GERMANIUM AND URANIUM IN COALIFIED WOOD FROM UPPER DEVONIAN BLACK SHALE

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ABSTRACT

Microscopic study of black, vitreous, carbonaceous material occurring in the Chattanooga shale in Tennessee and in the Cleveland member of the Ohio shale in Ohio has revealed coalified woody plant tissue. Some samples have shown sufficient detail to be identified with the genus Callixylon. Similar material has been reported in the literature as "bituminous" or "asphaltic" stringers.

Spectrographic analyses of the ash from the coalified wood have shown unusually high percentages of germanium, uranium, vanadium, and nickel. The inverse relationship between uranium and germanium in the ash and the ash content of various samples shows an association of these elements with the organic constituents of the coal.

On the basis of geochemical considerations, it seems most probable that the wood or coalified wood was germanium-bearing at the time logs or woody fragments were floated into the basins of deposition of the Chattanooga shale and the Cleveland member of the Ohio shale. Once within the marine environment, the material probably absorbed uranium with the formation of organo-uranium compounds such as have been found to exist in coals.

It is suggested that a more systematic search for germaniferous coals in the vicinity of the Chattanooga shale and the Cleveland member of the Ohio shale might be rewarding.

Black, vitreous bands of carbonaceous material (1/8 to 5/8 inch thick and as much as several feet long) occur in the Chattanooga shale in Tennessee and in the Cleveland member of the Ohio shale in Ohio. In descriptions of these Upper Devonian black shales, these bands have been sporadically reported as "bituminous" or "asphaltic" lenses or stringers. Stauffer (1) described similar occurrences up to 3 inches thick in the Huron member of the Ohio shale in northern Ohio as "gilsonite seams." Microscopic study of the material has invariably revealed coalified woody plant tissue identical with that observed in vitrain. Some of this material shows sufficient detail of vascular pitting to be identified with the genus Callixylon.

Nearly fresh vitrain (2) collected from the top black interval of the Chattanooga shale in Davidson County, Tenn., and weathered vitrain obtained from the Cleveland member in the Bedford Reservation in Cuyahoga County southeast of Cleveland, Ohio, were available in sufficient quantities to obtain the standard coal analyses (3) shown in tables 1 and 2. The vitrain from the Chattanooga shale corresponds in rank to high-volatile A bituminous coal; the rank of that from the Cleveland member is probably similar, but the properties that are critical for determination of rank in this specimen have been altered by weathering. The vitrain from the Chattanooga shale is from one of the thickest bands recently observed (about half an inch). Other bands a quarter of an inch or thinner have been reported to be sparsely scattered in the shale which contains on the average three to five thin bands in a 30-foot core in central Tennessee (4). Other streaks have been observed in the black Dunkirk shale member of the Perrysburg formation in western New York and in the black Ohio shale near Chillicothe, Ohio.

Tabular pieces of coal from the Chattanooga shale and Cleveland member of the Ohio shale were cleaned with particular care to remove extraneous mineral matter before initiating geochemical studies. Spectrographic analysis (5) of the ash from each sample showed unusually high percentages of germanium, uranium, vanadium, and nickel (table 3). An analysis of ash from a sample of Chattanooga shale is also shown in table 3 for comparison.

Table 1.--Analysis of vitrain from the Chattanooga shale.1/

	As received (percent)	Moisture free (percent)	Moisture and ash free (percent)
Proximate analysis			
Moisture	2.1	--	--
Volatile matter	40.6	41.4	42.4
Fixed carbon	55.1	56.3	57.6
Ash	2.2	2.3	--
Ultimate analysis			
Hydrogen	5.6	5.5	5.6
Carbon	77.1	78.7	80.5
Nitrogen	1.7	1.7	1.7
Oxygen	9.8	8.2	8.5
Sulfur	3.6	3.6	3.7
Ash	2.2	2.3	--
British thermal units	14340	14640	14990

1/ Analyses by U. S. Bureau of Mines, Lab. No. E-32291, Feb. 2, 1954.

Table 2.--Analysis of vitrain from the Cleveland member of the Ohio shale.1/

	As received (percent)	Moisture free (percent)	Moisture and ash free (percent)
Proximate analysis			
Moisture	12.7	--	--
Volatile matter	33.5	38.4	40.0
Fixed carbon	50.2	57.5	60.0
Ash	3.6	4.1	--
Ultimate analysis			
Hydrogen	5.0	4.1	4.3
Carbon	62.5	71.6	74.6
Nitrogen	1.5	1.7	1.7
Oxygen	26.4	17.4	18.2
Sulfur	1.0	1.1	1.2
Ash	3.6	4.1	--
British thermal units	10620	12170	12700

1/ Analyses by U. S. Bureau of Mines, Lab. No. E-32292 Feb. 2, 1954.

Table 3.--Semiquantitative spectrographic analysis.1/

Percent	Ash of coal from Chattanooga shale 2/ Element	Ash of coal from Cleveland member 3/ Element	Ash from Chattanooga shale 4/ Element
Over 10	Fe	Fe	Al Si
5 - 10	Si	Al Ca Si	Fe
1 - 5	Ge Al Ca V	V Ge	K
0.5 - 1	Ni U Mg	Co Mg Zn	Mg
0.1 - 0.5	Cu Ti Cr Mo Na Sr B	Cu Cr Ni Ti U	Ca Na Ti Ba
0.05 - 0.1	Y Pb Ba	Ba B Na Mn Sr Y	--
0.01 - 0.05	Co Sn Zr Mn Zn	Mo Sn Pb Zr	Co B Cu Sr Cr Mo Ni Mn
0.005 - 0.01	Yb	Yb	V Ga La Zr
0.001 - 0.005	Ga Sc Be	La Ga Sc	Y Pb Sc Ge
0.0005-0.001	--	Be	--
0.0001-0.0005	--	--	Yb Be Ag

1/ Analyses by Mona Frank, U. S. Geological Survey.
2/ Ash of coal = 1.27 percent.
3/ Ash of coal = 1.7 percent.
4/ Ash of shale = 77.32 percent.

Semiquantitative analyses were supplemented and confirmed by the quantitative data shown in table 4. Analytical techniques that have already been described (2) were employed to obtain percentages of moisture, ash, and uranium in the samples. Germanium was determined quantitatively using a sodium carbonate dilution technique and appropriate standards; vanadium and nickel were determined using the pegmatite-base dilution technique described by Gordon and Murata (6).

A small sample of Chattanooga shale from Davidson County, Tenn., containing several thin coal bands was investigated in detail to determine the relationships of germanium and uranium in the coalified wood and in the shale. The specimen was dissected to remove four coal bands ranging from 2 to 5 mm in thickness. Five shale layers (2 to 10 mm) between the coal bands were also isolated for analysis. Four of the shale samples were highly weathered. The fifth shale sample was thicker than the others, very compact, and unweathered. Surfaces of the coal samples were cleaned of adhering mineral matter, and the individual samples were than pulverized in an agate mortar and analyzed. Analyses are shown in table 5.

The data of table 5 show that all the coal samples contain unusually high percentages of germanium and uranium. The ash content of each coal band is low and approximates that to be expected for vitrain (7). Determinations of percentages of ash and uranium in the shale matrix adjacent to these coal samples indicate a decrease in ash and uranium probably as a result of weathering. The germanium content of the shale samples may be somewhat high because of the presence of very thin hair-line streaks of coal, which could not be entirely removed and which probably contribute a small amount of germanium to the shale samples.

Table 4.--Analysis of coals from the Chattanooga shale and the Cleveland member of the Ohio shale.

	Coal from Chattanooga shale (weight percent)	Coal from Cleveland member 1/ (weight percent)
Moisture	2.3	--
Ash	1.27	1.7
Uranium in ash	2.58	0.50
Germanium in ash 2/	4.0, 4.5	2.
Vanadium in ash 3/	2.90	--
Nickel in ash 3/	0.36	--
Uranium in dry coal	0.033	0.0085
Germanium in dry coal	0.051, 0.057	0.034
Vanadium in dry coal	0.037	--
Nickel in dry coal	0.0046	--

1/ Analysis on dry basis by Audrey Smith, U. S. Geological Survey.
2/ Analyses by Katherine Valentine and Mona Frank, U. S. Geological Survey.
3/ Analysis by A. T. Myers, U. S. Geological Survey.

Table 5.--Analyses of shale and coal bands from the Chattanooga shale.

Sample	Ash (percent)	Uranium		Germanium 1/	
		In ash (percent)	In sample (percent)	In ash (percent)	In sample (percent)
Coal	4.23	0.42	0.0178	0.6	0.025
Coal	3.80	0.55	0.0209	2.0	0.076
Coal	2.45	0.57	0.0140	1.5	0.037
Coal	1.69	1.32	0.0223	3.0	0.051
Shale (unweathered)	77.32	0.0068	0.0053	0.001	0.0008
Shale	56.17	0.0038	0.0021	--	--
Shale	55.46	0.0049	0.0027	--	--
Shale	54.19	0.0083	0.0045	--	--
Shale	43.83	0.0099	0.0043	0.004	0.0018

1/ Analyses by Mona Frank, U. S. Geological Survey.

The inverse relationship (table 5) between uranium in the ash and the ash content of the coal samples shows an association of uranium with the organic constituents of the coal. The same relationship is true for germanium.

The association of uranium with coalified logs or coalified woody debris has long been known (8), and the occurrence of germanium in such materials has been well established (9, 10, 11). An association of both uranium and germanium in the same specimen, such as has been described in this paper, has not previously been reported.

Stadnichenko (11), in reporting on occurrences of germanium in American coals, states, "The highest concentrations of germanium have been found in coalified logs and pieces of woody coal occurring isolated in sediments." Germanium in the coalified wood from the Chattanooga shale represents another occurrence similar to those which Stadnichenko and her coworkers have described.

The germanium content of coal ash has been reported to range from less than 0.001 to 9 percent (9, 10, 11). Because germanium is frequently concentrated at the top and bottom of coal seams, it has been suggested that the element has entered the coal through the medium of ground water. Unusually high percentages of germanium may also have been introduced into ancient buried tree stumps by the movement of ground waters. Aubrey and others (10, 12) have suggested that germanium is retained in coals in intimate association with the organic constituents rather than with the mineral matter.

The concentration of germanium in sea water has been reported to be less than 10^{-8} percent (13). Shales have been reported by Preuss (14) to contain, on the average, approximately 7×10^{-4} percent of germanium.

From these data it would appear that sedimentation in a marine environment may concentrate germanium to an appreciable extent from sea water, but the content of the element in marine sediments is considerably lower than has been found in many coals or coalified logs from fresh-water environments. The highly anomalous concentration of germanium in coalified wood from the Chattanooga shale and the Cleveland member of the Ohio shale is several orders of magnitude greater than any concentration yet noted in marine sediments and can hardly be explained on the basis of absorption from a marine environment.

As has been noted by McKelvey and Nelson (15) and others, fine-grained shales deposited from marine environments may be uranium bearing. Two examples of such shales are the Swedish alum shale (16) and the Chattanooga shale (15). Sea water contains about 2 x 10^{-7} percent of uranium (17), marine formations normally contain approximately 10^{-4} percent of uranium (18), and certain strata in marine formations such as the Chattanooga and Swedish alum shales are known to contain from several thousandths to several tenths of 1 percent of uranium indicating even greater concentration of the element from sea water.

Several explanations are possible to account for this association of germanium and uranium, but it seems most probable that the wood or coalified wood was germanium-bearing at the time logs or woody fragments were floated into the basins of deposition of the Chattanooga shale and the Cleveland member of the Ohio shale. Once within the marine environment, the material probably absorbed uranium with the formation of organo-uranium compounds such as have been found to exist in coals (19).

The presence of germanium in the coalified wood from these shales suggests that a more systematic search for germaniferous coals in the vicinity of the Chattanooga shale and the Cleveland member of the Ohio shale might be rewarding.

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REFERENCES AND NOTES

1. C. R. Stauffer, Am. J. Sci. 242, 251 (1944).

2. I. A. Breger, R. Meyrowitz, and M. Deul, Science 120, 310 (1954).

3. A. C. Fieldner and W. A. Selvig, U. S. Bur. Mines Bull. 492 (1951).

4. T. M. Kehn, Personal communication.

5. C. L. Waring and C. S. Annell, Anal. Chem. 25, 1174 (1953).

6. M. Gordon, Jr., and K. J. Murata, Econ. Geol. 47, 169 (1952).

7. G. C. Sprunk and H. J. O'Donnell, U. S. Bur. Mines Tech. Paper 648, 3 (1942).

8. R. P. Fischer, Econ. Geol. 45, 1 (1950).

9. A. J. W. Headlee and R. G. Hunter, West Virginia Geol. Survey Rept. Invest. 8, 1 (1951).

10. K. V. Aubrey, Fuel 31, 429 (1952).

11. T. Stadnichenko, K. J. Murata, P. Zubovic, and E. L. Hufschmidt, U. S. Geol. Survey Circ. 272 (1953).

12. E. A. Rudge and S. E. A. Moon, Chemistry and Industry, 40 (1946).

13. I. Noddack and W. Noddack, Ark. Zool. (Swed.) 32A, no. 4, 35 (1939).

14. E. Preuss, Z. Angew. Min. 3, 8 (1940).

15. V. E. McKelvey and J. M. Nelson, Econ. Geol. 45, 35 (1950).

16. J. E. Eklund, Quart. Rev. Skand. Banken 28, 5 (1947).

17. D. C. Stewart and W. C. Bentley, Science 120, 50 (1954).

18. I. A. Breger, Manuscript in preparation.

19. I. A. Breger, M. Deul, and S. Rubinstein, Abstracts of Papers, Am. Chem. Soc., 126th Meeting, New York, 6K (Sept. 12, 1954).