ened to increase the amount of nitrate, there is also a diminution of the amount of sulphide dissolved. These points are shown in Table II.

TABLE II.

 $Ag_0S = 0.2g$.

 $HNO_2 = 71$ per cent.

Acid boiling					Acid cold.					
No. of expt.	Time of action.	Per cent. Ag ₂ S dissolved.	Per cent. nitrate formed.	No. of expt.	Time of action.	Per cent. Ag ₂ S dissolved.	Per cent. nitrate formed.			
21	Heated just to boiling		39 · 5	31	ı hour	37.0	32.8			
22	15 sec.	97 · 5	37 · 5	32	3.5 hrs.	53.6	20.8			
23	30 sec .	96.6	2I.I	33	9 hours	85.2	22.9			
24	ı min.	. 91.4	8.4	34	18 hours	95	7.2			
25	5 min.	99.7	3.6	35	42 hours	99 - 7	0.8			
26	70 min.	100	I.I	36	66 hours	99.8	0.3			

Summary.

Nitric acid, when of concentration above 5 per cent., dissolves precipitated silver sulphide rapidly. Very strong acid yields silver sulphate alone, while acid of lower concentration forms some nitrate in proportion to its dilution. 20–15 per cent. acid yields the maximum, about 95 per cent. nitrate, greater dilution again resulting in a smaller percentage. Heating the acid, or prolonging its time of action is unfavorable to the formation of nitrate.

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GRAHAMITE, A SOLID NATIVE BITUMEN.

By Clifford Richardson. Received June 24, 1910.

Grahamite is a solid native bitumen, the type of which was first found in Ritchie County, West Virginia, in the early sixties of the last century. It was named for the Messrs. Graham, who were interested in the commercial development of the deposit, by Henry Wurtz. The early literature of the subject¹ is largely devoted to the origin of the material and to its relations to coal, asphalt and albertite, as the latter occurs in Nova Scotia.² It is largely controversial, which is not surprising in view of the fact that there had been little opportunity up to that time of studying and differentiating the native bitumens.

In 1890 Prof. Wm. P Blake, who had been interesting himself in the solid native bitumen found in such large amounts in veins in Utah and

¹ J. P. Leslie, *Proc. Am. Phil. Soc.*, 9, 183 (1863). Henry Wurtz, *Am. J. Sci.*, [2] 42, 420 (1865); *Proc. A. A. A. S.*, 18, 124 (1869); *Am. Gas Light J.*, 11, 98. S. F. Peckham, *Am. Gas Light J.*, 11, 164 (1869). W. M. Fontaine, *Am. J. Sci.*, [3] 6, 409 (1873). J. P. Kimball, *Am. J. Sci.*, [3] 12, 277 (1876).

² Wetherill, Trans. Am. Phil. Soc., 1852, 353.

Colorado, presented a paper¹ before the American Institute of Mining Engineers at its Washington meeting entitled "Uintaite, Albertite, Grahamite, and Asphaltum, Described and Compared with Observations on Bitumens and its Compounds," in which he stated, after reference to preceding papers, that the grahamite of West Virginia is neither albertite nor gilsonite (uintaite) but that all of these bitumens are plainly differentiated from each other by definite characteristics, although he relied on the statements of his predecessors for his characterization of grahamite. His conclusions, we shall see from the data which are to be presented, were entirely justified.

Grahamite attracted no further attention until 1899 when J. A. Taff, of the U. S. Geological Survey, published a paper² on "An Albertite-like Asphalt in the Choctaw Nation, Indian Territory," in which he describes a deposit of solid native bitumen occurring in the Impson Valley. Dr. Wm. C. Day, who examined it for him, concluded that it "resembled albertite more than any other asphaltic substance" though "the solubility in carbon disulphide classes the material with the asphalts rather than the coals." Dr. Day should have known that the albertite is practically insoluble in carbon disulphide and that, consequently, the material he had in hand could not be an albertite. He, like many other writers, had not had a sufficiently wide experience with the solid native bitumens to recognize their relations to each other and to identify them.

In 1901 a voluminous paper on "The Asphalt and Bituminous Rock Deposits of the United States," by George H. Eldridge, was published in Part I of the Twenty-second Annual Report of the U. S. Geological Survey. Most of the occurrences of grahamite came under his observation but, strangely enough, he failed to recognize the relations and similarity of any of them to the type grahamite of West Virginia. He went so far as to give the name "impsonite" to the grahamite found in the Impson Valley and writes of that found in Middle Park, Colorado, as asphalt. It is but fair to say that Mr. Eldridge, when his attention was called to the matter by the writer, after the appearance of his report, recognized the fact that many of the bitumens which he had described were, actually, as will be seen later, grahamites.

The confusion as regards bitumens of the three types, grahamite, albertite and gilsonite and also, to a limited extent, manjak continued.

In 1909 there appeared a Bulletin No. 380 of the U. S. Geological Survey "Contributions to Economic Geology" in which, under the heading "Asphalt" two papers appear, one, "An Occurrence of Asphaltite in Northeastern Nevada," by Robert Anderson, and another, "Grahamite Deposits of Southeastern Oklahoma," by Joseph A. Taff. Anderson

¹ Trans. Am. Inst. Min. Eng., 18, 563.

² Am. J. Sci., [4] 8, 224.

undoubtedly uses the term asphaltite in the sense proposed by Eldridge in the classification of the native hydrocarbons and allied substances which he gives in his "Report," where he includes under asphaltites, albertite, impsonite, grahamite, nigrite and uintaite (gilsonite) although not distinguishing them from the true asphalts which do not appear in his table in any form. Anderson, no doubt, intends to convey the idea that the Nevada bitumen is not an asphalt. He says: "The asphaltite found here would be commercially known as 'grahamite' but its characteristics show it to differ from the variety so known scientifically. A few tests revealed a close relationship to the variety from Indian Territory described by G. H. Eldridge as impsonite." Anderson shows, therefore, that he is not aware that impsonite is grahamite. Taff's description of the solid bitumens of Oklahoma in the pages immediately following Anderson's paper shows that he is in accord with the ideas advanced by the writer some years ago1 that many, if not all of the solid bitumens of Oklahoma are grahamites, taking that from West Virginia as a type.

The confusion which has existed for many years as to what grahamite is becomes apparent from the preceding statement. It has arisen largely because no individual investigator has had in hand for comparison at one time, all of the very numerous deposits of solid native bitumen which are so widely distributed, particularly in North America and in the islands of the West Indies. Within the last fifteen years the writer has been so fortunate as to have referred to him specimens of nearly all the well-known occurrences of solid bitumen and of those which have been discovered during that period and was particularly fortunate in obtaining a large specimen of the original grahamite taken early in the seventies from the deposit in West Virginia, to which the name was originally applied and which must be regarded as the type. For this he is indebted to Prof. Charles F. Chandler, of Columbia University, whose identification of the material is, of course, authoritative.

In addition, specimens of this same bitumen, obtained when the vein was again worked for a short time in 1904–5 were available. The solid native bitumens which have been examined and which have the characteristics of grahamite are identified as to locality in the following list. Wherever possible reference is made to description of the deposits by geologists and others.

List of Occurrences of Grahamite.

WEST VIRGINIA.

No. 19,399 The type of material from Ritchie County. 25 miles a little north of east from Parkersburg, on McFarlan's Run near the South fork of Hughes River, taken

¹ Report on the "Mineral Resources of Cuba in 1901." Gussenheimer. Weil & Co., not properly accredited to the author, and "The Modern Asphalt Pavement." John Wiley & Sons, N. Y. First edition, 1905, 203, second edition 1908, 211.

from the vein at the time the mine was originally worked between 1868 and 1875. From the cabinet of Prof. C. F. Chandler.

No. 75,637 From the Ritchie County deposit in 1904.

No. 75,673 10 ft. below No. 75,637 at the same time.

No. 82,088 From the Ritchie County deposit in 1905.

COLORADO.

No. 19,162 From the Middle Park deposit, Grand County, on Willow Creek, 21 miles from Grand River and 12 miles west of Grand Lake, 8 miles east of Park White Mt., 4 miles north of Grand Mt. S. W. 15-6 and 22, T. 4 N. Range 77 West, specimen of 1898.

No. 19,260 Same.

No. 71,963 Same-Specimen of 1900.

No. 71.746 Same-Specimen of 1904.

OKLAHOMA.

No. 53,788 Impson Valley deposit, on a branch of Tenmile Creek, in the west side of Impson Valley near the south side of sec. 21, T. 1 S., R. 1 SE (Taff), specimen of IQOI.

No. 74,989 Same shaft No. 3, from "Old Slope," 24 ft. depth, specimen of 1904.

No. 74,990 Same shaft No. 3, from "Old Slope." 40 ft. depth, specimen of 1904.

No. 74,991 Same shaft No. 3, from "Old Slope," 70 ft. depth, specimen of 1904. No. 74,992 Same shaft No. 3, from "Old Slope," 90 ft. depth, specimen of 1904.

No. 74,993 Same shaft No. 3, from "Old Slope," 110 ft. depth, specimen of 1904.

No. 74,994 Same shaft No. 3, from "Old Slope," 135 ft. depth, specimen of 1904.

No. 114,041 Same, from the stock of the Barber Asphalt Paving Company, Maurer, N. J. Four samples running from "A" with least luster to "D" with greatest luster, specimens of 1909.

No. 76,503 McGue Creek Valley deposit, Williams mine, on the west side of McGee Creek in the S. W. 1/4 sec. 23, T. 1 N., R. 14 E. (Taff), specimen of 1905.

No. 76,504 Same.

No. 81,424 From the Choctaw Mining and Development Company, South McAlester. 1905.

No. 80,847 LeGrand's Stringtown deposit, in so called "red bank" near Loco, Chickowaw Nation, Okla. This specimen is characterized by an infiltration of pyrite. in crystals readily recognized with the naked eye.

No. 59,398 Exact locality not known, 1902.

No. 80,824 From 21/2 miles southeast of Stringtown, Okla., at South edge of Boggy Creek Valley filling fissures in Ordovician or Silurian shales.

TEXAS.

Fayette County. Webb County.

WYOMING.

No. 75,093 Locality not known, 1905.

MEXICO.

No. 12,113 Huasteca, Cristo deposit. The original material described by Kimball from the cabinet of Lehigh University.

No. 12,114 Same.

No. 64,152 From Victoria, 1903.

No. 83,982 From near the Eastern coast, 1905.

CENTRAL AMERICA.

No. 109,503 Unknown locality, 1909.

CUBA.

Pure bitumens.

No. 22.216 From "La America" mine near Bahia Honda, Province of Pinar del Rio, specimen of 1899.

No. 35,901 Same—Specimen.

No. 22,222 From "La Havana" mine near Campo Florida. Province of Havana, 1899.

No. 31.135 From an unidentified mine, twelve miles east of Havana, 1900.

Grahamites associated with mineral matter.

No. 21,415 From "Magdalena" mine, District of Mariel. Province of Pinar del Rio, Sample of 1899.

No. 21,657 Same.

No. 44,626 Same-Sample of 1901.

No. 52.000 Same-Sample of 1901.

No. 75,755 Same—Sample of 1905.

No. 21,416 From Mercedes mine, District of Mariel, Province of Pinar del Rio, 1899.

No. 25,131 From "Santa Eloisa" mine, near Santa Clara City, sample of 1899.

No. 47,617 Same—Sample of 1901.

No. 55,195 Same-Sample of 1901.

TRINIDAD, B. S. I.

No. 61.726-8 From Vistabella mine. near San Fernando, Trinidad, B. W. I., put on the market as "manjak," specimens of 1902.

No. 80,659 Same-Specimen of 1905.

METAMORPHOSED GRAHAMITES.

No. 69,235 Unknown locality, Oklahoma.

No. 69,482 From the Choctaw Mining and Development Company.

No. 69.242 Black Fork Mountain. Oklahoma.

Two samples.

- (a) Near top of outcrop.
- (b) Entry running in on vein from side of hill at a point probably 15 ft. below surface.

It will be seen from the number of occurrences mentioned in the preceding list that, if we are justified in considering them all as the same material, that is to say, as native bitumens corresponding to the type originally found in West Virginia, grahamite is very widely distributed.

The results of the examination of the specimens which have been studied are given in Table I.

In considering the data given some consideration must first be given to the subject of native bitumens in general and especially to the solid native bitumens from which grahamite is to be differentiated.

The native bitumens consist of a mixture of native hydrocarbons and small amounts of their nitrogen, sulphur and, in some cases oxygen derivatives, the character of any bitumen being dependent on that of the different series of hydrocarbons of which it is composed and their state of aggregation. Natural gas, petroleum in its various forms, maltha, asphalt, gilsonite, ozokerite and grahamite are bitumens, the four last

being solids. They are all characterized by being soluble in carbon disulphide, but are differentiated by their physical and chemical characteristics. They all originate in petroleum and are products of metamorphosis, depending for their character on that of the petroleum from which they are derived and the environment to which this has been exposed during the last periods of time during which the changes have been going on. Petroleums are known to be of various types and include the paraffin oils of the Eastern states, which contain but a small amount of sulphur derivatives, the more sulphurous oils of the Ohio and Canadian type, which are largely made up of the paraffin series of hydrocarbons, the semi-asphaltic oils of Illinois, Texas and the midcontinental fields, varying in character as they are more or less asphaltic in nature, and the asphaltic oils of California, Mexico and the West Indies, which are practically free from paraffin hydrocarbons. As yet no petroleum of the Russian type has been found in the western hemisphere.

Solid bitumens are, apparently, formed from all of these types of petroleum. Ozokerite consists of solid paraffins and is plainly der ved from paraffin petroleum. The type grahamite of West Virginia is found where paraffin petroleums alone are available as its source. That occurring in Middle Park, Colorado, must have had its origin in petroleum of the type found in that State at Florence, which is a paraffin oil. The grahamite of Oklahoma must have been derived from oil of the type of the mid-continental field which contains a large amount of paraffin hydrocarbons, although it is also asphaltic. All of the grahamites of the United States originate, therefore, in petroleums which are more or less of a paraffin nature. The contrary is the case with the grahamite of Trinidad, where the petroleum is purely asphaltic, as far as we know it to-day, but in appearance it can hardly be differentiated from that of the West Virginia deposit. The Cuban grahamites must, likewise, originate in asphaltic oils. These facts may prove of some value in differentiating the grahamites which have been examined.

From the non-paraffin oils are formed the asphalts, gilsonite, manjak and glance pitch, all of which have physical properties and chemical characteristics which differentiate them from one another and from grahamite. Before attempting to characterize grahamite, therefore, and to differentiate it from asphalt and the other solid bitumens something must be known in regard to these latter bitumens. Some data in regard to them are presented in Table II for comparison with which similar data in regard to the type grahamite from West Virginia are presented.

The native bitumens, it will be observed, are soluble in carbon disulphide. This is an essential characteristic. If the material is not soluble and, nevertheless, has been derived from petroleum it is regarded as a

	•	-		Specific
No.	Locality.		Luster.	gravity.
19,399	West Virginia, 1870		Dall	1.130
75.637	West Virginia, 1905	Schistose or backly	Dull	1.137
75. 6 7 3	West Virginia, 1905			1.121
82,088	West Virginia, 1905			• •
19.162	Colorado, 1898	Schistose or hackly	Lustrous	1.160
19.260	Colorado, 1898		Linstronia	1.159
31.963	Colorado, 1900.	- · · · · · · · · · · · · · · · · · · ·	Lustrous	1.152
71.746	Colorado, 1904.	Schistose of Mackey	Destroits	
•				••
53,788	Impson Valley, Okla., 1901		Lustrous	1.184
74. 989	Impson Valley, Okla., 1904	Schistose or hackly		
74.9 9 0	Impson Valley, Okla., 1904			
74.99 1	Impeon Valley, Okla., 1904	·		• •
74.992	Impson Valley, Okla., 1904			
74, 99 3	Impson Valley, Okla., 1904			
74. 994	Impson Valley, Okla., 1904			• •
114.0416		Schistose or hackly	Very dall	• •
Р	Impson Valley, Okla., 1909		Dull	
с	Impson Valley, Okla., 1909		Sub-instrous	
t d	Impson Valley, Okla., 1909		Lustrous	••
76, 503	McGee Creek, Okla., 1905	Schistose or hackly	Sub-lustrons	
76,504	McGee Creek, Okla., 1905,	Schistose or hackly	Lustrous	• •
81.424	South McAlester, Okla., 1905	Schistose or hackly	Lentrous	
80,824	Stringtown, Okla., 1905	Schistose or hackly	Sub-lustrous	
64.847	LeGrand, deposit, Okla., 1903	Schistose or hackly	Dull	
59,398	Unknown. Okla., 1902	Schistose or hackly		.:
	Fayette Co., Texas, 1909			
	Webb Co., Texas, 1909,			••
75,09 3	Wyoming. unknown. 1901			
	MRXICO.			
64.152	Victoria, 1903			
83.982	Near Eastern Coast, 1905	Smooth semi conchaidel	Lustrous	••
12.113	Huasteca, 1876	(MIOOCH, SCHI-CONCHORM	Lusuous	1,145
12.114	Huasteca, 1876			
12,117				• •
	CENTRAL AMERICA.			
109.503	Unknown locality, 1909			• •
	CUBA.			
22,2 16	Bahia Honda, "La America" mine, 1899	Distinct cleavage, thin layers	Semi-bright, coal like	1.157
3 5,9 01	Bahia Honda, "La America" mine, 1900		Semi-bright, coal like	1.235
22,222	Campo Florida, "La Havana mine." 1899 .		Dull	1.175
31,135	Unidentified mine, 12 m. E. Havana, 1900.		Dull	1.163
21,415	Mariel. "Magdalena" mine, 1899	Couchoidal	Dall	1.444
21,657	Mariel, "Magdalens" mine, 1899		Dull	1.409
44,626	Mariel. "Magdalena" mine, 1901		Dull	1.460
52,000	Mariel, "Magdalens" mine, 1901	Conchoidal	Dull	1.4341
75,755	Mariel, "Magdalena" mine, 1905			••
21,416	Mariel, "Mercedes" mine, 1899		Dull	1.562
25. 131	Santa Clara, "Santa Eloisa" mine, 1904		Lustrous	1.2735
47.617	Santa Clara, "Santa Eloisa" mine, 1905		Lustrous	1.2935
55,195	Santa Clara. "Santa Eloisa" mine, 1901	Smooth, semi-conchoidal	Lustrous	1.2859
	Trinidad.			
61,726	Vistabella "Manjak." 1902		Dull	
61,727	Vistabella "Manjak." 1902		Lustrous	••
61.728	Vistabella "Manjak." 1902		Bright	• •
80,659	Vistabella "Manjak." 1905		= -	1.156
	METAMORPHOSED OR ALTERED GRAHAM	1790		
69,235	Unknown locality, Okla., 1904	· 4 A G		
69,482	South McAlester, Okla., 1904.			• •
69.2424		Schietose	Sub-lustrous	••
	Black Fork Mountain, Okla., 1904		Sub-lustrous	••
	waster a surface	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	A	••

¹ Contains pyrite.

		Inor-		Per ce total men so in nar	bitu. oluble	Bitu. men		Re•		nate cor pure bit		on		
Loss 100°.	Bitu- men.	ganic matter		88° B.	62° B.	ins. CCl4.	pen- tine.	sidual coke.	c.	H.	s.	N.	Diff.	Test No.
0.4%	97.7%	2.0%	0.3%	9.4%	10.7%			36.8%	86.56%	8.68%	1.79%		2.97%	19.399
0.0	97.8	2.1	0.1	3.4	3.5	55.0	0.8	40.1			• •	• •		75.63 7
• • • •	97.6	1.9	0.5	1.4	2.7	• •	• •	39.7	•••	• •	• •	• •	• • •	75.673
0.4	• •	1.8	• •	• •	• •	••	• •	41.4	• • •	••	••	• •	• • •	82,088
• • •	98.2	0.1	1.7	0.8		80.6		47.4	85.97	7.65	0.93		5.45	19,162
• • •	99.0	0.1	0.9	. • :	. • •	• •	• •	48.4	86.08	7.63	0,95		5.34	19,260
	98.7	trace	1.3	1.3	1.3	• •	• •	48.3	85,90	7,75	0.99	• •	5.36	31.963
0 .7	99.3	0.1	0.6	0.9	1.0	• •	• •	49.3		• •	• •	• •	• • •	71.746
0.4	90.5	1.1	8.4	0.8	1.1	• •		56.4						53,788
• • •	96.2	3.0	0.8	0.7	• •	• •	• •	52.9	.83 ,90	7.14	2.24	• •	6.72	74.989
• • •	95.7 95.5	4.1 4.2	0.2 0.3	0.4 0.2	• •	••	• •	51.4 52.6	• • •	• •	• •	• •	• • •	74,990 74,991
	95.3	3.9	0.9	0.7			• •	52.9		• •		• •		74,991
• • • •	93.5	5.0	1.5	0.7				52.0	• • •	• •		• •		74,993
• • • •	93.0	5.3	1.7	0.7				52.0		.,				74,994
0.1	92.4	6.6	1.0				43.0	49.1			1.04			114.041a
0.1	95.4	3.8	0.8					51.1			1.56			Р
0.0	94.0	6.0	0.0	• •			• •	49.1		• •	1.52	• •	• • •	" с
0.2	93.3	6.7	6.0		• •	• •	• •	48.5	• • •	• •	1.40	• •	• • •	!! d
••	99.7 95.7	0.3	0.0 4.0	6.8 4.5	8.2 5.4	••	• •	43.5 45.7	•••	••	••	• •	• • •	76,503 76,504
• •	99.4	0.6	0.0	6.8		58.2	• •	44.0	• • •	• •	• •			81,424
0.7	83.7	7.1	9.2	5.0		37.9		41.0		• •	• • • • • • • • • • • • • • • • • • • •	• • •	• • •	80,824
0.6	76.4	23.61	0.0	6.3	7.5	• •		39.4		• •	••	• •		64.847
	96.8	2.6	0.6	0.9	1.0			54.0						59.398
0.3		4.2	• •	• •	• •	٠.		37.7	76.2	6.6	7.4	0.4	5.2	
0.3		2.9	• • •		• •	• •	• •	52.8	78.6	7.5	5.4	1.2	5.1	77.000
• •	99.0	• •	0.8	0.5	• •	• •	• •	51.2	• • •	• •	••	• •	• • •	75,093
••	• •	3.4 2.8	• •	••	• •	• •	••	54 .0	• • •	• • •	• •	••	•••	64,152
••	93.8	2.8	3.4	8.4		• •	40.5	38.0 35.3	83.14	8.09	5.47	• •	• • •	83.982 12,113
• • •			• • •	• • •	• •				77.67	8.06	7.51	• •	• • •	12,114
								• •						•-
	25.6	0.4	74.0	38.1		12.2		43.2						109.503
0.4	99.4	0.5	0.1	20.0	38.8	24.3	9.8	40.0	81.94	7.45	7.65		2.96	22,216
0.2	99.6	0.4	0.0	17.4	22.2	0.9	0.3	42.2	81.28	7.17	6.23		5.32	35,901
0.1	98.9	0.4	0.7	6.0	22.5	• •	• •	45.0	82.53	7.47	6.42	••	3.58	22,222
0.2	99.2	0.5	0.3	11.3	12.6	• • •	••	44.0				••		31,135
2.8 2.0	58.1 58.0	41.2 38.1	0. 7 3.9	37.7 40.2	53.5 55.9	2.2 1.5		36.0 38.2	77.82	8.69	6.86 7.59	• •	6.63 9.70	21,415
3.8	54.8	39.9	5.3	39.8	48.5	2.0		33.6	74.13 72.49	8.58 8.45	7.68	• • •	11.38	21.657 44.626
3.0	58.2	37.9	3.9	48.2	57.3		10.6					• • • • • • • • • • • • • • • • • • • •		52.000
	58.0	38.3	3.7					22 .3				••		75,755
3.6	49.8	48.4	1.8	42.3	55.0		4.3	37.4	75.91	7.81	7.81		8.48	21,416
0.8	79.1	19.1	1.8		47.1		19.1		82.43	6.99	8.72		• • •	25,131
2.5	77.4	20.4	2.2	• •	39.7		19.0		• • •	• •	• •	• •	• • •	47,617
• •	77.8	20.0	2.2	• •	43.7	2.9	11.4	34.9	• • •	• •	• •	• •	• • •	55.195
0.2	97.5	2.5	0.0	14 0	15.2			40.0						61 706
0.2	97.5 98.8	1.2	0.0 0.0	14.8 12.4	15.2 13.2	· •	• •	40.0	• • •	• •	• •	••	•••	61,726 61 ,7 27
0.3	91.5	4.9	0.0	14.5	18.2	· •	• •	35.0 33.0		• •	• • •	• •	• • •	61,728
• • •	94.2	5.8	trace	19.2		38.8		31.0	83 . 95	5.66	3.83	2.24		80,659
•												-		
0.5	41.6	0.03	58.1	8.4	8.9			48.0						69.235
	41.1	0.2	58.7					47.0						69.482
1.6	3.6	3.3	93.1	0.0	0.0			75.0		• •	••	••	• • •	69,242a
0.3	2.6	0.6	96.8	0.0	0.0	• •	• •	77.0	• • •	••	••	••	• • •	" ь

TABLE II.

Test No.	W. Va. Cam Grahamite. 75.637.	po Florida, Cuba. Grahamite. 22,222,		Egypt, Glance pitch, 14,145.	Barbadoes, Manjak, 14,144.	Utah. Gilsonite. 68,941.	I,ake Asphalt. Dry Trinidad. 63,260.	Wurtzelite. 72,684.	Ozokerite.
Physical Properties.									
Sp. gr. 25°/25° original substance Streak	. Black . Dull . Fractured . Hackly	1.175 Brownish-black Dull Semi-conchoidal Intumesces	1.075 Black Lustrous Uniform Conchoidal Intumesces	1.097 Black Lustrous Uniform Conchoidal 127° C.	1.100 Black Lustrous Uniform Conchoidal 221° C.	1.0433 Red-brown Lustrous Uniform Conchoidal 152° C.	1.40 Blue-black Dull Homogeneous Semi-conchoidal 88° C.	1.064 Black Lustrous Uniform Conchoidal Intumesces	Brown-black Dull Paraffin Irregular 72 ° C.
Chemical Characteristics.									
Bitumen soluble in CS3, air temperature. Difference	. 0.1	98.9% 0.7 0.4	5.9% 94.1 0.0	99.7% 0.2 0.1	98.3% 0. 5 1.2	99.4% 0.3 0.3	56.4% 6.4 36.9	6.7 92.5 0.8	100.0 0.0 trace
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Malihenes.									
Bitumen soluble in 88° naphtha, air temp This is per cent, of total bitumen		6.0%	1.5%	23.5% 23.6	22.2% 23.6	53.9% 54.2	3 5.6% 63.1	0.0	94.1
Carbones.									
Bitumen insoluble in CCl ₄ , air temperature bitumen yields on ignition	55.0%	•••	•••	0.1%	1.2%	0.5%.	1.3%	•••	•••
Residual coke	. 41.0%	45.0%	29.8%	15.0%	24.7%	14.5%	10.8%	8.3	0.0
Ultimate Composition.									
Carbon	. 86.56%	82.53%	83.44	80.87	89.95	89.28	82.33	80.00	85.25
Hydrogen		7.47	10. 08	10.42	9.04	8.66	10 .69	1 2.33	15.09
Sulphur		6 .4 2 3. 58	0. 44 6. 04	8.52 0. 19	0. 73 0.2 8	1.7 9 0. 79	6.5 6 0.82	5.83 1.84	0 .00 0 .00

pyrobitumen. Such a material is represented in the table by albertite. This may be regarded as a bitumen in which the metamorphosis, beginning in petroleum and extending through maltha, asphalt and grahamite, has terminated in a material which is no longer soluble. On this ground grahamite is an intermediate material between asphalt and albertite. The extent of the metamorphism may be measured, it will be observed, by a comparison of the relative solubility of the bitumens in light petroleum distillates, and in the heavy petroleum residuals, known as fluxes, by the amount of residual coke which they yield on ignition and to a certain extent by their density and melting points. For this purpose data in regard to bitumens of the series extending from petroleums which are mobile liquids to grahamite and albertite are here presented.

				Solubility in				
,	Melt. Spec. ing			carbon disul-	light naph-	heavy residuals		
	grav,			phide.	tha.	paraffin.	asphaltic.	
Paraffin petroleum	0.83	liquid	0.0	100.0	100.0			
Asphaltic petroleum	0.93	liquid	I.O	100.0	98.0			
Maltha	0.99	viscous	3.0	98.0	94.0			
Asphalt, medium	1.03	60°	12.5	96.0	70.0	homogenous		
Asphalt, hard	1.04	80°	14.5		63.0	homogenous		
Gilsonite	1.04	130°	15.0	99 · 4	53.0	non-hom.	homogenous	
Glance pitch	I.IO	130°	15.0	99.7	23.5	non-hom.	homogenous	
Manjak	1.10	200°	24.7	98.3	22,2	non-hom.	homogenous	
Grahamite, Trinidad	1.16	intum.	35.0	98.8	14.5	non-hom.	homogenous	
" West Va	1.14	intum.	41.0	97.8	3.3	non-hom.	homogenous	
" Oklahoma.	1.18	intum.	56.4	95.5	0.8	non-hom.	homogenous	
Albertite	1.08	intum.	29.8	6.0	1.5	insol.	insol.	

The preceding data present a fairly regular rate of metamorphism from petroleum to grahamite and illustrate very well the relation of grahamite to the other native bitumens, as well as the justification for its differentiation from asphalt and gilsonite. Grahamite does not melt. Asphalt, gilsonite and glance pitch become liquid on the application of heat. Grahamite is but slightly soluble in naphtha, whereas the other solid bitumens contain a considerable percentage which is soluble, corresponding in amount to the degree to which they have been metamorphosed. The grahamites yield a higher percentage of residual coke, this too corresponding to the extent of the metamorphism. The density of this form of bitumen is greater than that of the bitumens which melt readily.

Grahamite in its outward physical appearance is as a rule, and where it is not associated with mineral matter, characterized by a peculiar structure and fracture, which is found in no other form of solid native bitumen. While the material is homogenous or uniform as far as composition is concerned for any one specimen, the fracture is not conchoidal or that of a homogeneous solid such as gilsonite, glance pitch, manjak

or the pure asphalts. On the contrary it presents a surface which shows that the bitumen has been subjected to pressure and to motion from movement of the vein walls which it is too brittle to resist. The result has been a fine fracture carried entirely through the mass, which results in a surface, when grahamite is broken, which is more or less schistose in structure. It has been described as hackly and also termed pencillate. It is found in all the grahamites occurring in the United States, in that from Trinidad and in the pure bitumens from Cuba. The deposit at Huasteca, Mexico, has a lustrous fracture like that of glance pitch while in some of the grahamites of Cuba the fracture is masked by the high percentage of mineral matter which is present.

In powder, grahamite, like asphalt and glance pitch, is black and it gives a black streak. This differentiates it sharply from gilsonite, which yields a light brown powder.

It does not melt readily, as has been said, and this alone differentiates it from all the other bitumens and justifies us in putting all the grahamites in a class by themselves. It intumesces and swells up at high temperatures with the evolution of gas, but softens to some extent so that it can be in part drawn out into threads. In this respect it resembles the pyro-bitumen albertite, although it differs entirely from it by its solubility in carbon disulphide.

In their ultimate composition the grahamites show some interesting differences from the other solid bitumens and among themselves, which are of importance and without which any consideration of this form of bitumen would be incomplete.

An ultimate analysis by combustion of the grahamite from West Virginia shows that it consists of

C, 86.56: H, 8.68; S, 1.79: undetermined, 2.97,

the preceding figures being calculated on a basis of bitumen free from mineral matter. For comparison with these figures data in regard to the ultimate composition of three well-known asphalts will serve.

	Pure bitumens. Trinidad.	Pure bitumens, Bermudez.	Waldorf, Cal.
Carbon	82.33	82.88	82.77
Hydrogen	10.69	10.79	10.62
Sulphur	6.16	5.87	6.47
Nitrogen	0.82	0.75	0.35
			
	100.00	100.29	100.21

The West Virginia grahamite differs from asphalt by containing a much smaller amount of sulphur derivatives, more carbon and less hydrogen. The relation of carbon to hydrogen, considering sulphur as an equivalent to two atoms of hydrogen, is as follows:

	Grahamite.	Asphalt.
Carbon	90.9	88.5
Hydrogen	9.1	11.5
	100.0	100.0

This relation and the presence of the larger amount of carbon may be regarded as explaining, to a certain extent, the differences between the two forms of bitumen as well as the larger yield of residual coke from grahamite and the fact that it does not melt readily.

Having shown the characteristics of the type grahamite, the next step is the differentiation of the various other deposits on the basis of their behavior with certain solvents, their purity or admixture with mineral matter and their ultimate composition; this with a view of determining whether they may all be properly included under the one designation "grahamite," whether they should be separated into classes, or whether specific names should be applied to some of the bitumens as has been done by some writers who were not familiar enough with the native solid bitumens to recognize grahamite when it was met in a new locality. Of course, in so doing, the material from West Virginia which was described in the early sixties of the last century must serve as the type.

This, it appears, contains 86.6 per cent. of carbon and 1.8 per cent. of sulphur. Some of the other grahamites have a similar ultimate composition, notably those from Middle Park, Colorado, and various localities in Oklahoma. The carbon in these occurrences lies within the extremes, 86.6 and 83.9, the latter figure for the Impson Valley material which was called impsonite by Eldridge. This approaches the amount found in asphalt and is smaller by 2.7 per cent. than the carbon in the type grahamite.

It is questionable whether this is sufficient to authorize a specific name, especially in view of the fact that the two materials in other respects are so strikingly alike, in their fracture and general appearance, in not melting and in their insolubility in light naphtha and dense paraffin residuums. From the writer's point of view the West Virginia, Colorado and Oklahoma bitumens may safely be recognized as all being grahamites.

So closely allied to these three occurrences that it cannot be distinguished from them in external appearance is the grahamite of Trinidad. It has the same hackly fracture as the type material, does not melt or flux smoothly with the paraffin oils, yields from 31 to 40 per cent. of residual coke and is readily recognized by the trained eye as a grahamite. It differs from the bitumen of this type as found in the United States only by the presence of nitrogen to the extent of over 2 per cent., in which it is unique, a higher percentage of sulphur, 3.83 as compared to 1.79.

and its considerably greater solubility in light naphtha, 13.0–15.0 per cent. as compared with fractions of a per cent. in the Colorado and Oklahoma material and 1.4 to 9.4 in the original grahamite from West Virginia, the higher figure in the latter case being for the product of the operations in the sixties and the latter for material taken out in recent years. Further, the two materials differ in a marked degree in ultimate composition, as far as the percentages of carbon and hydrogen are concerned, the Trinidad grahamite containing but five per cent. of hydrogen whereas the West Virginia carries nine, and only 84 per cent. of carbon as compared with 86.5.

	West Va.	Trinidad.
Carbon	86.56	83.95
Hydrogen	8.68	5.66
Sulphur	1.79	3.83
Nitrogen		2.24
Difference	2.97	4.32

It may be held that the Trinidad bitumen differs sufficiently from the type grahamite to make it a distinct form, but the difference can be readily explained by the different character of the two petroleums from which the two deposits have been derived, the West Virginia grahamite originating in a paraffin oil and that from Trinidad in an asphaltic one. It is possible that grahamite must be considered as a class of bitumens. rather than a species, or genus, and this will be further confirmed as the characteristics of the other individual deposits are examined. seems to be no reason, however, why the Trinidad bitumen should not be regarded as a grahamite. It is certainly not a manjak, although it has been put upon the market as such; a manjak being a bitumen which has a smooth fracture like glance pitch and melting readily. The comparatively high percentage of residual coke which manjak yields does, however, show that it is a material which, in its metamorphism, is somewhat related to grahamite. In this connection it is worthy of note that in Barbadoes, where alone manjak occurs, a continuous series of bitumens is found ranging from maltha to one of the hardest consistency.

If we look further into the ultimate composition of the remaining grahamites which have been examined, it is seen that they all contain more sulphur than those which we have had under consideration, from 5.4 to 8.7 per cent. as compared with 0.93 to 3.83 per cent. It is possible, therefore, to divide the grahamites into two classes, those containing less than four per cent. and those having more than five per cent. of sulphur. The presence of sulphur may be attributed in part to sulphur derivatives of hydrocarbons existing in the original oils from which the grahamites are derived, but we know of no petroleums which contain a sufficient amount of such components to account for the high percentage of sulphur found in the second class of grahamites. The assumption

that this might be accounted for by concentration due to evaporation during the long period during which the metamorphosis has gone on will not serve, since this change has taken place, if we may judge from the location of the deposits, under conditions where volatilization could not occur, so that it must be adventitious in most, if not in all cases. bitumen of Trinidad asphalt, however, contains 6.5 per cent. of sulphur and this may be considered as the source of grahamite of that island and of that of the sulphur which it carries, as the two bitumens are found not far apart. The bitumen of the asphalt, on the other hand, is associated with an asphaltic petroleum, issuing from wells sunk immediately adjoining the deposit, which contains only about 1.5 per cent. of sulphur. It is difficult, therefore, to say definitely what the source of the sulphur in grahamite is, but it must be in certain cases adventitious, as the bitumen found at the Le Grand deposit in Oklahoma contains quite large and well defined crystals of pyrite, visible to the naked eye, which have been deposited by infiltration through the fractures of the material.

In Cuba deposits of bitumen are found which carry a very considerable amount of adventitious earthy matter, resembling in this respect Trinidad asphalt, but the characteristics of the bitumens are such that they may be considered as grahamites, since these yield a high percentage of residual coke, over 30 per cent., and have a high density, although they are, like the Trinidad grahamite, more soluble in light naphtha than the type grahamite and, possibly, should be classed by themselves on this account, and because of their peculiar ultimate composition, as they contain, in addition to a high percentage of sulphur, much organic matter the nature of which is not revealed in the ordinary methods of combustion and which may be oxygen.

Very pure grahamites are also found in Cuba at Bahia Hondo and Campo Florida, equalling in this respect those from West Virginia, Colorado and Oklahoma, and differing from them only in their higher percentage of sulphur and greater solubility in light naphtha. The Bahia Honda bitumen resembles in outward appearance the type grahamite, having the schistose or hackly fracture.

The grahamite from Huasteca, Mexico, described by Kimball¹ is a unique one in that it resembles gilsonite in its high lustre and fracture and in that it melts. It is quite insoluble in light naphtha, however, yields a high residual coke and corresponds in ultimate composition with grahamite. Kimball seems, therefore, to have been justified in classing it as such.

In this connection it is not out of place to call attention to the resemblance of grahamite to that portion of the bitumen of the asphalts which is soluble in carbon disulphide but insoluble in light naphtha and which

¹ Am. J. Sci., [3] 12, 277 (1876).

has been defined as a class as "asphaltenes" by the writer in distinction from the more soluble form which has been termed "malthenes" from their resemblance to natural maltha. The asphaltenes, like grahamite, do not melt, are not soluble in light naphtha, yield a high residual coke and have a similar ultimate composition, as can be seen from the following data:

	Trinidad asphalt. Asphaltenes.	Grahamite. Bahia Honda.	Bermudez asphalt. Asphaltenes.	West Va. Grahamite.
Specific gravity	I.I2I	1.157	1.110	1.130
Residual coke	32.00	40.00	37.00	36.80
Carbon	82.01	81.94	87.19	86.56
Hydrogen	7.82	$7 \cdot 45$	8.47	8.68
Sulphur	10.86	7.65	4.83	I.79
Difference		2.96		2.97
	100.69	100.00	100.49	100,00

The agreement in the ultimate composition, specific gravity and yield of residual coke between the asphaltenes in the asphalts and the grahamites which contain larger and smaller amounts of sulphur is striking, and is evidence of the gradual metamorphosis of petroleum into grahamite.

In the table of analyses of grahamites data are given of several materials from Oklahoma under the heading "metamorphosed or altered grahamites." These are distinguished by their smaller solubility in carbon disulphide than that of the grahamites. They illustrate the intermediate stages between that bitumen and the pyrobitumens such as albertite and the transition of one form into the other, although it has not been positively shown that the type albertite, from Nova Scotia, is derived from petroleum, as are the solid native bitumens which have been described in this paper. There is a great probability that it is a type of coal.

The behavior of the grahamites with other solvents than those which have been mentioned is also of interest. Oil of turpentine and carbon tetrachloride do not have the same solvent power with all of them. In studying the solvent power of the former on various bitumens it was found that it dissolved when cold but 0.8 per cent. of the bitumen in the grahamite from the Impson Valley, 4.8 in that from West Virginia, and in all the others but little, as on standing in contact with them for twelve hours it was practically uncolored. With gradual rise in temperature the action was not increased and no solution takes place until the boiling point of the turpentine is nearly reached, when at a definite point the bitumen dissolves. On cooling the bitumen separates out. The amount dissolved at high temperatures varies, as can be seen in the following table:

SOLUBILITY OF GRAHAMITES IN HOT OIL OF TURPENTINE.

		Solubi	Dan	
		hot turpentine.	carbon disulphide.	Per cent. of total bitumen sol, in turp.
35.901	Bahia Honda, Cuba	99.3	99.6	99 · 7
75,637	West Virginia	. 96.9	97.8	99.1
21.416	Mercedes Mine, Cuba	. 46.3	49.6	93.3
22,216	Bahia Honda, Cuba	. 89.6	99 · 4	90.1
21,657	Magdalena Mine, Cuba	. 51.2	58.0	88.2
44,626	Magdalena Mine, Cuba	47.2	54.8	86. I
55,195	Santa Clara, Cuba	. 66.4	77.8	85.3
25,131	Santa Clara, Cuba	. 66.0	79.I	83.4
52,000	Magdalena Mine, Cuba	. 47.8	58.2	82.1
21,415	Magdalena Mine, Cuba	. 51.6	58.1	81.9
47,615	Santa Clara, Cuba	. 58.4	77 · 4	75 · 4
	Impson Valley, Okla	. 48.9	91.8	53.2
	High			99 · 7
	Low			53.2
	Asphalt, Bermudez	. 94.9	95.6	99.2
	Gilsonite		99.8	99.9

On the ground of their relative solubility in turpentine the Impson Valley bitumen is differentiated from the West Virginia and the Cuban grahamites and all of them are more or less variable in this respect. This peculiarity should be further studied, including the bitumens from Colorado and Trinidad. In the case of the asphalts, it will be noticed, the bitumen is equally soluble in turpentine and in carbon disulphide, the lack of solubility in some of the grahamites undoubtedly being produced by changes due to environment and age.

It has been shown by the writer¹ that bitumens can be differentiated by the degree to which they are soluble in carbon tetrachloride, those showing the least solubility being the most metamorphosed by overheating, as in the preparation of residual pitches from asphaltic oils by distillation, or by age. The grahamites show decided differences in this direction. The proportion of bitumen in the several deposits examined varies, showing different degrees of alteration. The Colorado grahamite contains the largest amount of bitumen of this kind, over 80 per cent., the Oklahoma 58 and the Trinidad 39 per cent., while the Cuban deposits, with the exception of that at Bahia Honda, have but small amounts. This class of the components of bitumen has been called "carbenes" by the writer. A further study of this characteristic of the grahamites would prove of interest.

An interesting fact in connection with the mineral matter which is found in grahamite, and to which attention has been called by Messrs. Foster Hewitt and W. F. Hillebrand, is that, like the same component of some other bitumens, it contains vanadium, especially the ash of that

¹ J. Soc. Chem. Ind., 24, 310 (1905).

from the Impson Valley, which contains from 11 to 15 per cent. of V₂O₃. The West Virginia grahamite contains 3.38 per cent., while Trinidad asphalt has 0.089, manjak a small amount and albertite a trace, according to determinations furnished by Dr. Hillebrand.

From the facts and data given in the preceding pages grahamite can be characterized as a class of bitumens and further differentiated into sub-classes.

Grahamite may be defined as a brittle, solid native bitumen, the result of the metamorphosis of petroleum, generally pure but at times associated with adventitious mineral matter, characterized, when pure, by a peculiar schistose fracture, which has been termed hackly. It does not melt, but merely intumesces, on the application of heat, is soluble in carbon disulphide and only to a small extent in light naphtha and yields a high percentage of residual coke on ignition out of contact with air.

Various deposits of grahamite vary sufficiently to make it possible to divide them into several sub-classes:

- 1. Pure bitumens, 90 per cent. or more soluble in carbon disulphide.
- 2. Bitumens associated with adventitious mineral matter.

They may be subdivided again on a basis of solubility in naphtha, that is to say, the amount of malthenes which they contain, into:

- 3. Bitumens but a small proportion of which is soluble in light naphtha.
- 4. Bitumens of which a considerable part is soluble in naphtha, more than 15 per cent.

And still further, as regards the percentage of sulphur derivatives of the hydrocarbon which are present:

- 5. Bitumens with less than 5 per cent. of sulphur.
- 6. Bitumens with more than 5 per cent. of sulphur.

Individual grahamites can belong to more than one of these classes, but to only one in any group.

It is evident that the form of bitumen which we have had under examination is sharply differentiated from coal, asphalt and albertite and that there is no reason for confusing these minerals, as was done by the early writers. Whether there is any justification for further differentiating the grahamites and assigning names to special deposits, such as impsonite for the grahamite from Oklahoma, is a matter of opinion. From the writer's point of view this is, at present, hardly necessary. Particular grahamites have individual characteristics, but as a whole they are sufficiently alike to justify the application of the name to one class of bitumens, those which have been described in this paper, of which the original grahamite from West Virginia may be regarded as the type.

Eldridge, in his "Asphalt and Bituminous Rock Deposits of the United

States," classifies the solid native bitumens, excluding the melaterite and wurtzelite for some remarkable reason and giving no place whatever to asphalt, as asphaltite and coal, the former including albertite, impsonite, grahamite, nigrite and uintaite (gilsonite). Hofer has recently proposed to the writer that the solid native bitumens which are not asphalt shall be so denominated. It seems, however, that all these materials are so entirely different in character that we are hardly justified in putting them in one class, except for the fact that they are not asphalt, and the proposition does not, at present, commend itself.

In conclusion, the writer must acknowledge his indebtedness to the several assistants who have engaged in the investigation of the various grahamites and especially Mr. Kenneth Gerard Mackenzie, and Mr. J. S. Miller, Jr., for the study of the action of turpentine and tetrachloride of carbon on this bitumen. Prof. Jamieson and Mr. Ralph Langhy, of New Haven, have contributed ultimate analyses of several of the specimens, and have determined the presence of nitrogen, by the absolute method, in the Trinidad grahamite, Mr. Mackenzie has also aided in assembling the data and examining the cross references.

30 CHURCH ST., NEW YORK CITY.

PROGRESS IN SYSTEMATIC QUALITATIVE ORGANIC ANALYSIS.2

By S. P. MULLIKEN. Received June 29, 1910.

A general procedure in organic qualitative analysis that may be trusted to lead to the discovery of the proximate composition of any unknown organic substance whatever, whether this be a simple compound or a mixture, is demonstrably incapable of practical realization. Before proceeding to the discussion of the main subject of this paper, it therefore behooves us to pause for a moment to note certain limits which Nature seems to have set against the too curious advances of the analyst.

The most clearly insuperable of these limitations are associated with high molecular weight. If a paraffin hydrocarbon of the formula $C_{35}H_{72}$ were to be isolated in a state of perfect purity and in large quantity from some natural product, it would be impossible to absolutely identify it as a compound corresponding to any particular structural formula by any combination of methods of investigation now known, or whose future discovery appears probable. Such a hydrocarbon would not differ by one one-hundredth of one per cent. in its hydrogen or its carbon content from its adjoining homologues, while in chemical and physical properties there would be no measurable differences between it and

¹ 22nd Annual Report U. S. Geological Survey, Part I, 209-452.

² An address delivered at the Second Decennial Celebration of Clark University, Worcester, Mass., Sept. 16, 1909.