

*The mica of certain coal-measure shales in South Wales.*¹

By G. NAGELSCHMIDT, D.Ph.

Chemistry Department, Rothamsted Experimental Station, Harpenden,

and D. HICKS, M.Sc., A.I.C.

Officer in Charge, Coal Survey Laboratory, Cardiff.

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DURING a study of the sources of the dusts in South Wales coal mines, carried out on behalf of the Industrial Pulmonary Disease Committee of the Medical Research Council,² a mineral of the mica group was found as the main constituent of the shales overlying the coal in several mines. Of six shales investigated four were associated with anthracite, one with semi-bituminous, and one with bituminous coal. Between the coal seam itself and the shale which forms its roof there usually occurs a more coaly shale referred to locally as 'clod'. Five of the samples investigated were isolated from 'clods' and one from a roof. Table I gives the chemical analyses of the six shales and the carbon:hydrogen ratio of the corresponding coals in order to indicate the rank of the coal. Petro-

TABLE I. Analyses of shales from which the fine fractions were prepared.

(Analyses of residues after igniting the shales at 800° C. to a constant weight.)

Sample number	1	2	3	4	5	6
Colliery code number	A. 1	A. 2	A. 3 D. 1	A. 3 D. 2	S. 4	B. 3
Carbon : hydrogen ratio of coal	34.0	31.5	30.0	30.0	19.5	17.0
Residue at 800° C., % of air-dried shale	90.40	87.52	84.50	93.60	88.77	78.99
% of residue:										
SiO ₂	62.91	55.82	56.40	58.30	56.27	56.18
TiO ₂	1.14	0.82	0.68	0.46	0.94	0.86
Al ₂ O ₃	23.30	26.83	31.01	27.45	25.15	28.50
Fe ₂ O ₃	4.32	5.93	2.77	4.53	8.84	5.44
MgO	1.67	1.95	1.42	1.34	1.50	1.74
CaO	nil	0.07	0.17	0.13	0.14	0.18
BaO	trace	nil	0.10	0.33	nil	nil
Na ₂ O	1.17	0.98	0.95	0.92	0.62	0.52
K ₂ O	4.10	4.72	5.40	4.52	4.38	5.17
SO ₃	0.06	0.34	0.04	0.10	0.19	0.21
P ₂ O ₅	0.13	0.16	0.24	0.21	0.26	0.24
Loss on ignition at 800° C.	1.03	2.45	n.d.	n.d.	1.33	0.58
Total	99.83	100.07	99.18	98.29	99.62	99.62

¹ Published by permission of the Director of Fuel Research.

² D. Hicks and G. Nagelschmidt, Spec. Rep. Ser. Medical Research Council, London, 1943, no. 244 F.

logical descriptions of these shales are given by Brammall and Leech.¹ The colliery code numbers given in table I are identical with those used in the reports quoted.

Isolation.—The powdered shales were allowed to settle in water at 18° C. and the material in suspension after 100 hours at 8 cm. depth was repeatedly removed by siphoning. The accumulated suspensions were passed through an ultrafilter and the residues dried at room-temperature. Assuming a density of 2.7 of the material in water and the validity of Stokes's law, the diameter of the particles would be below 0.5 micron, but as the particles probably are not spherical no great importance should be attached to this figure. The six samples separated in this way will in the following be called the fine fractions.

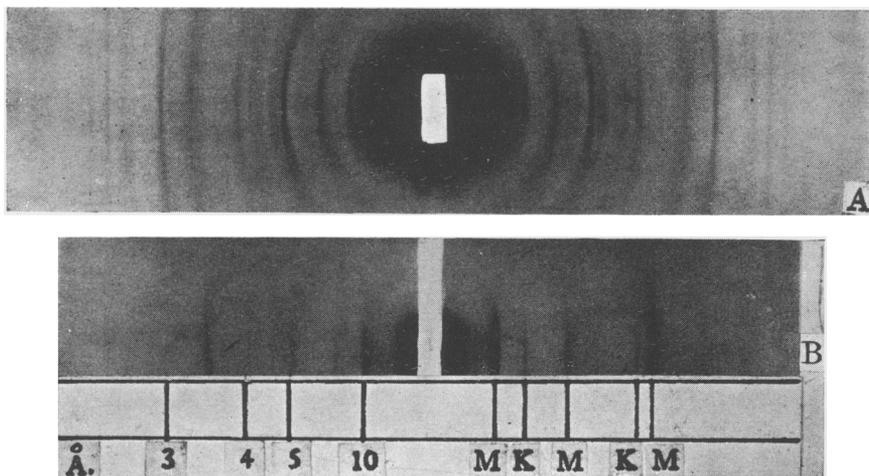


FIG. 1. X-ray diagrams of fine fractions from shales taken with cobalt $K\alpha$ radiation. Actual size. A, Powder diagram. Cylindrical camera, 57.4 mm. diameter. B, Aggregate diagram. Flat photographic plate 45 mm. from specimen. (M = mica, K = kaolin.)

X-ray data.—The six fine fractions gave almost identical powder and aggregate X-ray diffraction diagrams with cobalt or iron radiations and typical diagrams are shown in fig. 1. The aggregate diagrams revealed strong basal reflections at 10 and 3.33 Å., and a weaker one at 5.0 Å., indicating a mineral of the mica group; and weak reflections at 7.1 and 3.55 Å., indicating a mineral of the kaolin group. Diagrams of aggregates heated to 500° C. for 24 hours showed only the mica but not the kaolin basal reflections. On the powder diagrams the diffraction lines were wide and no kaolin lines were observed. Table II shows the evaluation of a powder diagram of the fine fractions and the corresponding data for illite given by Grim, Bray, and Bradley² and by Maegdefrau and Hofmann.³ It will be seen from this that the X-ray diagrams are very similar indeed.

¹ A. Brammall and J. G. C. Leech, *ibid.*, no. 244 E.

² R. E. Grim, R. H. Bray, and W. F. Bradley, *The mica in argillaceous sediments*. Amer. Min., 1937, vol. 22, pp. 813–829. [M.A. 7–12.]

³ E. Maegdefrau and U. Hofmann, *Glimmerartige Mineralien als Tonsubstanzen*. Zeits. Krist., 1937, vol. 98, pp. 31–59.

TABLE II. X-ray diffraction lines of fine fractions from shales and of illite.

Fine fraction.		Illite (M. & H., 1937).		Illite (G. B. & B., 1937).		Fine fraction.		Illite (M. & H., 1937).		Illite (G. B. & B., 1937).			
<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.	<i>d.</i>	Int.		
10.0	vs	10.1	s	9.98	s	(002)	2.44	w	2.47	w	2.44	w	(133)
5.0	m	4.9	m	4.97	w	(004)	2.37	wm	2.37	m	2.38	m	(133)
4.46	vs	4.45	vs	4.47	s	(110)	2.23	}	2.25	}	2.24	m	(221)
*				4.11	vw	(022)	2.17		w		2.18	w	2.18
*		3.67	vw	3.7	vw	(023)	2.14	m	2.13		2.11	w	(043)
*				3.4	vw	(114)	1.98	m	2.00	w	1.98	m	(0.0.10)
3.32	vs	3.31	ms	3.31	m	(006)	1.64	m	1.64	m	1.65	w	(1.3.10)
*				3.2	vw	(114)	1.49	vs	1.50	s	1.50	s	(060)
2.97	vw	3.05	vw	2.98	w	(025)	1.34	w			1.34	vw	(335)
2.80	vw			2.84	vw	(115)	1.29	m	1.30	m	1.29	m	(400)
2.55	vs	2.57	vs	2.56	s	(202)	1.24	w	1.25	w	1.24	w	(0.0.16)

d = interplanar spacings, Int. = intensities, vs = very strong, s = strong, ms = medium strong, m = medium, wm = weak medium, w = weak, vw = very weak.

* Reflections measured on aggregate diagrams, but not clearly observed on powder diagrams.

Attempts to separate the kaolin from the mica in the fine fractions were unsuccessful, but by using mixtures of kaolin-free illite from Grundy Co., Illinois (kindly supplied by Dr. Grim), and kaolin of comparable grain-size, the amount of kaolin in the fine fractions could be estimated to be about 10%.

As the original shales contained appreciable amounts of quartz (10–25%), one of the fine fractions was subjected to a 'rational analysis'¹ in order to determine chemically whether all the quartz had been removed. In the rational analysis the sample is treated with sulphuric acid followed by sodium carbonate-sodium hydroxide mixture. The residue obtained (A) is weighed and treated with hydrofluoric acid. Allowance is made for undecomposed silicates by determining Al_2O_3 (B) in the residue after treatment with hydrofluoric acid, and subtracting 5.4 times (B) from (A) on the assumption that the undecomposed silicate was felspar. In making the rational analysis of the fine fraction, part of the first residue (A) was removed for X-ray analysis and found to contain quartz, mica, and some kaolin. Therefore 2.5 times the Al_2O_3 in (B) was subtracted from (A) with the result that the quartz in the fine fraction was found to be 1.5%. Using the felspar factor would have resulted in a negative quartz content. Over-exposed X-ray diagrams of several of the fine fractions were taken subsequently, and very faint lines at 1.81, 1.38, 1.194, and 1.180 Å., indicating a trace of quartz, were observed.

Chemical data.—Chemical analyses of the six fine fractions are shown in table III. The samples are dark grey and may contain small amounts of carbon, especially sample 1; this may have affected the determination of FeO and the results for FeO are therefore possibly too high. The amount of carbon was not determined. The analyses of the six samples are very similar to each other except for variations in the amount of iron and for a small but regular decrease in sodium content with decreasing rank of coal accompanied by a slight increase in the $SiO_2:Al_2O_3$ ratio. In table IV the average composition of the fine fractions is shown (a) uncorrected and (b) after subtracting 10% of kaolin of theoretical composition, 1% of quartz, and water lost at 105°C. For comparison, analyses

¹ A. Shaw, *Analyst*, 1934, vol. 59, p. 446.

TABLE III. Analyses of air-dried fine fractions from shales.

Sample	1.	2.	3.	4.	5.	6.
SiO ₂	44.64	44.16	46.65	47.43	46.08	45.94
TiO ₂	0.56	0.50	0.51	0.44	0.61	0.59
Al ₂ O ₃	31.52	31.01	31.39	32.97	30.97	30.38
Fe ₂ O ₃	1.92	0.70	0.54	0.20	0.48	nil
FeO	1.24	2.28	0.98	1.02	2.01	1.80
MgO	1.73	1.69	1.24	1.37	1.33	1.26
CaO	nil	0.08	0.03	nil	nil	0.17
Na ₂ O	1.22	0.87	1.05	1.08	0.62	0.50
K ₂ O	5.22	5.34	5.12	5.23	5.34	5.22
H ₂ O + 105° C.	8.41	8.36	7.28	7.76	7.61	8.16
H ₂ O - 105° C.	3.25	3.05	3.13	3.00	3.25	2.89
CO ₂	0.06	0.14	n.d.	n.d.	n.d.	n.d.
Total	99.77	98.18	97.92	100.50	98.30	96.91
Mols. SiO ₂ : Al ₂ O ₃	2.40	2.42	2.52	2.44	2.52	2.57
Mols. K ₂ O : Na ₂ O	2.82	4.04	3.21	3.12	5.67	6.87

TABLE IV. Analyses of fine fractions and of illite (Grim et alii, 1937) and hydromuscovite (Brammall et alii, 1937).

	Average fine fraction.	Fine fraction corrected for kaolin & quartz.	Illite 1 (Grim, 1937).	Illite 2 (Grim, 1937).	Illite 5 (Grim, 1937).	Hydro-muscovite A (Brammall, 1937).
SiO ₂	45.82	47.55	50.10	51.22	44.01	46.54
TiO ₂	0.54	0.64	0.50	0.53	0.64	0.17
Al ₂ O ₃	31.37	32.45	25.12	25.91	26.81	36.37
Fe ₂ O ₃	0.64	0.76	5.12	4.59	11.99	0.72
FeO	1.56	1.85	1.52	1.70	—	0.36
MgO	1.44	1.70	3.93	2.84	2.43	0.50
CaO	0.05	0.06	0.35	0.16	0.11	0.22
Na ₂ O	0.89	1.05	0.05	0.17	0.07	0.46
K ₂ O	5.25	6.22	6.93	6.09	4.78	8.06
H ₂ O +	7.93	7.73	7.18	7.14	8.08	6.31
H ₂ O -	3.09	nil	1.90	1.45	2.33	0.52
Total	98.58	100.01	102.70	101.80	101.25	100.23
Mols. SiO ₂ : Al ₂ O ₃	2.48	2.49	3.39	3.36	2.79	2.17

of Grim's samples 1, 2, and 5 and of hydromuscovite from Ogofau, Carmarthen-shire,¹ are given. The fine fractions contain less silica, magnesium, and iron oxides and more alumina than Grim's samples, a trend which is reflected in the silica : alumina ratios, which vary between 2.4 and 2.6 for the fine fractions and between 2.8 and 3.4 for Grim's illite.

Grim gives the composition of illite calculated to a basis of 24SiO₂ as 2K₂O.3MO.8R₂O₃.24SiO₂.12H₂O. The average of the fine fractions on the same basis gives 2.2(K,Na)₂O.1.2MO.9.9R₂O₃.24SiO₂.13.9H₂O, and after correcting for 10% of kaolin and 1% of quartz 2.5(K,Na)₂O.1.3MO.9.9R₂O₃.24SiO₂.13H₂O. Formulae computed to a basis of O + OH = 48, the oxygen content of the unit cell of muscovite, are given in table V, which shows the mica in the fine fractions on the assumption that the latter contain 10% of kaolin and 1% of quartz.

¹ A. Brammall, J. G. C. Leech, and F. A. Bannister, *Min. Mag.*, 1937, vol. 24, p. 516.

Hydromuscovite (Brammall's variety A) and Grim's illite sample no. 1 are added for comparison.¹ This shows the mica in the average fine fractions to be very similar to hydromuscovite in atomic composition and to be intermediate between hydromuscovite and Grim's illite no. 1 in Si, Al, Mg, total iron, and total alkalis, although the water content is slightly higher. All three analyses show more hydroxyl groups than are necessary to compensate the lack of K_2O in comparison with muscovite on the basis of $(K,Na)_{4-m} = (OH)_{8+m}$.

TABLE V. Atomic composition of muscovite, hydromuscovite, mica in fine fractions, and Grim's illite no. 1, calculated to a basis of $(O+OH) = 48$.

	Muscovite.	Hydromuscovite.	Mica in average fine fraction.	Illite, 1.
K	4	2.7	2.0	2.3
Na	—	0.2	0.5	—
Ca	—	—	—	0.1
Mg	—	0.2	0.6	1.5
Fe''	—	0.1	0.4	0.3
Al	8	7.1	5.8	4.5
Fe'''	—	0.1	0.1	1.0
Ti	—	—	0.1	0.1
Al	4	4.0	3.9	3.1
Si	12	12.0	12.1	12.9
O	40	37.1	34.9	35.7
OH	8	10.9	13.1	12.3

Base-exchange.—The base-exchange capacities of the six fine fractions were determined by a micro-method (by Geochemical Laboratories, London, through arrangement by Dr. Brammall); the mean result was 32 milli-equivalents per 100 g. of air-dried sample (standard error ± 4.4). Values reported in the literature for illite vary from 20 to 40 milli-equivalents per 100 g.

Dehydration.—The samples were dehydrated in a current of nitrogen (to prevent oxidation of iron and carbon) and the losses in weight are given in table VI, which also includes Grim's data for illite, sample 1. All the fine fractions are alike and contain slightly more water than Grim's sample. The corresponding dehydration curves show no such clear break between adsorbed and lattice hydroxyl water as do the curves of kaolin or montmorillonite.

TABLE VI. Water loss on ignition.
(Per cent. of air-dried fine fractions.)

Sample	1.	2.	3.	4.	5.	6.	Grim's Illite, 1.*
Temperature,							
105° C.	3.25	3.03	3.13	3.00	3.25	2.89	2.60
200	5.02	4.35	4.25	4.28	4.87	3.71	3.18
300	5.78	5.13	4.80	n.d.	n.d.	4.25	3.90
440	8.37	8.00	7.47	7.34	8.96	7.16	6.70
600	10.92	10.63	10.03	10.42	10.32	10.53	8.62
800	11.66	11.39	10.41	10.76	10.86	11.05	8.80
1000	—	—	—	—	—	—	9.60

* The figures have been obtained by interpolation from Grim's published data.

¹ Water lost below 105° C. is neglected in making these calculations.

Optical data.—All six fine fractions had very similar optical properties. The mean refractive index, measured with sodium-light in a mixture of cinnamon oil and olive oil, was 1.587. The highest and lowest refractive indices observed on optical aggregates were γ' 1.600 and α' 1.572. Irregular negative biaxial interference-figures could be observed which showed a small axial angle, but no measurements of $2V$ could be made.

Discussion.—The data given above lead to the conclusion that the fine fractions consist mainly of a mineral of the mica group. Grim, Bray, and Bradley (1937) adopted the name 'illite' for similar material because no existing name was found satisfactory and they proposed to use illite as a group-name until further data had accumulated to show its chemical variability. It seems appropriate, therefore, to use the term illite for the micaceous constituent of the South Wales coal-measure shales that have been analysed, although similar material may have been described as sericite in the past. The term sericite has according to Grim been used for so many different types of mica as to be almost meaningless. The illite in the South Wales shales is very similar in its chemical composition to hydromuscovite from Ogofau described by Brammall, Leech, and Bannister (1937), but hydromuscovite is a well-crystallized mineral comparable to pyrophyllite and dickite, whereas illite is a poorly crystallized clay mineral, comparable to montmorillonite and halloysite.

Mica of the illite type and glauconite, which is closely related to it,¹ are the only known clay minerals which contain appreciable quantities of non-exchangeable potash. They are in this respect intermediate between potash-felspar of the igneous rocks and kaolin and montmorillonite of the sedimentary rocks. The mode of formation of illite is not known with certainty, but at least three possible ways may exist: weathering of felspar, disintegration of muscovite, and alteration of montmorillonite.

The mechanism of the weathering of potash-felspar has been investigated in detail by Correns and Engelhardt.² Their work led to the conclusion that potash, alumina, and silica are all at first removed in ionic form or at least in such small size as to pass the ultrafilters used. The relative proportions of the three constituents depend to some extent on the acidity of the extracting medium. What secondary minerals are formed in the weathering of potash-felspar and where they occur will thus depend on local conditions, and it seems possible that under certain conditions, e.g. impeded drainage, a sufficiently high potash concentration is maintained in the presence of alumina-silica gels which would lead to the formation of illite.

Disintegration of muscovite, e.g. as produced during glaciation, might also lead to minerals of the illite type, but laboratory evidence on the products of grinding and leaching muscovite under various conditions is almost non-existent. Finally, the replacement of all exchangeable bases by potash in minerals of the montmorillonite group should lead to the formation of illite. The conversion of exchangeable potash into a non-exchangeable form by repeated drying and wetting of montmorillonite has been reported by several workers,³ and this may be considered as the first stage in the formation of illite. That illite might be

¹ S. B. Hendricks and C. S. Ross, *Amer. Min.*, 1941, vol. 26, p. 683. [M.A. 8-275.]

² C. W. Correns and W. von Engelhardt, *Chem. Erde*, 1938, vol. 12, pp. 1-22. [M.A. 7-405.]

³ L. K. Wood and E. E. De Turk, *Proc. Soil Sci. Soc. Amer.*, 1940, vol. 5, p. 152.

formed from montmorillonite in marine sediments by absorption of potassium from sea-water has recently been suggested by R. S. Dietz.¹

The conditions governing the stability of illite are not well known. The mineral is frequently found in soil colloids and clays and it is likely to be the main constituent of many shales. Although it is therefore probably comparatively stable, it might decompose under prolonged leaching. Laboratory experiments in this field do not seem to have been published.

The finding of an increasing sodium content of illite in the roofs and 'clods' of South Wales shales with increasing rank of the associated coal may have a bearing on the theory of coal formation. McKenzie Taylor² postulated that anthracite and bituminous coal, but not lignite or peat, were formed by the decomposition of plant material under alkaline anaerobic conditions. These conditions were in South Wales ascribed to the fact that the roofs of the coal seams became impermeable through base-exchange with sodium ions upon coming into contact with salt water: they also subsequently underwent hydrolysis in fresh water. Taylor submits that the gradual change of a seam from bituminous coal in the east to high rank anthracite in the west of South Wales is due to a longer period of the peat stage in the west, before the peat became covered by the sediment which now forms the roof. The finding of more soda in the anthracite than in the bituminous coal roofs might alternatively be interpreted as indicating that alkaline conditions were maintained for a longer period of time in the west than in the east, and consequently the period and effect of the second stage in the process of coal formation described by Taylor might be important in determining the varying rank of the coal from one part of the field to another. If further work confirms the finding of increasing amounts of soda with increasing rank of the associated coal, both in the 'clods' and roofs, it will be necessary to consider whether the nature of the roof is an indication of varying conditions from one part of the field to another, which might have affected the degree of coalification.

Summary.—Fine fractions were prepared from six shales overlying anthracite and bituminous coal in certain South Wales collieries. X-ray diffraction and chemical analyses show that these fine fractions contain illite with about 10% of kaolin and 1% of quartz; dehydration, optical, and base-exchange data are given, and the conditions of formation and stability of illite are discussed. The sodium content of the illite decreases slightly with decreasing rank of the associated coal, and a possible connexion with McKenzie Taylor's theory of coal formation is pointed out.

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¹ R. S. Dietz, *Amer. Min.*, 1942, vol. 27, p. 219.

² E. McK. Taylor, *Fuel*, London, 1928, vol. 7, p. 230; *Nature*, London, 1927, vol. 120, p. 448; 1928, vol. 121, p. 789.