The Occurrence of Minor Elements in Ash of Low-Rank Coal From Texas Colorado, North Dakota and South Dakota

GEOLOGICAL SURVEY BULLETIN 1036-H

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DEPARTMENT OF THE INTERIOR
March 3, 1849

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By MAURICE DEUL *and* C. S. ANNELL

A CONTRIBUTION TO GEOCHEMISTRY

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A CONTRIBUTION TO GEOCHEMISTRY

THE OCCURRENCE OF MINOR ELEMENTS IN ASH OF LOW-RANK COAL FROM TEXAS, COLORADO, NORTH DAKOTA, AND SOUTH DAKOTA

By Maurice Deul and C. S. Annell

ABSTRACT

The distribution of 27 minor elements in the ash of 319 samples of low-rank coal from five localities was studied to determine whether any elements were correlated with uranium in the coal and also whether any elements occurred in amounts large enough to be of commercial importance.

The coal samples were ashed in a muffle furnace at 800°C, and semiquantitative spectrographic analyses were made of six channel samples to establish analytical control on ash of this type. The uranium was determined chemically by a fluorimetric method.

None of the coal shows any general enrichment of minor elements over coal from any other area. Boron, barium, and strontium are enriched in all the ash samples analyzed. A correlation between uranium and molybdenum exists only for the coal from the Dakotas where enrichment from ground water has been postulated. No other correlation is apparent. Sufficient data for 18 minor elements permits a graphic comparison of the coal from the five localities. Histograms show high concentrations of tin, copper, zirconium, boron, barium, and strontium in the coal from Milam County, Tex.

INTRODUCTION

A study of uranium-bearing coal is being conducted by the U. S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission. Suites of coal samples from many localities have been analyzed for uranium and ash content. From them, five suites of samples from five localities were selected for spectrographic analysis for minor elements. This was done to determine whether any elements were correlated with uranium in the coal and also whether any elements occurred in amounts large enough to be of commercial importance.

This report is a compendium on the minor elements found in the ash of some low-rank coal. A complete coverage of the literature on minor elements in coal ash is not within the scope of this report. Reference is made to the encyclopedic work of Gibson and Selvig (1944), Goldschmidt (1935, 1937, and 1954), Headlee and Hunter (1953), and Butler (1953); their work, and that of many others, has been chiefly concerned with higher-rank coal. Salmi (1950) has reported on the content of 10 minor elements in the ash of 50 samples of peat; his data can not readily be compared to the data for the ash of low-rank coal because the changes in the minor-element content of the peat reflect the composition of the mineral soil and bedrock in the neighborhood of the bogs.

Low-rank coal has not generally been studied in as much detail as has bituminous coal, and consequently most compilations of coal and coal-ash analyses make little or no reference to the lower-rank varieties, especially lignite. Gibson and Selvig (1944, p. 5–6) reported only two complete analyses of lignite ash. Most of the ash samples analyzed for this report were obtained from cored coal. The lignite from North Dakota and South Dakota and the subbituminous coal from Colorado were sampled in divisions ranging from 4 to about 12 inches in thickness. The thickness was controlled by coal petrographic factors. Each lignite sample from Texas was a split of an entire core; bed thicknesses ranged from 2.5 to 19 feet. For this report 6 complete chemical analyses were made of lignite ash, and 284 samples of lignite and 35 samples of subbituminous coal ash were analyzed spectrographically.

Many analyses for one or more elements occurring in coal-ash samples are contained in the literature, and complete coal-ash analyses for commercial-grade coal are commonly made (Selvig and Gibson, 1945), but complete spectrographic analyses for minor elements in low-rank coal are lacking.

SAMPLES

Lignite from Harding County, S. Dak., occurs in the Ludlow member of the Fort Union formation of Paleocene age. Of the 151 samples taken in Harding County, six were from channels and 145 were from eight cored holes. Lignite from Bowman County, N. Dak., occurs in the Tongue River member of the Fort Union formation. All 26 samples from this county were taken from four cored holes. The lignite from Perkins County, S. Dak., also occurs in the Tongue River member of the Fort Union formation. All 59 samples from this county came from five cored holes. Subbituminous coal from Jefferson County, Colo., occurs in the Laramie formation of Late Cretaceous age. All 35 samples from Jefferson County were from three cored holes. Lignite from Milam County, Tex., occurs in the Wilcox formation of early Eocene age. Each of the 48 samples from Milam County represents an entire coal core.

Four samples from McKenzie County, N. Dak., furnished by the Boukal-Noonan Coal Co., were analyzed as shown in table 5 to provide a comparison of nonuraniferous lignite with uraniferous lignite from the Dakotas.

PREPARATION OF SAMPLES FOR ANALYSIS

The coal samples were crushed in a Blake-type jaw crusher to minus one-fourth inch. A split of minus one-fourth-inch material was oven dried at 105°C so that the sample could be pulverized to −80 mesh in a 6-inch disc grinder; undried material could not be pulverized in this type of grinder because the moist sample accumulates on the disc surfaces. Usually about 100 grams of −80-mesh material was prepared. A 1- to 2-gram sample of the pulverized coal was ashed in a muffle furnace at 800°C.

ANALYTICAL PROCEDURES

Six channel samples from Harding County, S. Dak. (p. 156 and table 1), were selected for chemical and spectrographic analysis of the ash. The samples were chosen from the 435 samples collected by N. M. Denson, G. O. Bachman, and H. D. Zeller of the U. S. Geological Survey in 1950. These samples were analyzed to determine the variability of the percentage of the major and minor constituents of the ash and also to determine whether the standard ashing methods used by the U. S. Bureau of Mines, as described by Fieldner and Selvig (1951, p. 7, 44), were suitable for preparation of the ash for uranium analysis. The uranium determinations, using the procedure developed by Guttag and Grimaldi (1954), were in no way hampered by the standard ashing method adopted. These six samples were selected for this purpose because: two from the same locality had the same percentage of ash but differing uranium percentages (samples SC–35 and SC–36), two from the same area had the same uranium content but differing ash percentages (samples F–95 and F–84), and one each from two areas was similar in uranium content of the ash to a sample from one of the pairs (S–29 and SC–35, and C–18b and SC–36).

TABLE 1.—*Channel samples of lignite from Harding County, S. Dak.*

[Analysts: W. Tucker, J. Warr, and J. J. McGee]

Sample no.	Laboratory no.	U in dry coal (percent)	Ash in dry coal (percent)	U in ash (percent)	Thickness of bed sampled (feet)	Location
SC-35	47933	0.028	25.1	0.116	Lower 1.75 of 3.5	Outliers south and west of South Cave Hills, NE¼SW¼ sec. 20, T. 20 N., R. 5 E.
SC-36	47934	.014	25.2	.056	Upper 1.75 of 3.5	Do.
F-95	42921	.012	32.1	.035	1.2	Table Mountain area, NW¼SE¼ sec. 5, T. 22 N., R. 4 E.
F-84	42922	.005	15.1	.033	2.8	Do.
C-18b	44269	.018	34.8	.053	1	North Cave Hills, NW¼SW¼ sec. 19, T. 22 N., R. 7 E.
S-29	45367	.030	25.5	.12	1.75	Slim Buttes area, NW¼SE¼ sec. 1, T. 17 N., R. 7 E.

The spectrographic analyses of these six samples (table 2) showed unexpectedly high percentages of barium, strontium, nickel, cobalt, zirconium, and molybdenum. These elements were determined chemically as a check on the spectrographic analyses, and the complete chemical analyses, along with ash and uranium determinations, are given in table 3.

SPECTROGRAPHIC ANALYSIS

The spectrographic analyses of the coal ash were made following a method described by Waring and Annell (1953). The equipment used was a 21-foot grating spectrograph with a d-c arc. A semiquantitative method of analysis was used by which the concentration of the elements was reported within limits differing by a factor of 10 (i. e., 0.001–0.01 percent, 0.01–0.1 percent, etc.).

There are no determinations listed for elements, such as sulfur and chlorine, which have been reported in lignite ash (Gibson and Selvig, 1944, p. 9). The spectral sensitivities for 68 elements, as shown by table 4, vary widely and if some of these elements were present in lignite ash they occurred in concentrations too low to be detected. The elements for which no determinations could be made using this one-exposure method are listed below:

Halogens: F, Cl, Br, I, At
Gases: H, O, N, He, Ne, A, Kr, Xe, Rn
Others: S, Se, C, Tc, Pm, Po, Fr, Ra, Ac, Pa

Table 4 lists the standard sensitivities for the elements determined by the semiquantitative spectrographic method and also the crustal abundances of the elements as compiled by Mason (1952, p. 41). Comparison of the maximum concentration of the elements (table 5) and the histograms to the abundances in table 4 makes it possible to

TABLE 2.—*Spectrographic analysis of selected samples of ashed lignite from Harding County, S. Dak. (in percent)*

Sample no.	More than 10	10–1	1.0–0.1	0.1–0.01	0.01–0.001	0.001–0.0001
SC-35	Fe	Al, Ca, Na, K, Si.	Mg, Mo, Sr, Mn, Zr.	B, Ti, Ba, Ni, Pb, Co, Sc, Ga, V.	Y, Cr, Cu	Yb.
SC-36	Al	Fe, Si, Ca, Na	Mg, K, Sr, Mo, Mn, Ba.	B, Ti, Zr, Ni, Pb, Co, Sc.	V, Ga, Y, Cr, Cu.	Yb.
F-95	Fe, Si, Al	Ca, Na	Mg, Mn, Ni, Sr, K, Zr, Co, Ti.	Ba, Mo, Pb, Sc, Y, V, Ga, B.	Cr, Cu	Yb.
F-84	Fe, Si, Al	Na, Ca	Mg, K, Mn, Mo, Ni, Ti, Zr.	B, Sr, Ba, Co, Pb, Sc, Y, V, Ga.	Cr, Cu	Yb.
C-18b		Na, Fe, Mg, Ca, Al, Si.	K, Sr, Ba	Mo, Zr, Ti, Mn, Ni, Pb, Sc, Ga, B.	V, Cr, Y, Cu.	Yb.
S-29	Fe	Al, Na, Si, Ca, K.	Mg, Mo, Sr	B, Mn, Ti, Ba, Ni, Pb, Co, Sc, Ga.	V, Zr, Y, Cr, Cu.	Yb.

TABLE 3.—*Chemical analysis of selected samples of ashed lignite from Harding County, S. Dak.*

[Analyst: A. M. Sherwood]

Sample no.	SC-35	SC-36	F-95	F-84	C-18b	S-29
LOI (1,000°C)	3.32	5.62	2.10	7.80	2.30	7.30
SiO_2	9.54	21.76	32.18	28.46	11.58	15.20
Al_2O_3	14.75	23.80	21.85	19.60	12.90	17.65
Fe_2O_3	22.50	12.40	31.20	33.81	14.40	34.50
TiO_2	.10	.10	.60	.60	.10	.10
CaO	20.15	14.35	10.80	4.00	14.70	12.00
MgO	.12	.18	.21	.21	7.30	.23
K_2O	1.11	1.11	.82	.82	.92	1.54
Na_2O	3.14	3.45	1.90	3.55	24.88	4.38
MnO	.26	.48	1.01	.26	.05	.14
SO_3 [1]	29.00	22.82	1.35	4.68	13.40	9.23
BaO_2	----------	----------	----------	----------	.30	----------
SrO [3]	----------	----------	----------	----------	.53	----------
NiO [2]	----------	----------	.15	----------	----------	----------
CoO [2]	----------	----------	.05	----------	----------	----------
ZrO_2 [2]	----------	----------	.27	----------	----------	----------
MoO_3 [2]	----------	----------	----------	----------	----------	.23
Summation [1]	100.67	100.45	102.39	95.99	101.06	95.20
Ash [3]	25.07	25.17	32.1	15.1	34.82	25.53

[1] The sulfur is calculated as SO_3 although part of the sulfur is present as sulfide and possibly sulfite. Inasmuch as varying conditions of ashing would result in different losses of sulfur and in varying proportions of sulfide, sulfite, and sulfate residues, it was not considered necessary to determine the exact form of the sulfur. Under these circumstances summation to 100 percent is not possible.

[2] These determinations were made as spot checks only as listed.

[3] From table 1.

determine the maximum enrichment of any element reported in these samples of coal ash. The writers believe little is to be gained by computing maximum, minimum, and average enrichments from semiquantitative analytical data; without considering the geochemical factors, numerical enrichment factors may be quite misleading.

ANALYTICAL DATA

In this report, all elements present in the earth's crust in weight percentages greater than 1 percent are considered major elements and will not be described in detail. Eight major elements—oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium—comprise more than 98 percent of the earth's crust and are present in coal ash in about the same aggregate percentage. Coal represents a geochemical concentration of carbon and hydrogen, and, although its ash differs little from rocks of the earth's crust in gross chemical composition, it is not surprising that some elements are concentrated in coal ash when the geochemical history of coal is considered.

TABLE 4.—*Standard sensitivities for the elements in samples of coal ash determined by the semiquantitative spectographic method of Waring and Annell (1953), with crustal abundances of the elements (Mason, 1952)*

[The standard plates were prepared with elemental concentrations differing by a factor of 10; hence, some elements were detected below the sensitivities listed but not necessarily to the next lower value. All elements detected below standard sensitivities were reported. All data in weight percent.]

Element	Sensitivity	Abundance	Element	Sensitivity	Abundance	Element	Sensitivity	Abundance
Minor elements (0.82 percent of crust)								
Ag	0.0001	0.00001	Ge	0.001	0.0007	Sn	0.01	0.004
As	.1	.0005	La	.01	.0018	Sr	.01	.03
B	.001	.0003	Li[1]	.0001(0.1)	.0065	Ti	.001	.44
Ba	.0001	.025	Mo	.001	.0015	U	.1	.0004
Be	.0001	.0006	Mn	.001	.10	V	.01	.015
Co	.01	.0023	Ni	.01	.008	Y	.001	.0028
Cu	.0001	.007	P	.1	.118	Yb	.0001	.00027
Cr	.001	.020	Pb	.01	.0016	Zn	.01	.0132
Ga	.01	.0015	Sc	.001	.0005	Zr	.001	.022
Major elements (51.99 percent of crust; 98.59 percent including oxygen)								
Al	0.0001	8.13	Fe	0.001	5.00	Na[1]	0.001(0.1)	2.83
Ca	.001	3.63	K[1]	.01(1.0)	2.59	Si	.0001	27.72
Elements not detected								
Au	0.01		Ho	0.01		Rh	0.01	
Bi	.001		In	.001		Ru	.01	
Cd	.01		Ir	.1		Sb	.01	
Ce	.1		Lu	.01		Sm	.1	
Cs[1]	.1(1.0)		Nb	.01		Ta	.1	
Dy	.01		Nd	.01		Tb	.01	
Eu	.01		Os	.1		Te	.1	
Er	.01		Pd	.01		Th	.1	
F[2]	.1		Pr	.01		Tl	.1	
Gd	.01		Pt	.01		Tm	.01	
Hf	.1		Rb[1]	.01(10.0)		W	.1	
Hg	.1		Re	.1				

[1] A second exposure is required for the high sensitivity listed.

[2] A special exposure is required for the fluorine estimation.

Twenty-seven minor elements have been detected in the ash of the samples of low-rank coal discussed in this report. Sufficient data for 18 of these elements permit a graphic presentation as histograms (pl. 2) of the analyses for each of the five localities from which coal samples were taken.

TABLE 5.—*Maximum concentration, in percent, of minor elements detected in samples of coal ash examined*

Number of samples	Locality	10–1	1.0–0.1	0.1–0.01	0.01–0.001	0.001–0.0001
151	Harding County, S. Dak.	------	B, Ba, Sr, Mn, Ti, Mo, Co, Ni, Zn, As, Pb, Zr, Be, U.	Cu, Cr, V, Li, Y, La. Ga, Ge, Sc.	Sn------------	Yb, Ag.
59	Perkins County, S. Dak.	------	B, Ba, Sr, P, Ti, Mo, Zr, U.	Cu, Cr, V, Ni, Co, Pb, Mn, Ga, Ge, Zn, La.	Y, Sc, Sn-----	Be, Yb, Ag.
26	Bowman County, N. Dak.	------	B, Ba, Sr, Mn, Ti, As, Pb, V, Zr.	Cu, Cr, Mo, Ni, Co, Ga, Ge, U.	Y, Sc, Sn-----	Be, Yb.
4	McKenzie County, N. Dak.	------	B, Ba, Sr, Mn, Pb.	Ti, V, Cu, Li, Sn, La, Zr, Co.	Y, Mo, Ga, Ge, Ni, Cr.	Be, Yb.
35	Jefferson County, Colo.	------	B, Ba, Sr, Mn, Ti, Mo, Y.	Cu, Cr, V, Ni, Co, Zr, Pb.	Sn, Sc, Ga, U, Ge, La, Yb, Be.	
48	Milam County, Tex---	P	B, Ba, Sr, Mn, Ti, Ni, Sn.	Cu, Cr, V, Co, Pb, Zr, Zn, Y.	Mo, Sc, Ga, Ge, Be, Yb.	

URANIUM

The coal from the Dakotas is from suites that contain samples enriched in uranium. The uranium is believed to have been concentrated from percolating ground water carrying uranium in solution (Denson, Bachman, and Zeller, in preparation). All these coal samples occurred in the same geologic environment and had a similar geochemical history. The cored coal from Harding and Perkins Counties, S. Dak., is from thicker beds than the cored coal from the Medicine Pole Hills area in Bowman County, N. Dak. Where present in thick coal beds uranium is generally concentrated near the top with the uranium content dropping to less than 0.001 percent in the middle and lower parts of the seam. Most of these samples contain at least 0.001 percent uranium in the ash.

The samples of coal from Jefferson County, Colo., showed a relatively low uranium content; 22 percent of the samples contained less than 0.001 percent uranium in the ash and 78 percent of the samples contained no more than 0.01 percent uranium in the ash.

The lignite from Milam County, Tex., showed such a low radioactivity that uranium determinations were not made.

In general, these coal ash samples, with the exception of those from Milam County, Tex., show an enrichment of uranium greater than the average percentage in the earth's crust. Other coal deposits, especially eastern anthracite and bituminous, are low in uranium content and their ash contains uranium in about the same, or lower, percentages as that in the earth's crust.

MOLYBDENUM

Molybdenum occurs in ash of these low-rank coal samples from the Dakotas in percentages somewhat higher than that in the earth's crust. The highest concentration of molybdenum which Goldschmidt (1954, p. 559) reported was 0.05 percent in the ash of coal from Northumberland. One sample of this low-rank coal ash, sample S–29 in table 3, shows a concentration of molybdenum 100 times that in the earth's crust, using the abundance estimate of Mason (1952, p. 41). Using the estimate of 1±0.5 parts per million given by Kuroda and Sandell (1954, p. 46), these coal-ash samples contain concentrations of molybdenum as much as 1,500 times the average for crustal rocks.

A possible explanation for the high molybdenum content of the coal samples from the Dakotas is that the molybdenum was transported in the same solutions which carried uranium into the coal. The histograms for molybdenum for the coal from Harding and Perkins Counties, S. Dak., closely resemble the histograms for uranium, and this comparison is supported by individual coal-ash analyses which show that a high uranium content parallels a high molybdenum content. The erratic distribution patterns of uranium and molybdenum in the thin seams of coal from Bowman County, N. Dak., may be due to greater irregularities in the entry and migration of mineralized ground water in thin seams of coal.

COBALT AND NICKEL

The relative abundances of cobalt and nickel are reflected in the histograms which show that nickel is below the limit of detection (0.01) in only 6 samples, whereas cobalt is below the same limit of detection in 58 samples. No unusual concentrations of cobalt or nickel are apparent in the samples examined.

VANADIUM

Vanadium, one of the generally more abundant minor elements, is present in these coal samples in relatively low concentrations. Only in the ash of coal from Milam County, Tex., does the percentage of vanadium approach the abundance of vanadium in the earth's crust.

CHROMIUM

All the samples of coal ash contained chromium in detectable amounts, but none of the ash showed an appreciable enrichment of chromium over that in the earth's crust. Chromium may be enriched in some of the individual components of the lignite from Milam County, Tex., but gross sampling of an entire coal core did not permit the careful study that proof of this would require. Similarly, the Milam County lignite may show greater enrichments for more than one element, and it is discussed separately in this report on page 169.

STRONTIUM AND BARIUM

Very few data are in the literature regarding the percentage of strontium in coal ash. This is in contrast to the abundant data for barium in coal ash and is not what would be expected considering the greater abundance of strontium. The coal ash analyzed for this study showed that strontium is about as abundant as barium and that both elements are enriched in coal ash as compared with the crustal rocks. Sample C–18b (table 3) which was chemically analyzed for both elements showed a SrO content of 0.53 percent and a BaO content of 0.30 percent. Goldschmidt (1954, p. 249) quotes Noll's figure of 100 to 200 ppm SrO in coal ash but this is not in agreement with the data of this report and of Headlee and Hunter (1953, p. 549), which coincidentally averages for 35 column analyses of coal ash 0.54 percent SrO, and 0.31 percent BaO.

TITANIUM

Twenty-seven minor elements have been detected in the ash of the coal samples examined and they comprise only 0.82 percent by weight of the earth's crust. More than half of this amount is titanium. The analyses of these coal samples show that titanium is present in the ash of low-rank coal in about the same abundance as in the earth's crust.

MANGANESE

The average concentration of manganese in these ash samples of coal is low, somewhat less than 0.1 percent which is the abundance of manganese in the crustal rocks. This is in agreement with the data of Headlee and Hunter (1953, p. 549) who, for 16 major coal seams in West Virginia, have determined the average manganese content to be 0.037 percent in the ash. Goldschmidt (1954, p. 639) gives preferential leaching of manganese under reducing conditions as the reason for the relatively low proportion of manganese to iron in reduced sediments.

BORON

The boron content of ash of these low-rank coals is high, averaging more than 0.1 percent (more than 1,000 ppm). This enrichment of boron is considerably higher than that in the earth's crust. Boron is perhaps the only element in coal ash which is directly attributable to the living plants which were the progenitors of coal.

Much information regarding boron in the ash of coal from various places is in the literature. Coal from Svalbard with an unusually high percentage of boron, as much as 2 percent in the ash, has been reported by Butler (1953, p. 11). Headlee and Hunter in their study of 16 major coal seams in West Virginia (1953, p. 549) report an average of 0.035 percent boron for coal ash.

ZIRCONIUM

The zirconium content of the ash of the low-rank coal studied is highly variable, ranging from less than 0.001 to more than 0.1 percent. Undoubtedly some of the zirconium occurs as detrital zircon, but not all of the zirconium can be accounted for in this way.

Goldschmidt (1935, p. 1101) reports as much as 0.5 percent zirconium in the ash of coal, and Headlee and Hunter (1953, p. 549) report a maximum of 0.089 percent ZrO_2 in ash from a cube of coal from West Virginia. Butler (1953) reports from 0.004 to 0.11 percent zirconium in ash of coal from Svalbard. Sample F–95 (table 3) contains 0.27 percent ZrO_2. The histograms show that the average zirconium content of these ash samples is in the hundredths of a percent.

SCANDIUM

The data for the occurrence of scandium in coal ash are scant except for Goldschmidt's estimate (1954, p. 305) ranging from 0.004 to 0.026 percent scandium in coal ash. The scandium content of the ash of the samples of low-rank coal examined for this report ranges from less than 0.0001 percent to 0.01–0.1 percent, which is in general agreement with Goldschmidt's findings.

GERMANIUM

Germanium is an element that most persons associate with coal ash, and the many recently published papers on germanium in coal ash (Stadnichenko and others, 1953, p. 11–12) show the interest in this element. The study of the ash of these samples of low-rank coal proved none to be highly germaniferous, and indeed in most of the samples of coal ash that were analyzed germanium was either not present or was below the limit of detection. Germanium tends to be concentrated in the upper or lower parts of coal seams or along partings in a coal seam (Stadnichenko and others, 1953, p. 6) and this is the relationship indicated in this study of low-rank coal.

The abundance of germanium in crustal rocks is 0.0007 percent and the average germanium content in the ash of these samples of low-rank coal is probably no higher. Only 4 of the 319 samples analyzed contained more than 0.01 percent germanium in the ash. The 35 columns of coal from West Virginia analyzed by Headlee and Hunter (1953, p. 549) contained an average of about 0.01 percent germanium in the ash.

To insure that the percentages of germanium in the coal ash were not abnormally low because of loss of germanium during ashing, as reported by earlier writers, experiments were designed to investigate the loss of germanium during ashing at temperatures as high as 1,000°C. Waring and Tucker (1954) demonstrated that there were no losses in germanium when coal ash was prepared at 800°C by the standard method (Fieldner and Selvig, 1951, p. 44). Their findings are confirmed by the work of Hawley (1955, p. 519). Aubrey and Payne (1954) did not report on ashing losses of germanium throughout the temperature range used by Waring and Tucker, but they did test the samples at 900°C, with no preheating. These samples showed a loss of as much as 20 percent germanium.

The geochemical cycle of germanium is not well understood because of the low percentage of germanium found in most rocks analyzed (Fleischer, 1955, p. 148). A clue to the behavior of germanium is contained in table 3 of a report by Breger, Deul, and Rubinstein (1955, p. 213) where spectrographic analyses of the ash of lignite and of sink-and-float separates show germanium to be present only in the sink fraction, composed essentially of the secondary minerals gypsum and jarosite, and not detectable in the original coal or in the organic separate. Goldschmidt, with his intuitive understanding of these problems, predicted this in his treatise on geochemistry (1954, p. 388), in which he states,

> It is therefore reasonable to expect that germanium dioxide during weathering enters into ionic aqueous solution more readily than silica.

Searching for an explanation as to why silica deposits, formed from nonvolcanic aqueous solutions connected with the processes of weathering and sedimentation, contain no detectable germanium, Goldschmidt concludes,

> It would appear that there must be one or more powerful precipitants for germanium in the course of soil formation and sediment formation, which prevent germanium from being collected either in sedimentary silica precipitation or in sea water.

TIN

Tin shows an erratic distribution pattern in the samples of low-rank coal studied. It was detected in only 7 of 151 samples from Harding

County, S. Dak., yet it was found in all 48 samples from Milam County, Tex., and 5 of these samples contained from 0.1 to 1.0 percent tin.

The occurrence of tin in such relatively high concentrations in the Milam County, Tex., coal is difficult to explain without additional investigation. Separating mineral matter from the coal might show where the tin is concentrated, but rather than work with a sample of a whole coal seam it would be more desirable to select a coal increment which has a concentration of tin. A high concentration of tin is to be expected in such an increment if a sample from a thickness of several feet of coal contains as much as 0.1 to 1.0 percent tin.

Goldschmidt (1937, p. 669) reports a maximum concentration of tin of about 0.05 percent in coal ash, and Headlee and Hunter (1953, p. 549) report a maximum of 0.15 percent tin in the ash of a cube of coal from West Virginia.

LEAD

Lead shows an erratic distribution pattern for the ash of samples of low-rank coal, much like tin, but, unlike tin, it is present in detectable percentages in most samples. Weathering may have been a factor in the occurrence of lead in the coal of the Dakotas, where uranium and perhaps molybdenum, lead, and other migrating elements were leached from the overlying tuffaceous rocks. Lead in coal from Harding County, S. Dak., (Breger, Deul, and Rubinstein, 1935, p. 213) is shown to have been present mostly in the minerals separated from the coal by sink-and-float techniques, and this is in direct contrast to other coal in which Deul (1955) has found lead to be concentrated with the organic separates.

Goldschmidt (1935, p. 110) has found a maximum of 0.1 percent lead in coal ash, and Headlee and Hunter (1953, p. 549) have found in coals from West Virginia a maximum of 0.24 percent and an average of 0.045 percent lead. Gibson and Selvig (1944, p. 12) report occurrences of coal with much higher percentages of lead but the coal has obviously been mineralized by ore-bearing fluids.

COPPER

The concentrations of copper in the ash of samples of low-rank, unmineralized coal appear to be uniformly low. Goldschmidt (1954, p. 184) found a maximum copper content of only 0.05 percent in coal ash, and Headlee and Hunter (1953, p. 549) show this concentration to be about average for coal from West Virginia. For coal from Svalbard, Butler (1953, p. 11) found a maximum of 0.02 percent copper in the ash and found most samples below 0.01 percent. The coal from

Milam County, Tex., has a somewhat higher copper content than the other coal and will be discussed on page 169.

GALLIUM

The enrichment of gallium in coal ash has been known since Goldschmidt's classic work. Almost every sample of low-rank-coal ash showed an enrichment of gallium greater than the percentage in crustal rocks. All available comparative data show that gallium is more abundant in coal ash than in rocks.

OTHER ELEMENTS

Beryllium, yttrium, and ytterbium occur in almost every sample of the low-rank-coal ash examined. Beryllium is usually present in the lowest reported range, 0.001 to 0.0001 percent. Ytterbium is usually present in the same low range, and yttrium is usually in a somewhat higher range. As shown in table 5, these elements reach a maximum percentage range that is unusual, but the variation in the data is insufficient to permit an evaluation that is geochemically significant.

Some elements have such relatively poor spectral sensitivities by this single-exposure semiquantitative method that insufficient information was provided to permit a meaningful graphic presentation. In most of the coal ash, phosphorus, arsenic, lithium, lanthanum, and zinc were not present in percentages high enough to be detected.

Silver has an extremely high spectral sensitivity, but is detected in only a few of the coal ashes in the lowest percentage range, 0.001 to 0.0001.

INTERPRETATION OF ANALYTICAL RESULTS

The results of the geochemical study of the occurrence of minor elements in the ash of low-rank coal are in general agreement with the results of detailed geologic investigations. The geology of the coal from the Dakotas and of the Jefferson County, Colo., coal has been recently studied; detailed regional studies of the coal from the Dakotas were being conducted by the Geological Survey in 1955. The Milam County, Tex., coal is, in minor element content, perhaps the most interesting coal, yet less detailed information on its occurrence is available and sampling has been less detailed than for any other coal discussed in this report.

COAL FROM THE DAKOTAS

Lignite from Harding and Perkins Counties, S. Dak., and from Bowman County, N. Dak., is much weathered in outcrops; abundant gypsum and jarosite are formed from oxidation of pyrite. Rarely is pyrite found in exposed lignite beds. Several samples of cored coal obtained from each of the counties were pulverulent and crumbly. Denson and his coworkers (in preparation) postulated that the source of the uranium was in the overlying Oligocene and Miocene strata of the White River group and the Arikaree formation, respectively, and that the uranium was leached from these rocks and transported by circulating ground water. Mechanisms by which uranium could have been introduced into the coal by ground water have been discussed by Breger, Deul, and Rubinstein (1955, p. 224–225) and by Breger, Deul, and Meyrowitz (1955, p. 620, 621) in reports on the geochemistry and mineralogy of a sample of uraniferous lignite and a sample of uraniferous subbituminous coal. These mechanisms and Denson's theory require the coal to be in contact with ground water and at least a limited circulation of water through the coal.

Some of the elements, both minor and major, must have been added to the coal from the Dakotas by circulating ground water. Uranium and molybdenum and their apparent parallel relationship have been discussed in the molybdenum section of this report. Uranium is correlated with no other minor element in the coal, but it is not unlikely that other elements were added or removed from the coal by circulating ground water. Although vanadium-bearing uranium minerals have been found in sandstone overlying the coal at Slim Buttes, Harding County, S. Dak., vanadium is not a controlling factor in the fixation of uranium by the coal and no vanadium and uranium correlation is apparent.

The histograms for cobalt and nickel for the ashed coals from the Dakotas are distinctly different from the histograms for the ashed coals from Texas and Colorado, which are similar to each other. The differences are certainly a reflection of the geochemical histories of the coal, but there is no evidence from these data that the distribution patterns of cobalt and nickel are not due to modification of their distribution before weathering of the coal. Barium and strontium provide an interesting contrast to cobalt and nickel and to each other in that the distribution pattern for strontium is similar in all five localities, but that the barium distribution shows no dependence on the source of the samples.

COAL FROM JEFFERSON COUNTY, COLO.

The coal in Jefferson County, Colo., which has been known since 1875 to contain uranium, has been studied in detail by the Geological Survey. The coal bed is cut by a shear zone and the uranium is believed to have been derived from hydrothermal solutions.[1] Min-

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[1] Gude, A. J., 3d, and McKeown, F. A., Results of exploration at the Old Leyden coal mine, Jefferson County, Colo.: U. S. Geol. Survey Trace Elements Memo. Rept. 292 (open-file rept.), 1953.

eralization of the coal, except for silicification, was weak; molybdenum is the only element that reaches a concentration high enough to indicate hydrothermal enrichment, except for uranium which occurs in concentrations below 0.01 percent in the ash. Vanadium, associated with the uranium in the rocks in which the coal occurs, is not enriched in this coal although it is present in higher percentages than uranium. A few samples of coal containing as much as 0.1 percent uranium are reported by Gude and McKeown, but these are exceptional.

COAL FROM MILAM COUNTY, TEX.

The ashed lignite samples from Milam County, Tex., show uniformly high concentrations of copper, zirconium, boron, and tin. This lignite may provide samples of smaller bed thickness which have substantially higher concentrations of these and other elements. Figure 17 shows the distribution of eight elements, each within a narrow percentage range. Such a uniformity of distribution is likely to be the reflection of an averaging effect of using as a sample a split of core from a full bed thickness of coal. Nevertheless the high concentration of tin is worthy of note.

SUMMARY

These data show the occurrence of 27 minor elements in the ash of samples of low-rank coal. The 319 ash samples analyzed were enough to permit a graphic presentation of the data. The general agreement with data obtained by other workers for most of these elements shows that, for coal from any one of the areas studied, there has not been any general elemental enrichment over that for coal from other areas. Certain elemental concentrations are apparent and these concentrations, on the basis of geological evidence, can be related to certain stages in the geochemical history of the coal. Boron is an element that is concentrated from the soil by living plants and is not lost during degradation of plant tissues in the early stages of coalification, hence the high concentration of boron in all these samples of coal ash. The addition of uranium and molybdenum to the coal from the Dakotas during a cycle of weathering by ground water is reflected in their distribution in the ash of this coal as compared to the coal ash from the other two areas. The coal from the Dakotas shows a correlation of molybdenum with uranium; from these data there is no detectable correlation of uranium with any other element. The unusual concentrations of tin, zirconium, and copper found in the coal from Milam County, Tex., probably represent elements com-

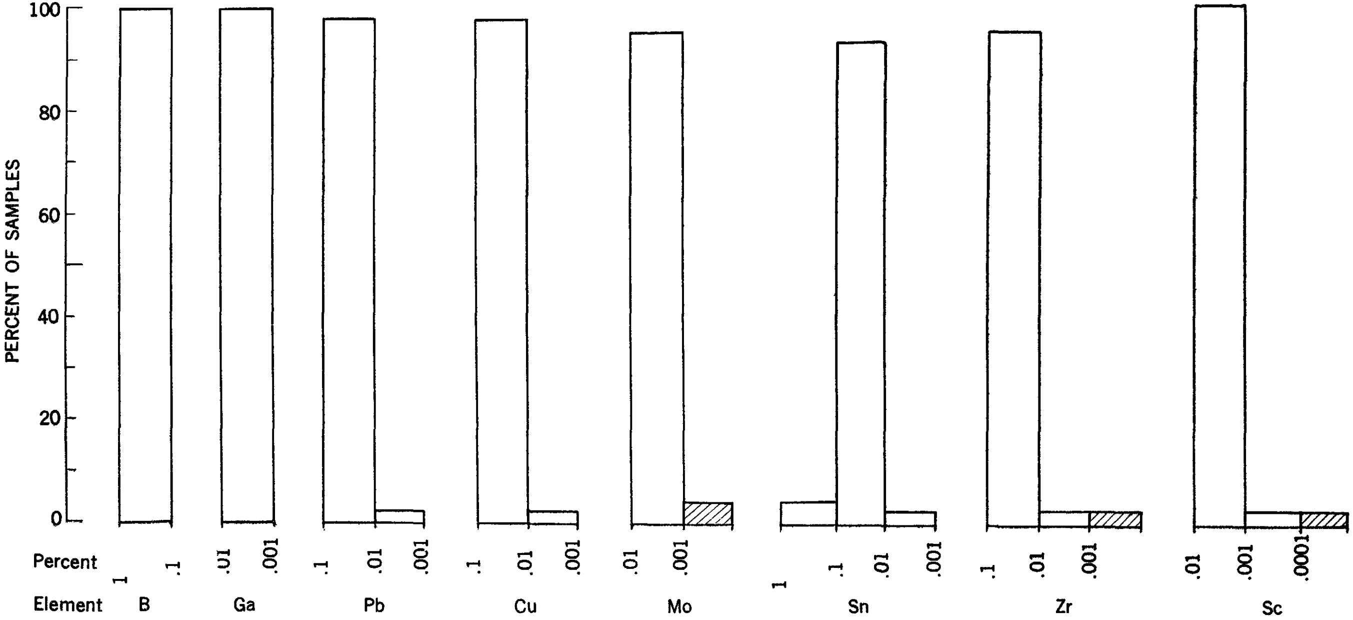

FIGURE 17.—Ashed lignite from Milam County, Tex. Shaded bars indicate samples in which the elements were below the limit of detection.

bined with the organic matter during degradation of the organic matter and during compaction and burial.

It is our experience that the most useful geochemical minor-element data are to be obtained from the analysis of the ash of a whole coal and of the ash of the mineral and organic separates derived from the original coal.

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