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THE ASSOCIATION OF URANIUM WITH CARBONACEOUS MATERIALS ON THE COLORADO PLATEAU*

By

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THE ASSOCIATION OF URANIUM WITH CARBONACEOUS MATERIALS ON THE COLORADO PLATEAU

By Irving A. Breger and Maurice Deul

ABSTRACT

On the Colorado Plateau uranium is associated with coalified wood, crude oil, carbonaceous shale, and carbonaceous matter of unknown origin. Investigations have shown that crude oil plays no role in the emplacement of uranium, although its ability to pick up small quantities of uranium while migrating through uraniferous zones may make oils an aid to general prospecting. Carbonaceous matter with no cellular structure that occurs as impregnations in sandstones or as pellets has been chemically related to coal and is thought to represent a coal extract. The reduction to U(IV) of uranium associated with coalified wood may take place after absorption of the uranyl ion. Study of a terrestrial shale shows that the uranium is associated with carbonaceous material similar to lignite in chemical composition. From these studies it is concluded that the fundamental association of uranium with carbonaceous material on the Colorado Plateau is with coalified wood and allied chemical substances.

INTRODUCTION

Coalified plant debris is the most common type of carbonaceous material occurring on the Colorado Plateau. Coal beds are absent in uraniferous zones, but ore-bearing rocks may contain several kinds of carbonaceous matter. Some of these carbonaceous materials are comparable to coals and as such vary in rank from lignite to bituminous. Replacements and impregnations of fossil wood by uranium minerals and by sulfide minerals, as well as by silica and calcium carbonate, are common, and it is not at all surprising that we have found evidence for the migration of extracts of organic material.

An unusual and perhaps unique situation exists in the Temple Mountain area, Emery County, Utah. There, in addition to an association with coalified wood, uranium is associated with crude oil and with carbonaceous substances apparently derived as extracts from coaly material. Because these various kinds of organic matter occur within the same or neighboring mines in the same formation, samples were collected from this area for detailed study to determine the relationship of the uranium to the different carbonaceous materials.

Uranium-bearing carbonaceous shale occurs within the Colorado Plateau province near Gallup, N. Mex., and a sample of this shale, which occurs in the Dakota sandstone in the Zuni uplift area, was studied in detail.

The carbonaceous substances studied have at various times been known by different names. Some of these names, although applied to substances of then unknown origins, have genetic connotations. "Asphalt" and "asphaltite" are two such terms that have been used to describe hard black impregnations in sandstone, rounded black pellets, viscous crude oil, and even coalified fragments of wood. These terms are misleading, hence they have not been used in this paper.

Soluble or extractable organic substances are amenable to study by standard physical and chemical techniques such as chromatography, fractional distillation, infrared and ultraviolet absorption analysis, and functional group (-OH, hydroxyl; -CHO, aldehyde; etc.) analysis. When organic material is found to be insoluble in any common solvent, physical and chemical methods of analysis become less effective and interpretation of results less reliable.

Furthermore, fine-grained mineral matter is often intimately associated with insoluble carbonaceous material and a problem arises in attempting to separate the organic material by mechanical techniques that result in only minor changes, if any, to its chemical structure and composition.

Of the various carbonaceous materials collected, only the crude oils, occurring as seeps or as impregnations in sandstone, are readily soluble. Because of the relative ease of working with oils they were studied first to determine the relationship of uranium to them and the manner by which uranium is retained by them.

CRUDE OILS, EXPERIMENTAL AND ANALYTICAL DATA

Samples for this study were collected from four operating uranium mines in the Temple Mountain area (table 1). One sample was an oil-impregnated sandstone exposed during mining operations. The other samples were collected from seeps by scraping the oils from mine walls or by chipping portions of the rock through which they were flowing. The viscosity of these oils varied greatly, the most viscous having a taffylike consistency.

In the laboratory each oil was first dissolved in benzene to free it from mineral matter. Multiple filtrations of the benzene solution were carried out to make certain that suspended mineral matter was removed from the oil. Benzene was removed from the filtered oils by distillation at room temperature and then by freeze-drying. Small samples (approximately 5 g) of the oils were redissolved in 25 to 30 ml of benzene and pure pentane was added to the solutions in the ratio of 40 volumes of pentane per volume of

Table 1.--Oils collected from mines in the Temple Mountain region, Emery County, Utah.

Source	Description	Collectors
AEC No. 8 mine	Seep through uraniferous zone. Consistency of taffy.	L. R. Stieff and T. W. Stern
Marsh Bank Canyon mine	Seep through uraniferous zone.	A. D. Weeks
AEC No. 5 mine	Oil seep on mine wall.	I. A. Breger and M. Deul
AEC No. 4 mine	Oil-impregnated sandstone.	I. A. Breger and M. Deul

benzene. This mixture was stored overnight at approximately 5° C to precipitate asphaltenes. The chilled solutions were filtered, and the asphaltenes were thoroughly washed with pentane. The filtrate and washings from the asphaltenes were mixed and diluted with pentane to assure complete precipitation of asphaltenes from the oil.

The asphaltenes were vacuum dried for two hours at room temperature and then analyzed for carbon and hydrogen by standard microcombustion techniques. Ash from each analysis was weighed and analyzed for uranium (Grimaldi et al., 1954). Nitrogen and sulfur were determined by combustion analysis. Analytical data for the asphaltenes are shown in table 2. Table 3 summarizes data showing the distribution of uranium in the oils.

OILS AS TRANSPORTING AGENTS FOR URANIUM

The uranium content of crude oils from nonuraniferous provinces is known to be low. Unkovskaya (1940) has reported from 0.0001 to 0.001 ppm of uranium in naphthenic base oils from Russia and, although these results may be low, an increase by one or even by two orders of magnitude will not make

Table 2.--Analysis of asphaltenes from oils of the Temple Mountain area.1,2/

	AEC No. 4 mine	AEC No. 5 mine	Marsh Bank Canyon mine	AEC No. 8 mine
Ash, percent	0.34	0.28	1.83	1.07
Uranium, percent	0.000147	0.0221	0.0386	0.0922
Carbon, percent	82.21	82.84	82.71	83.31
Hydrogen, percent	7.92	8.44	8.24	9.44
Nitrogen, percent	0.98	1.07	0.40	1.0
Sulfur, percent	5.7	5.1	5.7	6.3
Oxygen, by difference, percent	3.2	2.5	3.0	--

1/ Analysts: R. T. Moore and E. B. Brittin, U. S. Geological Survey.
2/ Asphaltenes isolated by H. M. Ezekiel, U. S. Geological Survey.

Table 3.--Distribution of uranium in the oils from the Temple Mountain area.

	AEC No. 4 mine	AEC No. 5 mine	Marsh Bank Canyon mine	AEC No. 8 mine
Original oil				
Uranium, percent	0.0000438	0.00445	0.0137	0.0310
Asphaltenes, percent	22.7	16.2	22.5	27.8
Asphaltenes				
Uranium, percent	0.000147	0.0221	0.0386	0.0922
Ash, percent	0.34	0.28	1.83	1.07
Uranium in ash, percent	0.0432	7.89	2.11	8.62
Percent of uranium in original oil held by asphaltenes	76.2	80.5	63.4	82.6
Uranium in extracted sandstone, percent	0.00020	--	--	--

them geochemically significant. Erickson, Myers, and Horr (1954) have also shown that oils from nonuraniferous provinces contain very small quantities of uranium--0.00001 to 0.064 ppm. Because crude oils normally contain extremely small percentages of uranium, it is reasonable to conclude that the oils collected from operating uranium mines on the Colorado Plateau have absorbed uranium during their migration through uraniferous zones.

Variations of from 45 to 310 ppm of uranium in the three oils collected from seeps probably reflect the migratory history of each oil. The uranium content of the oil extracted from impregnated sandstone from the AEC No. 4 mine is somewhat lower than might be anticipated considering the proximity of the oil to the uranium. Here the oil-impregnated sandstone occurs below the ore horizon, and the uranium in the oil (0.45 ppm) may represent only that which came into contact with it through a medium such as ground water. It is possible that the oil in this sandstone was already in place before the introduction of the uranium in the region and has remained static. If this is so, then oil in this sandstone might represent oil that originally migrated into the Temple Mountain area before the introduction of uranium into the region. Oil collected from seeps would then represent the same oil that had migrated by various paths within the area following introduction of the uranium.

Asphaltenes from crude oils range in sulfur content from 0 to as much as 11 percent (Sachanen, 1945; Mariani, 1951); the asphaltenes isolated from the oils that have been studied in this work contain from 5.1 to 6.3 percent sulfur. This narrow range of variation in sulfur contents suggests that these oils are from the same source.

In the oils that have been studied, 63.4 to 82.6 percent of the uranium is retained in the asphaltenes. Infrared studies of the asphaltenes indicate the existence of functional oxygen-containing groups which may be responsible for the retention of the uranium.

From these results, it is suggested that reconnaissance for uranium might be carried out in uraniferous provinces, such as the Colorado Plateau, by analyzing oils that may occur. Oils found to contain appreciable percentages of uranium might then be used as guides to uranium ore. A factor that must be considered is the unknown migratory course a crude oil may take. Use of an oil as an ore guide would, therefore, be based on the assumption of very limited movement of the oil or other geologic evidence that would indicate the course of migration.

CARBONACEOUS SANDSTONE, EXPERIMENTAL AND ANALYTICAL DATA

The ore-grade sample of carbonaceous sandstone used in this study was collected from the AEC No. 9 mine, Temple Mountain area, Emery County, Utah, by L. R. Stieff and T. W. Stern of the U. S. Geological Survey. The sample was taken from a sandstone member of the Chinle formation (Triassic), which is locally referred to as the Moss Back member. By means of lead-uranium isotope analysis, Stieff and Stern (oral communication) have shown the age of the uranium in an equivalent sample to be not older than 60 million years. In hand specimen the material is black and very dense and yields a faint X-ray powder pattern for uraninite; on being struck, the material emits a petroliferous odor which may have led to its being called an "asphaltite." In thin section the sandstone consists of clean rounded quartz grains. Voids between the grains are filled with black, carbonaceous material. Abraham (1945) describes similar material that, on the basis of physical tests, has been classified as glance pitch.

Soxhlet extraction of 80-mesh carbonaceous sandstone with 1:1 benzene-alcohol dissolved 0.09 percent by weight of the sample. Further treatment of the sample with pyridine, aniline, 6 N hydrochloric acid, 5 percent sodium hydroxide, or a pyridine-acetic acid mixture resulted in no further extraction.

Because of the difficulty in performing accurate organic microanalyses on a sample containing 72 percent ash (table 4), it was first necessary to concentrate the organic material. This separation was accomplished by using a technique (Deul, unpublished work) developed during studies of carbonaceous shales, namely, by ball-mill grinding with a mixture of kerosene and water. Under these conditions organic substances concentrate in the kerosene phase. As shown in table 4, an organic separate containing only 18.01 percent ash was isolated from the carbonaceous sandstone. Each separate was analyzed for ash, carbon, hydrogen, and uranium. Semiquantitative spectrographic analyses of the ashes obtained from the samples are given in table 5. Table 6 lists sensitivities for the elements determined by the spectrographic technique.

Table 4.--Analysis of fractions from carbonaceous sandstone ore.[1]

	Ash (percent)	Carbon (percent)	Hydrogen (percent)	Uranium (percent)
Original sample	72.46	20.49	1.53	2.4
Organic separate	18.01	62.63	4.01	1.1
Inorganic separate	95.35	1.92	0.35	0.63
Organic middlings	83.16	12.69	1.24	1.1
Inorganic middlings	88.38	9.05	1.22	4.9

[1] Analysts: C. Johnson, A. Sweeney, and E. Brittin, U. S. Geological Survey.

Table 5.--Semiquantitative spectrographic analyses of ashes from carbonaceous sandstone ore and separates.[1]

Sample	Original sandstone	Organic separate	Mineral separate	Organic middlings	Mineral middlings
Ash [2] (percent)	72.46	18.01	95.35	83.16	88.38
Uranium in ash [3] (percent)	3.2	6.1	0.66	1.3	5.5
Range (percent)					
> 10	Si	Si	Si	Si	Si
5-10	--	--	--	--	--
1-5	U Al Fe V	U Fe Al V	Fe Al V	Fe Al U V	Al U Ca Fe V
0.5-1.	--	Ca	U	--	--
0.1-0.5	Ca As	As Na Mg	Zr Ca	Ca As Mg Na Zr	Mg Na
0.05-0.1	Ba Mg	Sn Ba Zn	Mg As Ba	Ba	Ba As
0.01-0.05	Mn B Pb Ti Zn	Pb Mn B Ti Ni Zr Cu	Na Ti Mn B Pb Zn	Zn Pb Mn Ti B	Zr Mn B Pb Ti Zn Ni
0.005-0.01	Ni	--	Ni	Ni Sn	Sn
0.001-0.005	Sr Cu Zr Y Sn	Sr Y	Sn Y Sr Cu	Sr Cu Y	Sr Cu Y
0.0005-0.001	--	--	--	--	--
0.0001-0.0005	Cr Ag Be	Ag Cr Be	Cr Ag	Ag Cr Be	Cr Ag Be

[1] Analyst: C. S. Annell, U. S. Geological Survey.
[2] Data from table 4.
[3] Calculated from data of table 4.

Table 6.--Sensitivities for the elements determined by the semi-quantitative method.1/

Element	Percent	Element	Percent
Ag	0.00001	Nb	0.001
Al	0.0001	Na 2/	0.0003 (0.01)
As	0.01	Nd	0.006
Au	0.001	Ni	0.005
B	0.005	Os	0.1
Ba	0.001	P	0.07
Be	0.00005	Pb	0.001
Bi	0.005	Pd	0.003
Ca	0.01	Pr	0.01
Cd	0.005	Pt	0.003
Ce	0.03	Rb 2/	0.007 (7.)
Co	0.008	Re	0.04
Cr	0.0006	Rh	0.004
Cs 2/	0.01 (0.8)	Ru	0.008
Cu	0.00005	Sb	0.01
Dy	0.006	Sc	0.001
Eu	0.003	Si	0.005
Er	0.003	Sm	0.008
F 3/	0.08	Sn	0.004
Fe	0.0008	Sr	0.001
Ga	0.004	Ta	0.1
Gd	0.006	Tb	0.01
Ge	0.001	Te	0.08
Hf	0.03	Th	0.08
Hg	0.08	Ti	0.0005
Ho	0.001	Tl	0.04
In	0.0004	Tm	0.001
Ir	0.03	U	0.08
K 2/	0.005 (0.3)	V	0.001
La	0.003	W	0.07
Li 2/	0.00003 (0.04)	Y	0.003
Lu	0.005	Yb	0.0003
Mg	0.00003	Zn	0.008
Mo	0.0005	Zr	0.0008
Mn	0.0007		

1/ Waring and Annell (1953).
2/ A second exposure is required for the high sensitivity listed.
3/ A third exposure is required for the fluorine estimation.

ORIGIN OF CARBONACEOUS MATERIAL IN SANDSTONE ORES

The black, carbonaceous ore bodies of the Temple Mountain region have been known by several names since their discovery, and the terms used have implied genesis from crude oils. Because of the conclusions reached with regard to the association of uranium with crude oil, it was necessary to establish the composition and structure of these carbonaceous materials and their relationship to the oils.

From autoradiographic studies (Stieff and Stern, 1952) to investigate the relationship of uranium to the mineral and organic constituents of the sandstone the following observations were made:

1) There is no concentration of alpha-particle tracks at boundaries between the carbonaceous material and mineral fragments indicating that uranium is not present in the ore as a coating on the mineral grains.

2) Alpha-particle tracks are dispersed throughout the carbonaceous material with some areas containing greater or lesser concentrations of tracks.

3) Quartz and pyrite grains are practically devoid of tracks. Vanadium minerals show some tracks but not nearly as many as appear in the carbonaceous material.

Because permeable sandstones permit the flow of aqueous solutions, gases, petroleum, or other fluids, it is possible that uranium entered the interstices of the sandstone before the introduction of the organic matter. If this were true, there should be a concentration of uranium on the surfaces of the quartz and other mineral particles. Such evidence is lacking. On the contrary, the dispersion of uranium throughout the organic matter and the fact that the quartz grains are practically devoid of alpha-particle tracks suggest that the uranium and carbonaceous matter entered the sandstone in solution or as a nearly homogeneous suspension. The separation of uranium from the organic matter by fine grinding (table 4) indicates that most of the uranium is not now chemically associated with the organic matter. Had a chemical combination existed, separation has since taken place, perhaps as a result of bond cleavage by the alpha particles.

Recalculation to a moisture- and ash-free basis of the composition of the organic matter isolated by ball-mill grinding shows that the organic matter contains 76.5 percent carbon, 4.9 percent hydrogen, and, by difference, 18.6 percent oxygen, nitrogen, and sulfur. This composition is indistinguishable from that of lignite and suggests that the organic impregnation in the sandstone is derived from a low-rank coal.

The data of table 5 show that the organic separate from the carbonaceous sandstone, as compared to the mineral separate, has been enriched in uranium, arsenic, tin, copper, and beryllium. The same elements are also enriched in the ashes of organic separates from coal as compared to ash of minerals separated from coal (Deul, 1955). The organic separate from the sandstone contains a higher percentage of uranium than does the mineral separate, but both are lower in uranium content than the original sandstone ore.

Vacuum differential thermal analysis (Whitehead and Breger, 1950) provides further evidence that the impregnating organic material is related to coal. Carbonaceous material separated from the sandstone gives a decomposition curve similar to those obtained for low-rank coals (fig. 1) but different from those for such substances as gilsonite, wurtzilite, etc. (fig. 2). As can be seen from figure 1, the shape of the exothermic curves for carbonaceous material from the pellet and from the ore are similar to the shape of the curve for coals between 300° and 500° C (Breger and Whitehead, 1951). The small exothermic peaks at 300° C are superimposed on the general curve and are of unknown origin. The small endothermic peak on the curve for the carbonaceous

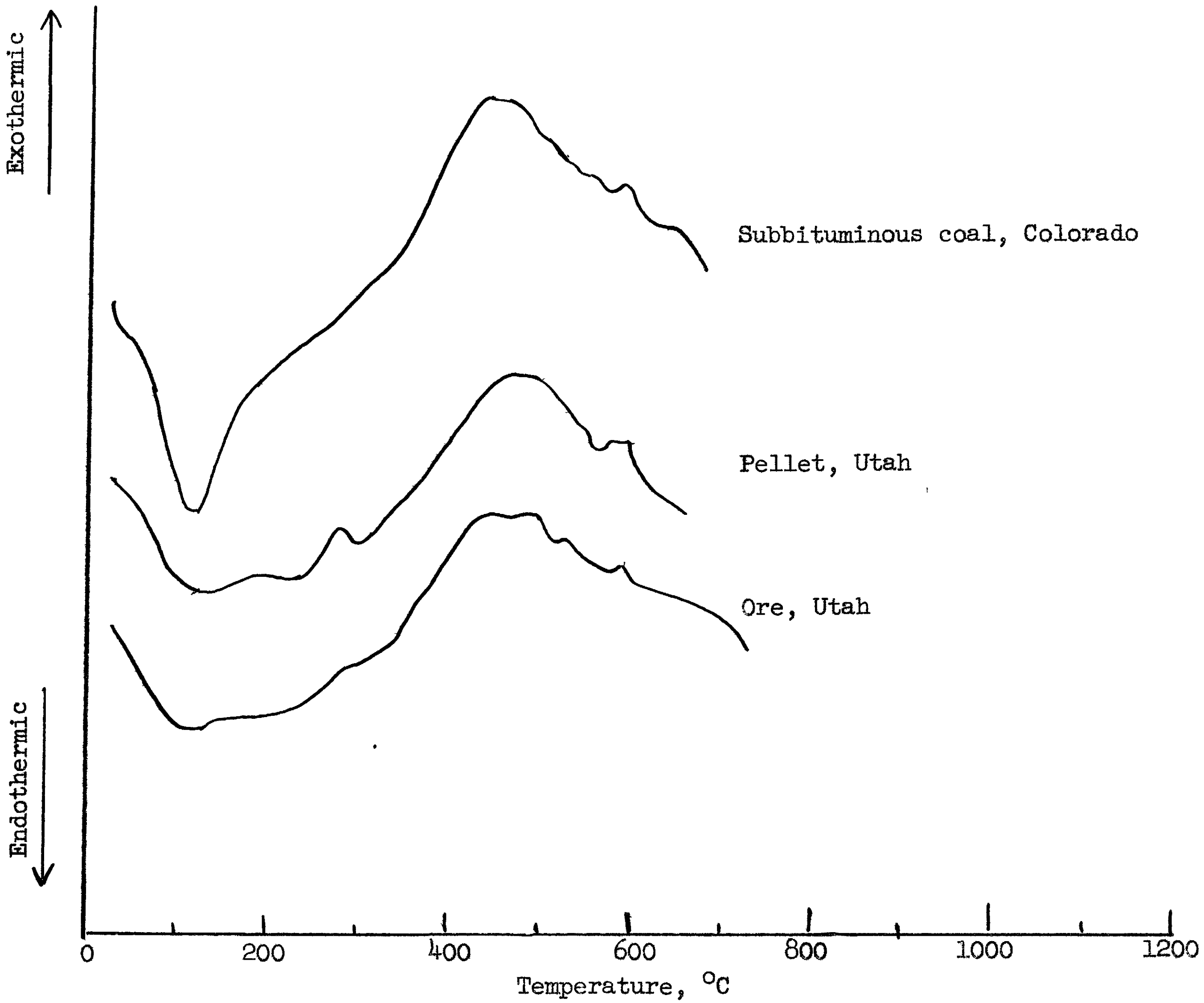

Figure 1.--Vacuum differential thermal analysis curves for a carbonaceous pellet and carbonaceous material isolated from sandstone ore. The curve for a subbituminous coal is shown for comparison. Small peaks at 575° C are caused by quartz used as an internal standard.

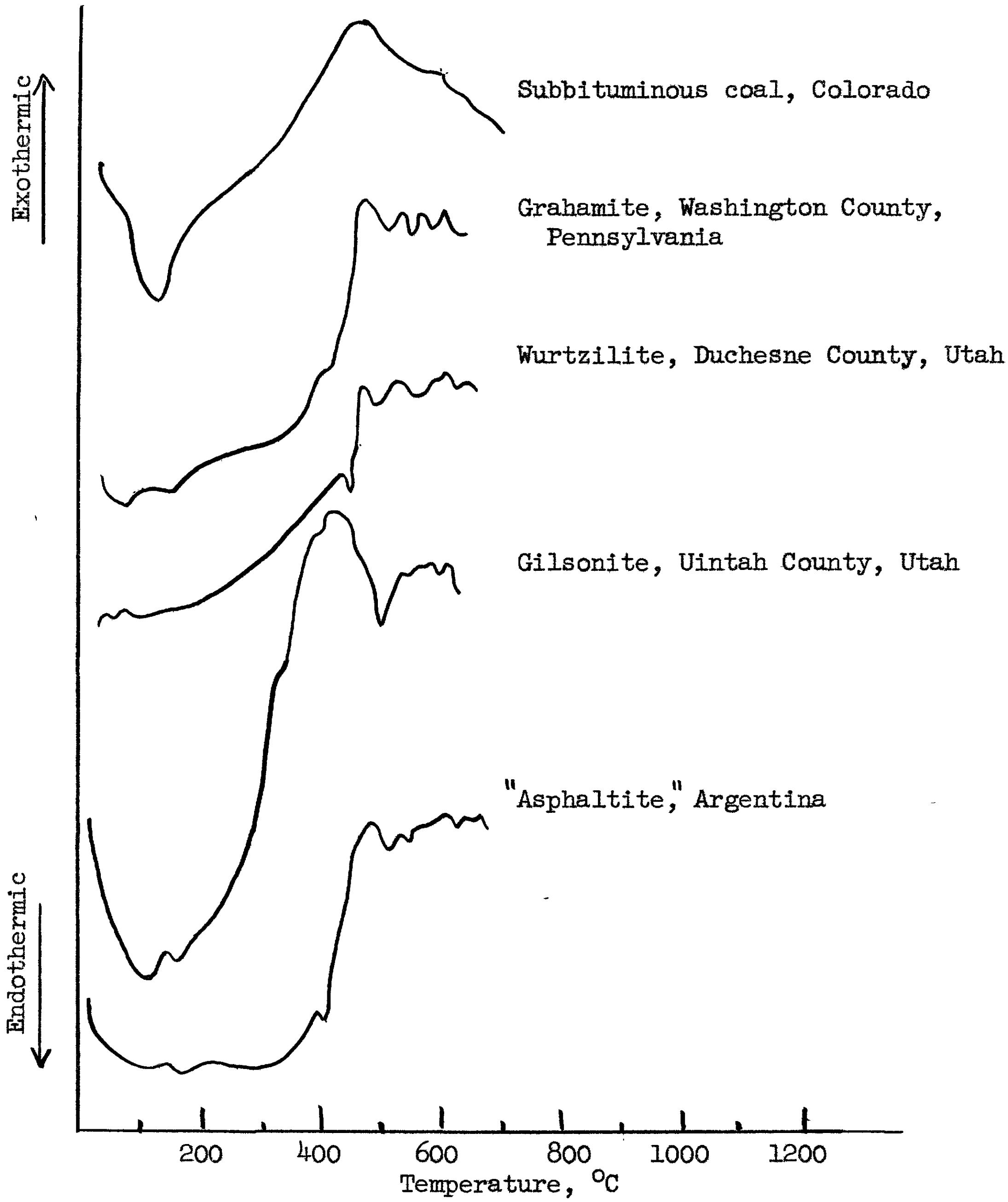

Figure 2.--Vacuum differential thermal analysis curves for "asphaltite." The curve for a subbituminous coal is shown for comparison. Small peaks at 575° C are caused by quartz used as an internal standard. Curves by S. Rubinstein, U. S. Geological Survey.

material from the ore at about 425° C is similarly superimposed on the general curve and is of unknown origin. It is possible that mineral matter may be the source of these small peaks. The curves of figure 2 for wurtzilite, gilsonite, and other "asphaltites" are quite different from the curves for coal.

Based on the analytical data, a possible explanation for the accumulation of uranium in the carbonaceous sandstones of the Temple Mountain region is that aqueous solutions carrying organic material extracted from low-rank coals in the region, along with uranium and vanadium, may have saturated the pores of the sandstone. Eventually the organic matter was devolatilized and converted to its present insoluble state, perhaps radiochemically.

CARBONACEOUS PELLETS, EXPERIMENTAL AND ANALYTICAL DATA

Pellets of black carbonaceous material, ranging from several millimeters to several centimeters in diameter, occur in certain strata of a sandstone member (Moss Back) of Chinle formation at Temple Mountain. In places these rounded masses merge with the carbonaceous material that impregnates sandstone. Gruner (oral communication) and Stieff and Stern (oral communication) have reported that some of the carbonaceous material replaces clay balls imbedded in sandstone. The carbonaceous material of the pellets also corrodes some of the quartz grains with which it comes into contact.

Pellets for this study were collected at three sites: The Rex No. 2 mine, the AEC No. 4 mine, and the AEC No. 8 mine, all in the Temple Mountain region, Emery County, Utah. Because many of the pellets were extremely small and weighed less than 100 mg each, detailed work on individual pellets has been limited.

Six pellets from a suite collected in the AEC No. 4 mine were selected on the basis of their specific gravities, which ranged from 1.29 to 1.56. One pellet from the AEC No. 8 mine was chosen because of its rather large size and its relatively high specific gravity. The specific gravity of the pellet from the Rex No. 2 mine was determined to be 1.38 ± 0.02. Analyses of these pellets are given in table 7.

Spectrographic analysis of ash (6.94 percent) from the pellet from the Rex No. 2 mine is shown in table 8.

ORIGIN OF CARBONACEOUS PELLETS

The origin of carbonaceous pellets occurring in the Temple Mountain region has been a subject for speculation for some time. Abraham (1945) states, "The asphaltite is characterized by the fact that it carries uranium and vanadium, which are assumed to have been incorporated in it during its migration from the underlying strata, thereby hardening the asphaltite and 'fixing' it in the present associated rocks."

With obvious exceptions, examination of the data of table 7 reveals certain trends: 1) ash rises with specific gravity; 2) carbon and hydrogen both decrease with specific gravity; and 3) the total of oxygen, nitrogen, and sulfur rises regularly with specific gravity. There does not appear to be any specific relationship between uranium and any of the other components or properties of the pellets.

In figure 3 data have been plotted for a number of carbonaceous pellets and other substances collected from the Colorado Plateau. Represented are analyses of pellets (table 7), analysis of the carbonaceous material isolated from the carbonaceous sandstone (table 4), analysis of vitrain (table 11),

Table 7.--Analytical data for carbonaceous pellets from the Temple Mountain region, Emery County, Utah.

Mine	Sp. gr.	Ash (percent)	Carbon (percent)	Hydrogen (percent)	Oxygen, nitrogen, and sulphur (percent) 1/	Uranium in original pellet (percent)
AEC No. 4	1.29	6.61	80.2	7.54	12.26	0.038
	1.34	9.13	80.8	6.52	12.68	2.54
	1.38	10.77	81.4	5.18	13.42	2.96
	1.43	15.88	79.7	6.12	14.20	2.44
	1.57	19.15	78.7	6.08	15.22	2.51
	1.56	8.26	77.7	6.20	16.10	1.67
Rex No. 2	1.38	6.94	76.1	4.93	18.97	2.77
AEC No. 8	1.63	9.72	76.3	5.53	18.17	1.68

1/ Moisture- and ash-free basis.

Table 8.--Semiquantitative spectrographic analysis of ash from carbonaceous pellet from Rex No. 2 mine.[1]

Percent	Elements
Over 10	U
5-10	Si
1-5	Al Fe V Ca
0.5-1.	As Pb
0.1-0.5	P Mg Y Ba Ti
0.05-0.1	B Ce Sr Nd
0.01-0.05	Zn Mn Ni Pr Dy Er Yb Gd Cr Co
0.005-0.01	Zr La Cu Sn
0.001-0.005	Sc Ho Lu
0.0005-0.001	Be
0.0001-0.0005	--

[1] Analyst: Helen Worthing, U. S. Geological Survey.

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and analyses of four samples of vitrain from the Corvusite mine, Grand County, Utah (tables 13 and 14).

The dashed lines enclose an area in which most normal, mined coals occur (Lowry, 1945). The deviation from this area for a coal that has been subjected to mineralization is clearly shown. Analyses for the pellets all fall close to the normal coal curve strongly suggesting that these materials are related to coal in origin. This conclusion has been confirmed by the differential thermal analysis of one pellet from the region (fig. 1). The evidence points to the materials as being coaly in nature.

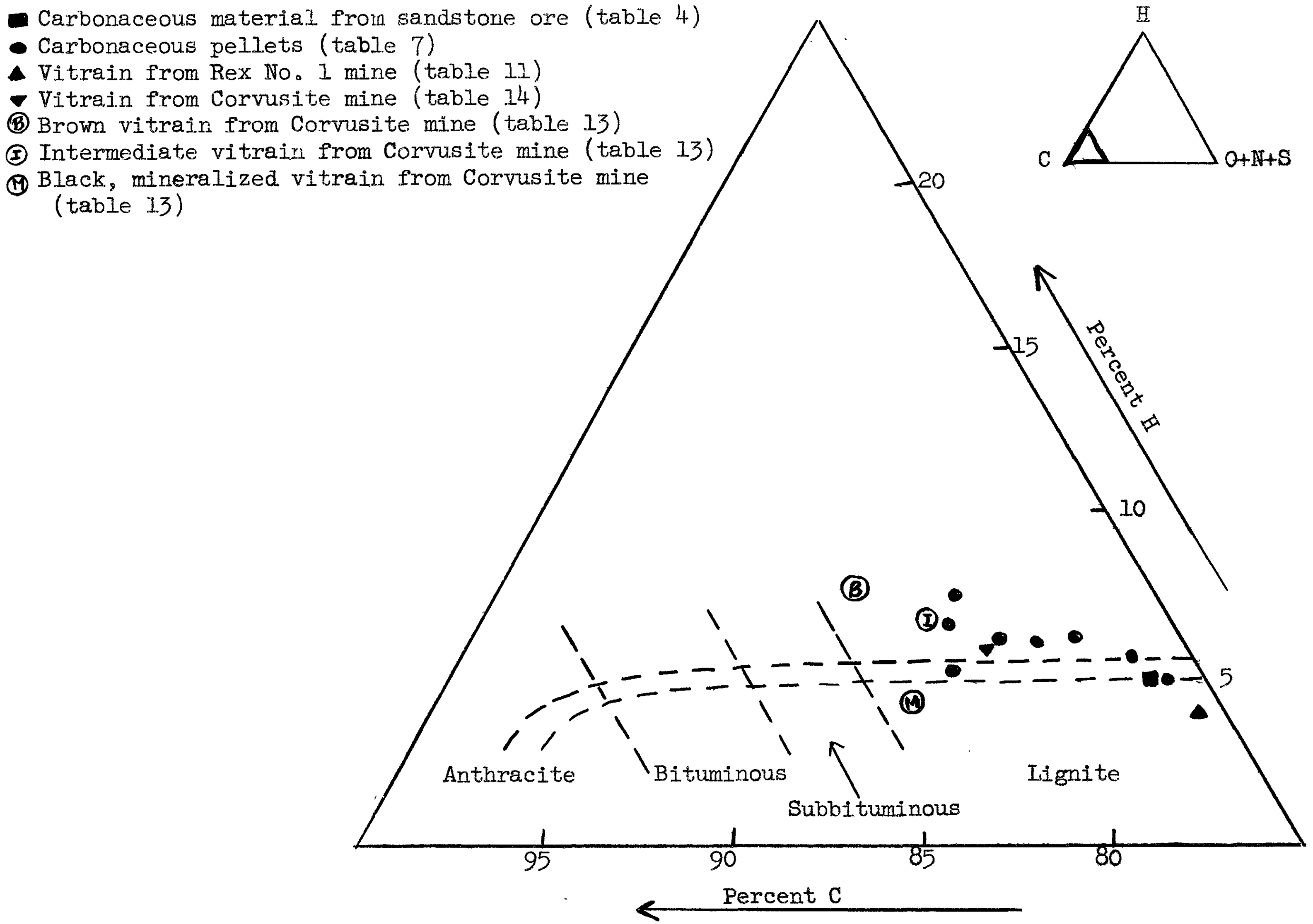

Figure 3.--Plot of analyses of carbonaceous materials from the Colorado Plateau on a standard coal curve. All analyses on moisture- and ash-free basis. Dashed lines enclose average analyses of most mined coals.

The occurrence of pyrite in the pellets indicates that they have not been subjected to appreciable oxidation. In view of this fact, it is not believed that the relatively high oxygen content of the pellets can be explained as resulting from oxidation of carbonaceous material of petroliferous origin.

Spectrographic analysis of the ash from the pellet from the Rex No. 2 mine (table 8) has shown the presence of 10 of the 15 rare earths. This is in contrast to analyses of petroleum ash (Erickson, Myers, and Horr, 1954) which normally show the presence of only the more abundant and more easily detectable rare earths. Sodium, on the other hand, should appear in the analysis of the ash if the pellet were derived from petroleum (Erickson, Myers, and Horr, 1954). These data may be interpreted as signifying a nonmarine and, therefore, a nonpetroliferous origin for the pellets.

CARBONACEOUS SHALE, EXPERIMENTAL AND ANALYTICAL DATA

Although uranium-bearing carbonaceous shales are quantitatively unimportant on the Colorado Plateau, a shale from the Zuni uplift area of New Mexico was studied to determine the relationship of the uranium to the carbonaceous material. The section of the Dakota sandstone containing the carbonaceous shale was deposited marginal to the sea. In contrast to marine shales, these stream and lagunal sediments are essentially terrestrial, exhibiting braided stream deposits and paleostream channels (Mirsky, 1953). Shale for this study was collected by T. W. Stern. Mineral and organic fractions were separated and concentrated by the ball-mill technique that has already been mentioned.

Table 9 gives the analytical data for carbon, hydrogen, ash, and uranium for the original shale and for the separates. The results of the spectro-

Table 9.--Analysis of carbonaceous shale collected from Dakota sandstone in Zuni uplift area, New Mexico, and of separates from shale.[1]

	Ash (percent)	Carbon (percent)	Hydrogen (percent)	Uranium (percent)
Original sample	76.22	12.97	1.62	0.091
Organic separate	30.21	48.47	2.98 [2]	0.41
Mineral separate	89.68	0.81	1.60 [2]	0.0051
Middlings	67.85	13.90	2.25 [2]	0.12

[1] Analysts: H. Levine and R. T. Moore, U. S. Geological Survey.
[2] High hydrogen values caused by hydration of shales during milling.

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graphic analyses of the ashes of the same samples are shown in table 10.

SIGNIFICANCE OF URANIUM-ORGANIC ASSOCIATION IN CARBONACEOUS SHALE

The shale from the Dakota sandstone yielded a mineral fraction which contained only about 1 percent organic matter, whereas the organic concentrate showed a fourfold enrichment of carbonaceous material (table 9). The direct association of uranium with organic material is shown in the analyses for uranium where the organic concentrate has a fourfold enrichment of uranium over that in the original sample and an eightyfold enrichment of uranium over that in the mineral concentrate. It is not at all unlikely that most of the uranium in the mineral fraction is associated with organic matter remaining with the mineral matter.

Table 10.--Semiquantitative spectrographic analyses of ash of original shale sample from Dakota sandstone formation and of ash of separates.1/

Sample	Original sample	Organic concentrate	Mineral concentrate	Middlings
Ash 2/ (percent)	76.22	30.21	89.68	67.85
Uranium in ash 3/ (percent)	0.12	1.35	0.0057	0.18
Range (percent)				
> 10	Al Si	Al Si	Al Si	Al Si
5-10	--	--	--	--
1-5	Ti K	Ca	--	Ca K Fe
0.5-1.	Fe Ca Mg	Fe K Ti Mg	K	Mg
0.1-0.5	--	Ba Na	Ca Fe Mg Ti Na	Ti Na
0.05-0.1	Na Ba V	Cu Sr Ce Pb	Ba Zr	Zr Ba Sr
0.01-0.05	B Pb Zr Co Sr	Zr V Zn B Co Mn Cr La Ni Y	Sr B Zn	Pb B Cu Cr Mn
0.005-0.01	Cu Ni Cr La Y	Ga	Cr Ni V	Ga Ni V Y Co Mo
0.001-0.005	Ga Mn Mo	Sc Sn Yb Ag Mo	Y Ga Pb Cu Mn Mo Co Sc	La Sn Sc
0.0005-0.001	Sc Be Yb	Be	--	Yb
0.0001-0.0005	--	--	Yb Ag Be	Be Ag
0.00005-0.0001	--	--	--	--
0.00001-0.00005	Ag	--	--	--

1/ Analysts: Mona Frank and K. Valentine, U. S. Geological Survey.
2/ Data from table 9.
3/ Calculated from data of table 9.

Spectrographic analyses of the fractions (table 10) show that the organic concentrate, with respect to the original shale, is enriched in uranium, cerium, tin, copper, manganese, silver, and ytterbium. In addition, the organic concentrate, as compared with the mineral separate, is enriched in lanthanum, cobalt, lead, and calcium. With the exceptions of calcium and silver, it has been shown that the minor and trace elements concentrated in the organic fraction are similar to the elements concentrated in organic separates from coal (Deul, 1955).

The analysis of this sample for carbon and hydrogen, when calculated on an ash-free basis (carbon, 69.5 percent; hydrogen, 4.3 percent), shows that, although too low in carbon content to fall on the coal curve as plotted in figure 3, the composition of the material is in the proper range for a lignite. The data, when considered in the light of the geologic interpretation for this deposit as given by Mirsky (1953), provide strong evidence that the uranium in the shale is associated with carbonaceous material similar to coal in composition.

COALIFIED WOOD, EXPERIMENTAL AND ANALYTICAL DATA

The association of uranium with coalified wood on the Colorado Plateau is universally recognized. Extensive studies conducted on uraniferous coals from other regions (Breger, Deul, and Rubinstein, 1955) have demonstrated the nature of the association of uranium with the coal substance. It was felt that our present studies could best be directed toward carbonaceous substances about which little was known, hence only few samples of coalified wood have been studied.

Although coalified wood from the Colorado Plateau has not yet been investigated in detail, hand-picked vitrain from a coalified log taken from the Rex No. 1 mine, Temple Mountain region, Emery County, Utah, was submitted to the U. S. Bureau of Mines for standard coal analysis. On the basis of data shown in table 11, the rank of this coal is subbituminous C. The uranium content of the coal is 7.54 percent, and X-ray diffraction patterns have weak lines indicating the presence of uraninite. Table 12 gives the semiquantitative spectrographic analysis of the ash from the vitrain. The radioactivity of fusain in contact with the vitrain is extremely low.

A small sample of coalified wood was collected in 1952 from the Corvusite mine, Grand County, Utah, by Alice D. Weeks of the U. S. Geological Survey. This sample of vitrain, about 2 inches long, graded longitudinally from brown at one end to black at the other end. The black end was highly mineralized. Analytical data for this sample are given in table 13.

Another sample of coalified wood from the Corvusite mine consisted of vitrain and fusain, analyses for which are given in table 14.

ROLE OF COALIFIED WOOD IN URANIUM FIXATION

The samples studied probably represent in rank most of the coalified wood in the region. The hand-picked vitrain from the Rex No. 1 mine has an extremely high content of organic sulfur for which no explanation can as yet be made. The presence of a very high concentration of zinc, of high copper, of cobalt in concentrations greater than nickel (table 12), and the unusually high sulfur content of the coal are undoubtedly related to the mineralization of the sample.

Examination of the analytical data shows that where vitrain is in contact with fusain, the vitrain contains the uranium. Fusain--mineral charcoal--is chemically inert and would not, therefore, be expected to contain

Table 11.--Analysis of coalified wood from Rex No. 1 mine.[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	10210	10480	13600

[1] Analyses by U. S. Bureau of Mines, Lab. no. E-61765, January 26, 1955.

chemically bound uranium. Vitrain, on the other hand, is chemically reactive because it contains functional groups which are capable of combining with uranium.

The data of table 13 illustrate variations in carbon-hydrogen ratios that exist within a single specimen of vitrain. When the data for vitrain shown in tables 11, 13, and 14 are plotted in figure 3, none of the points fall within the normal coal range as defined on the graph. This coal range is based on analyses of coals composed of vitrain, fusain, and other coal ingredients. Vitrain normally contains more hydrogen than do other major coal ingredients,

Table 12.--Semiquantitative spectrographic analysis of ash from vitrain from the Rex No. 1 mine.[1]

Percent	Elements
Over 10	U V
5-10	--
1-5	Si Pb Ca
0.5-1.	Al Fe
0.1-0.5	Zn
0.05-0.1	Ba Nd La Cu
0.01-0.05	B Ti Y Mg Mn
0.005-0.01	Sr Co Dy
0.001-0.005	Cr Ag Sc Zr
0.0005-0.001	--
0.0001-0.0005	Be

Notes: Na obscured by high Sn.
K obscured by high U.
Yb obscured by high V.

[1] Analyst: Mona Frank, U. S. Geological Survey.

while fusain contains less. It is not possible to determine from the few data available whether there is a direct relationship between increasing uranium content and decreasing hydrogen content in vitrains, but we suspect that this is so.

A hypothesis has been proposed that ground water solutions bearing alkaline- or alkaline-earth uranyl carbonates introduced uranium into coals; in acid environment below a pH of 4.5 such complex compounds decompose and

Table 13.--Analysis of coalified wood fragment from Corvusite mine, Grand County, Utah. Analysis on dry basis 1/

Description	Ash (percent)	Carbon 2/ (percent)	Hydrogen 2/ (percent)	Uranium (percent)	Atomic ratio carbon/hydrogen
Brown vitrain	3.01	82.7	7.7	0.057	0.90
Intermediate vitrain	0.64	81.3	6.7	0.0018	1.00
Black, highly mineralized vitrain	22.46	83.0	4.2	6.63	1.64

1/ Analysts: Jesse J. Warr, Jr., and Robert Meyrowitz, U. S. Geological Survey.

2/ Ash-free basis.

Table 14.--Analysis of coalified wood from Corvusite mine, Grand County, Utah. Analysis on dry basis 1/

Description	Ash (percent)	Carbon 2/ (percent)	Hydrogen 2/ (percent)	Uranium (percent)
Vitrain	13.06	80.1	5.8	2.28
Fusain	2.04	94.4	2.8	0.0038

1/ Analysts: Jesse J. Warr, Jr., and Robert Meyrowitz, U. S. Geological Survey.

2/ Ash-free basis.

release uranyl ions (UO_2^{++}) which are made available for the formation of ionic uranyl organic compounds, insoluble above a pH of about 2.2 (Breger, Deul, and Meyrowitz, 1955).

It is not known whether the uranium associated with coalified wood on the Colorado Plateau was introduced as the uranous ion, which was directly absorbed, or whether the uranyl ion was reduced by the carbonaceous material upon or subsequent to absorption. Experiments conducted by A. Pommer (written communication) on the reducing capacity of wood and lignite indicate that reduction of the uranyl ion is a distinct possibility. Mechanisms are known that would permit the retention of uranium by coal, coalified wood, or related substances regardless of the state of oxidation of the uranium in the ore solution.

SUMMARY AND CONCLUSIONS

Studies of the carbonaceous materials from the Colorado Plateau lead to several conclusions:

1) The crude oil that occurs in seeps in the operating mines seems to have no effective role in the emplacement of uranium. The association of uranium with oil results from the ability of oil to pick up and carry small quantities of the element. The association of crude oil with the other carbonaceous substances in the Temple Mountain region is fortuitous--the result of geological conditions which permit the flow of crude oil through strata containing uranium and vanadium. The ability of crude petroleum to pick up small quantities of uranium may make oils an aid to geochemical prospecting.

2) The carbonaceous material associated with the sandstone ore is apparently derived from plant material that has been coalified, or from the low-rank coals of the region. It is possible that uranium- and vanadium-

bearing solutions extracted organic matter from degraded plant debris in the sediments and that the mixture of carbonaceous material, uranium, and vanadium was subsequently deposited in porous sandstones. The present insolubility of the carbonaceous matter may be the result of cross-linkage of coal molecules caused by irradiation by the alpha particles from the uranium and its daughter products.

3) The carbonaceous pellets are believed to have much the same origin as the carbonaceous material that is impregnating the sandstone ore. Some samples of sandstone ore show impregnations of carbonaceous material that appear to coalesce into pelletal groups replacing sandstone, and the rank of the materials, as reflected by their composition, is similar. Discussion of the mechanics of such replacements is beyond the scope of this paper.

The carbonaceous pellets are by no means uniform and it is not at all surprising that this is so. Plant materials and coals vary in composition and type, and migrating solutions or dispersions of colloidal material derived from coal could not be expected to be uniform in composition. Analyses have shown that coals from the Colorado Plateau can deviate more from the normal coal curve than do the carbonaceous pellets. This is illustrated in figure 3.

4) The direct association of uranium with carbonaceous material separated from the shale from the Dakota sandstone is further evidence of the potency of certain kinds of carbonaceous material for the fixation of uranium. That this particular shale is of terrestrial rather than of marine origin supports the conclusion that the organic material separated from the shale is related to lignite.

5) Coalified fragments of wood and coalified logs are the most abundant carbonaceous materials on the Colorado Plateau. We have shown that many of

the carbonaceous materials that are of unknown origin or that have been considered to be of petroliferous origin have probably been derived from woody or coaly material. Insofar as carbonaceous materials are concerned, on the Colorado Plateau, as well as in the Dakotas, in the Red Desert area of Wyoming, and in the Fall Creek area of Idaho (Vine and Moore, 1952), coal and humic materials related to coal are the major controls for the fixation of uranium.

Based on available evidence, it appears that the fundamental association of uranium with carbonaceous materials on the Colorado Plateau is with coalified plant debris and allied chemical substances.

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