

Chemistry

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

PRELIMINARY STUDIES OF COALIFIED WOOD ASSOCIATED
WITH URANIUM ON THE COLORADO PLATEAU*

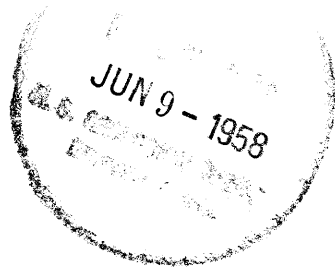
By

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PRELIMINARY STUDIES OF COALIFIED WOOD ASSOCIATED
WITH URANIUM ON THE COLORADO PLATEAU

By Irving A. Breger

ABSTRACT

In a study of the relationship of fossil plant debris to uranium on the Colorado Plateau, analyses of logs have shown that the composition of the coalified wood is dependent upon environment of burial. Equivalent rank varies from lignite to subbituminous on the British classification. Although uranium and carbon content cannot be correlated, organic hydrogen, volatile content, and Btu values decrease as uranium content increases. Several samples of coalified wood, both uraniferous and nonuraniferous, have lost all vestiges of cellular structure. Autoradiographic studies show concentrations of alpha particles along fracture zones of the coalified wood. Even where uraninite or coffinite is known to be present, however, the uranium is dispersed throughout the material. It is suggested that uranium, as the uranyl ion, was absorbed by the coalified wood, just as in massive uranium-bearing coals, and subsequently reduced from U^{+6} to U^{+4} .

INTRODUCTION

The geochemical relationship of plant debris to uranium and vanadium has long been a subject for speculation (Boutwell, 1904). Hess (1933) in discussing mineral deposits in the Shinarump member of the Chinle formation and the Morrison formation of the Colorado Plateau stated, "...uranium is nowhere found without carbonaceous material, either fossiliferous or petroliferous." As exploration for uranium intensified after 1945, more and more such occurrences

were described until today there is recognized nearly universally an association of fossil plant debris with oxidized and unoxidized uranium and vanadium ores that occur in sedimentary deposits. The literature is replete with such descriptions, and fossil wood has even been suggested as a guide to uranium ore (Weir, 1952; McKay, 1955).

In spite of the widespread descriptions covering such associations, there have been no specific studies of the plant debris. This report summarizes studies carried out to date to answer two specific questions:

- 1) What is the nature of the coalified plant debris, uraniferous and nonuraniferous, that occurs on the Colorado Plateau?
- 2) Can any relationships be recognized between uranium and other elements of or associated with the coalified plant debris?

The work summarized in this report is of a preliminary nature and will be augmented by additional investigations.

ACKNOWLEDGMENTS

Among his colleagues at the U. S. Geological Survey the author is particularly indebted to Kenneth G. Bell who accompanied the author during the collection of samples in 1955; his comments were both helpful and stimulating. R. C. Robeck, D. P. Elston, and L. S. Hilpert suggested areas of particular interest. Alice D. Weeks, L. R. Stieff, and T. W. Stern provided samples from their collection. Standard coal analyses were obtained through the courtesy of Roy F. Abernethy of the U. S. Bureau of Mines.

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SAMPLES

Locations and descriptions are presented in table 1 for samples collected from Triassic and Jurassic sedimentary rocks of the Colorado Plateau. Plant debris was recognizable by its morphology at each collection site.

With the exception of sample RF-1, the first 9 samples shown in table 1 were relatively large--several pounds. To obtain additional data, pieces of coalified plant debris, although too small for coal analyses or for petrographic work, were also studied. These samples are also listed in table 1.

U. S. Bureau of Mines standard coal analyses (Fieldner and Selvig, 1951) for samples RF-1, DD-2, DD-3, P-1, AG-1, JJ-2, SF-1, NA-1, V-1, and MD42B-3 are shown in tables 2 through 11. Uranium analyses together with carbon, hydrogen, and ash values are summarized in table 12.

Table 1.--Description of coalified wood specimens from the Colorado Plateau.

Sample number	Description
RF-1	<p>Collection site: Robby Ford, Chimney Canyon, San Rafael Swell, Emery County, Utah. Unsurveyed sec. 23; surveyed T. 25 S., R. 8 E., SIM. Field description: Coalified wood in white sandstone. Moss Back member of Chinle formation (Triassic). Sample about 6 inches above bottom of channel. Petrographic description: <u>1/</u> No histologic structure--a red translucent limpid gel. No visible minerals or opaque organic matter.</p>
DD-2	<p>Collection site: Dirty Devil No. 4 mine, School section, San Rafael Swell, Emery County, Utah. Field description: Coalified log from roof in corridor about 100 yards from adit. Highly vitrained. Smells asphaltic when broken. Moss Back member of Chinle formation (Triassic). Petrographic description: <u>1/</u> Questionable histologic structure. Matrix very dense, mostly opaque or brown including some translucent ovoid organic bodies. Some of the ovoid bodies are grouped in files reminiscent of ray-resin groupings in wood. However, no cell-wall differentiation is visible. Pyritic (?) and transparent mineral matter show equivocal relation to possible histologic features.</p>
DD-3	<p>Collection site: Same as DD-2. Field description: Several small coalified logs, each several inches wide and about 18 inches long. Sample about 2 feet below DD-2 and 8 feet from it laterally. Sample about 2 feet above ore-bearing sandstone. Moss Back member of Chinle formation (Triassic). Petrographic description: <u>1/</u> Evident wood structure, resinous cell contents scarce. Opaque spheroids with pyritic nuclei.</p>

Table 1.--Description of coalified wood specimens from the Colorado Plateau.--Continued.

Sample number	Description
SEF-1	<p>Collection site: Santa Fe pit, Poison Canyon mine, sec. 19, Valencia County, N. Mex. Field description: Coalified log from sandstone. Brushy Basin shale member of Morrison formation (Jurassic). Petrographic description:<u>l</u>/ Evident wood structure throughout, visible from polished surfaces viewed by reflected light. Variable translucency. Tissue structure generally resembles fusain in being uncompressed; opaque cell walls, however, have organic contents which usually are semitranslucent (brown). More translucent areas show vitrained appearance common in anthraxylon.</p>
AG-1	<p>Collection site: Rocky Mountain Uranium Co., A and G mine no. 2, Dry Canyon, San Rafael Swell, Emery County, Utah. Unsurveyed sec. 26; surveyed T. 24 S., R. 8 E. Field description: Sample taken at mine-face workings 121 feet from outcrop. Coalified log 6 inches in diameter extending over approximately 10-20 feet in the mine. Section 12 to 18 inches long mined out for sample. Interior of log filled with clay. Moss Back member of Chinle formation (Triassic). Petrographic description:<u>l</u>/ Evident wood structure. Moderate amount of resinous cell contents. Dark opaque areas along cracks and as small spheroids around disseminated pyritic (?) nuclei.</p>
JJ-2	<p>Collection site: J. J. mine, San Miguel County, Colo., T. 46 N., R. 102 E. Field description: Sample of one or possibly two coalified logs from mineralized lower sand. Salt Wash sandstone member of the Morrison formation (Jurassic). Petrographic description:<u>l</u>/ Evident wood structure. Contains areas of abrupt transition to opaque organic matter, and darkening around some rays and small spheroids associated with disseminated pyritic (?) mineral.</p>

Table 1.--Description of coalified wood specimens from the Colorado Plateau.--Continued.

Sample number	Description
VNA-1	<p>Collection site: Vanadium King No. 7 mine, north adit, middle workings, Temple Mountain, San Rafael Swell, Emery County, Utah. Field description: Coalified log containing much pyrite and other minerals and surrounded by halo of black impregnation in sand having a faint appearance of banding. Sample 2 to 3 feet above base of member and 150 feet in from adit on west face just southwest of the airhole. Moss Back member of Chinle formation (Triassic). Petrographic description:1/ No histologic structure. Consists principally of opaque organic matter with smaller areas of homogeneous red-translucent organic matter. A few isolated, translucent ovoid bodies, similar to those in sample DD-2, but lacking any organized grouping, are present in the dense matrix. The transition between opaque and translucent areas is fairly abrupt and the contact has a colloidal, diffusion-type (botryoidal ?) outline. Needle-shaped crystals of an opaque mineral are preferentially concentrated in red translucent areas.</p>
P-1	<p>Collection site: Peanut mine, Montrose County, Colo., T. 46 N., R. 102 E. Field description: Large sample of coalified wood. Low-grade ore just above and below sample. Clay above and below coalified wood.</p>
V-1	<p>Sample 6 inches below top layer of ore and 26 inches above bottom layer. Morrison formation (Jurassic). Petrographic description:1/ Evident wood structure, moderate amount of resinous cell contents. Shows a little disseminated pyritic mineral and very little darkening of organic material.</p> <p>Collection site: Virgin No. 3 mine, Montrose County, Colo., sec. 21, T. 29 S., R. 101 W. Field description: Coalified log from roof of mine. Morrison formation (Jurassic). Petrographic description:1/ Evident wood structure. No minerals noted.</p>

Table 1.--Description of coalified wood specimens from the Colorado Plateau.--Continued.

Sample number	Description
LAB9C-1	Sample AW-8-54 collected by Alice Weeks in the Corvusite mine, Grand County, Utah. Sample is a large tree.
LAB9C-2	Brushy Basin shale member of Morrison formation (Jurassic). (0.94 g)
LAB9C-4	Second specimen from AW-8-54. (3.04 g)
LAB9C-4	Third specimen from AW-8-54. This sample (separately numbered AW-10-54) is a very black shiny portion of the tree. (4.48 g)
LAB9C-5	Fourth specimen from AW-8-54. This sample of the coalified wood was very hard and light brown when ground. (Approximately 3 g)
LAB9C-6	Fifth specimen from AW-8-54. Coalified wood was dark brown when ground. (1.63 g)
LAB9C-3	Sample of coalified wood collected by Alice Weeks (AW-73-54) in the Camp Bird No. 7 mine, Emery County, Utah. Material was black, dense, had a conchoidal fracture, and emitted a very sulfurous odor when ground. This sample was similar to RF-1. Chinle formation (Triassic). (2.13 g)
LAB9C-8	Sample of pyrite-bearing coalified wood from Rex No. 1 mine, Temple Mountain, Emery County, Utah. Sulfurous odor (not H ₂ S) emitted on grinding. Moss Back member of Chinle formation (Triassic). (Approximately 3 g)
LAB9C-12	Second sample from Rex No. 1 mine. Material dark brown, woody, and soft. (2.03 g)
LAB9C-13	Third sample from Rex No. 1 mine. Black to dark brown, brittle, coalified wood. (0.84 g)
LAB9C-15	Fourth sample from Rex No. 1 mine. Single piece of coalified wood grading from soft brown to nearly brittle black material. No odor on grinding. (1.41 g)

Table 1.--Description of coalified wood specimens from the Colorado Plateau.--Continued.

Sample number	Description
LIAB9C-16	Fifth sample from Rex No. 1 mine. Small piece of very dark brown coalified wood emitting no odor when ground. (2 g)
LIAB9C-17	Sixth sample from Rex No. 1 mine. Very bright shiny black coal. Brittle and emitting peculiar odor when ground. (0.35 g)
LIAB9C-18	Seventh sample from Rex No. 1 mine. Dull dark-brown coalified wood. Peculiar odor when ground. (1 g)
LIAB9C-9	Coalified wood from Utex mine, San Juan County, Utah. Black and tough, but no odor on grinding. Small films of calcite removed. Chinle formation (Triassic). (1.12 g)
LIAB9C-10	Coalified wood from Happy Jack mine, San Juan County, Utah. Black, shiny, and brittle. Slight sulfurous odor on grinding. Shinarump member of the Chinle formation (Triassic). (1.56 g)
LIAB9C-19	Woody material from the A. E. C. No. 4 mine, Temple Mountain, Emery County, Utah. Small amount of shiny, conchoidal coal associated with woody material. Moss Back member of Chinle formation (Triassic). (0.88 g)
LIAB9C-20	Woody material from the Virgin No. 3 mine, Montrose County, Colo. Dark brown; no odor on grinding. Morrison formation (Jurassic). (1.03 g)
LIAB9C-22	Coalified wood from Rex No. 2 mine, Temple Mountain, Emery County, Utah. Dark brown and odoriferous when ground. Moss Back member of Chinle formation (Triassic). (2.71 g)
LIAB9C-23	Coalified wood collected by Alice Weeks (AW-61-54) from Lucky Strike mine, Emery County, Utah. Chinle formation (Triassic).

Table 1.--Description of coalified wood specimens from the Colorado Plateau.--Continued.

Sample number	Description
AMD42B-3	Coalified wood from Rex No. 1 mine, Temple Mountain, Emery County, Utah. Moss Back member of Chinle formation (Triassic). <u>2/</u>
AW-16-52A	Brown coalified wood from the Corvusite mine, Grand County, Utah. Brushy Basin shale member of Morrison formation (Jurassic). <u>2/</u>
AW-16-52B	Dark-brown coalified wood from above sample. <u>2/</u>
AW-16-52C	Black, brittle coalified wood from above sample. Sample AW-16-52 was a small plant fragment, about 2 inches long. <u>2/</u>
AW-18-52	Coalified wood from the Corvusite mine, Grand County, Utah. <u>2/</u>

1/ Petrographic studies made by James M. Schopf, U. S. Geological Survey, Columbus, Ohio.

2/ Irving A. Breger and Maurice Deul, U. S. Geological Survey, written communication, 1955.

Table 2.--Analysis of coalified wood sample RF-1 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	1.5	--	--
Volatile matter	54.6	55.5	55.7
Fixed carbon	43.4	44.0	44.3
Ash	0.5	0.5	--
Ultimate analysis			
Hydrogen	7.6	7.5	7.5
Carbon	79.4	80.6	81.0
Nitrogen	0.4	0.4	0.4
Oxygen	7.6	6.4	6.5
Sulfur	4.5	4.6	4.6
Ash	0.5	0.5	--
Forms of sulfur			
Sulfate	0.02	0.02	0.02
Pyritic	0.05	0.05	0.05
Organic	4.46	4.52	4.55
British thermal units	15,550	15,780	15,860

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-9307⁴, December 13, 1955.

Table 3.--Analysis of coalified wood sample DD-2 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	1.1	--	--
Volatile matter	31.1	31.4	33.8
Fixed carbon	60.9	61.6	66.2
Ash	6.9	7.0	--
Ultimate analysis			
Hydrogen	4.7	4.6	5.0
Carbon	67.0	67.7	72.8
Nitrogen	0.2	0.2	0.2
Oxygen	7.8	7.0	7.5
Sulfur	13.4	13.5	14.5
Ash	6.9	7.0	--
Forms of sulfur			
Sulfate	0.04	0.04	0.05
Pyritic	1.33	1.34	1.44
Organic	12.00	12.14	13.05
British thermal units	13,140	13,290	14,280

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93069, December 13, 1955.

Table 4.--Analysis of coalified wood sample DD-3 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	1.3	--	--
Volatile matter	60.2	61.0	61.7
Fixed carbon	37.4	37.9	38.3
Ash	1.1	1.1	--
Ultimate analysis			
Hydrogen	6.9	6.8	6.9
Carbon	81.1	82.1	83.0
Nitrogen	0.4	0.4	0.4
Oxygen	8.4	7.5	7.6
Sulfur	2.1	2.1	2.1
Ash	1.1	1.1	--
Forms of sulfur			
Sulfate	0.03	0.03	0.03
Pyritic	0.11	0.11	0.11
Organic	1.96	1.98	2.00
British thermal units	15,330	15,530	15,700

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93070, December 13, 1955.

Table 5.--Analysis of coalified wood sample P-1 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	1.8	--	--
Volatile matter	54.7	55.7	56.6
Fixed carbon	42.0	42.7	43.4
Ash	1.5	1.6	--
Ultimate analysis			
Hydrogen	6.5	6.4	6.5
Carbon	80.1	81.6	82.9
Nitrogen	0.3	0.3	0.4
Oxygen	10.8	9.3	9.4
Sulfur	0.8	0.8	0.8
Ash	1.5	1.6	--
Forms of sulfur			
Sulfate	0.4	0.4	0.4
Pyritic	0.15	0.16	0.16
Organic	0.63	0.64	0.65
British thermal units	14,820	15,090	15,330

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93073, December 13, 1955.

Table 6.--Analysis of coalified wood sample AG-1 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	4.2	--	--
Volatile matter	48.1	50.2	51.8
Fixed carbon	44.7	46.7	48.2
Ash	3.0	3.1	--
Ultimate analysis			
Hydrogen	6.0	5.8	6.0
Carbon	69.6	72.7	75.0
Nitrogen	0.2	0.3	0.3
Oxygen	19.8	16.7	17.2
Sulfur	1.4	1.4	1.5
Ash	3.0	3.1	--
Forms of sulfur			
Sulfate	0.51	0.54	0.55
Pyritic	0.17	0.18	0.18
Organic	0.69	0.72	0.74
British thermal units	12,690	13,250	13,680

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93068, December 13, 1955.

Table 7.--Analysis of coalified wood sample JJ-2 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	1.7	--	--
Volatile matter	38.8	39.5	42.2
Fixed carbon	53.2	54.1	57.8
Ash	6.3	6.4	--
Ultimate analysis			
Hydrogen	5.7	5.6	6.0
Carbon	76.9	78.3	83.6
Nitrogen	0.3	0.3	0.4
Oxygen	8.9	7.5	8.0
Sulfur	1.9	1.9	2.0
Ash	6.3	6.4	--
Forms of sulfur			
Sulfate	0.06	0.06	0.07
Pyritic	0.71	0.72	0.77
Organic	1.10	1.11	1.19
British thermal units	14,150	14,440	15,380

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93072, December 13, 1955.

Table 8.--Analysis of coalified wood sample SF-1 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	9.9	--	--
Volatile matter	20.9	23.2	28.0
Fixed carbon	53.5	59.4	72.0
Ash	15.7	17.4	--
Ultimate analysis			
Hydrogen	3.5	2.7	3.2
Carbon	55.5	61.6	74.6
Nitrogen	0.4	0.4	0.5
Oxygen	18.5	10.8	13.1
Sulfur	6.4	7.1	8.6
Ash	15.7	17.4	--
Forms of sulfur			
Sulfate	0.73	0.81	0.98
Pyritic	5.19	5.76	6.97
Organic	0.46	0.51	0.62
British thermal units	9,520	10,560	12,790

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93075, December 14, 1955.

Table 9.--Analysis of coalified wood sample NA-1 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	2.2	--	--
Volatile matter	23.1	23.6	29.5
Fixed carbon	55.3	56.6	70.5
Ash	19.4	19.8	--
Ultimate analysis			
Hydrogen	3.5	3.3	4.2
Carbon	61.3	62.6	78.1
Nitrogen	0.2	0.2	0.3
Oxygen	7.3	5.7	6.9
Sulfur	8.3	8.4	10.5
Ash	19.4	19.8	--
Forms of sulfur			
Sulfate	0.06	0.06	0.07
Pyritic	1.44	1.47	1.83
Organic	6.77	6.92	8.63
British thermal units	11,060	11,310	14,100

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93071, December 13, 1955.

Table 10.--Analysis of coalified wood sample V-1 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	2.4	--	--
Volatile matter	54.5	55.8	56.9
Fixed carbon	41.3	42.4	43.1
Ash	1.8	1.8	--
Ultimate analysis			
Hydrogen	6.5	6.4	6.5
Carbon	78.3	80.2	81.7
Nitrogen	0.4	0.4	0.4
Oxygen	12.2	10.3	10.5
Sulfur	0.8	0.9	0.9
Ash	1.8	1.8	--
Forms of sulfur			
Sulfate	0.5	0.6	0.6
Pyritic	0.14	0.14	0.15
Organic	0.65	0.66	0.67
British thermal units	14,250	14,600	14,860

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-93076, December 14, 1955.

Table 11.--Analysis of coalified wood sample MD42B-3 from the Colorado Plateau.^{1/}

	As received (percent)	Moisture-free (percent)	Moisture- and ash-free (percent)
Proximate analysis			
Moisture	2.6	--	--
Volatile matter	24.2	24.8	32.2
Fixed carbon	50.9	52.3	67.8
Ash	22.3	22.9	--
Ultimate analysis			
Hydrogen	3.3	3.1	4.0
Carbon	56.8	58.3	75.6
Nitrogen	0.1	0.1	0.2
Oxygen	8.9	6.8	8.8
Sulfur	8.6	8.8	11.4
Ash	22.3	22.9	--
Forms of sulfur			
Sulfate	0.07	0.07	0.09
Pyritic	1.04	1.07	1.39
Organic	7.45	7.65	9.92
British thermal units	10,210	10,480	13,600

^{1/} Analysis by U. S. Bureau of Mines, Lab. no. E-61765, January 26, 1955.

Table 12.--Analyses for plant debris from the Colorado Plateau
(in percent).

Sample	Ash <u>1,3/</u>	Carbon <u>2,3/</u>	Hydrogen <u>2,3/</u>	Uranium in dry sample <u>4/</u>	Org.
RF-1	0.5	81.0	7.5	0.001	4.5
DD-2	7.0	72.8	5.0	2.02	12.1
DD-3	1.1	83.0	6.9	0.018	1.9
SF-1	17.4	74.6	3.2	3.08	.51
AG-1	3.1	75.0	6.0	0.036	.72
JJ-2	6.4	83.6	6.0	1.31	1.11
NA-1	19.8	78.1	4.2	7.51	6.92
P-1	1.6	82.9	6.5	0.036	.64
V-1	1.8	81.7	6.5	0.016	.66
IAB9C-1	2.7	79.3	5.9	0.50	
IAB9C-2	4.5	79.1	6.5	0.73	
IAB9C-4	9.5	83.2	3.4	5.4	
IAB9C-5	1.0	82.6	6.8	0.043	
IAB9C-6	3.1	83.8	6.9	0.031	
IAB9C-3	12.6	80.2	4.6	7.7	
IAB9C-8	40.9	79.5	5.7	1.7	
IAB9C-12	5.3	72.7	6.0	0.001	
IAB9C-13	1.4	76.4	5.9	0.001	
IAB9C-15	4.2	74.7	5.9	0.0032	
IAB9C-16	9.1	82.6	6.5	0.014	
IAB9C-17	12.5	74.5	3.8	5.5	
IAB9C-18	1.3	78.8	6.1	0.19	
IAB9C-9	2.2	82.7	5.7	0.19	
IAB9C-10	4.5	81.5	4.8	1.0	
IAB9C-19	5.6	81.4	6.6	0.012	
IAB9C-20	0.8	82.6	6.2	0.003	
IAB9C-22	4.4	81.0	6.7	0.11	
IAB9C-23	20.8	74.5	4.4	6.9	
MD42B-3	22.9	75.6	4.0	7.54	7.65
AW-16-52A	3.0	82.7	7.7	0.057	
AW-16-52B	0.64	81.3	6.7	0.0018	
AW-16-52C	22.5	83.0	4.2	1.64	
AW-18-52	13.1	80.1	5.8	2.28	

1/ Dry basis.

2/ Moisture- and ash-free basis.

3/ Analyses by U. S. Bureau of Mines and by E. B. Brittin and R. Meyrowitz, U. S. Geological Survey.

4/ Analyses by Roberta Smith, Carmen Johnson, and Jesse Warr, Jr., U. S. Geological Survey.

DISCUSSION

Nature of the plant debris

Petrographic studies of the nine samples made by James M. Schopf, U. S. Geological Survey (written communication), show that the majority contain evident wood structure (gymnospermous pycnoxylic). Schopf states, "Coaly material from the Colorado Plateau has usually been regarded as corresponding in classification with subbituminous rank. Probably this is correct as far as the effects of metamorphism alone are concerned. The microscopical results reported here, however, show a correlation between opaque or poorly translucent organic matter and decrease in volatile content. This indicates that mode of preservation, rather than metamorphism, is primarily responsible for the wide range of analytical values."

Inspection of the Bureau of Mines reports indicates that the 10 samples of coalified wood that were analyzed in detail are equivalent to lignite or subbituminous in rank according to the British system of classification (Seyler, 1948). According to the American system, these coals correspond in classification to subbituminous or high volatile bituminous rank (Fieldner and Selvig, 1951). Classifications are tabulated in table 13. It should be noted that sample DD-2 can be classified a lignite, whereas DD-3, taken only several feet from it, is equivalent to subbituminous rank.

Analyses of the 33 samples of table 12 are plotted in figure 1 on Seyler's Fuel Chart 47 (Seyler, 1948). The dark lines enclose the analyses of most mined coals. Lignites contain 63 to 75 percent carbon; subbituminous coals, 75 to 84 percent carbon. The random distribution of analytical data (fig. 1) illustrates the abnormal coalification process noted in Schopf's petrographic studies. Had coalification proceeded through normal burial of

Table 13.--Equivalent classification of samples of coalified wood.

Sample	Rank correspondence	
	British <u>1/</u>	American <u>2/</u>
RF-1	Subbituminous	High volatile A bituminous
DD-2	Lignite	High volatile B bituminous
DD-3	Subbituminous	High volatile A bituminous
SF-1	Lignite	Subbituminous B
AG-1	Subbituminous	High volatile C bituminous
JJ-2	Subbituminous	High volatile A bituminous
NA-1	Subbituminous	Medium volatile bituminous
P-1	Subbituminous	High volatile A bituminous
V-1	Subbituminous	High volatile A bituminous
MD42B-3	Subbituminous	Subbituminous B

1/ Based on Seyler (1948).

2/ Values for bed moisture not known. Equivalent rank, therefore, is based on "as received" value.

wood in a swamp environment, most analytical points would be expected to fall within or close to the normal coal curve. Low hydrogen values for a number of samples plotted in figures 1 and 2 may be related to uranium content of the coalified wood. This point is discussed in another section of this paper.

Variations in coalification for the same specimen and within the same mine are shown in figure 2. Three samples from the Corvusite mine range in carbon content from about 79 to 83 percent. One of these three samples was divided into three segments, individual analyses for which are shown. Samples from

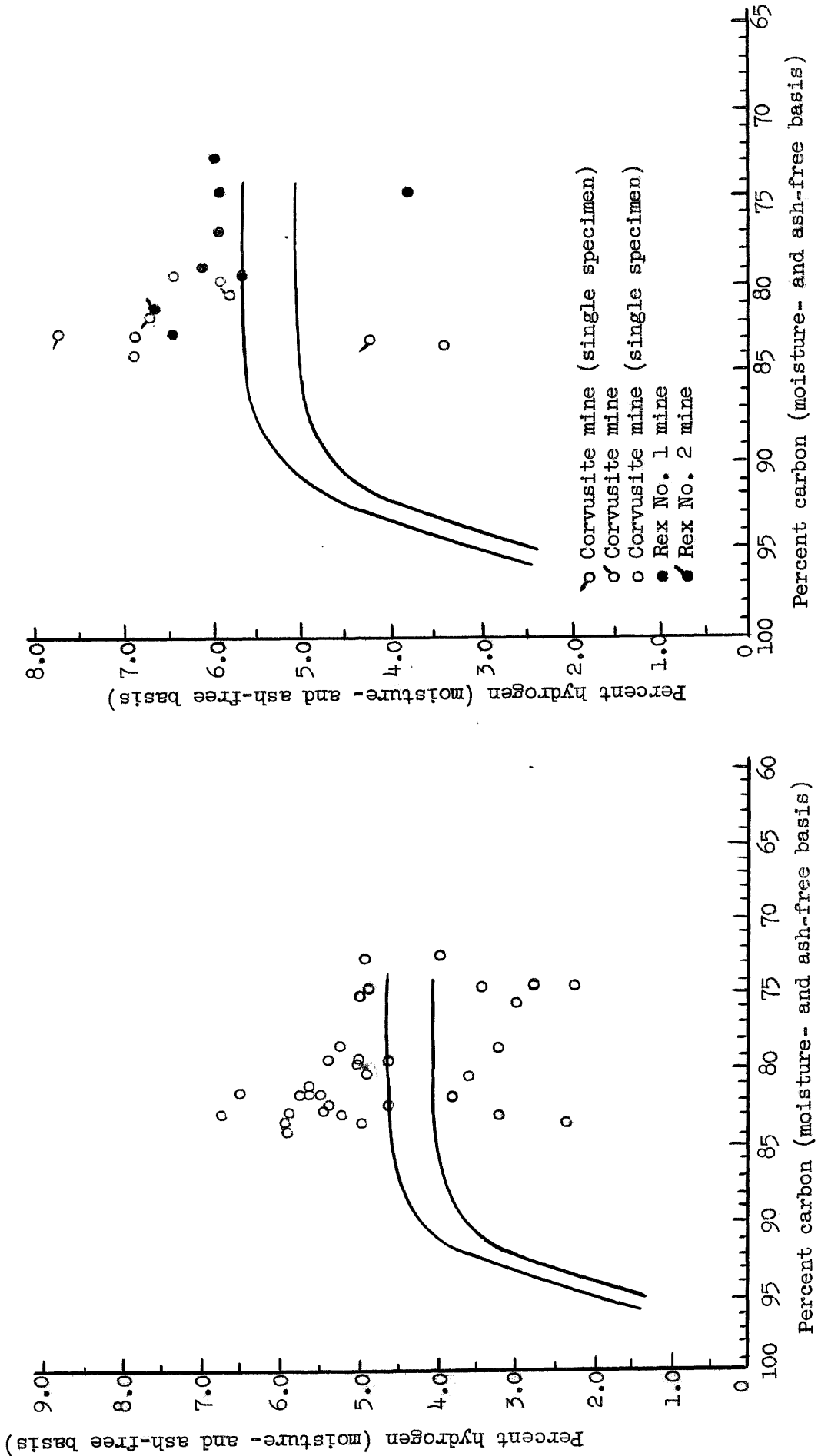


Figure 1.--Analyses of coalified wood samples from the Colorado Plateau plotted on Seyler coal chart.

Figure 2.--Variations in coalification with the same specimen and within the same mine.

the Rex No. 1 and No. 2 mines, which are adjacent to each other, range in carbon content from about 72 to 83 percent. The hydrogen contents of these samples range from about 3.3 to 7.7 percent.

Coalification is extremely variable within the same sample or within a particular mine. It is important to note from figure 1 that not one of the 33 samples analyzed contains more than 84 percent carbon. This sharp limiting value indicates that coalification took place only through the relatively rapid biochemical stage, and that dynamochemical metamorphism (Hendricks, 1945) was not a factor in coalification.

Correlation between uranium and constituent elements of the coalified wood

Samples of coalified wood that have been studied were, as already noted, deposited during Triassic and Jurassic time. A number of proposals, reviewed by Fischer (1956), have been made to account for the age relationships between the uranium ore and the sediments. It is beyond the scope of this report to compare the features of the various opinions. As a basis for discussion, however, it will be assumed that uranium was introduced into the sediments not earlier than Late Cretaceous time, about 60 to 90 million years ago (Stieff, Stern, and Milkey, 1953). An epigenetic origin for the uranium deposits is also supported by the geological considerations of Wood (1956). It is reasonable to assume that coalification of the wood was essentially complete for Triassic logs during Triassic time and for Jurassic logs during Jurassic time. During coalification chemical differences in the composition of the logs would be expected to disappear.

Data plotted in figure 3 show the relationship between organic carbon and uranium in the samples of coalified wood. It is evident that, especially as the uranium differs by nearly four orders of magnitude, there is no dependence of uranium on carbon content.

When organic hydrogen is plotted against uranium (fig. 4), there is no apparent relationship for samples containing less than 0.1 percent uranium. As uranium content rises from 0.1 to 7.5 percent, however, hydrogen seems to decrease.

The data of figure 4 are presented on a semilogarithmic plot for convenience. Were the data plotted on a linear diagram, the change in slope at about 0.1 percent uranium would not be apparent. To illustrate this point, the data of figure 4 have been replotted in the linear diagram of figure 5. The line drawn on figure 5 is based on a least-squares calculation on the assumption that the relationship is linear. If this assumption is correct, then hydrogen decreases by 0.25 percent for every increase of 1 percent of uranium retained by the coal.

The relationship between hydrogen and uranium can be explained as arising from a radiochemical dehydrogenation of the coalified wood by the alpha particles from uranium and its daughter products. It is well known that high-energy radiation initiates chain mechanisms that result in the crosslinking of molecules (Charlesby and Ross, 1953). Dehydrogenation is also a common phenomenon when organic compounds are irradiated (Breger, 1948). Aromatic compounds generally polymerize or condense with a relatively low production of hydrogen. Inasmuch as coal is basically aromatic in structure, a major radiochemical product would be polymerized or condensed coal. The natural dehydrogenation of coal by alpha particles has not been noted before but is suggested from

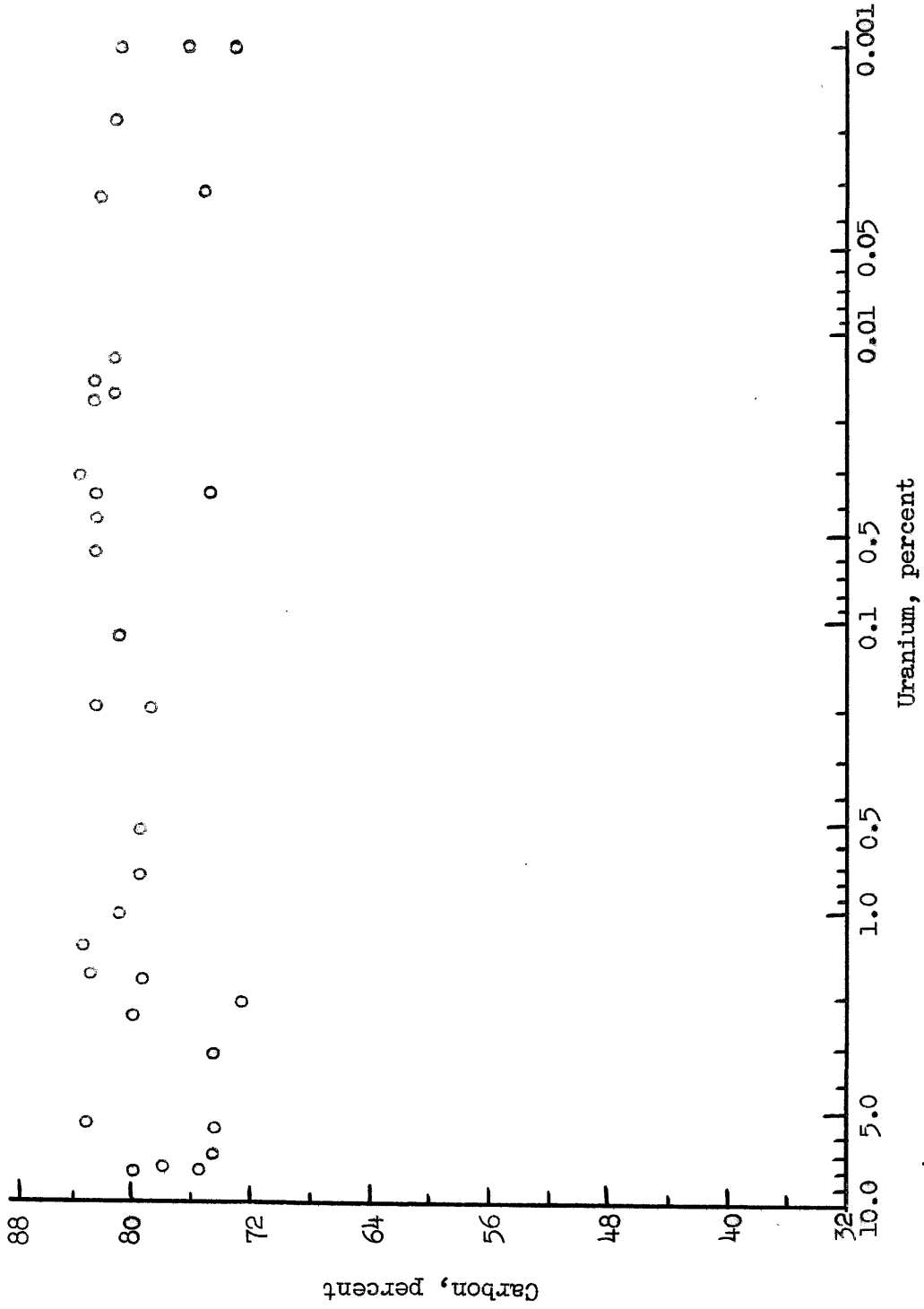


Figure 3.--Relationship of organic carbon (moisture- and ash-free) to uranium in coalified wood.

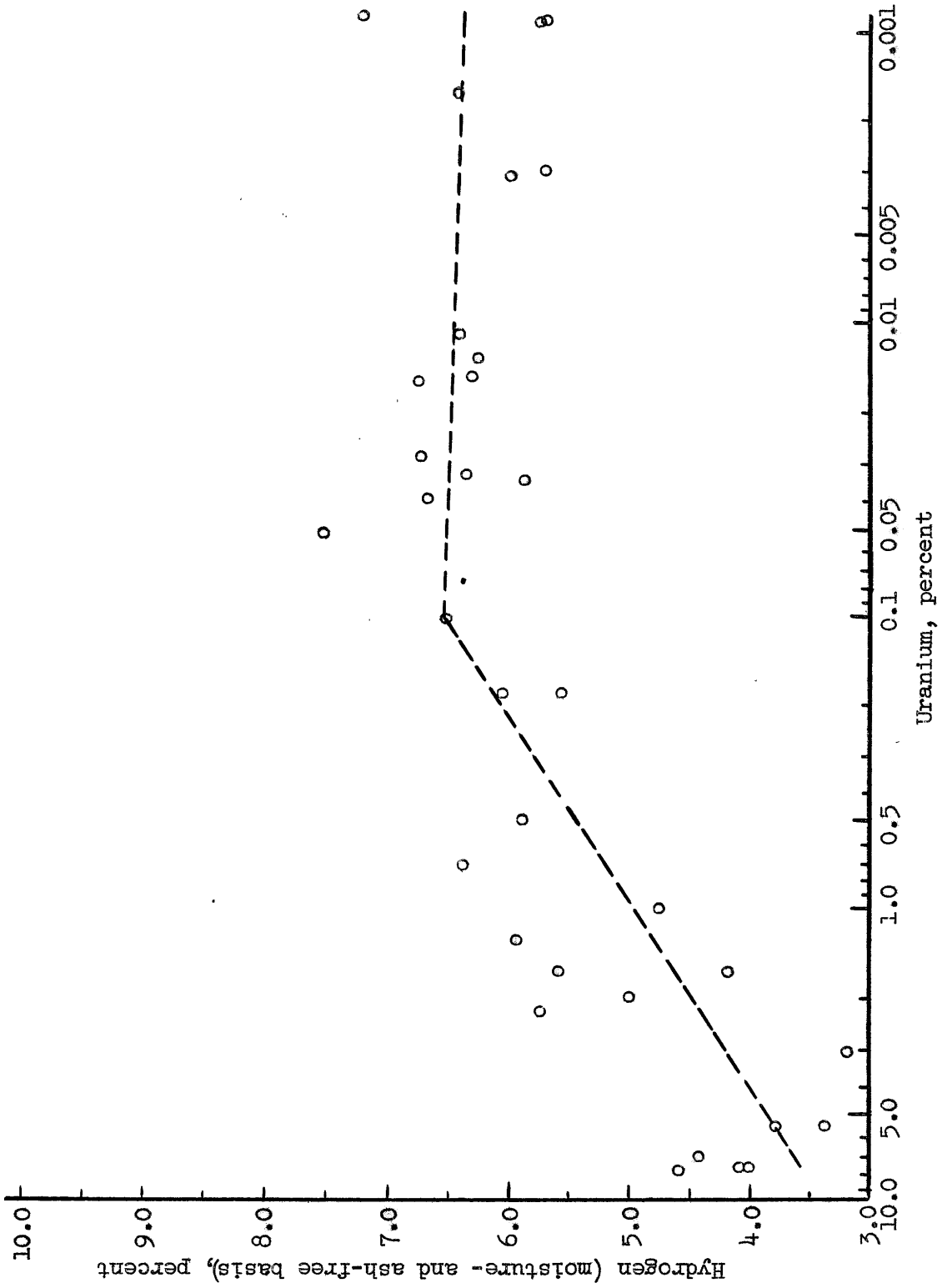


Figure 4.--Relationship of organic hydrogen (moisture- and ash-free) to uranium in coalified wood, semilogarithmic plot.

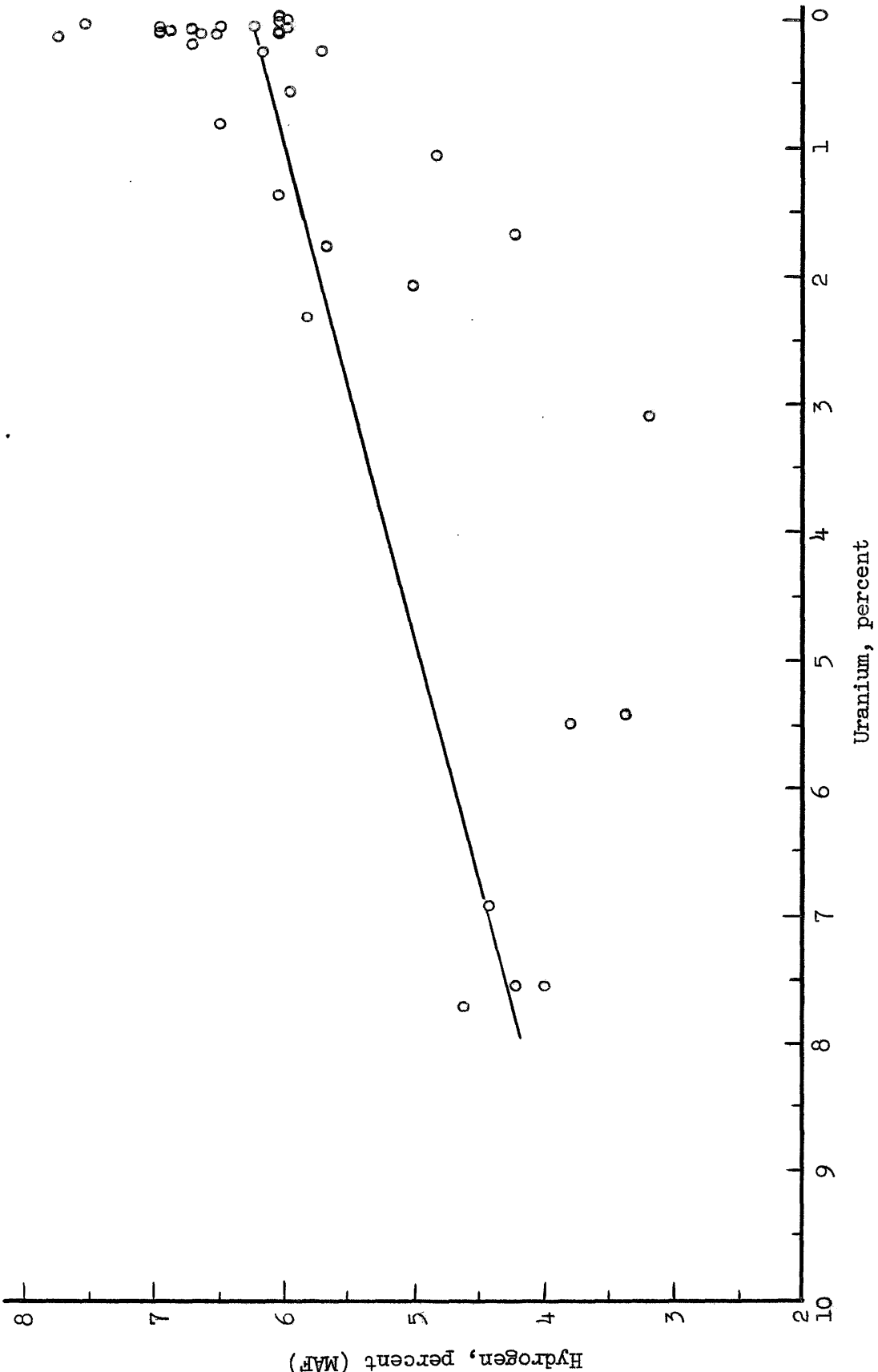


Figure 5.--Relationship of organic hydrogen (moisture- and ash-free) to uranium in coalified wood, linear plot. Straight line based on a least squares calculation assuming straight line relationship.

inspection of figures 4 and 5. If uranium was introduced into the sediments in Late Cretaceous or Tertiary time, then the Triassic and Jurassic coalified logs have been subjected to irradiation for approximately the same time.

An inverse uranium-hydrogen relationship should appear throughout the entire range of values for uranium (0.001 to 7.7 percent), but it must be remembered that small percentages of uranium will result in the elimination of minute and undetectable quantities of hydrogen. Above uranium contents of 0.1 percent, however, it appears that the loss of hydrogen becomes analytically significant and the inverse relationship becomes detectable. The scatter of points about the dashed lines of figure 4 can be explained in two ways: (1) If the uranium is not homogeneously dispersed throughout the coal, radiochemical dehydrogenation would take place only in part of the sample analyzed. Although an attempt was made to eliminate any such error by taking extremely small samples (approximately 1 to 3 g) of 23 of the specimens analyzed, the effects of a microscopically inhomogeneous distribution of uranium, since demonstrated by autoradiography, are difficult to predict and indicate this to be a possible explanation. (2) Another explanation for the scatter of points in figure 4 is based on the variable coalification that the wood samples have undergone. Differences in hydrogen content are evident in figure 1 and are undoubtedly reflected in figure 4. It is apparent, however, that the secondary effect of radiochemical dehydrogenation is imposed upon such variations.

Although only 10 samples were large enough for the determination of volatile content by the Bureau of Mines, the semilogarithmic plot of volatile matter and uranium (fig. 6) is roughly similar to that for hydrogen and uranium (fig. 4). The loss of hydrogen from a sample of coalified wood is undoubtedly related to crosslinking of the coal and to decrease in the volatile constituents produced when the coal is pyrolyzed during the determination of volatile matter.

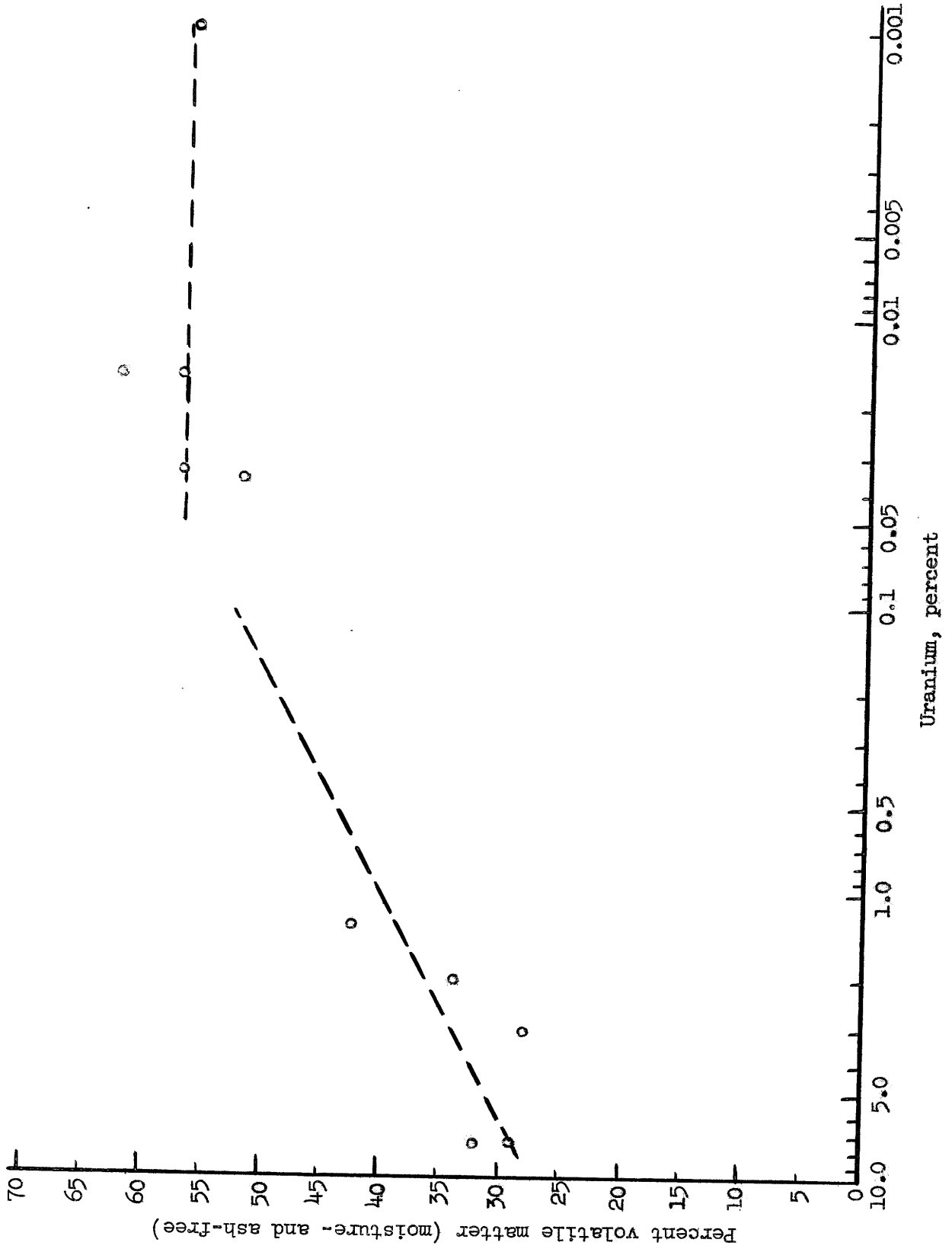


Figure 6.--Relationship of volatile content (moisture- and ash-free) to uranium in coalified wood.

Correlation between sulfur and uranium for the 10 samples of coalified wood for which data are available is shown in figure 7. Total sulfur rises abruptly as the uranium content increases above about 2 percent. Organic sulfur also increases sharply above this value for all samples except SF-1, which was collected from the Morrison formation, Valencia County, New Mexico.

The limited number of samples provides insufficient basis for any conclusions regarding the relationship between uranium and organic sulfur. Sulfur may have become associated with the coalified wood before, during, or after introduction of uranium.

The occurrence of coalified wood with high organic sulfur content is unusual and worthy of special note. The high organic sulfur content of sample MD42B-3 (9.92 percent) has already been observed (I. A. Breger and Maurice Deul, written communication, 1955); this amount has now been exceeded by that of sample DD-2 (13.05 percent) and nearly equalled in sample NA-1 (8.63 percent). The Tangorin high organic sulfur seam of Australia (Marshall and Draycott, 1954) contains only 4.84 to 4.96 percent organic sulfur, and the Rasa coal of Istria contains 11 percent (Kreulen, 1952). As far as can be ascertained, sample DD-2 contains the highest percentage of organic sulfur yet reported for coal or coalified wood. The organic sulfur of samples DD-2, NA-1, and MD42B-3 may be related to the composition of the ore-bearing fluid and may indicate that sulfur was introduced along with uranium. Sample SF-1, on the other hand, comes from a different part of the Colorado Plateau and, although it contains high total sulfur, has a low organic sulfur content.

Figure 8 shows that the Btu content of the coalified wood decreases slightly with increasing uranium content (135 Btu per percent U based on a

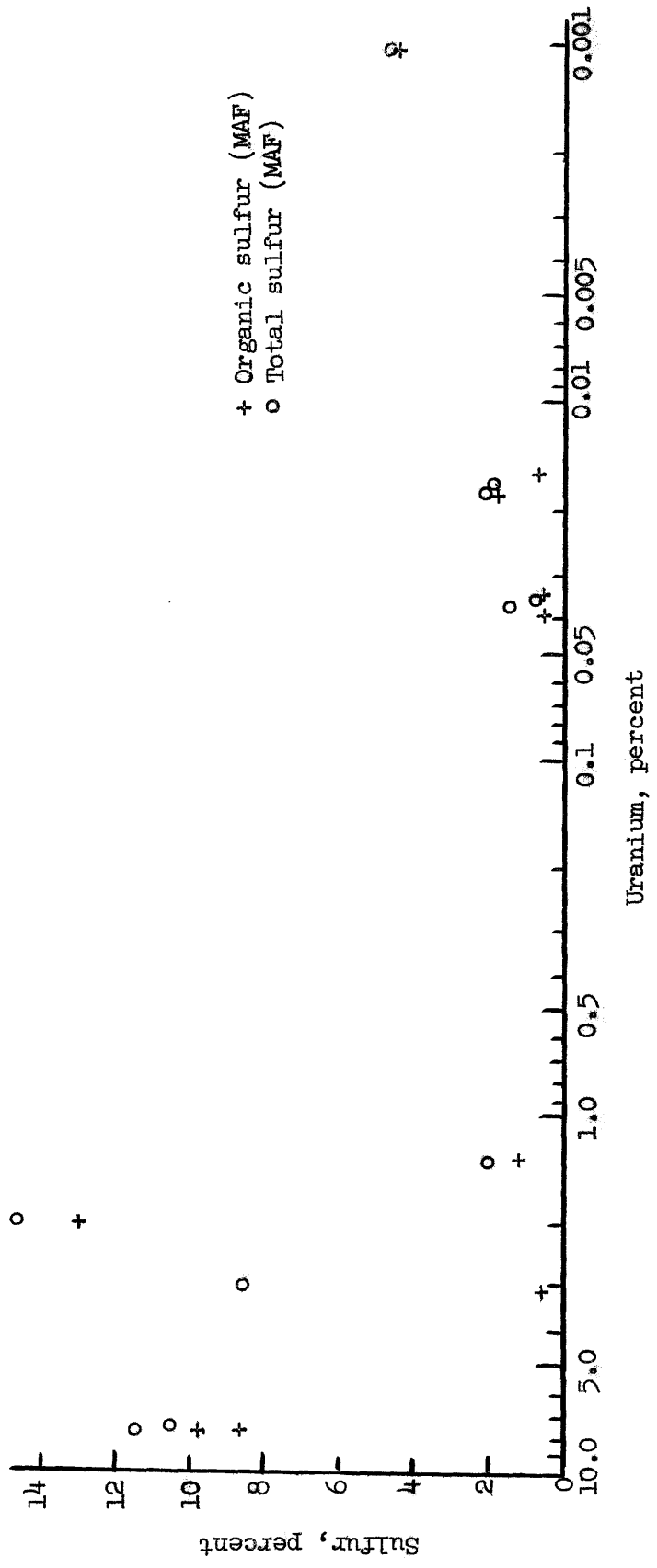


Figure 7.--Relationship of sulfur (moisture- and ash-free) to uranium in coalified wood.

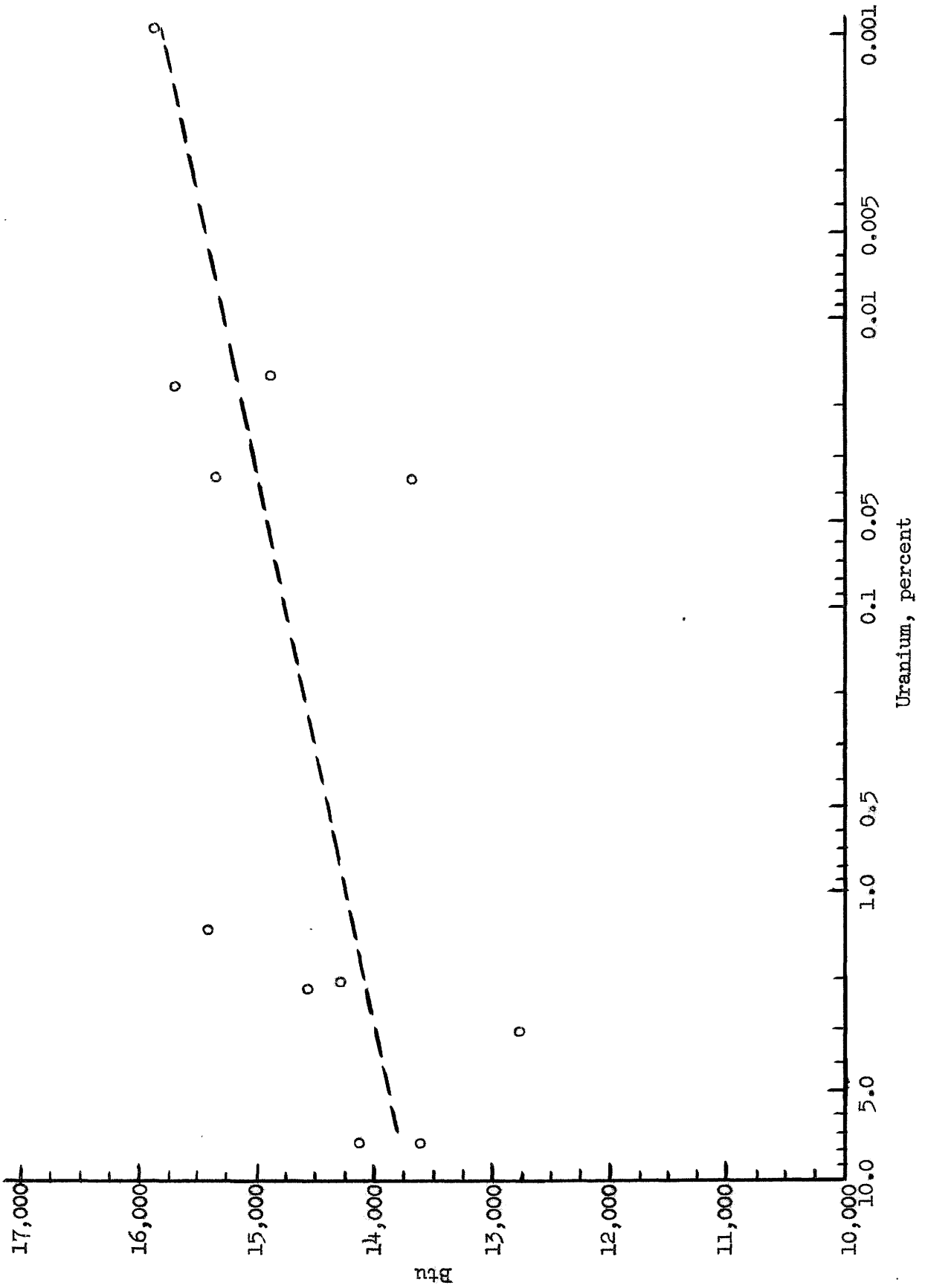


Figure 8.--Relationship between Btu content of coalified wood and its uranium content.

least squares calculation). This relationship, as in the case of hydrogen or volatile matter, is probably connected with the effects of alpha-particle radiation on the coal.

Aside from the correlations of uranium with hydrogen, volatile matter, Btu, and sulfur, no other relationships could be detected from available data. Figure 9 shows that there is little, if any, correlation between oxygen of the coalified wood and uranium. Any relationship between uranium and the sum of oxygen, nitrogen, and total or organic sulfur hardly reflects more than the correlations between sulfur and uranium shown graphically in figure 7. Data for figures 7 and 9 are summarized in table 14.

Correlation of uranium with elements in ash from coalified wood

Semiquantitative spectrographic analysis of the ash from each of the 10 samples of coalified wood was carried out to determine if any clear correlation could be detected between uranium and any other elements present in the ashes from the coalified wood (table 15). Because the ash content of sample RF-1 was small and insufficient material was available for complete analysis, analysis for this sample was carried out on a 1-mg specimen.

Attempts to correlate various elements with increasing uranium content, with increasing ash content, or on a geographic basis have met with only partial or minor success. More apparent relationships may be exposed with the analysis of additional samples. The data of table 15 were compared on an ash-free basis on the assumption that the elements were inherent to the coalified wood. Although this assumption may be valid for samples with low ash content, the assumption may or may not be sound for samples MD24B-3, NA-1, and SF-1 containing, respectively, 22.9, 19.8, and 17.4 percent ash.

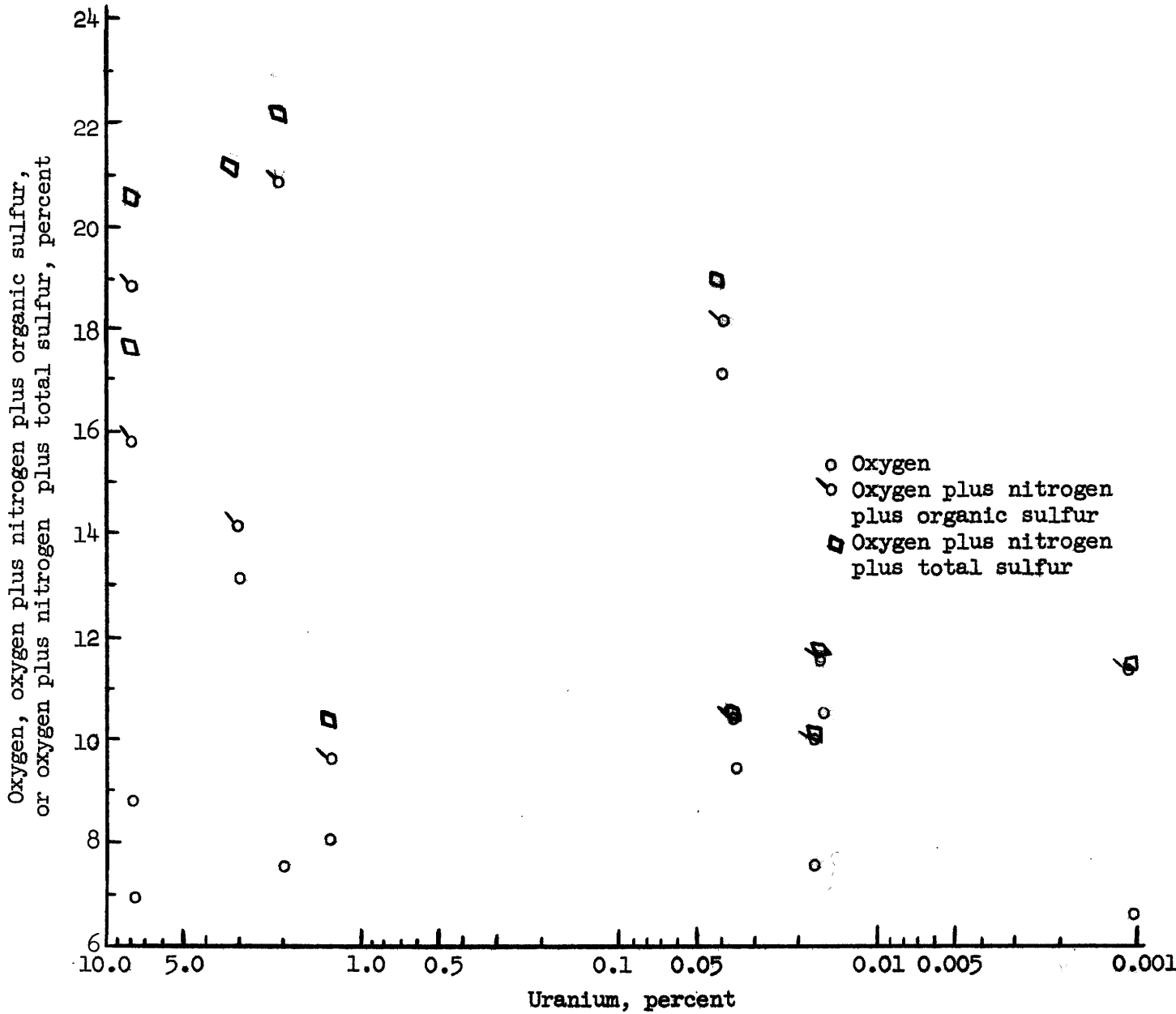


Figure 9.--Relationship between oxygen, (O + N + total S), or (O + N + organic S) and uranium for coalified wood.

Table 14.--Data for the correlation of oxygen, nitrogen, and sulfur with uranium in coalified wood.

All figures in percent, except Btu.

Sample	U	Total S	Organic S	Btu	Volatile matter	C	H	O	N	O + N + organic S	O + N + total S	Ash
RF-1	0.001	4.6	4.55	15,860	55.7	81.0	7.5	6.5	0.4	11.4	11.5	0.5
DD-2	2.02	14.5	13.05	14,280	33.8	72.8	5.0	7.5	0.2	20.8	22.2	7.0
DD-3	0.018	2.1	2.00	15,700	61.7	83.0	6.9	7.6	0.4	10.0	10.1	1.1
SF-1	3.08	8.6	0.62	12,790	28.0	74.6	3.2	13.1	0.5	14.2	21.2	17.4
AG-1	0.036	1.5	0.74	13,680	51.8	75.0	6.0	17.2	0.3	18.2	19.0	3.1
JJ-2	1.31	2.0	1.19	15,380	42.2	83.6	6.0	8.0	0.4	9.6	10.4	6.4
NA-1	7.51	10.5	8.63	14,100	29.5	78.1	4.2	6.9	0.3	15.8	17.7	19.8
P-1	0.036	0.8	0.65	15,330	56.6	82.9	6.5	9.4	0.4	10.5	10.6	1.6
V-1	0.016	0.9	0.67	14,860	56.9	81.7	6.5	10.5	0.4	11.6	11.8	1.8
MD42B-3	7.54	11.4	9.92	13,600	33.2	75.6	4.0	8.8	0.2	18.9	20.4	22.9

Table 15.--Semiquantitative spectrographic analyses of ashes from samples of coalified wood from the Colorado Plateau.

Analysts, Mona Frank and Katherine V. Hazel, U. S. Geological Survey.

Percent range	RF-1	DD-2	DD-3	SF-1	AG-1	JJ-2	NA-1	P-1	V-1	MD42B-3 <u>1/</u>
Over 10	Si V	U	Si	U Si	Fe	U V Si	U V	Fe	Fe	U V
5-10	--	Fe	Ti	Fe	K	--	Si	Si	Si	--
1-5	Ni Mg Ca Al Fe	Si Zn Pb	U Fe Ca Zn Al	--	Na U Si Ti	Fe K Ca	Fe Ca Pb	Ca Na Mg U Ba	Ca Mg	Si Pb Ca
0.5-1.	K U	Ca	K V Mg Na	Y Ca	Al Mg Ca	Al Na Mg Pb	Al Zn K	K Al	Al U K Ba	Al Fe
0.1-0.5	Na B Ti Mn	Ti Al Y	Ge Ba	Al Mo Pb	V Zn Mo Co	Ba	--	Y Ti	Y Na Zr Ti	Zn
0.05-0.1	Cu Mo	Mo Ni Co	Mo B Sr Cu Pb	--	Pb	--	Ti Co	Pb Cu Sr Zr	Mn B Cu	Ba Nd La Cu
0.01-0.05		V Mn Ba B Mg Yb Sr	Mn Ni Co Y Cr	Sr Mg Co Yb Cu Mn V Ti B	Cu Ni Sr Mn Y Ge B	Sr Ti Cu Mo B Co	Ba Mn B Cu Sr Cr	Mn B Mo V Zn	Sr Pb V Ge Mo Ni	B Ti Y Mg Mn
0.005-0.01		Zr Ga Cu Bi Sc La	Zr Ga	Ga Ni	Ba Cr	Ga La Y Mn Ni	Y Mg Ga Bi	Yb Ni	Yb Co Cr	Sr Co Dy
0.001-0.005		Cr	La Yb Sn	La Cr Zr Ba Sc Sn	Ga Zr Yb Sc Sn	Cr Zr	Zr	Co Ga Cr Ge Sn Sc	Ga Sn Sc	Cr Ag Sc Zr
0.0005-0.001		--	--	--	--	Yb	Yb	--	--	--
0.0001-0.0005		Be	Be	--	Be	--	Be	Be	--	Be
Ash, percent	0.5	7.0	1.1	17.4	3.1	6.4	19.8	1.6	1.8	22.9

1/ In the spectrographic analyses: Na obscured by high Sn; K obscured by high U; and Yb obscured by high V.

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Comparison of data for ash from relatively uraniferous and nonuraniferous samples from the same mine was carried out in a further attempt to determine if introduction of uranium was accompanied by the absorption of particular elements from the ore-bearing fluid by the coal substance. The following observations were made for samples DD-2 and DD-3:

- (1) The uraniferous coalified wood contains appreciable concentrations over the relatively nonuraniferous coal of U, Pb, Y, Yb, Fe, Ni, La, and Co.
- (2) The coalified wood with the higher percentage of uranium may contain a concentration of Mn, Zn, Zr, Ga, and Mo.
- (3) Uraniferous coalified wood is not enriched in Si, Ca, Ti, Al, V, Ba, B, Mg, Sr, Cu, or Cr.

These observations may not be the same as those noted for organic-free sandstone deposits (E. M. Shoemaker, A. T. Miesch, W. L. Newman, and L. B. Riley, written communication), inasmuch as the coalified wood presents an unusual environment conducive to the absorption of only certain elements from the ore-bearing fluid. Although no conclusions can be drawn from this single set of analyses, the data provide a guide for further studies.

Autoradiographic studies

Polished sections of three uranium-bearing coalified logs (JJ-2, DD-2, and NA-1) have been studied to determine the distribution of radioactivity. The technique used was that developed by Stieff and Stern (1952).

Sample JJ-2: Although alpha-particle tracks are well distributed throughout the specimen, there are zones of both high and relatively low concentrations of alpha-particle tracks. High track concentrations seem to follow straight or curved paths and may indicate that uranium in solution penetrated the

coalified wood preferentially along microscopic fractures. There is no evidence of specific mineral masses from which the alpha-particle tracks selectively emanate. This point is of particular interest indicating that coffinite, which occurs in the sample (table 16), must be colloiddally dispersed.

Sample NA-1: This sample (7.5 percent uranium) has been shown to contain uraninite (table 16). The alpha-particle track density in the stripping film is very high but, as in the case of sample JJ-2, the distribution of tracks indicates colloidal dispersion of the mineral.

Sample DD-2: This sample (2.0 percent uranium) has been shown to contain pyrite and a mineral having a cubic lattice with $a_0 = 5.41 \text{ \AA}$. There is little doubt that this mineral is uraninite. On examination, the polished section was found to have a narrow mineralized zone containing, as identified by R. G. Coleman of the U. S. Geological Survey (personal communication), pyrite and galena as the most abundant minerals along with sphalerite and native arsenic (?). Although the organic material on either side of and in immediate contact with this mineralized zone apparently contains relatively little uranium as evidenced by a lack of alpha-particle tracks, the density of tracks rapidly rises to a maximum and then gradually decreases as shown in figure 10. As in the previous two samples, the tracks in this sample indicate colloidal dispersion of any uranium mineral present, assuming emanation of the tracks from such a mineral.

The observations that concentrations of alpha-particle tracks occur along straight or curved paths suggest that a uranium-bearing fluid entered the coalified wood along zones (possibly fracture zones) on either side of which maximum absorption of uranium occurred (fig. 10). These fractures may be too small to be seen or may have been healed during or after introduction of uranium as a result of plastic flow of the coal. Such plastic flow has been observed

by R. A. Scott of the U. S. Geological Survey (personal communication) in his studies of coalified and silicified logs from the Colorado Plateau.

It cannot be determined whether the arsenic and mineral-forming elements of the pyrite, galena, and sphalerite entered sample DD-2 prior to or after introduction of uranium. Scarcity of alpha-particle tracks along the fracture zone in which these minerals occur, however, suggests that they were formed subsequent to the introduction of uranium. If uranium entered the coalified wood by way of such fractures, then it would be reasonable to expect the highest concentration of alpha-particle tracks at the boundaries of a fracture zone, and diffusion of uranium to lower concentrations within the coal substance where permeability to the uranium-bearing solution was lower.

Table 16.--X-ray diffraction analyses of several samples of coalified wood.

<u>Sample</u>	<u>Uranium in coalified wood (percent)</u>	<u>Minerals in coalified wood</u> ^{1/}
DD-2	2.0	Pyrite plus a cubic pattern with $a_0 = 5.41 \text{ \AA}$
SF-1	3.1	Pyrite and coffinite
JJ-2	1.3	Coffinite
NA-1	7.5	Uraninite

^{1/} Analyst, Evelyn Cisney, U. S. Geological Survey.

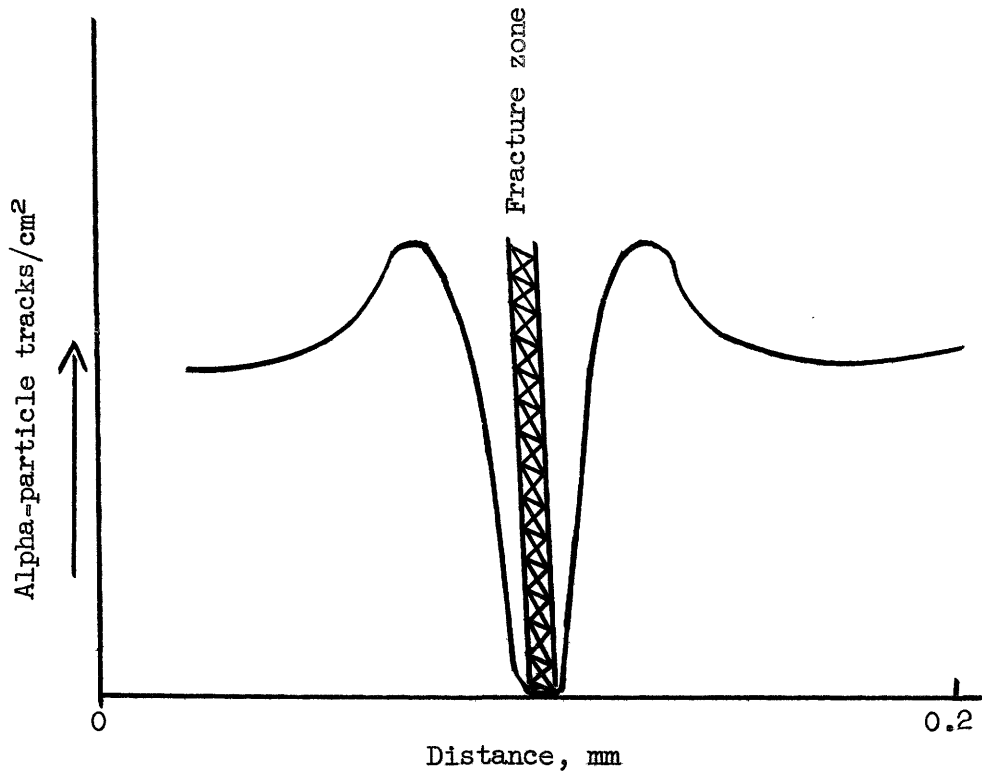


Figure 10.--Concentration of alpha-particle tracks about fracture zone in autoradiographic study of sample DD-2 (diagrammatic).

INTRODUCTION AND RETENTION OF URANIUM

Distribution of uranium in the several sections of coalified wood that have been studied suggests that the element was initially introduced in a solution that followed paths of least resistance, namely, fracture zones. Previously reported studies of uranium-bearing coals from South Dakota (Breger, Deul and Rubinstein, 1955) and Wyoming (Breger, Deul, and Meyrowitz, 1955) showed that the uranium was probably retained in a complex of organo-uranium compounds soluble below a pH of about 2.2. It is reasonable to expect absorption of uranium from the mineralizing fluid in the form of similar compounds in the coalified wood of the Plateau. Furthermore, it has been suggested in the case of the coal from Wyoming (Breger, Deul, and Meyrowitz, 1955) that uranium traveled in the form of alkaline or alkaline earth uranyl carbonate complexes. Studies of impregnated sandstones ("uraniferous asphaltites") and other sandstones from the Plateau by Waters and Granger (1953) and by Fischer, Gruner, Stieff, and Stern, the author, and others (personal communication) have invariably led to the conclusion that mineralization was accompanied by solution of quartz grains as evidenced by the occurrence of re-entrant and filamentous structure, an observation that provides evidence for an alkaline mineralizing solution. The similarity between absorption of uranium from mineralizing fluid by massive coal beds in Wyoming or by coalified wood in the Colorado Plateau area is striking.

The occurrence of uraninite or coffinite in coalified wood from the Plateau indicates that, after absorption, conditions in the Plateau area were conducive to reduction of the uranyl ion. If uranium were initially introduced into the coalified wood of the Colorado Plateau in the form of the uranyl ion, the presence of uraninite or coffinite indicates that, following absorption, the

uranyl ion was reduced. The rapid reduction of the uranyl ion by lignite in the laboratory at elevated temperature (150° C) has been demonstrated (I. A. Breger and R. T. Moore, written communication, 1955).

The general distribution of alpha-particle tracks in specimens of coalified wood known to contain uraninite or coffinite indicates that these minerals are probably colloiddally dispersed and present at sites where uranyl ions were originally absorbed. Had reduction of the uranyl ion to insoluble uranium minerals occurred simultaneously with its introduction, dispersion of uranium throughout the coal would probably have been prevented.

CONCLUSIONS

The studies outlined in this preliminary report are not yet complete; sufficient data have been accumulated, however, to indicate trends. The importance of coalified wood as a precipitant for uranium on the Colorado Plateau makes it desirable to present available data and suggestions prior to completion of the work.

The conclusions that have been reached on the basis of these studies are outlined below:

(1) Composition of coalified wood is dependent upon environment of burial. Both mineralized and unmineralized specimens have been found in which all traces of cellular structure are absent.

(2) Distribution of radioactivity is dispersed throughout the coalified wood, but concentrations of alpha-particle tracks along zones suggest that the uranium-bearing fluid entered the coalified wood through paths of least resistance--probably fracture zones.

(3) Conditions for the introduction of uranium and its retention by coalified wood seem to be geochemically similar to those that resulted in the

formation of uraniferous coals of the Dakotas and Wyoming. Uranium is thought to have first been absorbed and then to have been reduced.

(4) Samples of coalified wood containing more than one percent of uranium also contain inordinately high percentages of organic sulfur.

(5) High uranium contents are accompanied by decreases in organic hydrogen, volatile content, and Btu values for the coalified wood. Dehydrogenation by alpha-particle bombardment is thought to lead to these changes.

(6) There is no correlation of uranium with organic carbon.

Insufficient data have been accumulated with which to relate uranium to minor elements in coalified wood.

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