ELEMENTAL DISTRIBUTION AND ASSOCIATION WITH INORGANIC AND ORGANIC COMPONENTS IN TWO NORTH DAKOTA LIGNITES

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Introduction

The associations of major, minor, and trace elements in lignite-bearing strata of the Fort Union Region present a challenge in understanding their geochemical relationships and history. In an earlier work (1), the spatial patterns of elemental distribution within a lignite-bearing sequence were examined and were related to factors of accumulation of vast amounts of plant materials and to the depositional and post-depositional influx of inorganic matter. Lignite-bearing sediments, including the lignite, lignite overburden, and underclay, were sampled from two beds, the Kinneman Creek and the Beulah-Zap, which are part of the Sentinel Butte Formation of North Dakota. These samples were examined to determine the spatial patterns of elemental distribution within the lignite seam, modes of elemental occurrence, and organic/inorganic affinities of the inorganic constituents.

The inorganic constituents within lignites from the Fort Union Region have been classified as being very heterogeneous (2), which leads some investigators to believe that the study of geochemical relationships is futile. The modes of occurrences of the elements are generally similar from one mine to another within the Fort Union Region lignites (3). The inorganic matter in the lignites is distributed as adsorbed ions on the organic acid groups, coordinated species, detrital minerals, and authigenic minerals. The distribution of elements is determined by natural processes, and, therefore, is expected to be systematic even though complex.

The methods to qualitatively identify the interrelationships of major, minor, and trace elements include examining the spatial patterns of distribution of elements within a stratigraphic sequence (1), consideration of results of chemical fractionation procedures (4), and evaluation of organic/inorganic affinities (5,6). The spatial pattern of elemental distribution was correlated with the chemical fractionation behavior, organic/inorganic affinities, and ionic potentials of elements to infer the association or combination of associations an element may have within these coals.

Methods and Procedures

The samples were collected from freshly exposed faces within open pit mines. The lignite, lignite overburden, and underclay were collected from two pits at the Beulah Mine where lignite is mined from the Beulah-Zap seam. Samples were also collected from the Kinneman Creek seam in the Center mine. The sample collection procedures have been summarized by Karner (7) and Benson (8). Bulk channel samples were also collected and homogenized to provide large quantities for additional experiments.

The lignite samples collected at various intervals within the stratigraphic sequence were subjected to the following analyses: proximate, ultimate, heating value, ash analysis, and trace element analysis by neutron activation analysis (NAA) (9) and x-ray fluorescence (10). Minerals in the coal and the associated sediments were determined by x-ray diffraction and by scanning electron microscopy and electron microprobe analysis. A split from the bulk sample was examined by chemical

fractionation to selectively extract inorganic constituents based on how they are bound in the coal. Briefly, the chemical fractionation procedure involves extracting the coal with 1M ammonium acetate to remove soluble and ion-exchangeable inorganic components. The coal is subsequently extracted with 1M hydrochloric acid to remove elements present as carbonates, oxides, or coordinated species. The extracts and residues from the chemical fractionation procedure are analyzed by a combination of NAA, XRF, inductively coupled argon plasma (ICAP), and atomic absorption spectroscopy (AA).

Results and Discussion

The major, minor, and trace element determinations along with locations within the seams and lithology of the stratigraphic sequence are summarized in Tables I and II for the Beulah coals. The data from Center Mine stratigraphic sequence was summarized in a previous report by Karner and others (1).

In previous work (1), the spatial distribution of elemental constituents has been described as fitting into several patterns: 1) concentration at one or both margins, 2) even distribution, and 3) regular patterns. The various ways inorganic constituents accumulated in the lignite during and after deposition affect where certain elements will concentrate within the seam. The detrital constituents carried in by wind and water will most likely be enriched near the margins of the coal seam. Included in this group of inorganic constituents are clay minerals, quartz, and volcanic ash. Solutions containing ions flowing through the lignite can exchange with the coal matrix and precipitate as stable authigenic phases. Inorganic constituents are also present in the original plant material that was deposited. Even patterns of elemental distribution are characteristic of organically bound elements. Irregular distribution patterns are characteristic of concentrated occurrences of authigenic minerals.

Table I includes data from two seams within the south Beulah mine. Table II summarizes the data from a high-sodium pit (Orange Pit) of the Beulah mine. The Center mine data used in this work was reported by Karner and others (1).

In this study, the spatial patterns of enrichment and depletion of major, minor, and trace elements have been expanded to include four categories: 1) even distribution, 2) enrichment at margins (top, bottom, or both), 3) enrichment at the center of the seam, and 4) irregular. The patterns of enrichment and depletion are listed in Table III for Beulah and Center mine lignite seams.

The bulk coals were subjected to chemical fractionation analysis (3) which can be used to categorize how a particular element is associated in the coal. The elemental associations within the coal were divided into three categories: 1) ion-exchangeable, 2) acid-soluble, and 3) residual. The elements are associated in the coal in one or more of the groups described above. The categories for the elements are listed in Table III.

The organic and inorganic affinities of elemental constituents have been determined by a number of investigators (5,6). The relationship between the concentration of an element in moisture-free coal and the ash content can be used as a guide to the affinity of that element for, or incorporation in, the mineral matter or the carbonaceous material. If the concentration of an element increases with increasing ash content that element may be characterized as being associated with the inorganic species that form ash, or in other words may be said to have an inorganic affinity. If the concentration shows no correlation with ash content, that element may be said to have an organic affinity. Linear least squares correlation coefficients were calculated for the concentrations of the elements versus the ash content. For example, organic and inorganic affinities for elements from the Center mine indicate the following affinities. Seven elements - Na, Ca, Mn, Br, Sr, Y, and Ba - had correlation coefficients below 0.200 and thus show organic affinity in this suite of samples. An additional seven elements - Mg, K, Cu, As, Rb, Ce, and Eu - had correlation coefficients ranging from 0.201 to 0.600

and may be associated with both the carbonaceous and mineral portions of the coal. The remaining 24 elements show inorganic affinity.

The ionic potentials of all the elements, Z/r, where Z is the ionic charge and r is the ionic radius, are summarized in Table III. The ionic potentials of elements have a large effect on the association of the element in mineral-forming processes (13). Elements having low ionic potential ($Z/r < 3$), such as sodium, magnesium, and calcium, associate as hydrated cations. Insoluble hydrolysates have ionic potential of $3 < Z/r < 12$, which include, for example, the elements aluminum, silica, and titanium.

The elements displaying an even distribution within the coal seams have the following characteristics: 1) ion-exchangeable, 2) organic affinity or both organic and inorganic, and 3) ionic potential less than 3. The elements that are included in this group are Na, Mg, Ca, Mn, Sr, and Ba. Slight variations in distribution patterns and chemical fractionation behavior may be indicated; these generalizations were made on the basis of average trends. The elements showing enrichment of the margins in the lignite seams display the following characteristics: 1) chemical fractionation suggests association with the acid soluble and residue portions or, in some cases, distribution in all three groups, 2) inorganic affinity, and 3) ionic potential $3 < Z/r < 12$. The elements that have these characteristics include Al, Si, Cl, K, Sc, Ti, V, Cr, Co, Br, Zr, Ra, Cs, La, Ce, Sm, Eu, Yb, Th, and U. These elements are primarily associated with detrital constituents. The elements that have a random or irregular distribution within the coal seams, for the most part, have the following characteristics: 1) chemical fractionation behavior which suggests that the elements are insoluble and remain in the residue, 2) inorganic affinity, and 3) formation by authigenic mineralization. The elements included in this group are Fe, Ni, Zn, As, Se, Cd, and Sb. The irregular distribution of these elements is the result of syngenetic and epigenetic mineralization in the formation of sulfides. All of these elements have chalcophilic characteristics.

The possible associations of the elements included in this study are given in Table IV which summarizes distribution patterns, chemical fractionation behavior, organic and inorganic affinities, and ionic potential.

Acknowledgment

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Table I. Elemental Analysis of a Stratigraphic Sequence Containing Two Lignite Seams at the Beulah Mine, North Dakota, part per million unless otherwise indicated, dry coal basis

ID	Lithology	Height, m*	% Ash[1]	Na	Mg	Al	Si**	P**	S**	Cl	K	Ca	Sc	Ti
3-1-A	Underclay	-0.3	--	1964	10364	84699	321178	436	2803	750	10062	3398	11.7	3574
3-2-A	Lignite	0.0	17.0	7767	722	8394	19572	679	17182	100	530	6888	11.9	829
3-3-A	Lignite	0.1	8.47	14348	678	1935	5068	332	10142	8	500	6101	2.1	207
3-4-A	Lignite	0.5	7.30	3479	642	2584	3139	286	8302	100	500	7249	4.9	100
3-5-A	Lignite	0.9	22.20	753	1598	27082	34145	387	13513	100	1908	2191	10.6	438
3-6-A	Clay	1.0	--	1821	13741	113270	298737	0	8009	750	13269	3720	15.0	4211
3-7-A	Clay	1.6	--	2159	12454	111945	307620	0	3204	750	13585	2559	16.1	4560
2-1-A	Lignite	1.7	10.80	3991	671	9428	10956	282	8823	16	500	7062	10.8	125
2-2-A	Lignite	2.1	7.20	7497	707	5192	3971	471	7698	100	500	5281	0.9	119
2-3-A	Lignite	2.6	7.60	9482	717	4542	5045	364	8522	100	713	6206	0.8	140
2-5-A	Lignite	2.9	7.10	6598	731	3431	3086	0	8046	100	500	6031	1.7	226
2-6-A	Lignite	3.3	7.40	6988	571	3886	4981	355	9720	100	500	3973	0.5	59
2-7-A	Lignite	3.4	5.60	6692	564	2664	11048	122	3453	24	500	4615	0.3	100
2-8-A	Lignite	3.6	15.28	6583	3386	7312	10072	800	20071	100	500	8261	0.8	502
2-10-A	Lignite	4.2	6.40	5907	472	4308	5475	223	6561	100	500	12635	2.4	77
2-11-A	Lignite	4.8	12.0	5631	1242	7557	12398	366	10476	100	500	8927	6.1	121
2-13-A	Top of Lignite	5.1	9.10	5561	914	5937	5360	436	10823	100	500	6423	11.5	196
2-14-A	Clay	5.2	--	3518	16012	118373	290790	436	4405	750	16692	4520	15.5	3647
2-15-A	Clay	6.3	--	4385	14031	88995	293127	0	1201	750	15654	4983	13.9	3630
2-16-A	Silt	7.3	--	3440	14605	88403	288453	0	2803	750	9177	2880	12.0	3082
2-17-A	Chert	7.5	--	464	3800	13052	56100	0	9211	1250	1000	1709	12.1	1000
2-18-A	Sandstone	7.8	--	4084	9826	49621	250117	0	2803	750	7608	27085	8.3	2426
2-19-A	Clay	8.9	--	1771	14771	81163	287518	436	4405	750	4162	6110	14.5	4017

Table I. Elemental Analysis of a Stratigraphic Sequence Containing Two Lignite Seams at the Beulah Mine, North Dakota, part per million unless otherwise indicated, dry coal basis (Continued)

ID	Lithology	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Ru	Cd	Sb
3-1-A	Underclay	99	66	177	24853	5.9	>25	150	66	2.51	0.20	1.10	86.00	2.50	0.65
3-2-A	Lignite	66	37	44	15358	5.5	>20	58	19	21.8	1.42	1.70	12.00	1.00	4.61
3-3-A	Lignite	4	5	42	6580	4.0	9	10	25	22.5	0.69	4.98	5.00	1.00	0.05
3-4-A	Lignite	6	6.5	40	2561	1.7	>25	11	25	2.17	0.55	1.69	5.00	1.00	0.04
3-5-A	Lignite	148	39	57	26129	13.0	90	25	9	374	4.28	3.28	16.00	1.00	5.74
3-6-A	Clay	205	91	96	15258	18.0	95	150	30	24.1	0.20	0.77	108.00	1.00	1.78
3-7-A	Clay	181	94	98	11929	2.7	>25	150	94	6.66	4.12	0.76	126.00	2.50	1.35
2-1-A	Lignite	25	16	36	3100	1.9	>25	52	33	11.5	0.43	1.73	3.26	1.20	1.33
2-2-A	Lignite	3	2.8	41	1502	1.2	>25	25	8	3.55	0.10	1.18	5.00	1.00	0.12
2-3-A	Lignite	2	2.9	46	1467	1.1	>25	25	25	5.18	0.52	1.25	5.00	1.00	1.28
2-5-A	Lignite	5	3.1	46	1489	0.7	>25	48	0	2.22	1.00	1.29	5.00	1.00	0.04
2-6-A	Lignite	3	2.5	31	6193	1.0	>25	25	30	31.5	0.39	0.45	1.42	0.65	0.01
2-7-A	Lignite	1	1.3	36	1035	1.1	>25	25	25	0.66	0.32	0.53	5.00	1.00	0.03
2-8-A	Lignite	1	4.4	58	2928	0.6	>25	25	25	4.37	0.59	0.46	5.00	1.00	0.21
2-10-A	Lignite	6	8.6	27	8711	5.2	>25	25	20	21.2	1.27	0.55	5.18	1.00	0.34
2-11-A	Lignite	5	6.5	79	2821	1.5	7	25	19	3.45	0.56	1.24	5.00	1.00	0.29
2-13-A	Top of Lignite	34	9.3	70	2405	3.0	10	10	25	7.03	0.20	1.16	5.00	1.00	0.60
2-14-A	Clay	177	81	212	22282	17.0	121	150	30	14.8	0.20	0.50	115.00	2.50	1.52
2-15-A	Clay	144	64	735	27448	12.0	15	150	30	2.63	0.20	0.50	90.00	2.50	1.04
2-16-A	Silt	136	56	1000	28123	11.0	>20	150	30	2.75	0.20	0.89	77.80	2.50	0.63
2-17-A	Chert	73	18.9	8046	273475	2.7	>25	300	200	0.50	0.20	0.89	10.00	2.50	0.19
2-18-A	Sandstone	73	55	611	15853	8.6	>20	150	52	6.09	0.54	0.25	50.64	2.50	0.49
2-19-A	Clay	134	68	738	35592	12.0	>20	150	30	2.48	3.22	1.12	87.00	2.50	0.73

Table I. Elemental Analysis of a Stratigraphic Sequence Containing Two Lignite Seams at the Beulah Mine, North Dakota, part per million unless otherwise indicated, dry coal basis (Continued)

ID	Lithology	Cs	Ba	La	Ce	Sm	Eu	Yb	U
3-1-A	Underclay	4.96	786	32.18	48.66	2.51	1.36	1.59	1.91
3-2-A	Lignite	5.50	746	8.07	19.81	1.31	0.71	2.22	2.09
3-3-A	Lignite	0.02	756	1.29	8.46	1.42	0.36	1.37	0.50
3-4-A	Lignite	0.05	1114	2.95	9.21	1.04	0.46	1.62	0.23
3-5-A	Lignite	4.56	683	45.36	71.90	8.29	1.95	1.38	3.32
3-6-A	Clay	8.10	676	45.36	41.00	2.45	1.13	1.20	3.32
3-7-A	Clay	10.00	644	36.00	45.32	2.58	0.98	1.60	2.34
2-1-A	Lignite	1.49	1005	2.49	8.32	1.05	0.49	1.41	1.86
2-2-A	Lignite	0.05	988	9.75	14.35	0.52	0.21	0.40	0.41
2-3-A	Lignite	0.05	1158	3.75	6.98	0.35	0.12	0.38	0.36
2-5-A	Lignite	0.05	1284	11.36	16.00	0.43	0.11	0.41	0.56
2-6-A	Lignite	0.16	844	0.84	1.00	0.17	0.07	0.11	0.23
2-7-A	Lignite	0.12	1041	0.58	1.66	0.17	0.06	0.07	0.10
2-8-A	Lignite	0.05	21	2.07	4.08	0.42	0.26	0.63	0.50
2-10-A	Lignite	1.15	3045	7.47	39.27	0.63	0.55	0.42	0.24
2-11-A	Lignite	0.34	1749	4.06	9.69	0.81	0.37	1.11	0.90
2-13-A	Top of Lignite	0.02	226	3.52	6.77	0.82	0.43	1.39	2.08
2-14-A	Clay	8.50	811	36.20	52.50	2.73	1.11	1.72	2.88
2-15-A	Clay	5.31	813	35.00	45.61	3.28	1.30	1.83	1.82
2-16-A	Silt	4.35	613	28.00	39.00	2.54	1.06	1.17	2.30
2-17-A	Chert	0.40	274	11.60	10.00	1.27	0.40	1.09	0.20
2-18-A	Sandstone	3.00	725	26.70	37.00	2.65	1.18	1.26	1.54
2-19-A	Clay	5.28	851	25.60	46.70	2.63	1.43	1.81	1.75

*Height from base of first seam.
**Determined by x-ray fluorescence.
†Ash on a moisture-free basis

Table II. Elemental Analysis of a Stratigraphic Sequence Containing One Lignite Seam from the Orange Pit of the Beulah Mine, North Dakota, ppm (dry basis)

ID	Lithology	Height, m*	Ash, %	Na	Mg	Al	Si**	S**	Cl	K	Ca	Sc	Ti	V
B-1	Lignite	-0.5	7.1	7041	1041	2824	10800	65890	44.3	500	7317	2.16	132	3.02
B-2	Lignite	0.00	6.8	5178	1004	3107	12950	46240	43.9	500	9072	0.64	132	2.84
B-3	Lignite	0.50	6.7	5833	1150	3472	7940	50030	52.8	500	8891	0.57	138	2.73
B-4	Lignite	1.00	6.8	6018	1043	2675	16760	51530	41.8	500	7803	0.57	144	2.22
B-5	Lignite	1.50	13.0	5826	3526	6710	12580	65160	132.7	500	8016	0.38	326	5.84
B-6	Lignite	2.00	6.9	5313	1238	2793	39940	59750	49.2	500	7828	0.36	150	2.20
B-7	Lignite	2.50	8.5	6169	1292	4348	93000	64240	63.2	500	11998	0.43	162	2.50
B-8	Lignite	3.00	15.7	6278	1449	5869	44510	64020	70.9	500	10872	0.48	167	2.12
B-9	Lignite	3.50	10.4	5096	1483	7929	104700	56470	54.1	500	11876	1.05	226	4.85
BR-1	Overburden	3.60	--	2246	15718	91958	275900	3130	750	9724	7094	15	2390	136.00
BR-3	Overburden	4.14	--	2773	13226	89901	259700	1100	750	14994	6673	18	4256	165.00
BR-5	Overburden	4.80	--	3098	15480	97158	281400	497	100	8653	7342	16	3880	158.00
BR-6	Overburden	5.10	--	2619	15475	84893	288900	1480	100	10800	6197	5.1	3674	134.00
BR-9	Overburden	6.10	--	2389	16774	88663	294000	1350	750	14971	9553	15.8	4557	142.00
BR-11	Overburden	6.70	--	2082	9982	51610	187700	3220	750	14971	9465	18.7	2760	119.00
BR-13	Overburden	7.30	--	2842	12634	66743	277400	12710	750	6441	12042	8.97	3796	80.1
BR-13A	Overburden	7.35	--	3028	14339	78427	284900	840	150	8994	123401	12.9	4131	117.0
BR-18	Overburden	8.90	--	3028	12471	75153	286200	1070	750	8994	13916	14.0	4360	117.0
BR-19	Overburden	9.20	--	2863	12793	78030	290700	<100	750	10006	14862	14.0	3451	117.0

Table II. Elemental Analysis of a Stratigraphic Sequence Containing One Lignite Seam from the Orange Pit of the Beulah Mine, North Dakota, ppm (dry basis) (Continued)

ID	Lithology	Cr	Mn	Fe	Co	Ni	Cu**	Zn	As	Se	Br	Sr**	Y**	Zr**
B-1	Lignite	2.24	22	5147	1.68	5.75	53	12.62	10.67	0.05	1.62	360	6	8
B-2	Lignite	1.62	28	3261	0.75	10.23	33	5.48	3.90	0.40	1.40	445	6	11
B-3	Lignite	1.41	29	3462	0.70	10.71	53	6.08	3.52	0.39	1.49	480	4	13
B-4	Lignite	1.37	28	3289	0.39	13.17	58	4.78	3.34	0.50	1.04	410	2	9
B-5	Lignite	2.08	136	22202	0.37	5.00	23	25.00	27.18	0.91	0.84	320	2	<5
B-6	Lignite	1.89	37	3308	0.80	15.34	64	25.00	5.24	0.54	0.99	360	2	8
B-7	Lignite	2.30	33	1706	0.59	11.36	59	3.46	3.55	0.49	0.55	520	2	15
B-8	Lignite	2.60	48	30530	0.69	15.66	30	25.00	39.17	0.79	0.81	330	2	10
B-9	Lignite	3.51	47	2897	0.70	9.36	62	8.57	7.85	0.36	0.92	520	6	17
BR-1	Overburden	86.2	611	36878	14.02	28.88	86	30.00	12.66	1.56	0.92	262	26	112
BR-3	Overburden	93.2	2092	50756	13.57	72.84	73	30.00	2.50	0.57	1.05	223	28	94
BR-5	Overburden	92.4	467	30865	10.97	22.93	87	30.00	5.25	1.40	0.27	239	26	109
BR-6	Overburden	32.4	979	14308	3.99	95.69	81	25.00	6.23	0.42	0.55	234	31	126
BR-9	Overburden	88.0	885	39106	13.78	63.45	84	30.00	3.52	1.25	0.92	230	25	108
BR-11	Overburden	72.3	3542	147377	11.26	39.66	46	30.00	2.50	0.20	1.07	104	18	66
BR-13	Overburden	63.0	308	36902	10.14	50.09	64	30.00	27.16	1.01	1.41	255	22	169
BR-13A	Overburden	78.7	424	26437	9.95	20.00	71	30.00	5.01	0.84	1.46	274	28	165
BR-18	Overburden	90.8	670	31472	11.33	45.09	80	30.00	5.01	0.53	1.46	285	25	131
BR-19	Overburden	90.8	435	28566	11.44	36.64	73	30.00	3.34	1.08	1.08	265	27	164

Table II. Elemental Analysis of a Stratigraphic Sequence Containing One Lignite Seam from the Orange Pit of the Beulah Mine, North Dakota, ppm (dry basis) (Continued)

ID	Lithology	Ru	Ag	Cd	Sb	Cs	Ba	La	Ce	Sm	Eu	Yb	Th	U
B-1	Lignite	2.00	0.15	5.00	0.01	0.01	714	7.84	8.30	0.53	0.11	0.36	0.57	0.40
B-2	Lignite	1.37	0.53	5.00	0.04	0.04	917	3.30	5.61	0.49	0.09	0.28	0.75	0.24
B-3	Lignite	2.00	0.48	5.00	0.10	0.03	943	3.62	6.39	0.43	0.06	0.24	0.81	0.23
8-4	Lignite	2.00	0.79	0.34	0.10	0.03	844	3.24	4.92	0.24	0.05	0.09	0.83	0.75
B-5	Lignite	2.00	0.05	1.10	0.07	0.01	930	12.78	13.14	0.34	0.03	0.01	0.78	0.40
B-6	Lignite	2.00	0.53	0.19	0.01	0.03	704	0.98	2.42	0.26	0.01	0.06	0.49	0.31
B-7	Lignite	2.00	0.75	5.00	0.06	0.03	1138	1.52	3.18	0.31	0.05	0.09	1.01	0.56
B-8	Lignite	2.00	0.37	1.87	0.04	0.05	1242	2.20	9.98	0.28	0.07	0.08	1.12	1.26
8-9	Lignite	2.00	0.15	5.00	0.22	0.08	720	2.38	4.97	0.55	0.12	0.38	1.75	0.99
BR-1	Overburden	114.48	0.08	2.50	0.44	6.57	1075	12.19	63.46	1.17	1.30	1.07	10.37	1.51
BR-3	Overburden	131.48	0.08	2.50	0.50	7.56	732	14.58	67.26	1.23	1.29	1.77	10.14	1.03
BR-5	Overburden	164.19	0.08	2.50	0.49	7.53	685	13.82	61.24	1.25	1.12	1.33	9.50	0.80
BR-6	Overburden	35.87	0.49	5.00	0.51	0.79	285	12.70	18.50	1.26	0.31	0.73	3.26	0.76
8R-9	Overburden	127.44	0.08	2.50	0.38	6.38	567	12.31	61.70	1.12	1.33	1.59	9.39	1.09
BR-11	Overburden	77.75	0.00	2.50	0.69	4.50	401	16.88	82.93	1.59	1.37	1.46	7.02	2.99
BR-13	Overburden	72.16	0.08	2.50	0.40	3.39	444	12.36	69.63	1.15	1.26	1.15	7.84	1.12
BR-13A	Overburden	108.76	20.08	2.50	0.38	4.53	619	14.57	63.00	1.28	1.35	1.50	9.35	0.80
BR-18	Overburden	101.83	0.08	2.50	0.38	5.10	567	14.00	63.00	1.35	1.43	1.52	9.45	1.27
BR-19	Overburden	94.82	0.08	2.50	0.30	4.69	511	13.55	64.46	1.22	1.46	1.71	10.18	1.13

*Height from base of first seam.
**Determined by x-ray fluorescence.
† Ash on a moisture-free basis

Table III. Qualitative Geochemical Relationships Between Geochemical Properties and Elemental Distribution Within Seams

	Distribution Within Lignite Seams at the Beulah Mine					Distribution Within Lignite Seam at the Center Mine			
		Beulah							
	Beulah Orange Pit	Upper Seam	Lower Seam	Chemical Fractionation Behavior	Affinity	Center	Chemical Fractionation Behavior*	Affinity	Ionic Potential Z/r
Na	E	E	CE	IE	Organic	E	IE	Organic	1.0
Mg	E	E	E	IE	NC	E	IE>>AS	NC	3.0
Al	T-MA	MA	B-MA	AS, RS	Inorganic	MA	AS, RS	Inorganic	5.9
Si	T-MA	IR	E	RS	Inorganic	MA	RS	Inorganic	9.5
P	ND	IR	B-MA	ND	Inorganic	IR	ND	Inorganic	14.3
S	IR	IR	MA	RS, IE	Organic	MA	RS, IE	Organic	17.1
Cl	E	E	E	ND	NC	B-MA	ND	Inorganic	
K	E	E	E	RS, AS	Inorganic	B-MA	IE, AS, RS	Inorganic	0.13
Ca	E	CE	E	IE, AS	NC	E	IE, AS	NC	2.0
Sc	MA	MA	MA	RS, AS	NC	MA	AS, RS	Inorganic	3.7
Ti	T-MA	IR	B-MA	RS	Inorganic	B-MA	RS	Inorganic	5.9
V	E	MA	B-MA	AS	NC	B-MA	AS, RS	Inorganic	4.0
Cr	MA	MA	B-MA	RS	Inorganic	B-MA	RS	Inorganic	4.8
Mn	E	T-MA	T-MA	AS, IE	NC	E	AS, IE	NC	2.5/6.7
Fe	IR	IR	B-MA	RS, AS	Inorganic	MA	AS	Inorganic	2.7/4.7
Co	B-MA	ND	ND	AS, RS	Inorganic	MA	AS, RS	Inorganic	2.8
Ni	IR	E	MA	RS	Inorganic	MA	RS	Inorganic	3.0
Cu	IR	E	B-MA	ND	Inorganic	B-MA	RS	Inorganic	1.0/2.8
Zn	IR	ND	ND	RS	Inorganic	MA	ND	Inorganic	.88/2.7
Ge	ND	ND	ND	ND	ND	B-MA	ND	ND	2.7/7.5
As	IR	IR	IR	RS	Inorganic	MA	RS	NC	10.8
Se	CE	IR	B-MA	RS	Inorganic	B-MA	RS, IE	Inorganic	14.3
Br	B-MA	MA	CE	ND	NC	ND	ND	Organic	
Rb	ND	ND	ND	ND	ND	IR	RS, AS	ND	0.68
Sr	E	ND	ND	IE	Organic	E	IE	Organic	1.8
Y	MA	ND	ND	ND	ND	IR	ND	ND	3.4
Zr	T-MA	ND	ND	RS	ND	MA	ND	Inorganic	5.1
Ru	E	E	B-MA	ND	Inorganic	B-MA	ND	Inorganic	6.0
Ag	IR	ND	ND	ND	ND	MA	ND	Inorganic	2.2
Cd	ND	E	E	RS	NC	IR	ND	Inorganic	.87/2.1
Sb	IR	B-MA	B-MA	RS	Inorganic	B-MA	AS, RS	Inorganic	4.0
Cs	T-MA	B-MA	B-MA	RS	Inorganic	B-MA	RS	Inorganic	0.6
Ba	E	T-MA	T-MA	IE, AS	NC	MA	IE, AS	NC	1.5
La	B-MA	IR	MA	AS, RS	Inorganic	B-MA	AS, RS	Inorganic	2.6
Ce	B-MA	IR	B-MA	AS, RS	Inorganic	MA	AS, RS	NC	2.9
Sm	MA	MA	E	AS, RS	Inorganic	MA	AS	Inorganic	3.1
Eu	MA	MA	MA	AS, RS	Inorganic	MA	AS	NC	3.2
Yb	MA	MA	MA	AS, RS	NC	MA		Inorganic	
Th	T-MA	MA	B-MA	RS	Inorganic	MA	RS	Inorganic	3.9
U	T-MA	MA	B-MA	AS, RS	Inorganic	MA	AS, RS	Inorganic	4.2

Patterns of Distribution

E - Even Distribution
MA - Enrichment at both margin
T-MA - Enrichment at top margin
B-MA - Enrichment at bottom margin
CE - Enrichment at the center of the seam
IR - Irregular

*Chemical Fractionation Behavior

IE - Ion-exchangeable
AS - Acid soluble
RS - Remains in the residue
NC - No Correlation
ND - Not Determined

Table IV. Association of Elements in North Dakota Lignites

Element		Possible Association
Na	-	Organically bound
Mg	-	Organically bound, carbonates
Al	-	Clay minerals, possibly hydroxide or coordinated
Si	-	Clay minerals, quartz
P	-	Organically bound, phosphates*, associated with rare earth elements
S	-	Sulfides, sulfates, organically bound
Cl	-	Inorganic association
K	-	Associated with illite and other k-bearing minerals, organically bound
Ca	-	Organically bound, carbonates
Sc	-	Inorganic association, clay minerals
Ti	-	Rutile, associated with quartz
V	-	Possibly has both an organic and inorganic association
Cr	-	Totally an inorganic association
Mn	-	Organically bound, carbonate minerals
Fe	-	Oxides, hydroxides, sulfides
Co	-	Inorganic association, possibly sulfides
Ni	-	Inorganic association, possibly sulfides
Zn	-	Inorganic association, possible sulfides
As	-	Inorganic association, possible sulfides
Se	-	Inorganic association, possibly sulfides
Br	-	May have an organic association
Rb	-	Organically bound
Sr	-	Organically bound
Y	-	Inorganic association, possibly carbonates
Zr	-	Zircon
Ru	-	Inorganic
Ag	-	Inorganic, possibly sulfides
Cd	-	Inorganic, possibly sulfides
Ba	-	Organic, sulfates
La	-	Detrital inorganic, phosphates*
Ce	-	Detrital inorganic, phosphates*
Sm	-	Detrital inorganic
Eu	-	Detrital inorganic
Yb	-	Detrital inorganic
Th	-	Detrital inorganic
U	-	Detrital inorganic

*Monazite has been found in Beulah lignite samples (12).