

GERMANIUM AND OTHER TRACE ELEMENTS IN SOME WESTERN CANADIAN COALS

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ABSTRACT

This paper is a report on the results of spectrographic analyses of the ash of twenty-four coal samples from British Columbia, the Yukon and the Northwest Territories. The samples were selected from the collection of coals in the geology Department of the University of British Columbia.

Traces of germanium were found in six of the samples examined. A concentration of germanium greater than 0.1% was apparent in coals from Hornaday River N.W.T., and from Cape Caution B.C. The distribution of germanium in the samples examined was erratic; especially in the coal sample from Cape Caution.

INTRODUCTION

V. M. Goldschmidt (1930, 1937, 1944, 1954) was the first worker to use carbon arc spectroscopy for the analysis of coal ash. During these studies Goldschmidt discovered an unexpectedly high concentration of germanium and other trace elements in the ash of some European coal samples. Later work has shown that Goldschmidt's findings were not unique, and that coals from many parts of the world contain similar concentration of trace elements. A comprehensive bibliography of previous work in this field of research is given by Stadnichenko *et al.* (1953).

THE ORIGIN OF TRACE ELEMENTS IN COAL

Goldschmidt (1930) suggested three ways in which elements might be concentrated in coal ash.

- (1) Concentration by growing plants.
- (2) Concentration by residual enrichment of soil after the more soluble elements have been leached away.
- (3) Concentration in a coal seam after burial by selective reaction of the elements in groundwater with the carbonaceous material in the coal.

THE DISTRIBUTION OF TRACE ELEMENTS IN COAL

Both Headlee (1953) and Goldschmidt (1944) have published figures for the concentration of elements in coal ash as shown in Table 1.

Headlee found that all the trace elements, with the exception of germanium, were evenly distributed across the coal seams which he examined, but germanium ions were concentrated in the top and bottom

TABLE I. THE CONCENTRATION OF ELEMENTS IN COAL ASH

Element	Maximum Concentration Factor (Goldschmidt)	Concentration Factor (Headlee)	Average amount in grams per ton (Goldschmidt)	Average per cent of metallic oxides (Headlee)
Boron	1,000	10-185 times	3,000	—
Silicon	—	Less than average	—	SiO ₂ = 44.8
Magnesium	—	Less than average	—	MgO = 0.99
Manganese	—	Less than average	—	MnO ₂ = 0.046
Copper	5	1-10 times	500	CuO = 0.062
Cadmium	300	—	50	—
Calcium	—	Less than average	—	CaO = 2.7
Beryllium	200	1-10 times	1,000	BeO = 0.008
Zinc	300	1-185 times	20,000	ZnO = 0.051
Lead	100	1-185 times	1,000	PbO = 0.048
Molybdenum	—	1-10 times	—	MoO = 0.016
Vanadium	10	1-10 times	1,200	V ₂ O ₅ = 0.050
Germanium	16,000	1-185 times	11,000	GeO ₂ = 0.013
Nickel	100	1-10 times	8,000	NiO = 0.046
Tin	—	1-185 times	—	SnO ₂ = 0.022

After Goldschmidt (1944) and Headlee (1953).

few inches of the seams which he examined, there being only a trace of germanium in the middle part of the seam. In a detailed study of the top three inches of a seam Headlee found that there was a gradation from 121 ppm. germanium in the quarter inch sample taken from the seam edge, to 2 ppm. in a sample three inches from the edge of the seam. A similar "contact enrichment" was found in the bottom four inches of another seam.

This experimental evidence appears to support Goldschmidt's third suggestion for the origin of trace elements in coal. Headlee's examination showed that all the germanium had been precipitated in the coal from the groundwater by the time such water had percolated more than a few inches into the coal seam. Rankama (1950, p. 736) in a discussion of the deposition of germanium in coal states "it (germanium) is precipitated as bivalent compounds because of the reducing action of the coal, and the enrichment is increased still more owing to the adsorptive properties of the carbonaceous material." Thus the experimental findings of Headlee appear to support the theories of deposition of both Goldschmidt and Rankama.

McClelland (1953) in a discussion of the germanium content of Canadian coals states that "germanium is not uniformly distributed

through a coal seam either vertically or horizontally." This is an important point because Headlee considered that the germanium content variation in a coal seam was only in the vertical direction.

To sum up, previous work has indicated that in general, trace elements, with the exception of germanium, occur uniformly throughout a coal seam. The germanium content of coal seams in at least one area has been shown to be concentrated at the edges of the seam, and in other areas the concentration varies laterally along the seam. In any systematic search for germanium in coal these factors should be considered.

PREVIOUS SPECTROGRAPHIC WORK ON COALS OF WESTERN CANADA

Newmarch (1953) describes spectrographic analyses of coal ash from the Michel area near Crowsnest Pass, British Columbia.

Newmarch was primarily interested in an analysis of coal seams for trace element content in order to discover if such data might be used for correlation of seams. He found the following germanium concentrations in the samples he analyzed.

TABLE 2. GERMANIUM CONTENT OF COAL FROM MICHEL B.C.

Seam	No. of Samples	Ash %	Germanium Content*
B	24	10.6	1.1
A		11.9	—
U ₃ ?	12	9.8	—
U ₃	9	7.5	.2
L ₃	5	25.9	—

After Newmarch, 1953.

* Numbers plotted do not equal percentages of element present but are relative to one another for any one element and approximate to percentage figures.

Newmarch states that he ashed his coals at 750° C. This temperature would tend to volatilize any germanium present as the dioxide.*

It would be interesting to examine a sample of Michel coal ashed below 500° C., especially if the sample were taken from the top or bottom few inches of the seam. The average of 1.1 units of germanium in 24 samples of Seam B would appear to be a relatively high percentage of the metal.

PROCEDURE

(1) *Sampling.* Each specimen was examined, and a representative sample taken from it. The sample was then pulverized in an agate mortar. Approximately 3 grams of the resulting powder was transferred to a wide mouthed crucible.

* Germanium oxides and sulphides are volatile above 700° C. (Powell *et al.*, 1951).

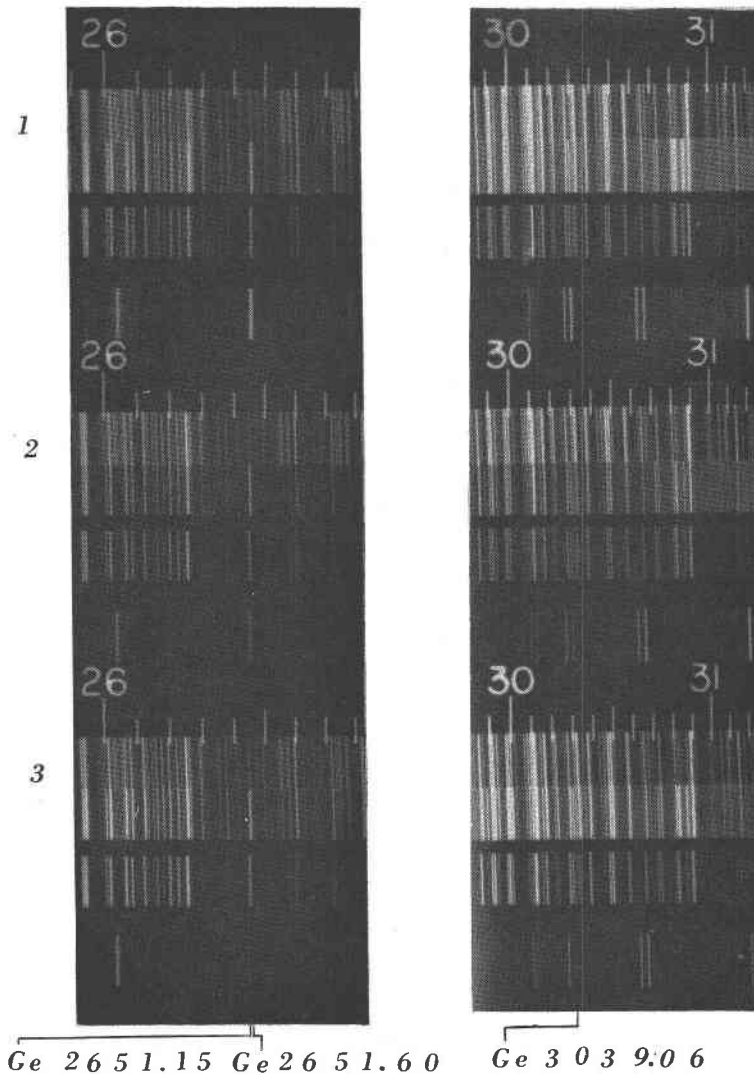


FIG. 1. 1, 2, 3 are photographs of the spectra of the Cape Caution coal ash sample. The individual spectra bands in each sample reading from top to bottom are: Iron Spectrum, Cape Caution Coal Ash 20 secs, Cape Caution Coal Ash 10 secs and Germanium Standard 10 secs. The germanium content of the standard samples is 1%, 0.1% and 0.01% in samples 1, 2, and 3 respectively.

(2) *Ashing.* a) The first two coal samples were ashed in crucibles without lids over a bunsen burner. Spectrographic analysis of such ash showed few trace elements present and as a result of this observation all later

TABLE 3. SPECTROGRAPHIC LINES USED IN THE IDENTIFICATION OF TRACE ELEMENTS IN COAL ASH

Element	Wave Length of Line in Armstrong Units	Intensity
Boron	{ 2496.78	(9)
	{ 2497.73	(10)
Manganese	2576.10	(3)
Germanium	{ 2651.15	(10)
	{ 2651.60	(10)
	{ 3039.06	(10)
Magnesium	2782.99	(6)
Lead	2833.07	(6)
Tin	2863.32	(8)
Silicon	2881.59	(10)
Beryllium	{ 3130.72	(10)
	{ 3131.06	(10)
Molybdenum	3132.60	(10)
Nickel	3134.10	(10)
Calcium	3158.87	(8)
Vanadium	{ 3184.00	(5)
	{ 3185.40	(5)
Cadmium	3261.05	(10)
Copper	3273.96	(10)
Zinc	3345.00	(10)

From Brode (1946).

ashing was carried out in a muffle furnace.

b) All the preliminary coal samples were ashed in a muffle furnace in which the temperature was not allowed to exceed 430° C. This temperature was considered low enough to minimize the danger of volatilization of trace elements (Powell, *et al.* 1951, p. 542).

c) After all the preliminary ashing had been completed and the spectrographic plates of the ash had been made, I received a copy of the report by Stadnichenko, *et al.* (1953). For all re-run samples the ashing method which they suggest was adopted, as follows.

- (i) 3 gms of coal dust placed in a shallow porcelain dish.
- (ii) The dishes were placed in a cold muffle furnace in which the following conditions were maintained.
 - 200° C. ± for 20-30 minutes with furnace door open.
 - 220° C. ± for 6 hours or until sample was ashed.
 - 410° C. for 30 minutes to drive off last trace of carbon.

During the ashing procedure each sample was raked over several times with a glass rod.

TABLE 4. DESCRIPTION OF SAMPLES ASHED

No.	Locality	Description	Ash Colour	Remarks
1	Cape Caution B.C.	Bituminous?	Orange brown	—
2	Flint Vermillion Bluffs, Princeton, B.C.	Bituminous?	Orange brown	—
3	Camp Robertson	Bituminous?	Light Grey	—
4	Near Port Haney C.P.R., B.C.	Lignite	Whitish Grey	—
5	Rashings, No. 4 Shaft Extension	Bituminous	Grey	—
6	Peel River, Y.T.	Albertite? Dyke	Greenish Brown	Very little ash about 10% by volume of sample
7	Sable Arm Baynes Coal Co.	Bituminous	White to Rose Pink	—
8	Princeton	Bituminous	Yellowish Brown	—
9	Coalmont	Bituminous	White	Resinous high gas content
10	Collings Gulch Nr Tulameen River B.C.	Sub Bituminous	Orange Brown	
11	Chua Chua N. Thompson, B.C.	Cannel Coal	Dark Grey	
12	Coal from Iron River	Bituminous	Grey	
13	6 Miles North Alexander ferry W. Bank of Fraser River B.C.	Lignite	Brownish Dark Grey	
14	Hamilton Lake	Fossil Wood	Dark Red	Probably incombustible
15	No. 4 Shaft Union Mine Comox	Sub Bituminous?	Light Brown	
16	Quatsino	Sub Bituminous?	Light Brownish Yellow	
17	Rocky Mt. Canyon Peace River	Bituminous	White	
18	Cape Caution B.C.	Lignite	Brownish Orange	
19	Glacier Gaulch B.C.	Sub Bituminous?	Medium Grey	Metamorphosed
20	"2" Hornaday River area N.W.T.	Lignite	Dark Grey	
21	"3" Hornaday River area N.W.T.	Fossil Wood	Orange	
22	"6" Hornaday River area N.W.T.	Fossil Wood	Orange grey	
23	"4" Hornaday River area N.W.T.	Lignite	Dark grey	
24	Cornwallis Island	Lignite	Yellowish Brown	

(3) *Spectrographic Method.* The ash samples were spectrographed with a Hilger Medium Quartz Spectrograph. Each sample was arced between National Special Graphite Electrodes at a current of 4.5 amp at 110 volts D.C. The spectra were recorded on Kodak 2×10 Spectrographic glass plates (Type 11-F (3)) which were developed for 5 minutes in D19 developer and fixed for at least five minutes in F5 fixing solution at room temperature (68° F.); then they were washed for one hour and air dried.

Four ash samples were exposed on each plate. Each sample was ashed for two periods of time; 10 seconds and 20 seconds. Two standard spectra were used for each *plate* sample, an iron spectrum above, and an R.U.* spectra below. These two spectra were used to locate the exact position of the characteristic lines used to identify each element.

* A standard prepared by Hilger Ltd. consisting of small quantities of 50 elements incorporated in a base of zinc, calcium and magnesium oxides. The quantity of each element is adjusted so that the "persistent lines" (Raies Ultimes) and the most sensitive lines appear for each element in the powder.

TABLE 5. ELEMENTS DETECTED IN COAL ASH SAMPLES

Sample	Boron	Manganese	Germanium 26 (lines)	Magnesium	Lead	Tin	Silicon	Germanium 3039.06	Beryllium	Molybdenum	Nickel	Calcium	Vanadium	Cadmium	Copper	Zinc
1	2	2	—	1	—	—	2	—	—	—	—	—	—	—	—	—
2	3	—	—	3	—	—	1	—	3	—	—	2	—	—	3	—
3	2	3	—	2	—	—	1	—	—	—	—	3	—	—	3	—
4	1	3	—	2	3	—	1	—	3	—	—	2	—	—	3	—
5	3	3	—	3	—	—	1	—	3	—	3	—	3	—	3	3
6	1	2	—	1	2	2	1	—	1	—	1	2	1	—	1	—
7	2	3	—	2	—	—	1	—	3	—	—	2	3	—	2	—
8	1	3	—	2	—	—	1	—	—	—	—	1	—	—	2	4
9	1	2	—	3	3	—	1	—	3	—	—	3	3	—	2	4
10	1	3	—	2	3	—	1	—	3	3	4	3	—	—	2	—
11	1	—	4	1	2	—	1	4	3	—	—	3	3	—	3	3
2	1	2	—	—	2	—	1	—	3	3	—	3	3	—	3	3
1	1	1	—	2	2	—	1	—	2	4	—	1	—	—	1	3
12	1	3	—	3	—	3	1	—	3	—	—	2	—	—	3	—
13	1	3	?	1	3	—	1	4	2	3	—	3	3	—	2	—
14	2	2	—	3	—	—	2	—	—	—	—	—	—	—	3	4
15	2	3	—	1	2	—	1	—	4	—	—	1	—	—	2	3
16	1	3	—	1	4	—	1	—	3	—	—	2	—	—	3	3
17	1	3	—	1	4	—	1	—	2	3	—	2	—	—	2	3
18A	2	3	3	1	3	—	1	3	2	2	2	1	—	—	3	3
19	2	3	—	1	3	—	1	—	3	—	—	3	—	—	2	3
20	1	1	—	1	3	—	1	—	3	—	—	1	—	—	2	3
21	1	3	2	1	3	—	2	1	3	—	—	1	—	—	2	—
22	1	2	2	1	—	—	2	1	3	—	—	1	—	—	—	—
23	1	2	—	1	?	—	1	—	—	—	—	1	—	—	2	4
24	1	1	4	1	1	4	1	3	2	3	4	1	3	—	2	3

Key to Intensity of lines: (1) Strong; (2) Medium; (3) Weak; (4) Pressure not detected.

Note: (1) The absence of a line or a very weak line may not mean that an element is absent. For example the manganese line used had an intensity of (3) and would appear as a weak line in all but the most strongly manganous samples. Hence the intensity of a line noted above may be taken as relative only.

(2) The absence of lines of common elements may be due to interference.

(4) *Reading of the Spectrographic Plates.* The spectra exposed on each plate were thrown onto a screen. The image of the iron spectrum above each sample was then compared with the standard iron spectrum in Brode (1946) and the presence or absence of the following elements in

TABLE 6. RESULTS OF REPEAT ANALYSIS OF GERMANIUM POSITIVE SAMPLES

	No	Ge 26	Ge 30	Ge Standard	Remarks	Ash Number
FIRST	11	3	3	.01	Trace only	2
RE-RUNS	13	3	3	.01	Trace only	2
	22	2	2	.01	Re-ash	2
	24	4	3	R.U.	Trace only	1
	22	—	4	.01	Suggest Re-ash	3
	21	3	3	.01	Trace only	2
	18A	1	1	.01	Re-ash	2
	6	—	—	.01	No Germanium present	2
SECOND	18B	2	2	.01		2
RE-RUNS	18B	1	1	1.0	Standard > Sample	3
	18B	1	1	0.1	Standard \approx Sample	3
	18B	1	1	.01	Standard < Sample	3
	22	1	1	.01	Standard < Sample	2
	22	1	1	1.0	Standard > Sample	4
	22	1	1	0.1	Standard \approx Sample	4
	22	1	1	.01	Standard < Sample	4

the sample was recorded. An estimate of the intensity of the lines present was made by eye; no densitometer was used.

DISCUSSION OF RESULTS

(1) *Detection of Elements Other Than Germanium.* Fewer elements were detected in samples ashed in a bunsen flame (No. 1 and No. 2) than in ash of the same coal samples ashed in muffle furnace.

The fact that zinc was undetected in several of the samples may be due to the fact that the zinc spectra are usually more sensitive to interference than the spectra of other elements, especially if only small amounts of zinc are present.

(2) *Germanium.* Six of the ashed coal samples showed detectable amounts of germanium. These samples were re-ashed and spectrographed again with a germanium (.01%) standard* used in place of the R.U. powder.

Two of these re-run samples showed relatively large concentrations of germanium and four showed only a trace of the metal.

* Ratio quantitative powder with either (.01%) or (0.1%) or (1%) of each of the following Be, Co, Ca, Ge, In, Rb, Se, Tl, Y, in a zinc base prepared and standardized for use in qualitative spectroscopy by Dr. S. J. Lewis for Adam Hilger Ltd.

The samples from Cape Caution and Hornaday River N.W.T. which were twice positive were re-ashed and spectrographed a third time against .01%, 0.1% and 1% germanium standards. A photograph of the third plate of the sample from Cape Caution appears as Plate I. It will be noted that this plate shows an apparent concentration of germanium of approximately .1% in the sample. No germanium was detected in three other samples of Cape Caution coal. The re-analysis of the original sample checked with the first result.

CONCLUSIONS

Many elements present in small amount in coal can be detected spectrochemically.

The finding of germanium in 6 out of 24 samples can be considered high because the coal seams were not selectively sampled for germanium analysis.

In any future work of this nature a satisfactory method of ashing should be evolved for each type of coal examined. In spite of the low oven temperature at which these coals were ashed there is still a possibility that germanium was lost due to local burning of the coal. This ashing problem is stressed by Stadnichenko *et al.* (1953, p. 3).

The results of the analysis of Cape Caution coal underline the importance of accurate and systematic sampling of coal seams if their true germanium content is to be discovered.

If systematic sampling and analysis were carried out on the coal seams from which the six germanium positive coals were taken, higher concentrations of germanium might be found in selected parts of the seams.

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