

URANO-ORGANIC MINERAL ASSOCIATION

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ABSTRACT

Semi-fluid asphalt which percolates through uranium ore bodies on the San Rafael Swell is indurated by heat at temperatures from 250° C.-300° C. The indurated material becomes brittle and generally similar in physical properties to naturally indurated "asphaltite." Infrared curves of artificially indurated material also compare favorably with curves for natural "asphaltite." Infrared curves for both indurated artificial and natural "asphaltite" show weak and indistinct absorption bands in contrast to the stronger absorption of semi-fluid asphalt.

Mineralogical investigation of the uranium silicate coffinite indicates that the mineral is similar to the synthetic coffinite, prepared by Fuchs and Hoekstra (1959), through the absence of an essential hydroxyl component.

The intimate and widespread association of indurated uranium-bearing "asphaltite" and the uranium silicate coffinite suggests that the two were formed contemporaneously. The urano-organic constituent could presumably have been hardened by irradiation, although this seems unlikely. However, such an origin is hardly even conceivable for the uranium silicate coffinite. Hydrothermal origin is believed to prevail both for the coffinite and the associated uranium "asphaltite."

INTRODUCTION

The widespread asphaltic association of uranium has long been recognized, and most workers attribute a petroliferous origin to this material. On the other hand, there appears to be a lack of agreement on the original source of the uranium and the temperature of formation. Gott and Erickson (1952) have suggested that uranium might have concentrated in the asphaltites directly from petroleum. Erickson *et al.* (1954) have also indicated that the similarity between the metal suite in crude oils and in uraniferous asphaltic deposits, and the uranium concentration in the latter, suggest that uranium and the other metals have accumulated in the heavier, more asphaltic portions of petroleum. Several believe that uraniferous asphaltites may have been formed through volatilization, oxidation, and polymerization of a petroleum enriched in these metals. Hail *et al.* (1956), however, concluded that most of the uranium present in the oil has been introduced during migration. At the same time, Breger and Deul (1956) have indicated that petroleum can be both a carrier and a collector of uranium.

Polymerization or condensation of hydrocarbons around an older radioactive source as a result of irradiation has been suggested by Elsworth (1928), Spence (1930), Davidson and Bowie (1951), Davidson (1955), Isachsen and Evensen (1956), and Pierce *et al.* (1958).

The exceedingly low uranium content of crude oils and asphalts com-

pared to the high content in uraniferous asphaltites indicates that petroleum is more likely to be a collector than a distributor of uranium. Kelley and Kerr (1958) have suggested that uranium-bearing hydrothermal solutions have introduced that metal into pre-existing liquid hydrocarbons which were indurated by the accompanying heat.

In this asphaltic association, uranium may be found in discrete minerals such as uraninite or coffinite, and it may occur as a urano-organic complex. The temperature range under which coffinite forms (Fuchs and Hoekstra, 1959) and the temperature of induration of "asphaltite" are believed to be significant in the interpretation of the temperatures which prevailed during uranium mineralization on the Colorado Plateau.

The objective of the current study has been essentially twofold: (1) to study the effect of heat on semi-fluid asphalt collected from fissure seepages in certain uranium deposits in order to compare the heat-treated material with naturally occurring uranium-bearing "asphaltite" from the same area, and (2) to study the association of coffinite, a frequent accompaniment of "asphaltite," in order to obtain more information on the nature of this unusual mineral and the significant association involved.

#### INDURATED URANIUM-BEARING ASPHALTITE

Numerous uranium deposits contain impregnations of asphaltic materials in which the impregnated rock types (Pierce *et al.*, 1958) range from igneous and metamorphic to terrestrial and marine sedimentary.

Elsworth (1928) applied the name thucholite to a thorium-uranium-rare earth hydrocarbon found in pegmatites at Parry Sound, Ontario. Thucholite was believed by Elsworth to have been formed by hydrothermal replacement of uraninite by hydrocarbons polymerized by  $\alpha$ -particle irradiation. Spence (1930) believed that migrating mineral oil was polymerized by radiation to form thucholite which in turn replaced uraninite.

Christie and Keston (1949) have described thucholite associated with gold in pitchblende veins in the Goldfields district of Saskatchewan, Canada. Bowie (1955) concluded that thucholite from the Nicholson mine, Saskatchewan had resulted from the polymerization of mobile, mostly gaseous hydrocarbons by radiation emitted by pre-existing pitchblende, a process similar to that postulated by Davidson and Bowie (1951) for the hydrocarbon-uraninite complex of the Isle of Man and the Witwatersrand.

Uraniferous hydrocarbons from Moonta, South Australia have been reported by Mawson (1944) in lodes cross-cutting bornite and quartz.

Davidson and Bowie (1951) studied a sample from this occurrence and found fine pitchblende associated with chalcopyrite, bornite, covellite, arsenopyrite, and quartz.

Linares (1956) has reported a uranium-bearing asphaltic material (thucholite) associated with uraninite, copper sulphides, galena, and sphalerite from the Eva Peron deposit of the Argentine Republic. The asphaltic material is thought to have originated through distillation of bituminous mud by thermal action related to magmatic activity. Uraniferous asphaltites have also been reported in the Soviet Union, Japan, Sweden, and Mexico.

In the United States occurrences of uranium-bearing "asphaltite" are widespread on the Colorado Plateau and in adjacent areas, but the nature and origin of such occurrences has been the subject of considerable discussion.

Breger and Deul (1955) have suggested that organic pellets in the Moss Back formation of the San Rafael Swell represent an organic extract from low-rank coals. Kelley and Kerr (1958) pointed out, however, that important factors of field occurrences support a petroliferous origin. Drill holes on the east side of the Temple Mountain show the transition from indurated uranium "asphaltite" to viscous non-uranium asphalt. There is also a widespread distribution of oil sand in the permeable strata of the area. At the same time coal is absent and the distribution of lignitic material is sparse.

Hydrocarbon occurrences of the Unita basin (Hunt *et al.* 1954) show four chemically different types (ozocerite, albertite, gilsonite and wurtzilite) which are believed to represent variations in the depositional environment of the source rock. Davidson (1955) has stated that many specimens of uranium "asphaltite" from the Plateau are indistinguishable under the microscope from thucholite derived from hydrothermal lodes or pegmatites and has expressed the opinion that both occurrences have a common origin.

Pierce *et al.* (1958) report that study by *x*-ray diffraction and infrared absorption with chemical organic analyses of various mineral oils and uranium "asphaltite" suggest a petroliferous origin for much of the "asphaltite" in the western United States.

Erickson *et al.* (1954) and Hail *et al.* (1956) have suggested that uranium which is present in small amounts in crude oil tends to be concentrated in the heavier, more asphaltic portion of the oil as an urano-organic complex and suggest crude oil as a transporting medium for uranium. However, analyses of many crude oil samples show only a few parts per billion of uranium, while in refinery residues the uranium con-

tent has been found by Hyden (1956) to lie within the comparatively low range of 0.33 to 1070 parts per billion. McKelvey *et al.* (1956) concluded that it is unlikely that migrating petroleum is the source of uranium in the Colorado Plateau. Kelley and Kerr (1958) have shown that an average urano-organic ore sample from Temple Mountain represents a uranium concentration two million times greater than the associated crude oil. They have concluded that the bulk of the uranium must have been provided by hydrothermal solutions. Breger and Deul (1956) also believe that water, because of its powerful solvent action, is probably the most effective medium for transporting uranium from its source to its eventual site of concentration in carbonaceous substances.

The highly irregular distribution of uranium in asphaltic ore and the wide occurrence of essentially non-radioactive, indurated material in the same localities support the conclusion that the asphaltic material is essentially a collector of uranium rather than a major transporting medium.

#### INFRARED ABSORPTION OF URANIUM-BEARING ASPHALTITE

Infrared absorption curves have been obtained from viscous asphalt and from three samples of the same material heated in an electric oven at temperatures of 100°, 200°, and 300° C. each for 72 hours. The asphalt was collected from fissure seepages which cut the uranium ore body in the Magor mine, San Rafael Swell, Utah.

The infrared curve of the unheated material (Fig. 1, curve No. 1) shows strong absorption at 3.4  $\mu$ , 6.8  $\mu$ , and 7.2  $\mu$  indicating aliphatic structures. It is identical in its principal absorption bands to a carbonaceous nodule from the Seven Rivers formation, Eddy County, New Mexico (Pierce *et al.* 1958, p. 193). According to Pierce *et al.* (1958) the 3.4  $\mu$  band is caused by stretching by aliphatic C-H groups, while 6.8  $\mu$  and 7.2  $\mu$  indicate bending by methylene CH<sub>2</sub> groups and terminal CH<sub>3</sub> groups respectively. A weak absorption band at 5.8–5.9  $\mu$  indicates acid carbonyl (C=O) groups. Although the absorption band near 6.3  $\mu$  falls in the region of aromatic absorption, the absence of aromatic absorption at 3.2–3.3  $\mu$  suggests that the 6.3  $\mu$  band is largely caused by water. The intensity of the 2.95  $\mu$  band tends to decrease greatly by prolonged evacuation, indicating water.

At 100° C. the asphaltic material shows increased fluidity compared to the highly viscous unheated material. At 200° C. (Fig. 1, curve No. 2) the major absorption peaks are essentially identical with those of the unheated material and the 100° C. product. Partial induration occurs at 200° C. as indicated by an increase in viscosity and the tendency of the

material cooled to room temperature to fracture conchoidally. The average hardness of a semi-fluid tar from Temple Mountain was found (Kelley and Kerr, 1958) to be 3.4 Knoop after being heated at 200° C. for 96 hours, and 10.7 Knoop after being heated at the same temperature for 142 hours.

At 300° C. a sharp decrease in the intensities of the aliphatic absorption bands at 3.4  $\mu$ , 6.8  $\mu$ , and 7.2  $\mu$  takes place (Fig. 1, curve No. 3) and is accompanied with increased induration. The product becomes brittle, with a conchoidal fracture, and the infrared absorption curve becomes

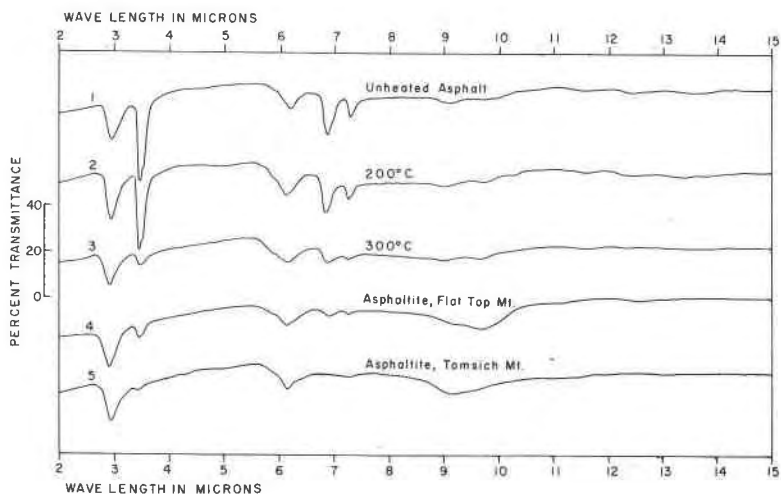


FIG. 1. The effect of heat on the infrared absorption of asphalt.

similar to the infrared absorption of the uraninite-bearing "asphaltite" from Flat Top Mountain and the Tomsich Mountain localities of the San Rafael Swell, Utah (Fig. 1, curves No. 4 and 5). The major difference between "artificial" and natural "asphaltites" lies in the presence of silica absorption in the 9–10  $\mu$  region caused by the presence of quartz in the Flat Top material and sulphur absorption near 8.9  $\mu$  caused by pyrite in the Tomsich Mountain material.

X-ray diffraction of semi-fluid asphalt, the heat-indurated (300° C.) product cooled to room temperature, and natural "asphaltite" from Flat Top Mountain show a single diffuse halo centered around the "d" spacing of 4.9 Å.

The experiment does not reveal the nature of changes during the heating process which resulted in the virtual disappearance of the absorption

bands of the semi-fluid asphalt. It is conceivable that a combination of devolatilization, oxidation, and polymerization takes place.

However, the similarity between the heat-treated product of the semi-fluid asphalt and the natural "asphaltite" in physical appearance and infrared absorption suggests the induration of natural "asphaltites" by high temperatures in the range 250°–300° C. as would be expected under hydrothermal conditions.

The effect of irradiation on hydrocarbons which causes polymerization and other radiation damage effects is widely recognized and may be an important factor in the induration of uranium-bearing asphaltic materials. Pierce *et al.* (1958) have shown that the total internal radiation dosage received by a number of "asphaltites" ranges from  $10^{24}$  to  $10^{27}$  electron volts per gram which corresponds to levels at which organic compounds are converted to coke in nuclear reactors. The indurated materials reported carry uranium or thorium in ore grade value amounting to several per cent. Many natural "asphaltites," however, contain little or no uranium, and spectrographic traces of uranium have not been reported to produce noticeable induration in petroleum.

#### THE URANIAN ASPHALTITE-COFFINITE ASSOCIATION

The frequent association of coffinite, a uranium silicaté (Stieff *et al.*, 1955, 1956) and "asphaltite" in many Colorado Plateau uranium deposits is believed to provide significant information on the temperature conditions which prevailed during uranium mineralization. Stieff *et al.* (1956) have called attention to some 40 occurrences of coffinite on the Colorado Plateau and in adjacent areas. Most of these contain associated organic material. Hydrothermal occurrences of coffinite in Colorado (Sims *et al.*, 1958), and the rather restricted hydrothermal conditions under which coffinite has been synthesized (Fuchs and Hoekstra, 1959), point to coffinite as a mineral of hydrothermal origin. The range in temperature of formation for coffinite coincides with the range in temperature at which semi-fluid asphalt becomes indurated. The similarity between the infrared absorption spectra of natural uranium-bearing "asphaltite" and asphaltite indurated by heat is an additional confirmatory factor.

Mineralogical investigation of coffinite has been carried out on material from a number of occurrences including the original coffinite from the La Sal No. 2 mine, Mesa County, Colorado kindly supplied by Dr. L. R. Stieff of the U. S. Geologic Survey; the Jackpile mine and Section 33 mine, New Mexico; the Green River district, and the Temple Mountain area, Utah.

## THE SEPARATION OF COFFINITE

Coffinite on the Plateau is found disseminated in hard "asphaltic" material which contains uraninite and quartz as prominent impurities. Those who have investigated the mineral have found it difficult to obtain even approximately pure coffinite. As a result, the literature shows a lack of chemical analyses of the pure material necessary to provide the exact chemical composition of the mineral.

Ordinary organic solvents fail to dissolve the associated organic material, but heating to 410° C. for two to three days has been found effective in removing the organic material. However, the presence of small amounts of uraninite and other finely disseminated uranium-bearing constituents in the organic complex may still cause uncertainty in the determination of the silica-uranium ratio of coffinite.

## X-RAY DATA ON COFFINITE

X-ray diffraction patterns of coffinite indicate (Stieff *et al.* 1956) that the mineral is tetragonal with a zircon type structure. X-ray patterns for a number of coffinite samples using copper radiation and a nickel filter are shown in Table 1. The coffinite localities represented are the Jackpile

TABLE 1. X-RAY DIFFRACTION POWDER PATTERNS OF COFFINITE  
(Copper radiation, Nickel filter)

hkl	Coffinite, Jackpile mine, New Mexico		Coffinite, Green River, Utah		Coffinite, La Sal No. 2 mine, Colorado		Coffinite, Temple Mountain, Utah		Coffinite, Arrowhead mine, Colorado*		Coffinite, USSR†	
	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
(011)	4.668	9	4.668	9	4.643	9	4.619	10	4.66	10	4.67	9
(200)	—	—	—	—	—	—	—	—	—	—	3.86	5
(200)	3.470	10	3.477	10	3.464	10	3.470	9	3.47	10	3.51	10
(121)	2.778	4	2.785	4	2.778	4	2.78	4	2.78	4	2.814	4
(112)	2.642	7	2.646	8	2.642	7	2.64	5	2.64	7	2.665	9
(220)	2.453	2	2.460	3	2.440	2	2.46	2	2.46	1	2.455	5
(031)	2.169	2	2.174	3	2.162	3	2.169	2	2.18	4	2.189	8
(013)	1.999	1½	2.003	3	1.999	1	2.01	1	2.01	1	2.002	7
(321)	1.839	2	1.850	4	1.836	2	1.835	2	1.841	4	1.855	3
(312)	1.799	5	1.799	4	1.793	3	1.80	7	1.801	7	1.813	9
(123)	1.735	2	1.732	3	1.732	2	1.73	2	1.737	4	—	—
(400)	—	—	—	—	—	—	—	—	—	—	1.742	4
(411)	1.623	1	1.627	1	1.623	½	1.63	2	1.629	1	1.632	5
(004)	—	—	—	—	—	—	—	—	—	—	1.562	5
(420)	1.551	1	1.554	1	1.551	1	weak	—	1.556	1	—	—
(332)	1.453	1	weak	—	1.448b	1	weak	—	1.451	1	1.449	2
(024)	1.427	½	weak	—	1.431	½	weak	—	1.435	1	1.430	2

\* Stieff *et al.*, (1956), ASTM card No. 8-304.

† Filipenko, Y. S. (1958). Interplanar spacings below 1.43Å are not reproduced.  
b=broad.

mine, New Mexico; Green River, and Temple Mountain, Utah; the La Sal No. 2 mine, and the Arrowhead mine, Colorado (Stieff *et al.*, 1956); and an undisclosed locality in the U.S.S.R. (Filipenko, 1958). Coffinite from the Jackpile mine and the La Sal No. 2 mine give relatively good *x*-ray patterns; all the reflections reported by Stieff *et al.* (1956) are duplicated, and most of the lines are sharp. The two samples from Green River and Temple Mountain, Utah give poor *x*-ray patterns with relatively low line intensities and some lines that are merged with the background. The removal of the organic material does not improve the line intensities, although the elimination of quartz does result in a slight improvement. Thus it is likely that crystallite size rather than dilution accounts for the poor quality of the *x*-ray pattern.

Three samples of coffinite were analyzed qualitatively for heavy elements with the *x*-ray spectrograph using tungsten radiation and a lithium fluoride crystal. The elements detected are shown in Table 2. It has been

TABLE 2. X-RAY SPECTROGRAPHIC ANALYSES OF COFFINITE

Coffinite, Jackpile mine, New Mexico	Coffinite, Green River, Utah	Coffinite, Section 33 mine, Grants, New Mexico
U	U As Fe V	U Pb

observed that in the *x*-ray fluorescence curve for coffinite from the Jackpile mine, New Mexico no reflections for heavy elements other than uranium are exhibited. Since this material also gives the best *x*-ray diffraction pattern obtained from samples used in this work, it may be inferred that arsenic, lead, iron, and vanadium noted in the other two samples are probably either absent or constitute non-essential impurities.

#### THERMAL BEHAVIOR OF URANIAN ASPHALTITE AND COFFINITE

Differential thermal analysis of coffinite-bearing "asphaltite" samples from Green River, Utah and the Jackpile mine, New Mexico show a strong and broad exothermic reaction which attains a maximum at 480°–500° C. (Fig. 2, curves Nos. 1 and 2). This reaction is believed to be caused by the oxidation of associated "asphaltite." The coincidence of the temperature at which this reaction takes place and the temperature at which the coffinite lattice is destroyed in air (500° C.) is probably accidental.



Differential thermal analysis of coffinite-bearing "asphaltite" from the Jackpile mine in vacuum shows no reactions up to 1000° C. (Fig. 2, curve No. 3). "Asphaltite"-free coffinite obtained by roasting at 410° C. for three days gives no thermal reaction in air (Fig. 2, curve No. 4). The lattice destruction of coffinite at 500° C. was not accompanied by any observable thermal reaction.

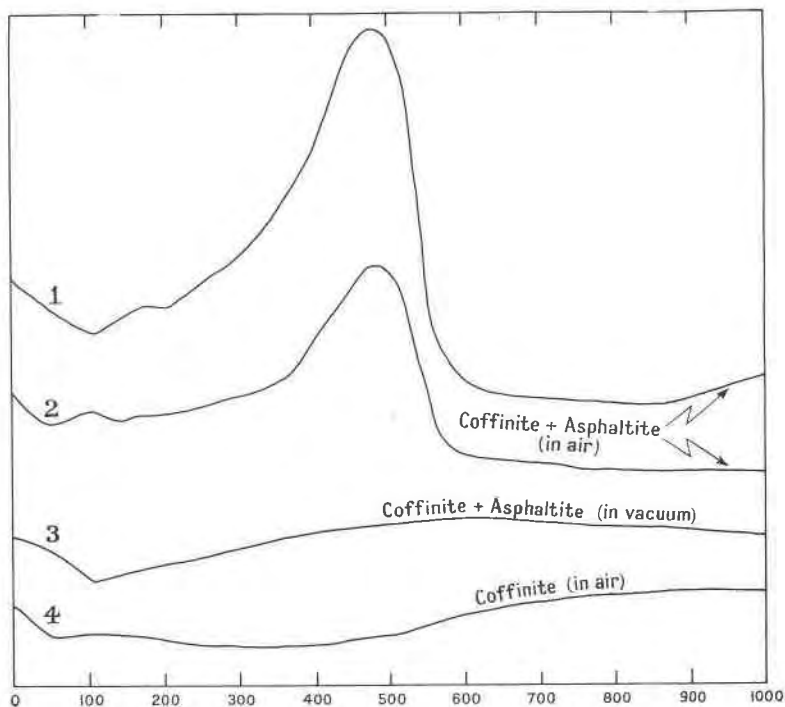


FIG. 2. D. T. A. of coffinite samples.

#### X-RAY DATA ON HEATED SAMPLES

A sample of coffinite-bearing "asphaltite" from the Jackpile mine was heated in an electric oven for two hours at each of the following temperatures. 200, 300, 400, 500, 600, 700, 840, 960 degrees centigrade, and an x-ray pattern was made of each product. The patterns were taken, after cooling to room temperature, using copper radiation and a nickel filter. The small amount of quartz which was present in the sample gave persistent lines throughout the temperature range. The strongest quartz line at 3.349 Å maintained approximately the same intensity in each pattern and served as a datum to which changes in the intensity of coffinite lines

could be referred. Table 3 shows the first four coffinite lines with intensities based on the quartz line at 3.349 Å considered as 10.

In the interval between 200° C. and 400° C. a slight decrease occurs in the intensity of coffinite lines. There is also a slight shift of the first three lines towards lower spacing values, although the significance of this shift is uncertain. At 500° C. there is a pronounced drop in the intensity of

TABLE 3. X-RAY DIFFRACTION OF COFFINITE HEATED IN AIR  
(Jackpile mine, New Mexico)  
Intensities computed taking strongest quartz line 10  
Cu/Ni Radiation

Unheated		200°-400° C.		500° C.		600° C.	
<i>d</i> Å	I	<i>d</i> Å	I	<i>d</i> Å	I	<i>d</i> Å	I
4.668	9	4.619	8	4.595	2½	4.595	1
3.470	10	3.437	9	3.424	3	3.386	1
3.349*	10	3.336*	10	3.349*	10	3.349*	10
2.778	4	2.761	3	2.761	1½	very weak	
2.642	6	2.642	5	2.627	1½	very weak	
700° C.		840° C.		960° C.		U <sub>3</sub> O <sub>8</sub> †	
<i>d</i> Å	I	<i>d</i> Å	I	<i>d</i> Å	I	<i>d</i> Å	I
4.110	1	4.110	7	4.110	8	4.110	4
3.386	1	3.386	8	3.386	6	3.390	10
3.349*	10	3.349*	10	3.349*	10		
2.627	1	2.627b	7	2.627	6	2.62	7
very weak lines		2.069	1	2.074	1	2.06	3

\* Strongest  $\alpha$ -quartz line.

† Milne (1951); ASTM card No. 4-0511.

b=broad.

the coffinite lines and the three strongest lines shift toward lower *d* values. At 600°-700° C. the intensity of the two strongest lines shows a further drop, and the other lines are extremely weak; also, the first line drops to 4.110, the value for the first line of U<sub>3</sub>O<sub>8</sub>. The strongest coffinite line drops to 3.386 Å at 840° C. It is noted that the three strongest coffinite lines 4.668 Å, 3.470 Å, and 2.642 Å shift to 4.110 Å, 3.386 Å, and 2.627 Å values respectively, which correspond to the three strongest lines of the pattern for U<sub>3</sub>O<sub>8</sub>. At 840° C. the intensities of the U<sub>3</sub>O<sub>8</sub> lines increase and some additional lines are developed. At 960° C. the pattern developed agrees with U<sub>3</sub>O<sub>8</sub>. Gruner and Smith (1955) report that cof-

finite showed some decrease in cell dimensions when heated in air at 500° C., while virtual destruction of the lattice occurred at 600° C. Fuchs and Hoekstra (1959) place the stability limits for synthetic coffinite at 500° C. in air and 1000° C. in vacuum.

In summary, the three strongest coffinite lines decrease sharply in intensity at 500° C. and show some shift toward the spacings of the three strongest  $U_3O_8$  lines. The shift in spacing toward  $U_3O_8$  lines is completed by 840° C. and is accompanied by an increase in line intensities and definition.

#### LOSS OF WEIGHT AND CHANGE IN COLOR

In a further attempt to investigate the nature of the reactions shown in the D. T. A. of coffinite-bearing "asphaltite," a dried sample from the Jackpile mine, New Mexico was heated in an electric oven for one hour at each of the following temperatures: 110, 200, 300, 400, 500, 600, 700, and 960 degrees centigrade. After each heating the sample was weighed on a sensitive balance after allowing to cool in a desiccator to room temperature. Up to 400° C. (Fig. 3) the loss of weight amounts to only two per cent of the weight at 110° C. Between 400° C. and 500° C. a sharp drop in weight occurs. The weight at this temperature is found to be 33.3 per cent of the weight at 110° C. From 500° C. to 960° C. the weight

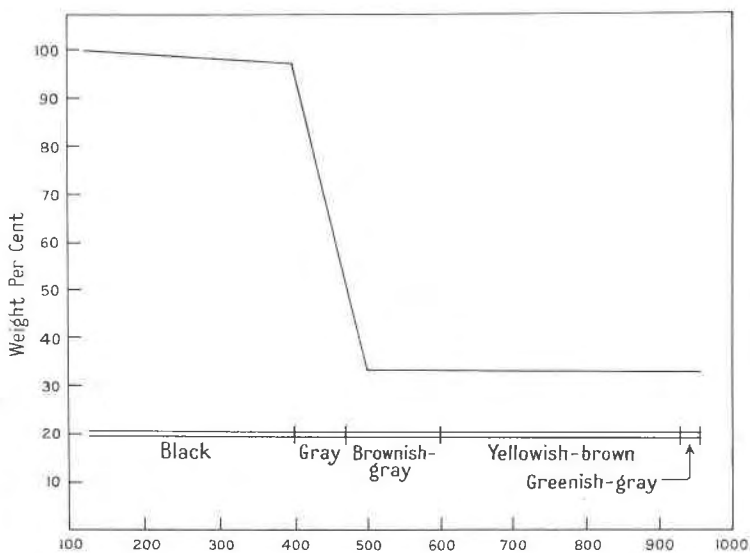


FIG. 3. Heat effects on weight and color of coffinite.

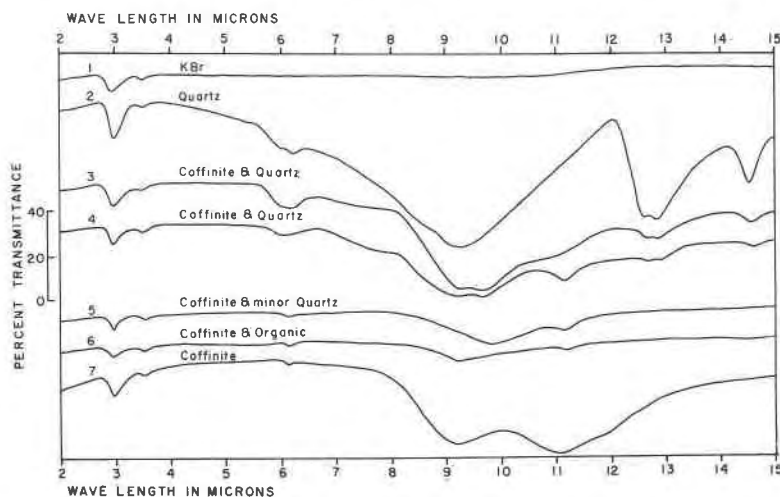


FIG. 4. Infrared absorption of coffinite.

is essentially stable, the final weight per cent of the sample at 960° C. being 33.28. Coffinite-bearing "asphaltite" from La Sal No. 2 mine lost 53 per cent of its weight on heating in air at 410° C. for two days. The loss of weight is accompanied by the evolution of CO<sub>2</sub> and H<sub>2</sub>O caused by the oxidation of the organic material.

Color changes in coffinite-bearing samples have been observed (Fig. 3) after several stages of heating. Up to 400° C. it remains black. Between 400° C. and 500° C. a rapid change is observed from black to gray to brownish-gray. At 600° C. it becomes yellowish-brown and retains this color until it becomes greenish-gray at 960° C. Similar color changes were observed by Stieff *et al.* (1956).

#### INFRARED ABSORPTION OF HEAT TREATED SAMPLES

Coffinite samples from the Jackpile mine and La Sal No. 2 mine were selected for infrared absorption study (Fig. 4). Curves were obtained both for samples containing organic material and for samples heated at 410° C. for two days to eliminate organic material.

The organic-free samples showed stronger silica absorption bands than samples contaminated with organic material as may be observed by comparing curves No. 6 and No. 7 (Fig. 4). Curve No. 6 represents organic material bearing coffinite from La Sal No. 2 mine; it shows two weak silica absorption bands near 9 and 11 microns. Increasing the thickness of the sample increases the opacity of the pellet and fails to

improve the absorption curves. Curve No. 7 represents coffinite from La Sal No. 2 mine free from the organic material; it shows two distinct and strong bands near 9 and 11 microns. Curve No. 6 is similar to a previously published curve of coffinite from the same locality by Stieff *et al.* (1956, Fig. 1, p. 687).

In a discussion of infrared absorption by the  $\text{SiO}_4$  group, Eitel (1954, p. 17) concludes that the active inner characteristic vibrations of the  $\text{SiO}_4$  group ( $\lambda = 10\text{--}12 \mu$ ) takes place at shorter wave lengths with increasing interlinkage of the  $\text{SiO}_4$  tetrahedra. Quartz has a framework structure with a maximum interlinkage between the silica tetrahedra groups and shows a strong absorption band which attains a maximum at  $9.3 \mu$  (quartz from Herkimer County, New York, Fig. 4, curve No. 2).

Quartz-free coffinite from the La Sal No. 2 mine shows an absorption band which attains a maximum at  $9.2 \mu$  corresponding to that of quartz. In addition, coffinite shows an absorption band at  $11\text{--}11.2 \mu$  indicating isolated tetrahedra (Launer, 1952).

The presence of a moderate amount of quartz as an impurity in coffinite causes an overlap of the  $9\text{--}10 \mu$  silica bands for the two minerals which results in a broadening of the silica absorption in this region. This broadening effect tends to impair the resolution of the  $11 \mu$  band of coffinite which often shows as a flexure rather than as a distinct band (Fig. 4, curve No. 3). Progressive removal of quartz causes a pronounced decrease in the intensity of the  $9\text{--}10 \mu$  band and the appearance of a distinct band near  $11 \mu$  characteristic of isolated silica tetrahedra (Fig. 4, curves No. 4 and 5). Quartz shows two additional bands at  $12.5\text{--}12.8 \mu$  and  $14.5 \mu$  but these do not appear in quartz-free coffinite.

The infrared absorption study of silica in coffinite points to agreement with the conclusion of Stieff *et al.* (1956) on natural coffinite and with Fuchs and Hoekstra (1959) on synthetic coffinite that the mineral has isolated silica tetrahedra in its structure.

Coffinite shows a rather broad O-H absorption band which attains a maximum at  $2.95 \mu$  with a weak band at  $3.5 \mu$ . These two bands also appear in KBr blanks and quartz. Prolonged pressure at  $200^\circ \text{C}$ . results in the virtual disappearance of the bands for the KBr blanks, but does not eliminate them from either quartz or coffinite samples.

A coffinite sample dried at  $410^\circ \text{C}$ . and another heated in air at  $750^\circ \text{C}$ . for two days to insure the destruction of the coffinite lattice shows no difference in the  $2.95 \mu$  band. This indicates that the  $2.95 \mu$  band is probably caused by absorbed water rather than by an (O-H) group in the coffinite lattice.

According to Keller and Pickett (1949) monomeric (O-H) within a

crystal lattice absorbs at  $2.75\ \mu$ , dimeric bonded (O-H) groups absorb at  $2.85\ \mu$ , and polymeric (O-H) groups absorb at  $2.95\ \mu$ . The O-H absorption of coffinite appears at  $2.95\ \mu$ , is absent at  $2.75\ \mu$ , and the slope of the absorption curve does not show any interruption at  $2.85\ \mu$ . This indicates that the  $2.95\ \mu$  band is caused by polymeric (O-H) groups caused probably by absorbed water. Water in the  $\text{H}_2\text{O}$  form absorbs in the  $2.8\ \mu$  and  $6.1\ \mu$  region, and therefore infrared absorption spectra do not distinguish between mechanically trapped  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$  which forms an integral part of the crystal as in gypsum or hydrogen bonded water (Keller and Pickett, 1954, p. 90).

A KBr disc, slightly thicker than the sample disc, placed in the path of the standard infrared ray of a split beam recorder produces a negative  $\text{H}_2\text{O}$  absorption band without any interruption in the  $2.8$ – $2.95\ \mu$  slope, indicating the absence of monomeric and dimeric (O-H) groups and also indicating that the absorption band in this region is caused by absorbed water. The absence of thermal reactions of coffinite free from organic material up to  $1000^\circ\text{C}$ . indicates the absence of the (O-H) group from the coffinite lattice. Fuchs and Hoekstra (1959) found that synthetic coffinite does not show any change in cell dimensions or line intensities for material heated to  $1000^\circ\text{C}$ . in vacuum and concluded that synthetic coffinite is  $\text{USiO}_4$  without an essential hydroxyl component.

Natural coffinite specimens from the Jackpile mine and La Sal No. 2 mine are believed to have no essential hydroxyl component in the structure and in this respect are similar to synthetic coffinite.

Chemical analyses of natural coffinite (Stieff *et al.*, 1956) show a lower silica content than would be stoichiometrically proportional to uranium in the formula  $\text{USiO}_4$  and have been considered to indicate a hydroxyl substitution of silica. However, Stieff *et al.* did not exclude the possibility that unseparated uranium oxide might account for the silica-uranium ratio discrepancy.

#### OPTICAL OBSERVATIONS

Under the microscope the black asphaltic material is opaque except in small fragments where it is translucent dark brown. "Asphaltite"-free coffinite obtained by heating at  $410^\circ\text{C}$ . for three days consists of a mixture of coffinite aggregates and quartz. Coffinite is isotropic, transparent greenish-yellow in small fragments and mottled translucent brown in thick aggregates. Intergrowth of coffinite with quartz and possibly surface replacement of the latter may be observed in many grains. The replaced surfaces of the quartz grains show parallel striations suggesting preferred orientation of replacement parallel to the  $c$ -axis of quartz. The

precipitation of quartz with synthetic coffinite was observed by Fuchs and Hoekstra (1959), and coffinite from the Soviet Union has been reported (Filipenko, 1958) to be associated with quartz.

#### ELECTRON MICROGRAPHS

Small portions of "asphaltite"-free and quartz-free coffinite from the Jackpile mine were optically examined and then ground to minus 350 mesh after which suspensions in collodion films were prepared for observation under the electron microscope. Aggregates of coffinite appear almost opaque on the screen, but a tracing of the aggregate outlines taken from several electron photomicrographs indicates crystal boundaries (Fig. 5).

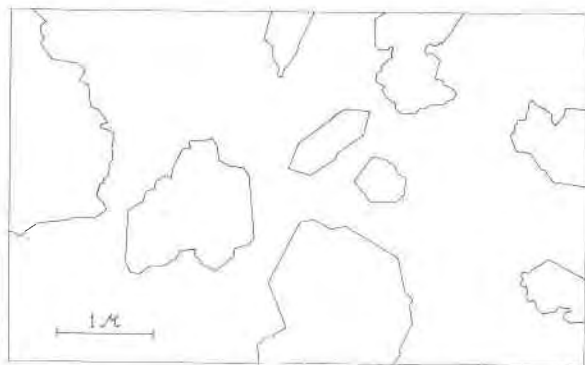


FIG. 5. Crystal outlines of coffinite aggregates, traced from electron photomicrographs.

#### COFFINITE AS AN INDICATOR OF HYDROTHERMAL ORIGIN

Descriptions of occurrences and synthesis suggest that coffinite is worthy of consideration as a temperature indicator for Colorado Plateau uranium deposits.

Coffinite has been reported (Sims *et al.*, 1958) associated with uraninite in the Copper King uranium mine, Larimer County, Colorado. The mine occurs near the central part of a Precambrian batholith of Silver Plume granite known as the Log Cabin batholith. Coffinite and uraninite occur along the Copper King fault and are associated with a hydrothermal assemblage of vein-forming minerals such as siderite, pyrite, marcasite, quartz, sphalerite, chalcocopyrite, and magnetite.

In the Soviet Union coffinite has been found (Filipenko, 1958) in fissures in granite. It occurs in the form of thin lenses and irregularly shaped nests associated with pyrite, galena, and chalcocopyrite, as well as quartz and several disintegration products of feldspars such as sericite and kaolinite.

Fuchs and Hoekstra (1959) synthesized coffinite by a hydrothermal procedure. They indicate that depolymerization of the polysilicate and the formation of  $\text{USiO}_4$  occurs during the heating process rather than during the precipitation step and report that co-precipitation of uranium and silica is necessary for coffinite synthesis. They also state that coffinite is not likely to form in nature by the reaction of finely divided  $\text{UO}_2$  and colloidal silica. Reducing and alkaline environment were found to be essential to the formation of coffinite and the temperature limits are set at  $200^\circ\text{C}$ . to  $360^\circ\text{C}$ .

#### CONCLUSIONS

The widespread urano-organic association in hydrothermal deposits suggests a hydrothermal source for the original uranium ions of the Colorado Plateau deposits.

Liquid hydrocarbons from the San Rafael Swell may be indurated under conditions of elevated temperature in the range between  $200^\circ\text{C}$ . and  $300^\circ\text{C}$ . The heated products give infrared curves similar to natural uranium-bearing "asphaltites" suggesting that the natural material could have been hardened by the action of hydrothermal solutions. Polymerization caused by irradiation is recognized as a possible originating mechanism for materials of high radioactivity. However, indurated "asphaltites" low in radioactivity are abundant, and their physical condition is better accounted for by the action of heat derived from hydrothermal solutions barren of uranium.

Infrared, x-ray, and D. T. A. study of coffinite indicates that the mineral is a uranium silicate without an essential hydroxyl component. Hydrothermal occurrences of coffinite and the temperature of its synthesis suggest a special significance as a temperature indicator.

The intimate coffinite-"asphaltite" association is not conceivable as a product of irradiation; at the same time, the uranium silicate is a likely product of hydrothermal action.

#### ACKNOWLEDGMENTS

The writers express their appreciation to Dr. L. R. Stieff of the U. S. Geological Survey for a sample of the original coffinite from the La Sal No. 2 mine, to Messrs. Vincent Perry and R. D. Lynn of The Anaconda Company for coffinite-bearing specimens from the Jackpile mine and to the American Museum of Natural History for coffinite specimens.

The assistance of Professor Brian Mason in reading this manuscript and offering suggestions is appreciated. This work has been made possible through fellowship aid by the United Arab Republic while field and laboratory assistance have been provided by the Division of Re-



search and the Division of Raw Materials of the U. S. Atomic Energy Commission.

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*Manuscript received June 22, 1960.*