Falkirk Mine; collected from working face April 24, 1979.

CGH Consolidated Coal Company, Glenharold Mine; collected from working face April 25, 1979.

CBF Slope Formation; collected from an outcrop at NW¼ sec.15, SW¼ sec.10, T. 105 N., R. 136 W., August, 1979.

FLS Fort Lincoln Site, Lower Middle Cannonball Formation; collected from an outcrop at NE¼ NW¼ sec.13, T. 138 N., R. 81 W., August, 1979.

TS Top shale.

LS Lower shale.

sp Shale parting.

spb Shale parting 2.

Numbers indicate location and sample number:
e.g. KRB 1-2 = Knife River, Beulah Mine, Location 1, sample 2.

Numbers in parenthesis indicate relative position in the bed:
e.g. (1) = Top of bed
(2) = Middle of bed
(3) = Bottom of bed.

Table 5. Elemental Analyses of North Dakota Lignite.

Sentinel Butte Formation

Beulah-Zap Bed

Sample No.	Position in bed		Al	As	Ba	Be	Ca	Cd	Co	Cr
			Elements in ppm							
KRB 1-1	bottom	(3)	3000	400	260	-	3870	-	-	90
KRB 1-2		(2)	5100	0	490	-	6820	10	40	0
KRB 1-3	top	(1)	12390	200	1100	-	7100	90	-	70
KRB 1-S		(2)	6700	120	350	-	7200	-	-	160
KRB 2-1	bottom	(3)	2790	300	540	-	4250	-	-	40
KRB 2-2	top	(1)	11120	90	590	-	7710	-	-	0
KRB 2-3		(2)	114640	50	830	-	7980	-	-	50
KRB 2-S		(2)	7000	90	1400	-	8460	-	-	30
KRB 3-1	bottom	(3)	4450	170	360	-	5760	-	-	10
KRB 3-2		(2)	3700	190	310	-	5020	-	-	0
KRB 3-3	top	(1)	7540	0	1030	-	9560	0	-	0
KRB 3-S		(2)	9870	0	700	-	5800	-	-	0
KRB 4-1		(2)	7480	450	1380	-	14380	-	-	140
KRB 4-2	bottom	(3)	1690	0	310	-	300	-	-	0
KRB 4-3	top	(1)	6230	410	190	-	2790	20	-	530
KRB 4-S		(2)	630	0	200	-	0	5	20	0
KRB 5-1	top	(1)	7290	330	160	-	4330	-	-	70
KRB 5-2		(2)	4020	60	1140	-	5360	-	-	0
KRB 5-3	bottom	(3)	3390	430	610	-	4550	-	-	110

Lehigh Bed

Sample No.	Position in bed		Al	As	Ba	Be	Ca	Cd	Co	Cr
HI 1-1	top	(1)	13490	250	1610	-	5720	-	-	70
HI 1-2	middle	(2)	1680	0	840	-	190	-	0	40
HI 2-1	middle	(2)	2000	30	90	-	13320	-	-	10
HI 2-2	top	(1)	18900	90	250	-	4430	-	-	0
HI 3-1	top	(1)	14900	230	20	-	6120	60	-	150
HI 3-2	middle	(2)	3190	200	1600	-	2790	-	-	390
HI 4-3	top	(1)	5730	0	170	-	3120	10	40	0
HI 5-1	middle	(2)	1720	0	550	-	34720	-	150	0
HI 5-2	top	(1)	4510	0	30	-	17400	-	80	0
HI 5-3	bottom	(3)	9510	250	1030	-	5680	-	-	70

Hagel Bed

Sample No.	Position in bed		Al	As	Ba	Be	Ca	Cd	Co	Cr
BNC TS*	top	(1)	78800	0	600	-	60	40	110	0
BNC 1-1		(2)	5380	0	240	-	4270	-	-	0
BNC 1-2		(3)	940	0	20	-	1780	10	-	0
BNC 1-3		(5)	3090	0	40	-	8040	-	-	40
BNC 1LS*		(4)	87300	0	760	-	0	0	70	0
BNC 2*		(1)	56750	0	540	-	1370	30	-	450
BNC 2-1		(2)	32090	0	270	-	3930	40	350	0
BNC 2sp*		(3)	37630	0	270	-	0	-	-	0
BNC 2-2	bottom	(4)	870	-	130	-	3980	-	70	0
BNC 3-1	top	(1)	4680	0	150	-	7060	-	-	0
BNC 3-2		(2)	1060	60	40	-	2890	0	2140	0
BNC 3sp*		(3)	45870	0	430	-	0	30	-	380

Sentinel Butte Formation

Hagel Bed

Sample No.	Position in bed		Elements in ppm Al	As	Ba	Be	Ca	Cd	Co	Cr
BNC 3-3		(4)	1590	0	50	-	1210	-	-	0
BNC 3spb*		(5)	36650	0	280	-	21440	30	20	280
BNC 3-4	bottom	(6)	2030	0	130	-	4950	-	-	0
NAF 2-1	top	(1)	5240	0	410	2	23290	0	180	170
NAF 2-2		(2)	2480	-	430	-	19050	-	90	30
NAF 2-3	bottom	(3)	3410	20	70	5	17450	-	90	140
CGH 1-1	top	(1)	2450	-	310	-	54410	-	70	20
CGH 1-2	bottom	(2)	1990	-	570	-	12150	-	140	70

Bullion Creek Formation

Harmon Bed

Sample No.	Position in bed		Al	As	Ba	Be	Ca	Cd	Co	Cr
KRG 1-1	top	(1)	4070	40	2810	-	4910	130	-	200
KRG 1-2*		(2)	48340	0	380	-	2410	-	30	0
KRG 1-3		(3)	690	0	30	-	0	-	20	0
KRG 1-4*		(4)	19540	-	160	-	2040	10	190	270
KRG 1-5		(5)	7840	150	300	-	33570	60	-	470
KRG 1-6*		(6)	14620	0	60	-	750	5	-	0
KRG 1-7	bottom	(7)	4900	0	30	-	5940	-	-	0
KRG 2-1*	top	(1)	29230	0	180	-	0	20	130	0
KRG 2-2		(2)	2890	120	80	-	2910	10	-	60
KRG 2-3*		(3)	33800	0	320	-	270	-	-	0
KRG 2-4		(4)	15200	-	80	-	7830	0	60	0
KRG 2-5*		(5)	7310	-	50	-	3240	10	40	0
KRG 2-6	bottom	(6)	3900	0	50	-	7700	-	20	0
KRG 3-1	top	(1)	4820	410	60	-	10810	10	-	0
KRG 3-2*		(2)	10860	0	200	-	25000	10	80	0
KRG 3-3		(3)	2900	-	30	-	10060	-	460	0
KRG 3-4*		(4)	26330	0	130	-	6560	30	-	90
KRG 3-5*		(5)	7170	0	50	-	0	10	130	0
KRG 3-6*		(6)	19110	260	100	-	3220	-	-	0
KRG 3-7	bottom	(7)	10730	200	10	-	5490	20	-	110
KRG 4-1	top	(1)	1670	0	380	-	4470	-	-	0
KRG 4-2		(2)	3060	0	-	20	5680	-	-	0
KRG 4-3*		(3)	35570	0	270	-	2970	-	-	0
KRG 5-1	top	(1)	4630	130	150	-	2930	-	-	0
KRG 5-2		(2)	3760	0	20	-	11620	-	-	0
KRG 5-3*		(3)	41820	300	250	-	5010	80	-	190
KRG 5-4		(4)	10890	200	80	-	22980	-	-	0
KRG 5-5		(5)	14450	70	170	-	2770	30	-	250
KRG 5-6	bottom	(6)	6620	0	5520	-	5760	-	-	0

Slope Formation

oyster lignite and oyster bed

Sample no.	Position in Bed		Elements in ppm Al	As	Ba	Be	Ca	Cd	Co	Cr
CBF 1-1*	bottom	(6)	55550	-	440	-	90240	40	470	90
CBF 1-2		(5)	1550	10	10	-	50610	-	40	40
CBF 1-3		(4)	1060	10	10	-	1280	10	100	40
CBF 1-4*		(3)	36470	-	260	-	1270	-	370	120
CBF 1-5*		(2)	48900	-	420	-	81570	10	650	110
CBF 1-6*	top	(1)	17350	-	170	-	19540	-	130	50

Cannonball Formation

Lower Middle Cannonball

FLS 1-1*	top	(1)	41680	-	430	-	44130	10	600	180
FLS 1-2*	bottom	(2)	58870	-	1130	-	27580	-	450	90

Sentinel Butte Formation

Beulah-Zap Bed

Sample No.	Cu	Fe	Ga	K	Li	Mg	Mn	Na	Ni	Si	Sr
	Elements in ppm										
KRB 1-1	-	2690	-	-	-	4320	140	2040	-	1750	380
KRB 1-2	0	1700	-	0	0	3950	0	1590	20	0	390
KRB 1-3	0	20100	-	540	0	7110	1470	3740	-	9700	870
KRB 1-S	140	1970	-	110	0	6700	90	3740	-	4960	910
KRB 2-1	0	1550	-	20	0	2350	100	1800	-	980	460
KRB 2-2	0	1810	-	140	0	6170	40	2250	-	7250	660
KRB 2-3	3050	6220	-	1320	0	7010	300	2060	-	26400	50
KRB 2-S	50	1660	-	160	0	6430	40	2640	-	6960	1170
KRB 3-1	0	1930	-	40	0	5340	110	1600	-	3920	640
KRB 3-2	100	1270	-	20	0	4500	60	2920	-	2600	730
KRB 3-3	90	2030	-	120	10	5250	70	3750	-	15780	980
KRB 3-S	20	2070	-	190	10	4710	50	7630	-	18190	880
KRB 4-1	0	2240	-	190	10	5970	200	7600	-	3370	1170
KRB 4-2	70	17670	-	100	0	1410	0	5640	-	2240	310
KRB 4-3	0	77180	-	160	5	2530	130	7240	-	2010	620
KRB 4-S	0	0	-	0	0	750	0	3650	30	1610	230
KRB 5-1	0	3750	-	110	10	2960	60	9480	-	3760	650
KRB 5-2	0	1250	-	50	0	4230	80	8170	-	2200	900
KRB 5-3	0	15750	-	40	0	3140	60	7410	-	1620	600

Lehigh Bed

HI 1-1	0	2080	-	500	20	6840	150	4870	-	16980	880
HI 1-2	0	440	-	140	0	3130	60	2810	-	240	5810
HI 2-1	0	120	-	0	0	2870	40	3690	-	1910	460
HI 2-2	0	930	-	200	5	5270	30	3900	-	19500	710
HI 3-1	0	4660	-	590	5	7670	150	4970	-	16760	1040
HI 3-2	0	460	-	160	0	3160	120	4320	-	2390	560
HI 4-1	0	1680	-	360	0	2650	40	3550	-	16890	390
HI 5-1	0	11720	-	-	0	3700	0	2820	-	82700	420
HI 5-2	0	3830	-	100	0	3560	0	3000	5	8850	450
HI 5-3	0	1130	-	200	0	6150	160	7140	-	3410	960

Hagel Bed

BNC TS*	0	24890	-	14410	20	11370	80	7450	-	>200000	200
BNC 1-1	0	48420	-	560	0	3690	0	3780	0	1520	510
BNC 1-2	0	730	-	-	0	2280	0	5220	-	0	420
BNC 1-3	5	1800	-	0	0	3660	60	3910	-	6960	560
BNC 1-LS*	0	25090	-	20660	30	11720	100	5340	-	>200000	180
BNC 2*	0	28910	-	11850	10	12980	180	5510	-	>200000	200
BNC 2-1	0	73560	-	5970	10	5140	30	4860	-	>200000	310
BNC 2sp*	10	8840	-	15130	10	1910	0	3770	0	>200000	60
BNC 2-2	0	160	-	5240	60	2230	0	3500	40	3340	5
BNC 3-1	0	3690	-	80	0	5910	0	4500	-	0	810
BNC 3-2	0	74030	-	2150	20	1630	0	2400	180	1620	310

Sentinel Butte Formation

Hagel Bed

Sample No.	Elements in ppm										
	Cu	Fe	Ga	K	Li	Mg	Mn	Na	Ni	Si	Sr
BNC 3sp*	0	8120	-	14060	10	5600	0	2920	-	>200000	20
BNC 3-3	0	1570	-	0	0	3140	0	4070	-	0	470
BNC 3spb*	50	5880	-	13020	10	3700	0	3130	20	>200000	170
BNC 3-4	0	1390	-	0	0	3140	0	4600	-	-	540
NAF 2-1	20	3830	-	1000	10	4870	70	400	30	13620	470
NAF 2-2	10	2080	-	630	10	3660	80	300	10	6120	400
NAF 2-3	50	3260	-	810	10	2910	70	320	40	6200	300
CGH 1-1	30	2060	-	140	10	3700	30	5510	-	7480	400
CGH 1-2	30	2450	-	700	80	2890	40	5320	-	8370	410

Bullion Creek Formation

Harmon Bed

Sample No.	Cu	Fe	Ga	K	Li	Mg	Mn	Na	Ni	Si	Sr
KRG 1-1	0	2410	-	200	0	5090	2060	1720	-	2850	510
KRG 1-2*	0	12220	-	14210	20	8090	20	1360	-	>200000	160
KRG 1-3	0	0	-	-	0	1730	0	1610	-	3920	310
KRG 1-4*	0	3230	190	15190	110	3000	0	1430	370	>200000	180
KRG 1-5	5	2830	-	230	10	7480	590	3490	-	39210	940
KRG 1-6*	0	0	40	0	30	1740	0	1460	-	>200000	210
KRG 1-7	0	0	-	0	0	5650	50	4470	-	400	550
KRG 2-1*	0	9430	10	15000	20	4840	0	560	-	187070	30
KRG 2-2	0	1670	-	0	0	4320	60	2220	-	2970	560
KRG 2-3*	0	4720	-	10290	10	5190	0	1070	-	>200000	200
KRG 2-4	0	80	80	7100	80	4520	0	2450	10	70270	390
KRG 2-5*	0	0	410	3540	70	1720	0	1260	40	>200000	220
KRG 2-6	0	0	-	0	0	4330	0	1930	-	2330	400
KRG 3-1	0	1030	-	400	0	5360	180	3710	-	7400	590
KRG 3-2*	0	6210	-	11080	20	2600	0	5500	-	138160	160
KRG 3-3	0	12330	10	7360	90	4750	10	2600	100	280	400
KRG 3-4*	20	2080	-	3500	20	9860	220	2830	-	73610	910
KRG 3-5*	0	2150	240	15910	70	110	0	930	-	>200000	10
KRG 3-6*	0	1090	-	380	30	2910	200	1720	-	>200000	360
KRG 3-7	0	900	-	260	10	620	250	4290	-	5010	670
KRG 4-1	0	0	-	110	0	7130	180	2280	-	4420	600
KRG 4-2	0	30810	-	0	0	5270	50	2370	-	0	490
KRG 4-3*	0	4180	-	9480	20	5580	20	1430	-	>200000	340
KRG 5-1	0	0	-	50	0	6460	110	2240	-	15640	590
KRG 5-2	0	20370	-	60	0	13790	120	2230	-	0	650
KRG 5-3*	0	8900	-	18680	30	6530	900	2310	-	>200000	90
KRG 5-4	0	90	-	120	10	6990	80	2350	-	36850	650
KRG 5-5*	0	2940	-	570	20	3950	90	1290	-	184030	300
KRG 5-6	0	20	-	0	0	4100	20	3300	-	6940	450

Slope Formation

oyster lignite and oyster bed

Sample No.	Elements in ppm										
	Cu	Fe	Ga	K	Li	Mg	Mn	Na	Ni	Si	Sr
CBF 1-1*	40	19880	250	13050	40	11210	190	4350	20	187300	120
CBF 1-2	20	1100	-	460	10	3040	50	2010	-	3090	820
CBF 1-3	20	3820	-	470	10	1640	40	1370	10	4220	10
CBF 1-4*	40	17160	290	9630	20	5700	80	4870	10	193100	40
CBF 1-5*	40	30090	230	9690	30	11420	280	4930	70	174700	280
CBF 1-6*	80	5640	160	7070	30	1900	20	3480	190	115300	70

Cannonball Formation

Lower Middle Cannonball

FLS 1-1*	40	26960	210	9330	40	10580	190	3450	90	123200	250
FLS 1-2*	40	19800	260	10780	30	7760	250	7000	30	119900	4860

Sentinel Butte Formation

Beulah-Zap Bed

Sample No.	Te	U	V	Zn	P	% water	% ash
				Elements in ppm			
KRB 1-1	-	-	-	0	-	31.7	16.7
KRB 1-2	-	-	0	110	-	28.6	-
KRB 1-3	-	-	950	1040	-	29.1	9.7
KRB 1-S	-	-	-	-	-	35.3	9.2
KRB 2-1	-	-	-	270	-	28.5	6.0
KRB 2-2	-	-	100	-	-	31.1	15.6
KRB 2-3	-	-	-	20	-	31.2	8.5
KRB 2-S	-	-	150	40	-	33.3	7.0
KRB 3-1	-	-	-	160	-	30.5	5.8
KRB 3-2	-	-	20	-	-	22.7	-
KRB 3-3	-	-	-	-	-	32.2	9.2
KRB 3-S	-	-	10	-	-	20.3	13.2
KRB 4-1	-	-	-	-	-	26.4	8.1
KRB 4-2	-	-	540	190	-	20.9	12.3
KRB 4-3	-	-	-	290	-	31.0	-
KRB 4-S	-	-	-	90	-	26.5	-
KRB 5-1	-	-	-	-	-	27.7	11.6
KRB 5-2	-	-	30	140	-	25.6	13.2
KRB 5-3	-	-	190	-	-	23.7	10.5
Lehigh Bed							
HI 1-1	-	-	0	330	-	39.1	10.2
HI 1-2	-	-	0	260	-	41.6	16.6
HI 2-1	-	-	0	600	-	43.3	6.1
HI 2-2	-	-	0	110	-	39.9	19.2
HI 3-1	-	-	510	650	-	38.7	10.4
HI 3-2	-	-	-	440	-	44.1	12.4
HI 4-1	-	-	-	160	-	43.0	-
HI 5-1	-	-	-	150	-	16.8	15.8
HI 5-2	50	-	-	110	-	38.3	8.4
HI 5-3	-	-	-	240	-	46.2	15.5
Hagel Bed							
BNC TS*	-	-	130	210	-	8.5	-
BNC 1-1	-	-	10	180	-	-	11.1
BNC 1-2	-	-	-	-	-	6.4	35.3
BNC 1-3	-	-	0	40	-	9.3	9.5
BNC 1LS*	-	-	60	130	-	22.4	-
BNC 2*	-	-	220	70	-	7.1	-
BNC 2-1	-	-	20	190	-	22.8	-
BNC 2sp*	-	-	0	0	-	10.5	-
BNC 2-2	-	-	0	210	-	9.8	33.8
BNC 3-1	-	-	10	0	-	-	-
BNC 3-2	-	-	0	730	-	-	25.9
BNC 3sp*	-	-	50	90	-	-	-

Sentinel Butte Formation

Hagel Bed

Sample No.	Te	U	V	Zn	P	% water	% ash
					Elements in ppm		
BNC 3-3	-	-	0	180	-	-	-
BNC 3spb*	-	-	90	70	-	19.2	-
BNC 3-4	-	-	0	-	-	-	-
NAF 2-1	-	5	20	40	5260	-	-
NAF 2-2	-	-	5	210	3280	-	-
NAF 2-3	-	-	10	70	5900	-	-
CGH 1-1	-	-	-	150	5280	-	-
CGH 1-2	-	-	40	50	4640	-	-

Bullion Creek Formation

Harmon Bed

Sample No.	Te	U	V	Zn	P	% water	% ash
KRG 1-1	-	-	280	-	-	25.1	7.4
KRG 1-2*	-	-	20	30	-	18.2	-
KRG 1-3	-	-	-	180	-	41.8	8.8
KRG 1-4*	30	-	-	160	-	11.3	-
KRG 1-5	-	-	-	290	-	27.7	12.6
KRG 1-6*	-	-	0	-	-	14.6	-
KRG 1-7	-	-	0	-	-	43.6	-
KRG 2-1*	-	-	70	170	-	15.5	-
KRG 2-2	-	-	10	250	-	18.2	-
KRG 2-3*	-	-	340	800	-	5.3	-
KRG 2-4	-	-	0	20	-	33.9	30.8
KRG 2-5*	120	-	0	330	-	17.9	-
KRG 2-6	-	-	-	280	-	61.5	-
KRG 3-1	-	-	-	890	-	54.4	-
KRG 3-2*	-	-	70	110	-	53.8	-
KRG 3-3	-	-	-	20	-	35.4	-
KRG 3-4*	-	-	-	-	-	42.5	-
KRG 3-5*	-	-	60	210	-	22.5	-
KRG 3-6*	-	-	320	-	-	32.0	-
KRG 3-7	-	-	-	120	-	-	14.6
KRG 4-1	-	-	-	80	-	38.6	12.8
KRG 4-2	-	-	-	140	-	36.7	-
KRG 4-3*	-	-	20	40	-	-	-
KRG 5-1	-	-	110	70	-	63.5	8.9
KRG 5-2	-	-	20	110	-	26.2	8.3
KRG 5-3*	-	-	700	-	-	14.4	-
KRG 5-4	-	-	0	-	-	39.2	17.9
KRG 5-5*	-	-	190	-	-	-	-
KRG 5-6	-	-	-	20	-	43.0	-

Slope Formation

oyster lignite and oyster bed

Sample No.	Te	U	V	Zn	P	% water	% ash
				Elements in ppm			
CBF 1-1*	-	20	90	250	130	-	-
CBF 1-2	-	-	10	20	4960	-	-
CBF 1-3	-	-	10	70	3820	-	-
CBF 1-4*	-	380	70	150	230	-	-
CBF 1-5*	-	-	100	600	-	-	-
CBF 1-6*	-	110	30	1560	1060	-	-

Cannonball Formation

Lower Middle Cannonball

FLS 1-1*	-	-	110	190	-	-	-
FLS 1-2*	-	50	100	240	-	-	-

Appendix 2. Chemical analysis of North Dakota groundwater: after Groenewold and others 1979.

Table 6. Chemical Analyses of North Dakota Groundwater.

Location	146-82-21* CCC	146-82-29* DAA	146-82-21' CCC	146-82-29' DAA
Concentration in mg/L				
Ca	66	69.6	42.6	36.2
Mg	38	39.9	18.3	20.4
Na	39	9.5	17.4	66.2
K	5.9	4.7	3.6	5.9
HCO_3	417	418.5	310	388
Cl	12.5	1.2	19.1	1.0
SO_4	159	45.1	21.7	20.6
Concentration in g/L				
Fe	67	266	16.0	4400
Mn	659	512	303	113
NO_3	0.1	1.2	6.1	0.1
F	0.29	0.2	0.2	0.14
Cu	4	9.1	9.8	3.8
Cd	0.32	1.1	0.65	1.2
Pb	2.1	11.2	4.6	2.8

* Indicates water sample was taken from the Kinneman Creek Interval.
' Indicates water sample was taken from the Hagel Bed.

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