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1993	**International Committee for Coal Petrology** **Nomenclature Sub-Committee**	**Rocks other than Coal**
SUPPLEMENT	**BITUMINITE IN ROCKS OTHER THAN COAL (Stopes-Heerlen System)**	R.L. Untreated Rock

I - ORIGIN OF TERM

According to H. Potonié[41] "Bituminite" is a general term for rocks which are especially rich in bitumen, i.e. which belong to the sapropelites. The name "bituminite" was used in former times by Szadeczky-Kardoss[55] and Malan[32] synonymously with the maceral group liptinite. Hamrla[20] used the term bituminite for an "unfigured" maceral of the liptinite group occurring in the Tertiary sub-bituminous coals of the Karst region in Istria where part of this maceral fills cracks and fissures.

In 1975 the International Committee for Coal Petrology introduced the term bituminite for a maceral of the liptinite group in lignites which is characterized by its lack of definite shape. Whereas the coal maceral bituminite was defined by M. Teichmüller[59] in 1974 (see also Stach et al.[54]), the name bituminite for an unfigured autochthonous maceral of the liptinite group, occurring in petroleum source rocks, had already been used by M. Teichmüller[58] in 1971 and has been applied since then by many authors, inter alia by Altebäumer[1], Bustin et al.[5], Cook[6,7], Creaney[8], Creaney et al[9], von der Dick et al.[10], Gormly and Mukhopadhyay[18], Hutton et al.[22], Kalkreuth and Macaulay[26], Kantsler[27], Littke and Rullkötter[30], Loh et al[31], Malan[33], McKirdy et al.[35], Mukhopadhyay et al.[36,37], Powell et al.[43], Robert[45,46], Rullkötter et al.[47,48,49,50], Sherwood and Cook[51,52], Spackman et al.[53], Stach et al.[54], Takahashi[56], M. Teichmüller and Ottenjann[60], M. Teichmüller and Wolf[61].

The name bituminite indicates the bituminous character of this maceral which gives high yields of soluble bitumen (v. Gaertner[11]) and volatile matter, as well as of tar (Hutton et al.[22]) and of hydrocarbons (Powell et al.[43]).

Etymology: BITUMEN (LATIN) = Mineral pitch, asphalt.

Synonyms and analogous terms:

Unfigured bitumen, partly	(M. Teichmüller[57]),
fine detrital polymerbitumen, partly	(Jacob[23,24])
amorphinite	(van Gijzel[12, 13])
amorphous matter in part of kerogen concentrates	(palynologists in petroleum industry, according to Hunt[21])
colloalginite	(Ginzburg et al.[15])
gels algaires et bactériens	(Alpern[2])
lamelles noir-rougeâtres or bituminite	(Alpern and Cheymol[3])
bitumodispersinit	(Malan[33])
sapropelic groundmass, partly	(Robert[46])
amorphous material	(Masran and Pocock[34])
structureless organic matter, bacterial liptinite	(Gutjahr[19])
alginite-collinite + sapropelic-collinite	(Timofeev and Bogoliubova[62])
sapropelinite	(Mukhopadhyay et al.[38,39])
vitrinite-like material	(Glickson and Taylor[17])
prebitumen	(Wehner and Hufnagel[64], Jacob and Hiltmann[25]).

II - DESCRIPTION

a) *Morphography*

Bituminite has no definite form. It is differentiated from exsudatinite (which, like bituminite, has no specific morphology), by its autochthonous occurrence as stringers or irregular lenses in the bedding and/or as a groundmass for other macerals and for minerals. In petroleum source rocks, bituminite commonly occurs as streaks or lenses as seen in perpendicular sections. In horizontal sections it forms more equidimensional particles of various shape, in some cases associated with fine vein-like occurences. In some rich oil shales bituminite occurs as thin layers. Bituminite may surround "impurities" of minerals and/or other macerals, mainly corroded algal remnants (Creaney[8]) and liptodetrinite (Teichmüller and Ottenjann[60]). Under the electron microscope (TEM-method) bituminite (of the Toolebuc oil shale, Australia) appears light grey (low electron density), loosely packed, granular or sponge-like, sometimes with filamentous organisms between (Glikson and Taylor[17]).

The internal structure of bituminite may vary between homogenous, streaky, sometimes fluidal and finely granular, the structure typically becoming visible often only under excitation with blue or violet light. Because bituminite is a product of different organic materials which have undergone alteration and/or degradation (see III, Genesis) its optical properties, especially fluorescence, may vary relatively widely. For this reason, different types of bituminite can be distinguished in individual source rocks, e.g., bituminite I, II and III in the Liassic Posidonia Shale of Germany (Teichmüller and Ottenjann[60], Loh et al.[31]), bituminite I and II in the Cretaceous Boundary Creek Formation of the Beaufort-Mackenzie-Basin (Creaney[8]), the non-defined amorphinites A, B and C of van Gijzel[12], bituminite I, II and III in various source rocks of Gormly and Mukhopadhyay[18], Mukhopadhyay et al.[37], Rullkötter et al.[48,49,50] and sapropelinites I, II of Mukhopadhyay et al.[38,39]. In the Posidonia Shale of Germany (and other oil shales) bituminites of types II and III are very rare. Bituminite II is distinguished from bituminite I by its much larger size (lenses of up to 1 mm length and 0.4 mm width), and by a negative alteration when irradiated with blue light. Bituminite II fluoresces yellowish or reddish brown and sometimes shows oil expulsions when irradiated. As with all bituminites, the very rare bituminite III of the Posidonia Shale is dark grey under white reflected light. Bituminite III is distinguished by a finely granular structure and by lack of fluorescence. It is often associated with faunal relics.

Note: the submicroscopic organic substances which are adsorbed or incorporated on or in minerals ("lipoid substances of the mineral-bituminous groundmass" of M. Teichmüller and Ottenjann[60], "matrix bituminite" of Creaney[8], "matrix of amorphous organic matter" = "AOM" of van Gijzel[14]) and which attracts attention only through certain fluorescence properties of the mineral matrix, does not belong to the maceral bituminite because, according to the definition in the International Handbook of Coal Petrography (1975), "a maceral is a microscopically recognizable individual constituent which does not contain any mineral substances resolvable with the light microscope". The "amorphous" fraction of kerogen concentrates contains the insoluble part of bituminite together with the non-soluble part of the submicroscopic organic matter of the mineral matrix.

b) *Physical Properties*

Colour: In transmitted light: orange, red or brown in thin sections.

Under reflected light, bright-field, oil immersion: dark brown (internal reflections at low levels of maturity), dark gray, sometimes almost black. Under polarized light (crossed polars) black and easily distinguishable from the mineral matrix.

Under reflected light, fluorescence: pale yellow , pale orange, light to dark brown depending on type and rank (M. Teichmüller and Ottenjann[60], Creaney[8], Sherwood and Cook[52]). In the vitrinite reflectance range $R_r = 0.5$ - 0.8% dark brown with reddish tint (Posidonia Shale), with loss of fluorescence at $R_r =$ 0.8 - 0.9%. Some varieties do not fluoresce in the immature stage (bituminite III of Teichmüller and Ottenjann[60]; Sherwood and Cook[52]). The alteration of bituminite may vary according to rank and type, but strong positive alteration is characteristic of low-rank bituminite, type I. Higher-rank varieties show a weak positive alteration (Sherwood and Cook[52]).

Reflectance: Markedly lower than reflectance of vitrinite, variable according to type and rank. Values are given by Alpern[2] for the marine Toarcian oil shale of France ($R_r = 0.10$ - 0.15%, corresponding to a vitrinite reflectance of $R_r = 0.46\%$). Cook[6] and Sherwood and Cook[52] measured $R_r =$ 0.2% for bituminite of the marine Cretaceous oil shales of the Toolebuc Formation, Australia (vitrinite $R_r = 0.5\%$). Glikson and Taylor[17] report values of $R_r = 0.3\%$ for bituminite (vitrinite-like material) against $R_r =$ 0.5% for vitrinite.

Polishing hardness: low for bituminite I of M. Teichmüller and Ottenjann[60] and Creaney[8].

Density: Barron et al.[4] measured density values of 1.20-1.30g/cm^3 on bituminite concentrates from a Devonian oil shale of Kentucky (vitrinite density = 1.28-1.35 g/cm^3).

c) *Chemical Properties*

Disregarding rank variations (see IV) the chemical properties of bituminite vary according to the different types, but a high hydrogen content, a high H/C ratio and high yields of tar and of soluble bitumen are characteristic. Oil shales rich in bituminite usually contain type II organic matter of the H/C:O/C diagram (Tissot et al.[63]), as was shown, e.g., by the atomic ratio of bituminite concentrates from a Devonian oil shale of Kentucky (Barron et al.[4]).

On the basis of a comparison between chemical and organic petrological analyses of kerogen concentrates containing bituminite I, Powell et al.[43] obtained data confirming a high H-content, a high H/C-ratio and a high yield of hydrocarbons formed during pyrolysis. Moreover these authors found a relatively low pristane/phytane-ratio, pointing to an anoxic depositional environment.

On the basis of solubility studies in thin sections, material described by v. Gaertner[11] and subsequently considered to be bituminite I, is partly soluble in benzene and in chloroform. According to Given[16], bituminite contains abundant linear alkane chains. Glikson and Taylor[17] found less than 1% humic acids in bituminite concentrations from the Toolebuc oil shale, but high nitrogen contents which they explain through high concentrations of carbohydrates and proteins in the cyanobacterial parent matter. ^{13}C is markedly depleted in bituminite according to Glikson and Taylor[17].

III - GENESIS

Bituminite is a degradation product formed under predominantly anoxic and suboxic conditions. Presumed source materials are algae, faunal plankton, bacterial bodies and bodies of higher animals (fish, crayfish, etc). An assumption of this kind of parent matter is supported by the chemical properties of bituminite (e.g., Powell et al.[43]), by experiments of artificial maturation (pyrolysis) of algae and bacteria (Lijmbach[29]) and by the main occurrence of bituminite in marine and lacustrine petroleum-source rocks. Cook[6] suggests a genesis of bituminite from algal-fungal mats growing on the surface of the sediment near the oxic-anoxic boundary, similar to algal-fungal mats found at present in the Santa Barbara Basin according to Kauffmann[28]. Ramsden[44] suggests that Coccolithophoridaceae could be a source material for the bituminite in the Toolebuc Formation oil shales, since he found abundant fragmented coccoliths in the mineral matrix of this oil shale (Sherwood and Cook[52]) (see also Glikson and Taylor[17]). Coccoliths are also very abundant in the Posidonia Shale of Germany (Müller and Blaschke[40]; Loh et al.[31]). According to Gutjahr[19] bituminite ("bacterial organic matter") is considered to be of bacterial origin. According to McKirdy et al.[35] bituminite of Cambrian carbonate source rocks in South Australia (Officer Basin) represents algal and cyanobacterial organic matter that has been extensively degraded and resynthesized by anaerobic bacteria. On the basis of electron microscopical methods (TEM and SEM), Glikson and Taylor[17] regard bituminite ("vitrinite-like material") in the Toolebuc oil shale of Australia as the product of cyanobacterial (*Oscillatoria*-like) mats formed in an oxygenated water layer. The great abundance of coccoliths remains and of planktonic foraminifera in the same oil shale, likewise, indicate oxygenated water layers. But the high concentrations of organic matter and of pyrite testify to highly anoxic conditions at the sediment surface, i.e. sapropelic conditions. Similarly Loh et al.[31] consider bituminite as the remnant of microbial mats, but formed at the sediment surface lying at or below the redox boundary. Wehner and Hufnagel[64] attribute bituminite (their "prebitumen") to "marine snow, flocculent amorphous macroscopic components of the nearshore epipelagic seawater which was inhabited by various kinds of microorganisms". The faecal pellets of zooplankton contain only 1-4% organic carbon (Porter and Robbins[42]). Therefore it is unlikely that they are precursors of bituminite (as suggested by some authors).

In source rocks belonging to kerogen type III (Tissot et al.[63]), bituminite may have assimilated degradation products of humic origin, in the same way as may bituminite in coals. According to Masran and Pocock[34] (who used strew mounts) "amorphous material" may be derived from either marine or terrestrial sources, although most of it was formed in a marine environment with reduced oxygen supply.

IV - CHANGES DURING MATURATION

With increasing degree of diagenesis the reflectance of bituminite rises and the fluorescence intensity decreases. The fluorescence colour of bituminite types with originally yellow or orange colours shifts to the red. At a vitrinite reflectance of $R_r = 0.8 - 0.9\%$ fluorescence is lost. During maturation ("oil window") hydrocarbons are generated from bituminite, leaving highly reflecting relics, mostly micrinite, as dehydrogenated residual products (M. Teichmüller and Ottenjann[60]; M. Teichmüller and Wolf[61]; Gormly and Mukhopadhyay[18]; Cook[6], Gutjahr[19]; Sherwood and Cook[52]; Loh et al[31]; Littke and Rullkötter[30]). Sherwood and Cook[52] describe "micrinitization of bituminite" as a prominent feature in the Cretaceous Toolebuc Formation oil shale from central and north-east Australia. Loh et al.[31] consider the bituminite type III (which does not fluoresce and is often associated with faunal remains) as a highly coalified form of bituminite I and II. According to Littke and Rullkötter[30] hydrocarbon generation from bituminite in the Posidonia Shale is almost complete at a vitrinite reflectance of R_r = 0.9%.. In the same oil shale micrinitization of bituminite I is complete at a vitrinite reflectance of R_r = 1.3%.

According to Gutjahr[19] and Masran and Pocock[34] oil generation from bituminite begins at lower rank levels than from alginite A (e.g., *Botryococcus, Tasmanites*). The same is assumed by Sherwood and Cook[52]. In the Toarcian oil shale of France, oil generation from bituminite begins at a bituminite reflectance of R_r = 0.3%, corresponding to a vitrinite reflectance of R_r = 0.5% (Alpern[2]); in Australian oil shales it starts at a vitrinite reflectance of R_r = 0.4%, reaches its maximum between R_r = 0.5% and 0.8% and ends at about R_r = 0.9% ("oil death line") (Cook[6]).

V - OCCURRENCE

Bituminite is a characteristic maceral of many oil shales and oil source rocks, especially of marine and lacustrine source rocks of kerogen type II, e.g., the Posidonia Shale or Toarcian of Western Europe (M. Teichmüller and Ottenjann[60]; Alpern and Cheymol[3]), the Kimmeridge Shale of the North Sea (Gutjahr[19]), the Antrim Shale of Michigan, the Chattanooga Shales of Kansas (USA), the Toolebuc oil shales of the Eromanga Basin in north-east Australia (Glikson and Taylor[17]; Sherwood and Cook[52]) and Cambrian carbonate source rocks of South Australia (McKirdy et al.[35]).

Bituminite is generally associated with the macerals alginite and liptodetrinite, sometimes also with fish remains (M. Teichmüller and Ottenjann[60], Sherwood and Cook[52], Loh et al.[31]). Transitions from corroded alginite to bituminite are reported by Creaney[8] and Gormly and Mukhopadhyay[18]. On the basis of a similar mode of occurrence (and the suggested similar origin from "algal or bacterial mats") Loh et al.[31] assume a genetic relationship between lamalginite and bituminite in the Posidonia Shale of Germany. Some very rich oil-source rocks (e.g., Kimmeridge Shale of the North Sea and the Triassic Fish Shale of Seefeld, Tyrol), contain layers of pure bituminite. Bituminite is generally associated with abundant framboidal pyrite, pointing to bacterial reworking (by sulphate reduction) of the digestible organic matter (Gutjahr[19]; M. Teichmüller and Ottenjann[60]; Glikson and Taylor[17]; McKirdy et al.[35]; Sherwood and Cook[52]; Loh et al.[31]). In the Toolebuc Formation of the Eromanga Basin (Australia), studied by Sherwood and Cook[52], bituminite constitutes 10 to 40 percent of the oil shales. Glikson and Taylor[17] stress the close association of bituminite and calcite in the Toolebuc oil shales.

VI - PRACTICAL IMPORTANCE

Bituminite is an important maceral of many oil shales and other oil-source rocks, and, together with the submicroscopic lipoid substances of the mineral matrix, the main source material for low-temperature tar (obtained up to 400-600°C) and crude oil, respectively. According to Powell et al.[43] "the presence of bituminite I in excess of 10% of the organic matter is clearly indicative of a potential petroleum-source rock". Also other authors (Sherwood and Cook[52]; Masran and Pocock[34]; Gutjahr[19]; Loh et al.[31]) found that bituminite (or "structureless organic matter") "possesses excellent hydrocarbon source characteristics"[34]. The high bituminite content of the lower part of the Posidonia Shale in Germany has made this part the "main target in the search for shale oil" (Loh et al.[31]). Mukhopadhyay et al.[39] state that bituminite ("sapropelinite II") is the characteristic maceral of the most abundant source rock for liquid hydrocarbons in nature. According to Sherwood and Cook[52] Fig. 4), the Cretaceous Toolebuc source rock of Queensland, which is very rich in bituminite, yields about 200 mg hydrocarbons per gram organic carbon, although part of the bituminite is already in the stage of micrinitization, i.e., natural oil generation is occurring.

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Plate I

Fig. 1a

Lenses and layers of bituminite with transitions into micrinite:
Blue Lias, Seven Point, Dorset, England.
reflected light, oil immersion, x520.

Fig. 1b

Same field as Fig. 1a, under crossed polars

Plate II

The three types of bituminite[60] *from the Posidonia Shale (Lias E) of Germany.*

Fig.1

The most abundant bituminite-type I:. dark long streaks (black) in light mineral-bituminous groundmass (gray) with many pyrite framboids (white).
reflected light, oil immersion, x 500.

Fig.2

The very rare bituminite-type II: dark gray, compact round lenses with scarred porous structure, surrounded by light mineral-bituminous groundmass, rich in pyrite.
reflected light, oil immersion, x 500.

Fig.3

The rare bituminite-type III: gray, granular masses associated with faunal remains (dark gray) in mineral bituminous groundmass (light).
reflected light, oil immersion, x 500.

Fig.4

Concentration of micrinite (white grains in the centre) as the solid relic ("dead carbon") of former bituminite-type II in the stage of overmaturity (vitrinite reflectance $R_r = 2.2\%$*).*
reflected light, oil immersion, x 500.

Plate III

Fig.1a

Bituminite (dark gray stringer), associated with pyrite framboids, embedded in mineral-bituminous groundmass: Toarcian oil shale, Fécocourt, Luxembourg.
reflected light, oil immersion, x590.

Fig.1b

Same field as Fig. 1a, under blue-light excitation.

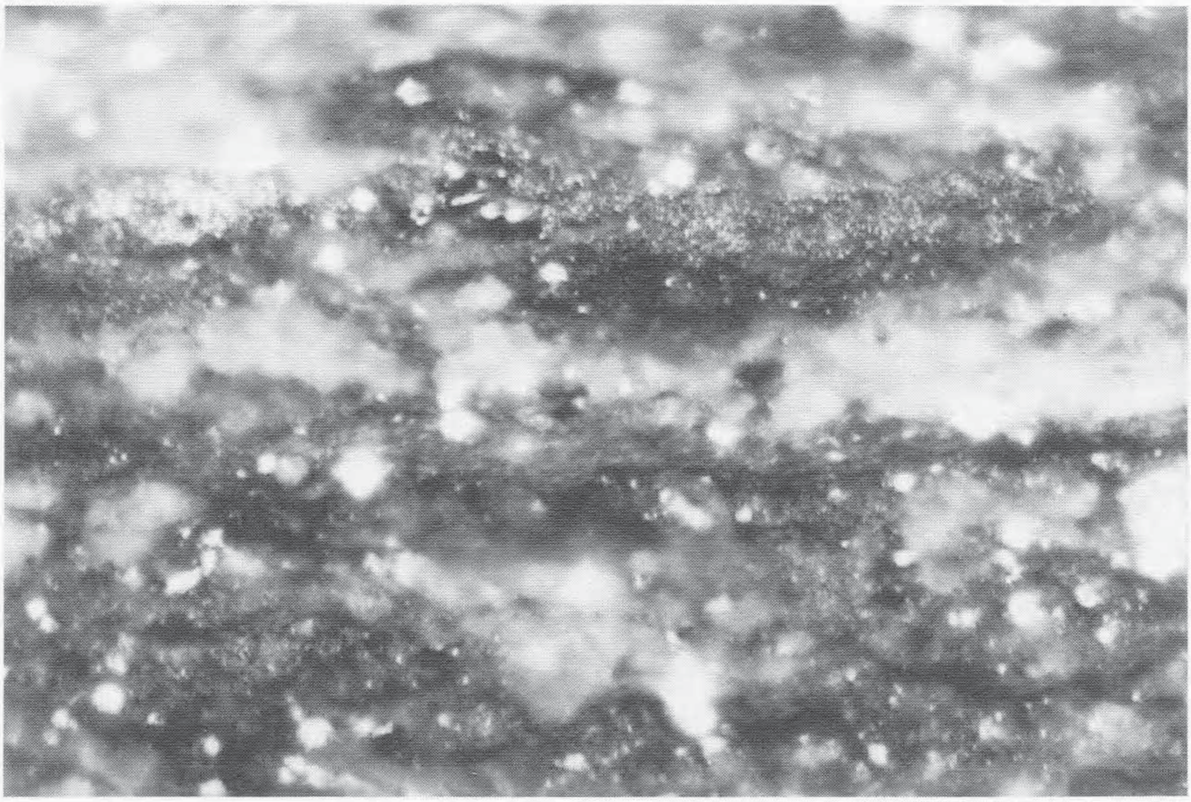
Fig. 2a

Bituminite (brown to dark gray) in a section parallel to the bedding plane: Toarcian oil shale, Fécocourt, Luxembourg.
reflected light, oil immersion, x590.

Fig. 2b

Same field as Fig. 2a under blue-light excitation:
(note the inclusions of yellow fluorescing liptinitic particles).

Plate I



1a

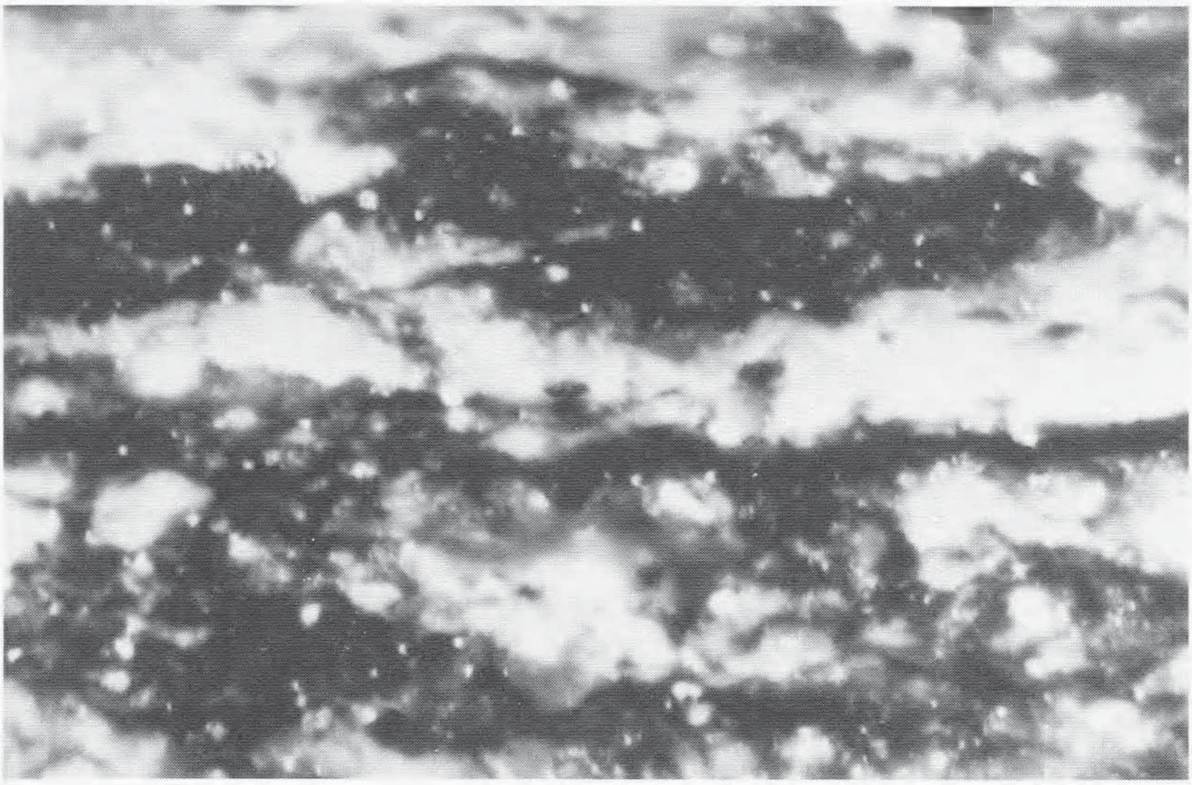


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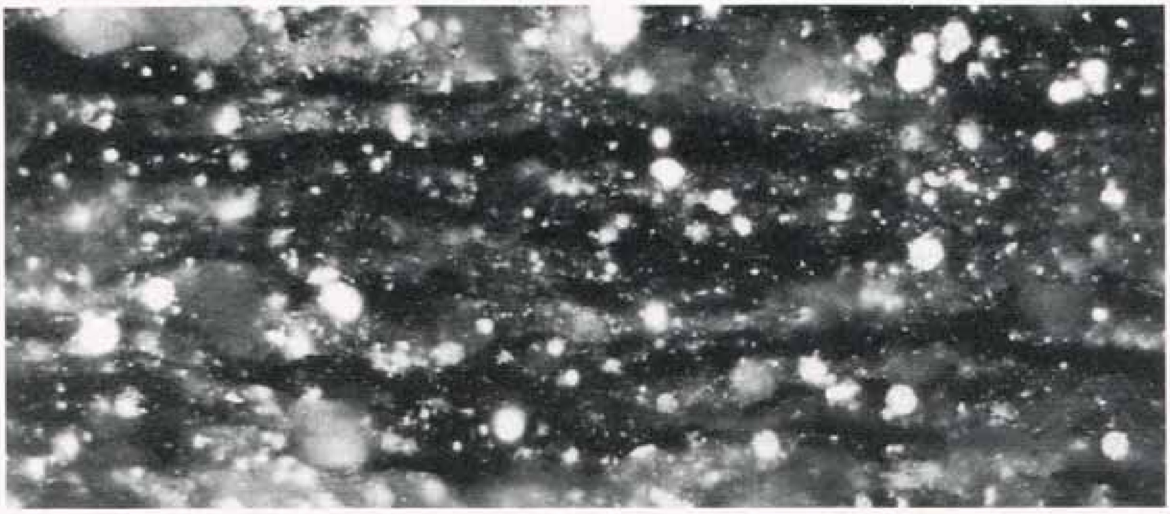
Plate II



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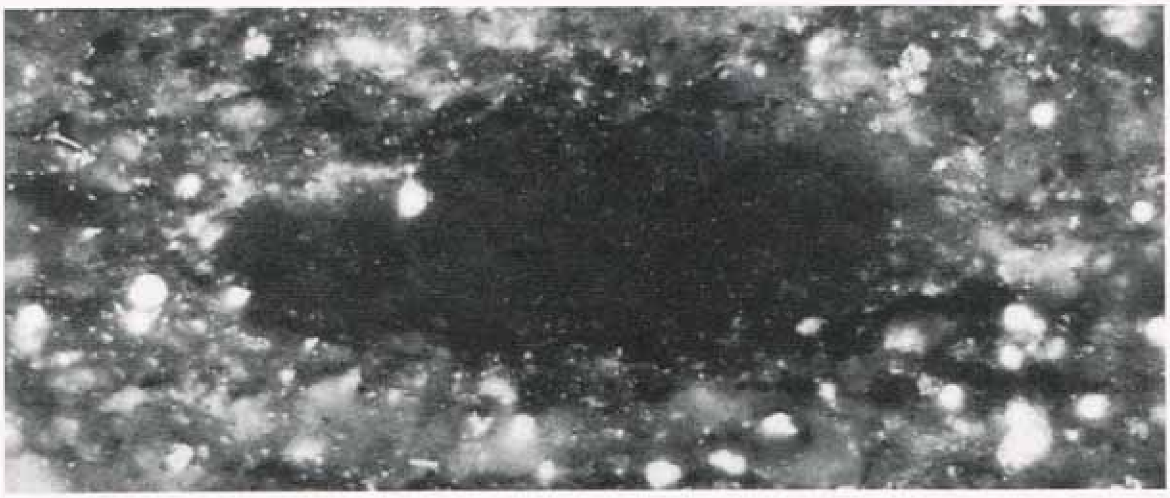

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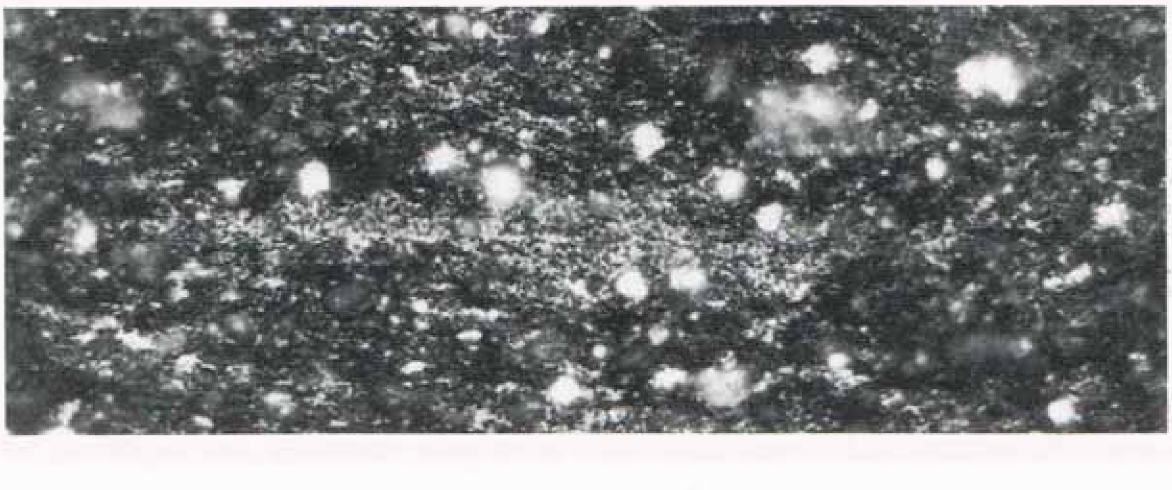

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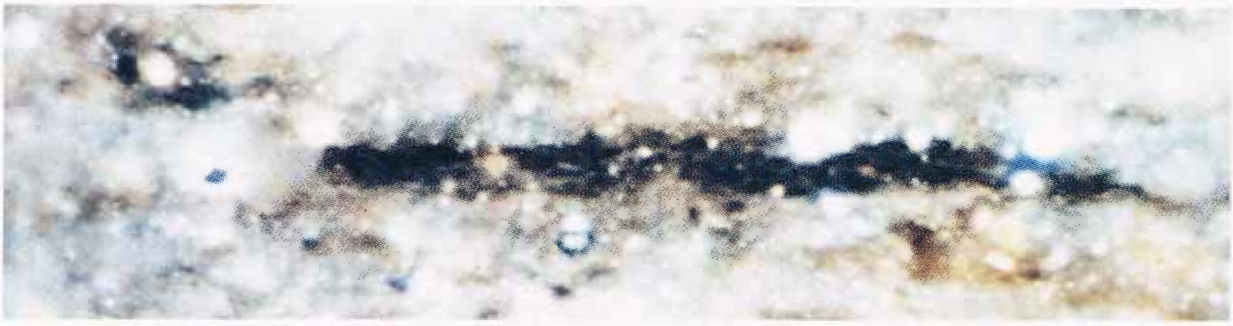
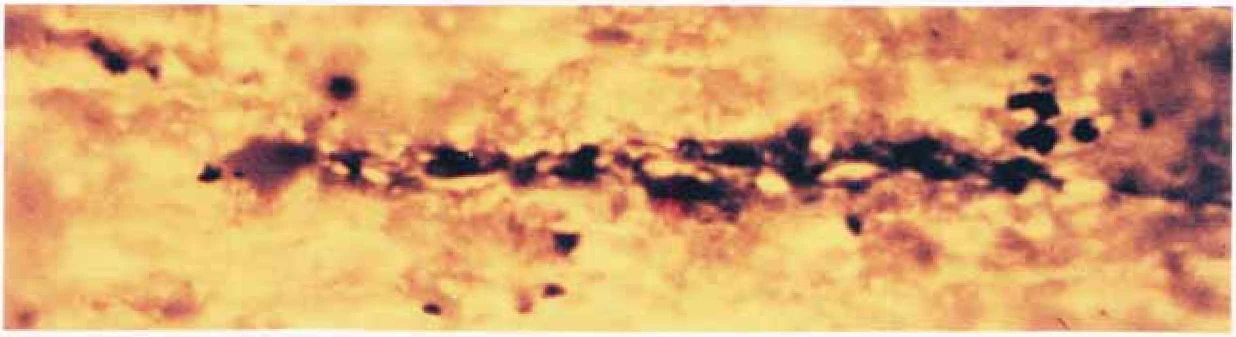
Plate III



6a



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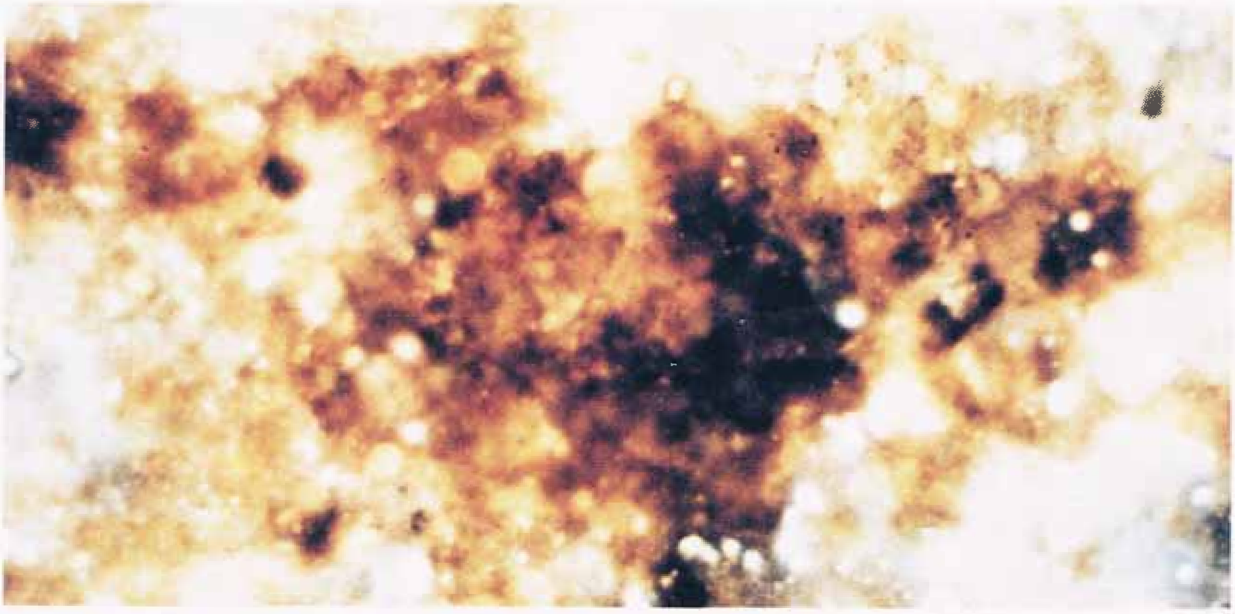
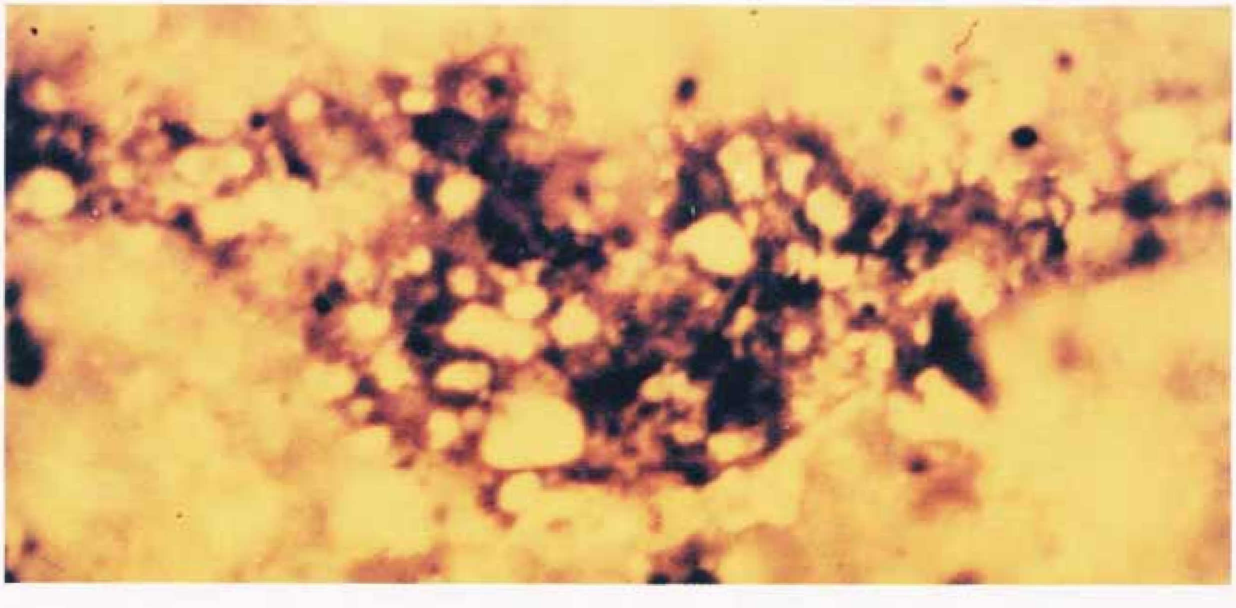


7a



7b

1993 SUPPLEMENT	**International Committee for Coal Petrology** Nomenclature Sub-Committee **MINERAL-BITUMINOUS GROUNDMASS**	Rocks other than Coal R. L. Untreated Rock

I - ORIGIN OF TERM

The term mineral-bituminous groundmass was introduced by M. Teichmüller and Ottenjann[15] for the mineral matrix of the *Posidonia* oil shale (Lias E) of Germany. It is applicable to all immature and mature oil source rocks (Stach et al.[14])

Synonyms and analogous terms:		
	matrice fluorescent	(Robert[11])
	organo-mineral associations or fluorescent groundmass	(Robert[12])
	mineral-bituminous matrix	(Kalkreuth and Macauly[7])
	background matter	(Rullkötter et al.[13]; von der Dick et al.[5])
	matrix bituminite, partly	(Creaney[2]; Powell et al.[10]; Creaney et al.[3])
	matrix of amorphous organic matter (="AOM"), partly	(van Gijzel[6])

II - DESCRIPTION

The mineral matrix of immature and mature source rocks is characterized by a more or less strong fluorescence caused by adsorbed organic matter. The organic character of this fluorescence is demonstrated by fluorescence alteration during irradiation as well as by the change of fluorescence intensity and fluorescence colour with increasing rank (maturity). The organic matter cannot be resolved in polished sections and thin sections of the untreated rock because of its submicroscopic size. Thus, it can be detected only indirectly under the microscope. In thin sections of the untreated rock, it causes an anomalous colouration (yellowish to brownish) of the mineral groundmass in normal white light. Therefore, it is considered to be adsorbed and/or incorporated on or in minerals, e.g. layered clay minerals such as montmorillonite, kaolinite, illite and chlorite which can bind organic cations and adsorb dispersed bitumen-like oil droplets (Weiss[16], Czarnecka and Gillot[4]).

Amount, maturity, and type of the organic substances which are extremely finely distributed between and within the minerals determine the fluorescence intensity and the fluorescence colour of the mineral-bituminous groundmass: the higher the amount in immature source rocks, the stronger the fluorescence. The amount of organic substances hidden in the mineral-bituminous groundmass of oil-source rocks is commonly much larger than that of the macerals, i.e., of the organic constituents which are visible under the microscope in untreated oil-source rocks (Leythaeuser[8], Robert[12]). After dissolution of the mineral matter by treatment of the source rock with HCl and HF, the organic substance of the mineral-bituminous groundmass is released and appears as part of the "amorphous" fraction in organic-matter concentrates (another part deriving from bituminites). The type of submicroscopic organic substances in the mineral-bituminous groundmass is indicated by its fluorescence properties which correspond to the fluorescence properties of liptinite macerals in oil-source rocks (Leythaeuser et al.[9]), inferring a lipoid (bituminous) character. Of the groundmasses distinguished by Robert[12,1)] only the "sapropelic groundmasses" correspond to the mineral-bituminous groundmass[1)].

With increasing maturity, the fluorescence intensity of the mineral-bituminous groundmass decreases, the decrease beginning at about a vitrinite reflectance of $R_r = 0.5\%$ and ending at about a vitrinite reflectance of $R_r = 1.3$-1.5% where minimum values of 1-2 I (546 nm) are reached (Fig. 1). As the fluorescence intensity decreases, the fluorescence colour changes from yellowish to reddish in a similar way to the fluorescence properties of liptinite macerals embedded in the mineral-bituminous groundmass (Fig. 2). This behaviour shows that the mineral-bituminous groundmass reveals characteristic changes during the stages of petroleum generation and migration. Fluorescence alteration during irradiation is especially characteristic of the mineral-bituminous groundmass and its submicroscopic constituents. The alteration changes from strongly positive in immature oil-source rocks to negative in mature oil-source rocks to zero in the overmature stage (Figs. 3 and 4). Thus, alteration measurements on untreated source rocks allow the determination of the three main stages of maturity (M. Teichmüller and Ottenjann[15]).

[1)] Robert[12] distinguishes A) "sapropelic groundmasses" of a) "lacustrine" and b) "marine" facies from B) "humic groundmasses".

Bertrand et al.[1] studied the petrographic and chemical (H/C:O/C, hydrogen index and Tmax) changes of the "organo-mineral groundmass" in samples of Toarcian oil shale during hydrous pyrolysis. According to their results oil formation begins at 250°C and is indicated by a high fluorescence intensity and a negative fluorescence alteration of the mineral groundmass. A few hydrocarbons exude even at the 200°C.

An internationally acknowledged subdivision of mineral-bituminous groundmasses according to, e.g., type and size of mineral matter, fluorescence colour, intensity, and alteration (facies, rank) does not yet exist.

III - PRACTICAL IMPORTANCE

Fluorescence properties and the large amount of lipoid organic matter hidden in the mineral-bituminous groundmass of many oil-source rocks indicate the importance of this material as an oil precursor.

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Fig. 1.

Relationship between fluorescence intensity (I) of the mineral-bituminous groundmass and vitrinite reflectance (%Rr) in samples of Posidonia Shale (Toarcian), Germany[15].

Fig. 2

Relationship between fluorescence intensity (I) of the mineral-bituminous groundmass and its spectral fluorescence parameters (λmax, Q) in samples of Posidonia Shale, Germany[15].

Fig. 3

Alteration curves for the mineral-bituminous groundmass of samples of Posidonia Shale (Toarcian, Lias E), Germany at different stages of maturity, related on the left to vitrinite reflectance. Immature ($<0.5\%\ R_r$*): positive alteration; mature (*$0.5\text{-}1.3\%\ R_r$*): negative alteration; overmature (*$>1.3\%\ R_r$*): no alteration. Abscissa: irradition time (min.). Ordinate: increase of fluorescence intensity (546 nm) in relation to the intensity at 4 min. after onset of irradiation*[14,15].

Fig. 4

Relationship between fluorescence alteration (A_I) (alteration of fluorescence intensity at 546 nm after an irradiation time of 30 minutes) of the mineral-bituminous groundmass and vitrinite reflectance (% R_r) in samples of Posidonia Shale (Toarcian) Germany[15].

Fig. 1

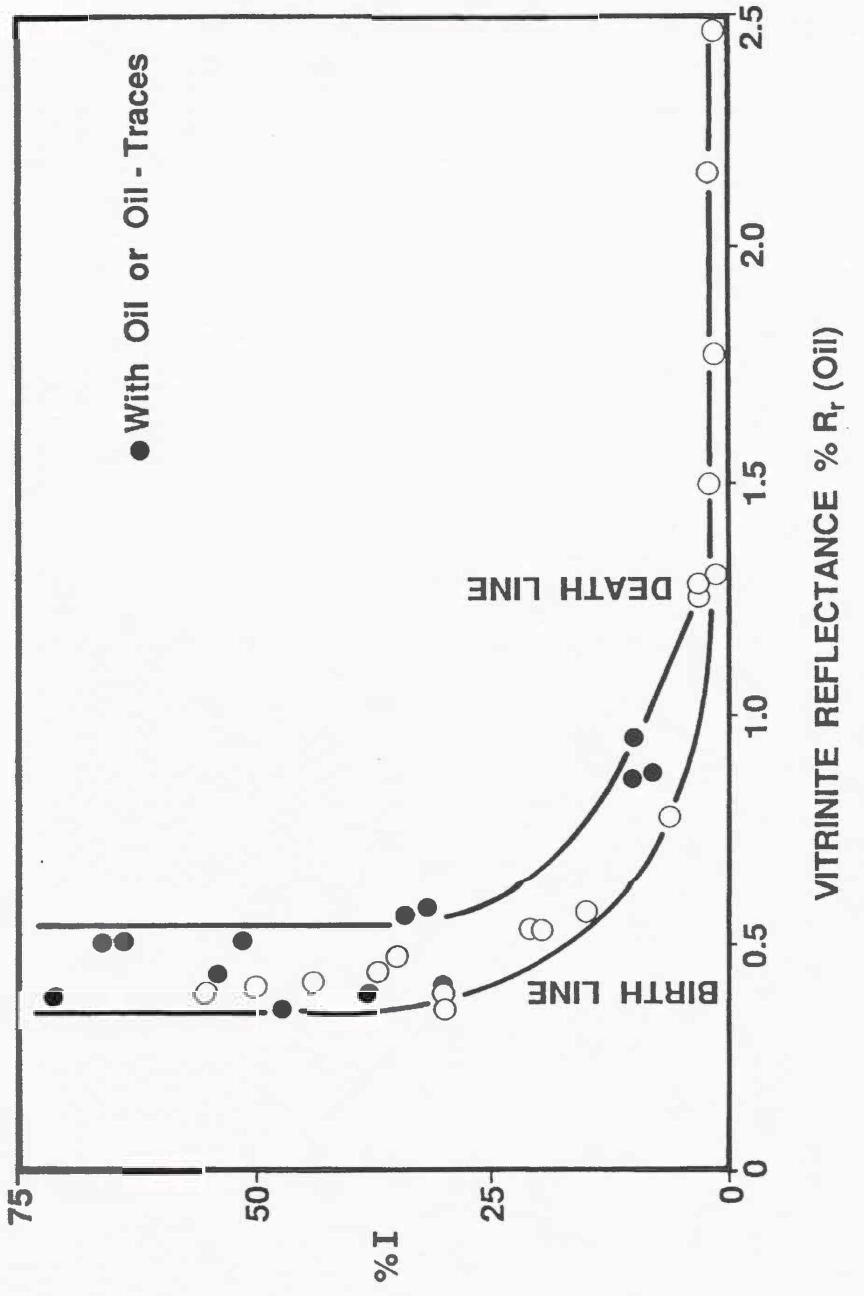

● With Oil or Oil - Traces
DEATH LINE
BIRTH LINE
%I
75
50
25
0
0
0.5
1.0
1.5
2.0
2.5
VITRINITE REFLECTANCE % R_r (Oil)

Fig. 2

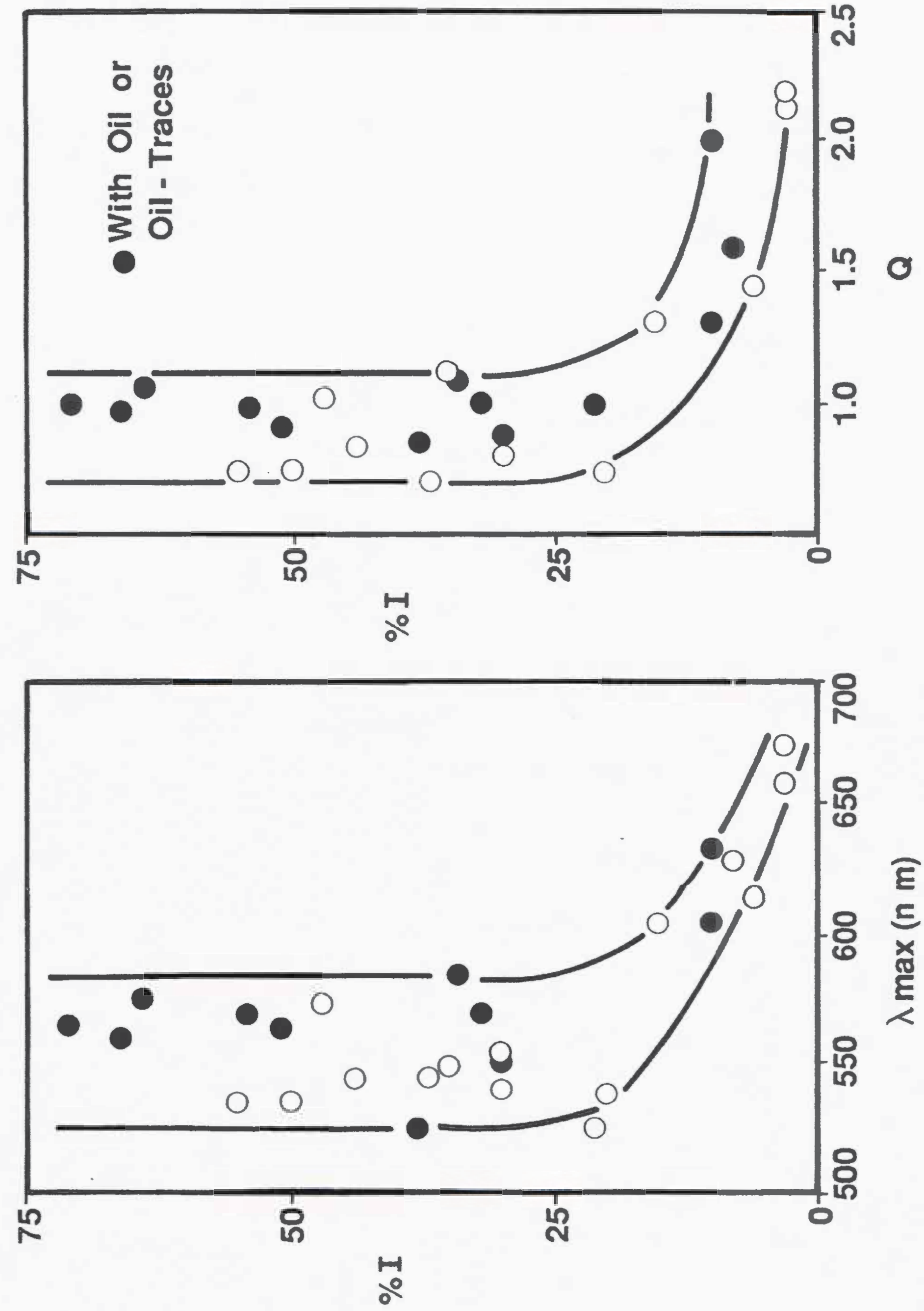

● With Oil or
Oil - Traces
%I
75
50
25
0
1.0
1.5
2.0
2.5
Q
%I
75
50
25
0
500
550
600
650
700
λ max (n m)

Fig. 3

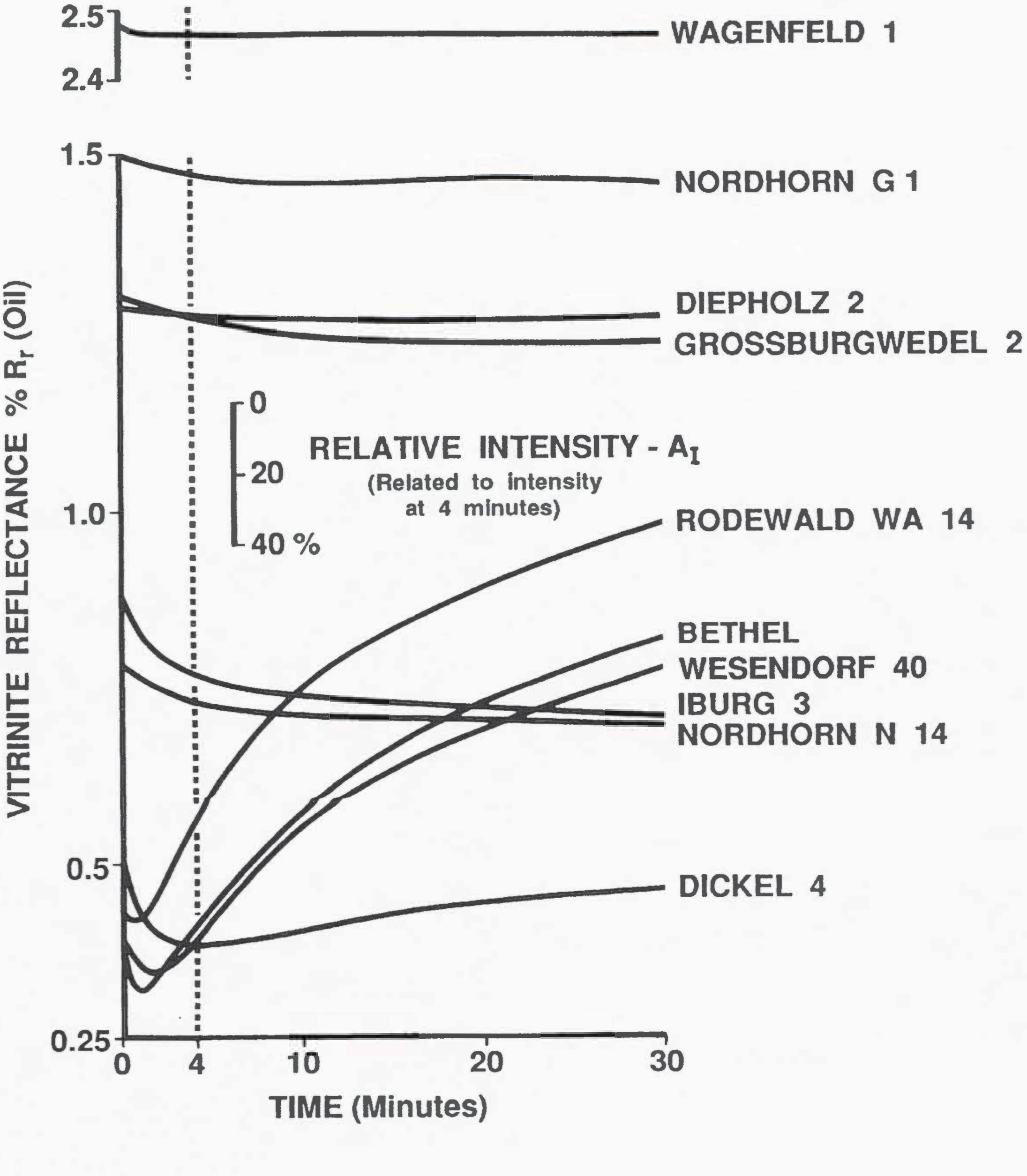
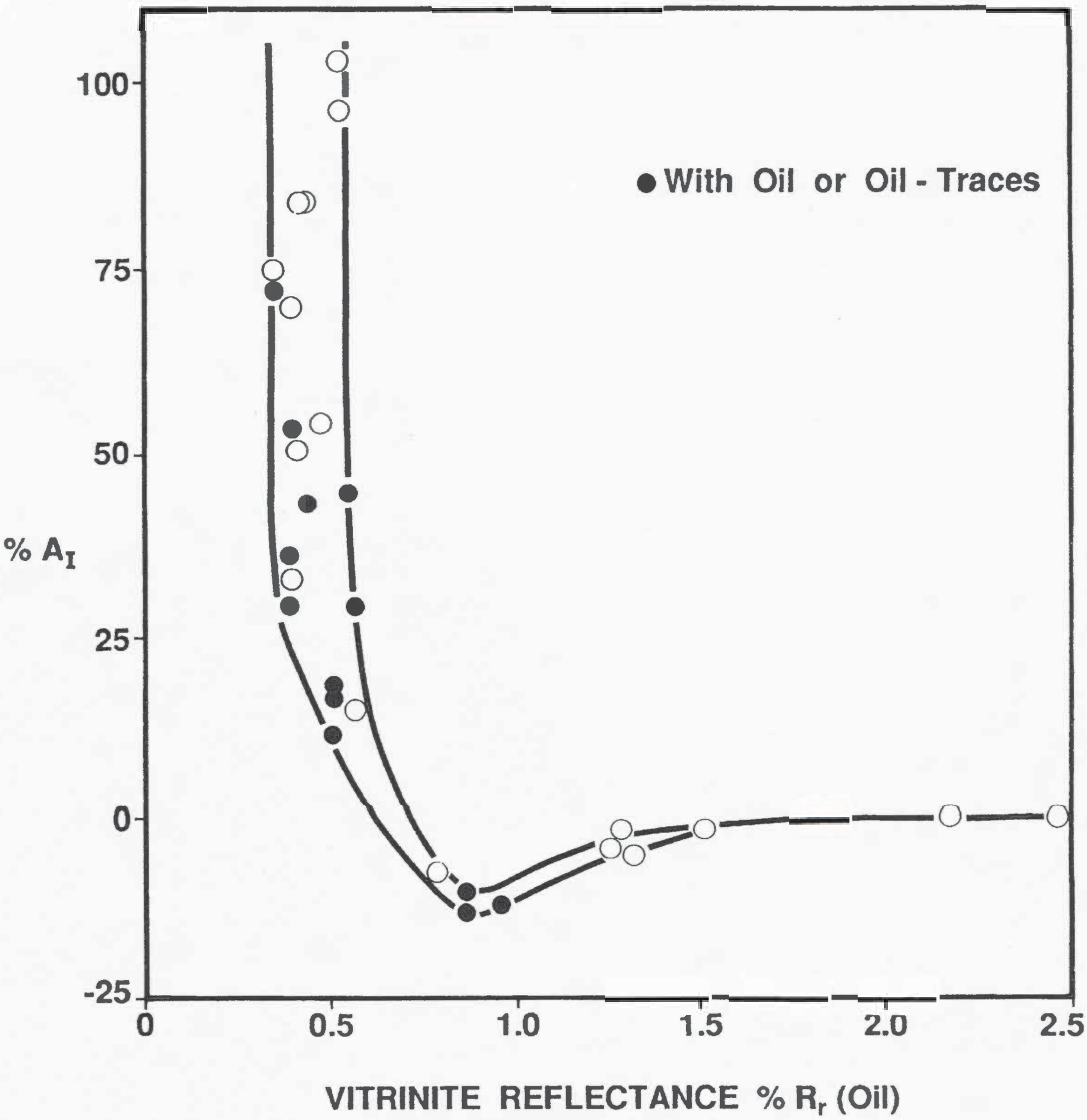

2.5
2.4
WAGENFELD 1
1.5
NORDHORN G 1
DIEPHOLZ 2
GROSSBURGWEDEL 2
1.0
0.5
0.25
VITRINITE REFLECTANCE % R_r (Oil)
0
20
40 %
RELATIVE INTENSITY - A_I
(Related to intensity at 4 minutes)
RODEWALD WA 14
BETHEL
WESENDORF 40
IBURG 3
NORDHORN N 14
DICKEL 4
0
4
10
20
30
TIME (Minutes)

Fig. 4



● With Oil or Oil - Traces
100
75
50
25
0
-25
% A_I
0
0.5
1.0
1.5
2.0
2.5
VITRINITE REFLECTANCE % R_r (Oil)

1993 SUPPLEMENT	**International Committee for Coal Petrology** Commission I	Hard Coal R. L. T. L.
	COLLORESINITE (Stopes-Heerlen System)	

I - ORIGIN OF TERM

The term was introduced in 1984 by the ICCP to denote a submaceral of resinite for discrete resinitic material having a reflectance closer to collinite than to liptinite* in a given coal.

II - DESCRIPTION

a) *Morphography*

Colloresinite has the form of bands and discrete round, oval or rod-shaped bodies, usually in a vitrinite matrix or as an infilling of telinite, or more rarely semifusinite, the shape depending on the plane of section and the degree of compression of the host tissue. Amorphous resinite, occurring as diffuse impregnations of vitrinite submacerals, is excluded from the definition.

Colloresinite is distinguished from desmocollinite by its homogeneous appearance, not being intimately associated with micrinite.

b) *Physical properties*

Colour: Transmitted light - orange red to reddish brown: closer to vitrinite than sporinite in the same coal.

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* Although colloresinite is classified as a submaceral of resinite, its recognition allows the petrographer to record such material separately, if required, so as to take account of its physico-chemical properties when evaluating a coal for technological purposes. It is assumed that its properties are closer to vitrinite than to the liptinite.

Reflected light (bright field, oil immersion) - grey, always slightly darker than the surrounding vitrinite. The difference becomes less with increasing rank.

Reflected light (fluorescence) - with UV excitation, very weak blue fluorescence; with blue-light excitation yellowish brown to light brown; always slightly lighter than surrounding vitrinite.

There is an inverse relationship between colour in white light and that under blue-light excitation. The darker the appearance in white light, the lighter the fluorescence colour.

Exposure to short-wave radiation under the microscope darkens the exposed area but enhances the visible structure.

Reflectance: rank dependent, but closer to vitrinite than to the sporinite and cutinite in the same coal. In any one coal the reflectance range of colloresinite overlaps the range of desmocollinite and to some extent that of telocollinite. No criteria can therefore be laid down for the recognition of individual bodies of colloresinite using the mean reflectance of any of the vitrinite submacerals. The recognition of colloresinite is based on a comparison with the unequivocal vitrinite in close association. It should be clearly recognisable by eye and have a lower reflectance than the surrounding vitrinite. The absolute reflectance difference in oil should be at least 0.05 % in high-volatile bituminous coals.

Polishing relief: weak to nil where colloresinite occurs infilling cell cavities; more marked where it occurs as discrete bodies in the vitrinite matrix.

c) *Chemical constitution and properties*

Not determined owing to the difficulty of separating and concentrating sufficient quantities of colloresinite from vitrinite. Coal containing appreciable amounts of colloresinite may be expected to yield a higher content of volatile matter than coals lacking this submaceral. In relation to their reflectance, such coals have been found to have a higher yield of volatile matter[1].

Effect of etching solutions: colloresinite is not attacked by etching solutions in contrast to desmocollinite and gelocollinite which then appear black in reflected light.

III - BOTANICAL AFFINITIES AND GENESIS

Plant excretions and plant-cell walls impregnated with resin. Resin is particularly characteristic of gymnosperms. Collapse of empty cells between infilled resin ducts after deposition will increase the relative proportions of resinite present in coals derived from woody tissue. It is not known whether the excretions now classified as colloresinite were initially chemically similar to the low-reflecting forms of resinite before polymerisation. Little is known of the chemical differences which now separate colloresinite from low-reflecting resinite, cutinite and sporinite on the one hand and vitrinite on the other. Transitions in reflectance covering the range of these macerals sometimes occur in the same fragment of telinite.

IV - OCCURRENCE

Colloresinite occurs in most coals, mainly in association with macerals of the vitrinite and inertinite groups. It is generally present as a minor component, although there are few published records of its occurrence. Marchioni[2] recorded 14 % resinite, most if not all of which is colloresinite, in a Permian seam from Australia. Colloresinite is not easily detected in coals with R_r oil > 1.5 % (VM < 20 % daf).

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Fig. 1

Colloresinite (r) filling cell cavities in telinite in a medium-rank coal from Welbeck Colliery, Nottinghamshire, England (R_{max} oil = 0.75 %).
reflected light, oil immersion

Fig. 2

Same subject as Fig.1, after etching in chromic acid, showing the unchanged appearance of the homogeneous portions of colloresinite in Fig.1.
reflected light, oil immersion

Fig. 3

Desmocollinite (d) filling cavities in a longitudinal section of telinite in medium-rank coal from the High Hazel seam, Clifton Airfield borehole, North Yorkshire, England (R_{max} oil = 0.80 %). Note the heterogeneous appearance of the darker infillings compared with the cell fillings in Fig.1.
reflected light, oil immersion

Fig. 4

Same subject as Fig.3 after etching in chromic acid to show the distinction between desmocollinite and colloresinite after etching.
reflected light, oil immersion

Fig. 5

Mottled vitrinite: the darker areas are not classified as colloresinite due to the amorphous and uncertain nature of this material: seam at 438.77m, Princethorpe Meadows borehole, Warwickshire, England (R_{max} oil = 0.40 %).
reflected light, oil immersion

Fig. 6

Same subject as Fig.5 after etching with chromic acid showing the accumulation of droplets in the darker areas: the droplets appear darker than the resin remaining after etching in Fig. 2.
reflected light, oil immersion

Fig. 7

Isolated elongate and oval bodies of colloresinite (r) embedded in matrix of desmocollinite in a medium-rank coal from the Silkstone seam, Hickleton borehole, Yorkshire, England (R_{max} oil = 0.95 %).

reflected light, oil immersion

Fig. 8

Isolated oval bodies of colloresinite (r) embedded in matrix of desmocollinite. The dark bodies are considered to be altered sporinite: medium-rank coal from the Swallow Wood seam, Orgreave Colliery, Yorkshire, England (R_{max} oil = 0.90 %).

reflected light, oil immersion

Fig. 9

Lamellae of colloresinite (r) in clarite from medium-rank coal: Meltonfield seam, Barnburgh Colliery, Yorkshire, England (R_{max} oil = 0.65 %).

reflected light, oil immersion

Fig. 10

Same subject as Fig.9 but showing fluorescence of colloresinite (r): note the fluorescence of colloresinite is intermediate between that of liptinite macerals (cutinite and sporinite) and desmocollinite.

reflected light, oil immersion, blue-light excitation

Fig. 11

Part of subject shown in Fig.10 at higher magnification to show that the apparently homogeneous lamellae at low magnification consist of cell tissue (telinite) under blue-light excitation: the fluorescent properties of such material may be due to the impregnation of the tissues with bitumen.

reflected light, oil immersion, blue-light excitation

Fig. 12

Aggregates of variably sized bodies of colloresinite (r) : Mesozoic coal, Greenland (R_{max} oil = 0.51 %).

reflected light, oil immersion

Fig. 13

Cells filled with colloresinite (r) : Mesozoic coal, Colombia (R_{max} oil 0.73 %).
reflected light, oil immersion

Fig. 14

Colloresinite (r) filling cell cavities showing elongate shape under compression: Liddell seam (Palaeozoic), New South Wales, Australia (R_{max} oil = 0.77 %).
reflected light, oil immersion

Fig. 15

Irregularly shaped masses of colloresinite (r) derived from cell fillings: the field contains material of variable reflectance but only the labelled material with absolute reflectance at least 0.05 % lower than the unequivocal vitrinite is classified as colloresinite: Palaeozoic coal, Morupule Coalfield, Botswana (R_{max} oil = 0.64 %).
reflected light, oil immersion

Fig. 16

Lamellae of colloresinite (r) between vitrinite (above) and sporinite and cutinite (below): Palaeozoic coal, Malagasy (R_{max} oil = 0.79 %)
reflected light, oil immersion

Fig. 17

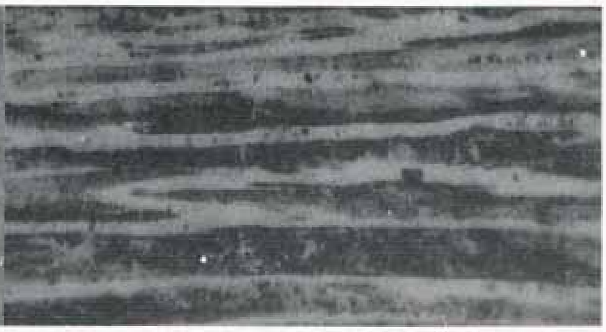
Aggregates of colloresinite (r) bodies collectively appearing as lamellae cut obliquely to the bedding: Palaeozoic coal, Hopeh Coalfield, China (R_{max} oil = 0.77 %).
reflected light, oil immersion

COLLORESINITE

1

2

3



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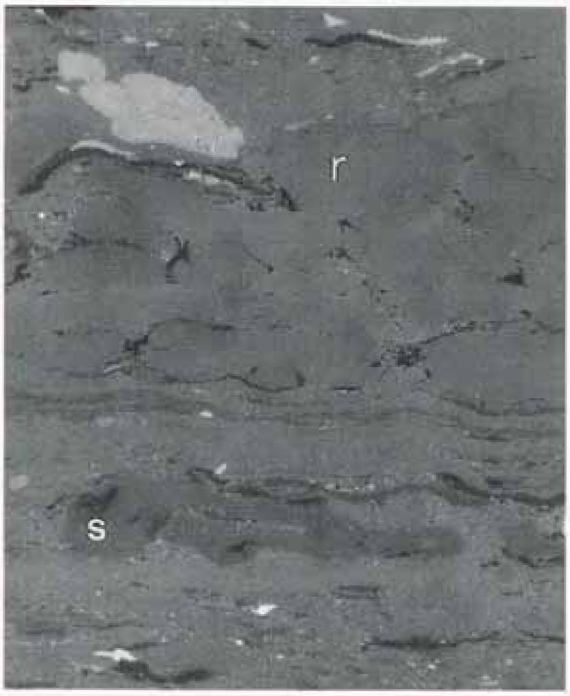
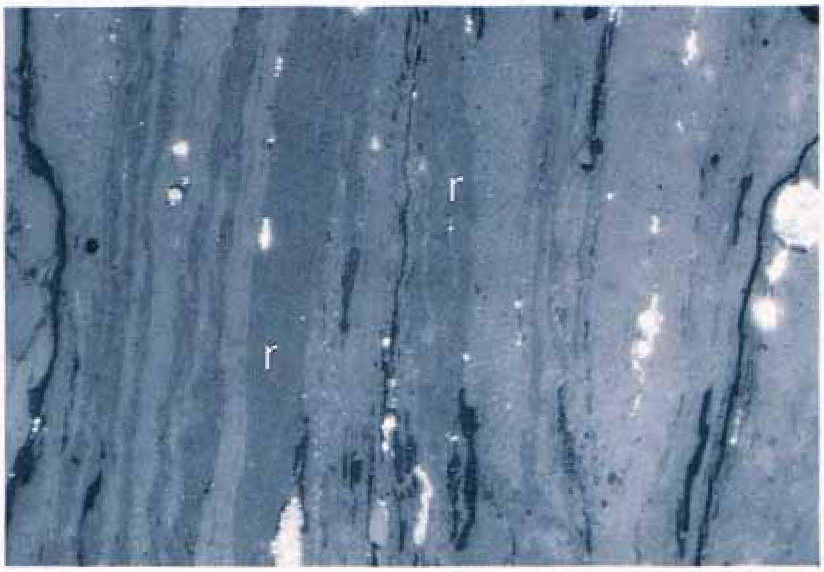


8

Scale 1-6 0 50um

7& 8 0 50um

COLLORESINITE



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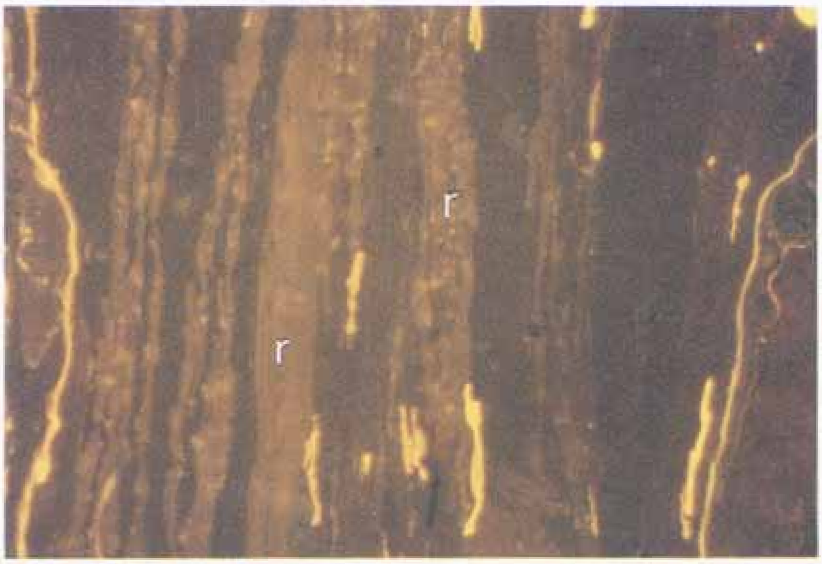

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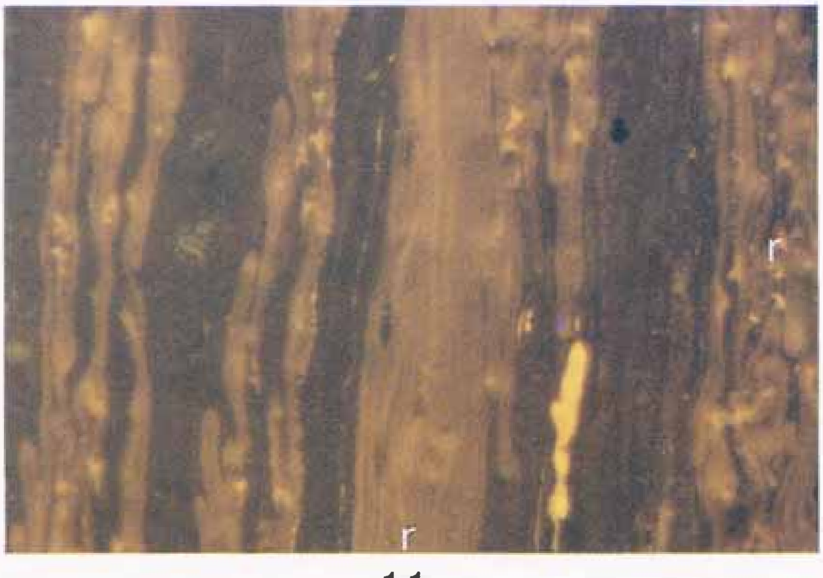
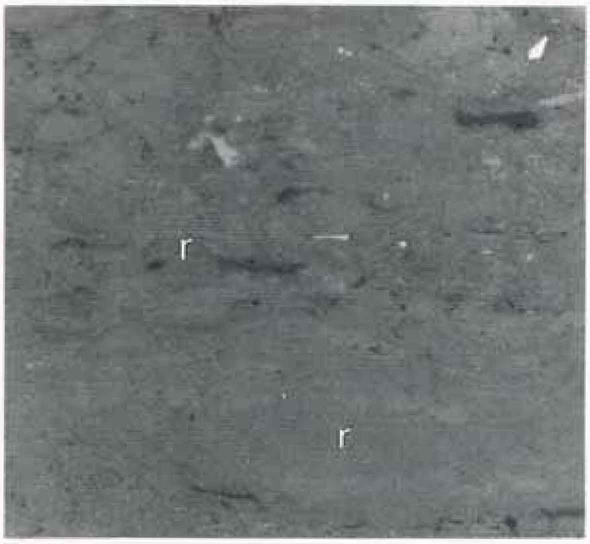


11

Scale 9 & 10 0 50um

COLLORESINITE



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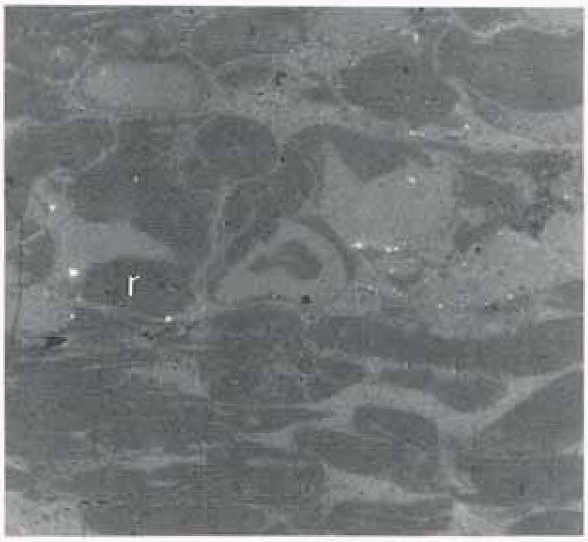

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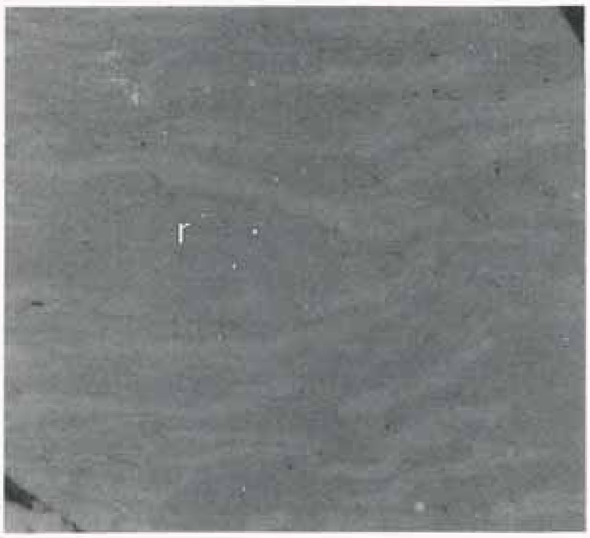

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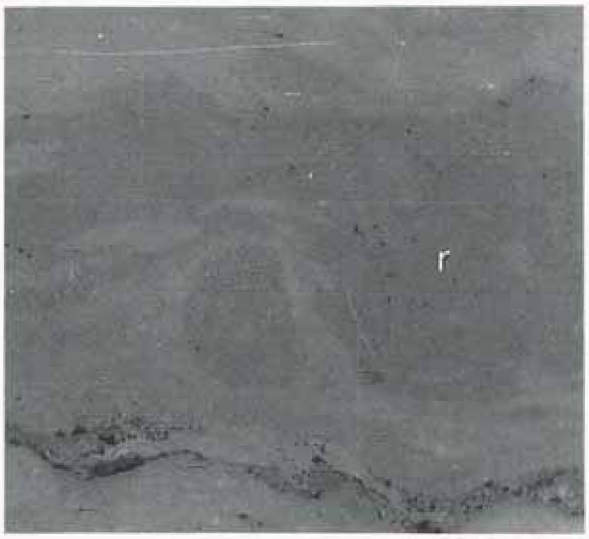

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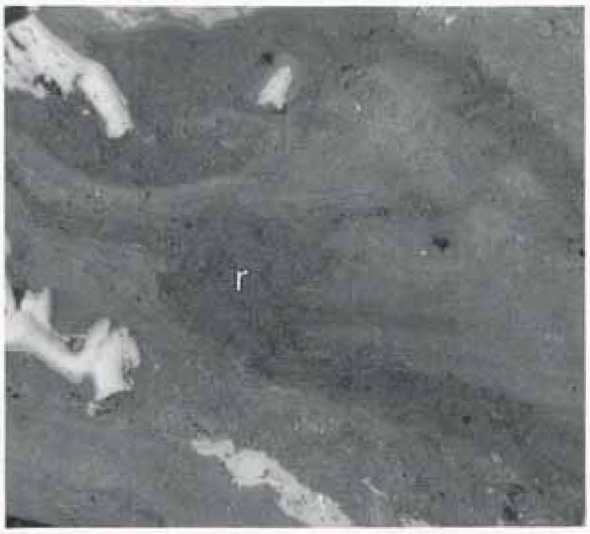

17

0 50 um

1993

SUPPLEMENT

International Committee for Coal Petrology
Analysis Subcommission

FLUORESCENCE MICROSCOPE PHOTOMETRY
PART I - DETERMINATION OF INTENSITY

Peat
Coal

R.L

I - GENERAL

Measurements of fluorescence intensity at approximately 546 nm (peak wavelength), excited with blue-light (peak wavelength at approximately 400 nm) are used for the investigation of humic substances in recent sediments and for the determination of the degree of coalification of huminite, vitrinite and liptinite, and the degree of bituminization of low- to medium-rank vitrinite. The method is also applicable to natural bitumens and to dispersed organic matter.

In many cases fluorescence intensity and reflectance (546 nm, standard immersion oil) are roughly inversely related to each other.

Descriptions of the equipment and the method are based on Jacob[1,2]: for instrumental details see also Krafft[3]. General aspects of microscope photometry are treated by Piller[4].

Recently the technique presented here has been modified by changing and/or extending the range of excitation and by altering the peak wavelength and bandwidth of the measured fluorescence, so as to achieve higher intensity (Diessel and McHugh[5]; Hagemann et al[6]). Measurements in those modes require the same analytical procedure and instrumental facilities (except for filters, beam splitter and standard). Using these methods some inertinites are found to fluoresce.

II - APPARATUS

The apparatus described in this section has to provide excitation radiation of high intensity with a wavelength range between 300 and 500 nm and a peak wavelength of approximately 400 nm, to suppress all other disturbing or interfering light, and to allow measurement of fluorescence intensities in the wavelength range at about 546 nm (half-band width up to 50 nm at maximum).

Intensity measurements sometimes require normal "white light" illumination in addition to the excitation source. The "white light" serves as a pilot illumination for the selection and focussing of objects for measurement, without subjecting them to the influence of excitation. Hence the lamp arrangement should be such as to allow a rapid change in the type of illumination.

The microscope equipment is basically similar to that used for reflectance measurements (see section DETERMINATION OF RANK-ICCP Handbook[7]), but with the following modifications (see Fig. 1):

a 100W high-pressure mercury lamp in addition to the tungsten lamp for normal "white light" illumination, which provides light of high intensity and suitable spectral distribution (peaks of high intensity at 365/366 nm, 405/408 nm, 435 nm, 546 nm, 557/579 nm), combined with long-term stability, and

an incident-light illumination system for fluorescence consisting of a high reflecting and transmitting beam splitter (dichromatic splitter) and the necessary filters to control excitation and emission. Sets of reflectors and filters for fluorescence microscopes are available from well established microscope suppliers. Here only the criteria for selecting those devices for coal application are described.

The excitation filter should restrict the wavelength range to between about 340 to 480 nm (peak wavelength approximately 400 nm) for blue-light excitation (see Table below for examples of the characteristics of (SCHOTT) BG 12 filters).

Properties of the blue-light excitation filter glass (SCHOTT BG 12)

Type[1]	**Designation**[2]	**max**	**max**	**HB**[3]	**Thickness**
BG 12	BP[4] 408/145	408	0.9	145 nm	1 mm
BG 12	BP 408/125	408	0.8	125 nm	2 mm
BG 12	BP 408/110	408	0.7	110 nm	3 mm

[1] SCHOTT

[2] DIN (German Industrial Standard)

[3] half bandwidth

[4] bandpass filter

Because the blue excitation filter allows transmission of red light, it is also necessary to use a red suppression filter (*e.g.* SCHOTT BG 38). Both filters have to be sufficiently thick to suppress any measurable reflectance in the wavelength range of detection. The weaker the fluorescence the thicker the filters need to be so as to keep the ratio of fluorescence to background light as low as possible.

The beam splitter (dichromatic splitter) which replaces the Berek prism or the plane-glass reflector is the highly efficient component of the fluorescence illuminating system. It provides high reflectance of the excitation light and high transmittance of fluorescence, even separating excitation and emission. A beam splitter with a separating line of approximately 500 nm is recommended.

The function of the barrier filter is to suppress any excess excitation light which could be reflected by the sample and interfere with observed fluorescence and its measurement. The filter also ensures that no harmful irradiation reaches the eyes of the observer. Its position is in the image-light path between the illuminating system and the eyepiece/photometer head. Hence it must be a so-called "long-pass" filter with a separation line of 490 to 520 nm with adequate extinction.

Objectives of moderately high magnification (x25 to x50) with a numerical aperture of not more than 0.8 are recommended (see Appendix). In addition to the use of dry objectives, which should be used when examining sub-bituminous coals and high-volatile bituminous coals, immersion objectives may be acceptable for work on peats and other substances which do not contaminate the immersion liquid (e.g. bituminous matter).

Interchangeable field diaphragms and photometer diaphragms from < 5 to approximately 40 µm (relative to the object surface) are required. The field diaphragm should be no more than 2 - 3 times the size of the photometer diaphragm (see Table below). For measurement of the small excited area a switchable luminous field diaphragm is required to allow an immediate change from the whole microscope field, used for observation, to the measuring area, and *vice versa*.

Examples of corresponding field diaphragms and photometer diaphragms (diameters of round-shaped diaphragms, relative to the object surface)

Example	Applications	Field Diaphragm[1]	Photometer Diaphragm[1]
1	sporinite microsporinite pollen grains	10 - 15 µm	5 µm
2	cutinite, alginite, megasporinite desmocollinite	30 - 100 µm	10 - 30 µm
3	ulminite	40 - 100 µm	20 - 40 µm

[1] The particular size and shape depend on the equipment and the objects under investigation

A bandpass filter (interference filter or coloured glass filter) in front of the photomultiplier window restricts the emission to the desired range. The filter is the same or similar to that used for reflectance measurements, possibly with a slightly extended bandwidth (546 nm/20-50 nm).

The common light sensor is a photomultiplier (e.g. S20-type), but any other light sensor is acceptable, if it is sufficiently free of electronic noise, has a low dark current and a sensitivity equal to or higher than an S20 cathode.

The method of recording and evaluating measurementS depends largely on the use which is made of microcomputers. Manual recording is possible, but computer-controlled transfer of values allows a greater number of measurements (see Jacob et al.[8]). For testing objectives and filter sets see Ottenjann[9].

III - FLUORESCENCE STANDARDS

To compare intensities of different objects within a given set of samples it may be sufficient to make all the required measurements while strictly maintaining the instrumental conditions. The relative values thus obtained may be useful for some purposes and do not require the use of a standard.

The use of any suitable material as a standard in combination with a predetermined outfit should provide repeatable but hardly reproducible data. Unlike reflectance photometry for which absolute standards are available, photometry of fluorescence intensity has no absolute standard at present. Relative standards must be used.

Standards should be solid fluorescent substances with an emission in the visible part of the spectrum. The emission must be as broad as possible, at least in that part around 546 nm. The intensity of the emitted radiation should be similar to the fluorescence intensity of coaly entities or related substances. Standards must not alter in their capacity to emit a defined intensity and spectral distribution, neither when stored nor during excitation. When the standard material is translucent, the effective thickness should be much reduced or restricted to the surface (see Appendix).

The intensity level of fluorescence standards is, like that of coal macerals, closely related to the strength of excitation which is an inherent disadvantage of fluorescent standards. The nominal intensity must be set arbitrarily to any value. Hence such standards need to be calibrated against a known master standard to give comparable results.

IV - TECHNIQUE OF MEASUREMENT VERSUS STANDARDS

Fluorescence is not a surface phenomenon like reflectance. Objects of different translucency become excited to different depths. In the case of translucent standards and more or less translucent objects, the results may only differ slightly because the excited volumes may not be different. Larger objects reduce the accuracy of the results. Hence the method of using microscope-photometric measurements to compare the properties of an object under investigation with those of any kind of standard introduces difficulties. The accuracy of the recorded values depends on the objective (magnification and aperture) as well as on the size of the field and photometer diaphragms (see Appendix).

V - SAMPLES

For intensity measurements any kind of polished block sample is suitable if its mounting medium is weakly fluorescent. A particulate block, as used for reflectance measurements or maceral analysis, is necessary to achieve a representative value for intensity from a bulk sample (particle size > 1mm but if possible > 2mm, to avoid boundary effects between the embedding resin and the coaly particles).

Prepared specimens should be air-dried and stored in a cool and dark place until required for measurement. A change of fluorescence properties was observed on very reactive samples after a storage time of a few days (Diessel[10]). Measurements should be made on freshly prepared samples within 24 hours after polishing. When using old specimen blocks grind at least 2 - 3 mm from the surface.

Measurements must be made on an unused block, otherwise pre-excitation or contamination with residues of immersion liquids may affect results.

VI - PROCEDURE

a) *Lamp adjustment*

The excitation lamp must be centred to give maximum brightness. If only a part of the image field is illuminated, centre the light closely to the field aperture. Avoid imaging the arc of the lamp on the specimen surface because this type of illumination is less stable. Do not open the aperture diaphragm more than is necessary to cover the back focal plane of the objective so as to avoid excessive illumination and an increase in background without enhancing the fluorescence.

b) *Handling background effects*

Background effects may be generated by the electronic equipment (dark current), fluorescence from lenses, fluorescence of immersion liquids and their enhancement by contamination, insufficient absorption of excitation filters (reflected excitation light) and stray light passing the eyepieces. Avoid such effects by using properly adjusted electronic equipment, tightly fitting excitation filters, appropriately selected objectives and a darkened working area. If any background value still occurs it must be measured. The measured background value must be subtracted from the calibration value as well as from the object value or it must be suppressed by means of electronic manipulation.

c) *Calibration*

The calibration procedure is the same as that used for reflectance measurement. The fluorescence emission reading of the standard is set to a value on the recording device which avoids readings which are too low or are off-scale. When using a computer-controlled photometer several (e.g. 3) measurements should be made on different parts of the standard surface and an average value calculated.

d) *Measurement*

Individual objects within a sample should be found, positioned and focussed in the fluorescence mode or under normal white light. Some material will rapidly change its intensity after onset of irradiation, lowering the accuracy of the result. The object must be measured within that time necessary for adjustment and focussing. That time interval should be accepted as being sufficient to reduce the scattering of values caused by alteration. The number of measurements per sample with respect to a particular maceral depends on the problem and on the nature of the sample (a minimum of 10 measurements appears to be necessary).

e) *Evaluation*

Evaluation depends on the equation:

$$I_0 = \frac{(MV_0 - B) \bullet I_s}{(MV_s - B)}$$

where

I_0 = fluorescence intensity of the measured object

MV_0 = measured value of the object

MV_s = measured value of the standard (average)

I_s = intensity value of standard (e.g. 1.07 for the secondary standard if the master standard is 1)

B = measured value of any background effects

It is recommended that the mean and standard deviation are calculated. The production of a histogram is possible if the number of values is sufficient. Using accepted statistical procedures the number of classes is given by the square root of the number of values.

VII - REPEATABILITY, REPRODUCIBILITY

Differences of excited volumes, alteration and storage conditions make measurements of fluorescence intensity less reliable and less repeatable and reproducible than reflectance measurements. Repeatability and reproducibility depend on the performance of the standard, the calibration technique and the method of measurement (see sections III and VI), as well as on the precision of the apparatus. At present specific values are unknown.

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(only those publications are listed which are relevant to equipment and method)

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Appendix

Unlike the reflectance phenomenon, which is exclusively a surface effect, fluorescence in translucent material is not only excited at the surface but also in the bulk of the material with a laterally distributed glare. The intensity of the fluorescence stimulated in bulk depends on the degree of translucency and on the particular spectral absorption for the wavelength of the excitation light beam. Furthermore the measure of the excited volume and the strength of excitation are a function of the objective properties: those of low magnification and low aperture produce less strong illumination in the mass and a slim light cone. High-magnification objectives with larger apertures cause a smaller but strongly excited volume with broad lateral extension because of the wide angle of aperture.

A part of the fluorescence radiation from the excited aperture "cone" (excited depth) and from its surroundings intensifies the fluorescence light flux of the area covered by the photometer diaphragm and makes the measured value increase. Thus a raised measurement on the standard causes a suppression of the related intensity values from the subsequently measured unknowns. A similar effect occurring with an unknown measurement will increase that intensity reading and will raise the relative intensity value of the unknown.

Most frequently the optical properties of the standard and the measured unknown are different. Hence the errors do not equalize.

To reduce inevitable errors use:

a standard from which a low fluorescence intensity comes mainly from the surface (for optimum calibration the standard should strongly absorb light in the excitation range),

medium-powered objectives of moderate magnification and aperture to restrict the range of possible deviation, and

well-adapted sets of field diaphragms and photometer diaphragms to reduce the influence of lateral glare.

Checking background: (reprinted from THE SOCIETY FOR ORGANIC PETROLOGY: NEWSLETTER. - vol.6, No. 2; June 1989.)

Microscopic photometric measurements of fluorescence intensity of spectral distribution are often influenced by: 1. the fluorescence of the microscope objective; and 2. filter systems which transmit light reflected from the sample.

Both of these permit additional light to contribute to the overall intensity or spectral distribution of an object's fluorescence. The former problem is specific to any given objective and to the intensity of the excitation light. For most weakly fluorescing objectives, this problem can be suppressed or compensated for electronically. The latter problem varies depending on the reflectance of the object being measured. Because macerals have different reflectances, the effect changes with each measurement. The error will be greater the higher the reflectance. This effect must also be suppressed or compensated for.

In order to test the suitability or efficiency of an objective or filter system the following procedures have been established and tested in our lab. My experience in interlab exchange studies have convinced me that the tests described below seem to be essential to reproducible results between laboratories.

Testing Your Objective

This test can determine which of your objectives is best suited for fluorometric measurements. Perform this test in a darkened room with no sample under the microscope. With your normal incident excitation light on, replace one of the eyepieces with a telescoping eyepiece. (Do this if you have a common microscope tube, if you have a more sophisticated POL tube use a Bertrand lens.) As you focus the eyepiece (or Bertrand lens) to the back focal plane the image of the objective's fluorescence will appear as a bluish-white glare. Test all your objectives in this manner, the objective exhibiting the weakest fluorescence is best suited for quantitative measurements. (The test is also very useful in determining the fluorescence effect from various immersion media.)

Testing Your Filter Set

This test will detect light reflected up through your objective which is allowed to pass through your filter system. Fluorescence intensity measurements can be made over the entire visible range or at specific wavelengths, i.e. whatever conditions you normally measure fluorescence under. Computerized normalization of the fluorescence intensity (for instance to a maximum of 100%) should not be performed. Thus, depending on your system, you may need to perform these measurements manually.

In a darkened room with your normal incident excitation light on, adjust the microphotometric equipment so that is is sensitive enough to measure a normal object's fluorescence. Remove the object and lower the objective into a black-painted metal box or cylinder (i.e., any small container free from reflectance and fluorescence). Altenatively, you may work in a completely darkened room but care must be taken so that absolutely no reflection light can reach the objective. Record a spectrum or single intensity value and do not correct it in any way. Call this spectrum or value, IO (intensity of the objective).

Place a highly reflective metal-surfaced mirror under the objective. The mirror must be free from dust, finger grease or any other fluorescing material. Focus on the mirror by momentarily switching to white light. Record a spectrum or single intensity as you did previously. Call this spectrum IM (intensity of the mirror).Compare IO and IM. If the intensity of these two spectra are clearly different (e.g., if IM is greater than IO), the filter system is insufficient for that level of gain, i.e., reflected light is passing through the filters.

If the intensity readings for IO and IM are similar (except for some of noise), your filter system has not allowed reflected light to pass through and is thus, well-suited for fluorometric measurements. In this case you may be sure that the background correction using IO is sufficient for maceral measurement. The intensity value or values of IO represents the static background (objective fluorescence and electronic effects such as dark current) of your system. This IO should be used for background corrections by subtracting it from the value or values for the maceral.
K. Ottenjann

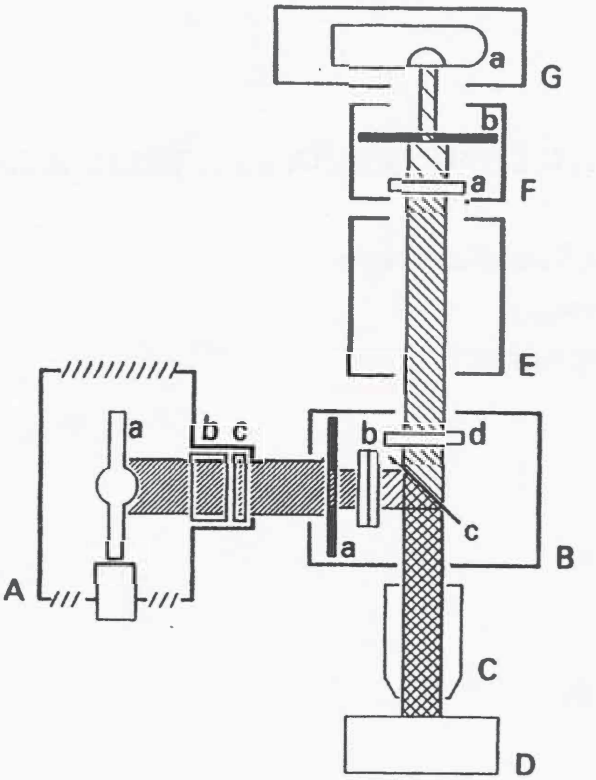
Comment
The two tests described by Mr. K. Ottenjann are very crucial to ensure a reliable and reproducible maceral (kerogen) fluorescence measurement, especially for weakly fluorescing objects such as vitrinite and certain amorphous kerogens. At a few times, I found that a measured and uncorrected spectrum of bituminous vitrinite would peak at 430 nm or below. This peak is apparently a result of excitation light reflection rather than fluorescence, probably due to contributions from the mercury emission bands at 405 and 435 nm. The reflected excitation light can be visible as a violet-blue 'tinting' on nonfluoresing or weakly fluorescing macerals.

The second test ("testing your filter set") is actually only for testing of the excitation filter. The 'IO' spectrum measured in a black-painted box (free from reflection and fluorescence) is basically electronic dark and random noise. The 'IM' spectrum measured with a mirror on focus, on the other hand, includes contributions from reflected excitation light as well as dark current and random noise. Therfore, the difference between 'IO' and 'IM', if any, is an evaluation of the excitation filter (band-pass or line-pass); a better (UV) excitation filter will be the one that permits the passage of a minimal amount of visible excitation light (400-700 nm). The emission optics which include lenses, objective, barrier filter(s) and the monochromator gratings need to be tested also. They, too affect the spectral distribution and intensity of fluorescence.

Rui Lin
Unocal Science and Technology
Brea, California .

Fig. 1

Diagram of a fluorescence microscope photometer



Scheme of a microscope photometer for intensity measurements of fluorescence

A LAMP HOUSING

- a) high-pressure mercury - vapour lamp
- b) collector
- c) heat filter

B FLUORESCENCE ILLUMINATION SYSTEM FOR INCIDENT LIGHT

- a) interchangeable field diaphragm
- b) excitation filter set
- c) dichroic splitting mirror
- d) barrier filter

C OBJECTIVE

D SPECIMEN

E MICROSCOPE TUBE

F PHOTOMETER HEAD

- a) bandpass filter
- b) interchangeable photometer diaphragm

G PHOTOMULTIPLIER HOUSING

- a) photomultiplier or other light detecting device

1993	**International Committee for Coal Petrology** Commission III	Coal Product
SUPPLEMENT	**INFORMATION SHEETS ON HYDROGENATION RESIDUES**	R.L.

Classification of Hydrogenation Residues

Unaltered Coal Macerals

Partially Reacted Coal Macerals

Vitroplast

Cenosphere

Granular Residue

Primary Semicoke

Secondary Semicoke

Pyrolytic Carbon

Unaltered Minerals

Altered Minerals

Neo-Minerals

1993	**International Committee for Coal Petrology** Commission III	Coal Product
SUPPLEMENT	**CLASSIFICATION OF HYDROGENATION RESIDUES**	R.L.

INTRODUCTION

I. Applications of the Study and Analysis of Residues and other Solids Produced during Hydrogenation.

1) The classification scheme described in the following pages will permit the petrographic measurement of relative percentages of major organic and inorganic liquefaction residue components. This can enable comparisons to be made of residues derived from different feed coals, liquefaction processes or run conditions. Even with our limited knowledge of liquefaction mechanisms, we do have some clear ideas as to what components should and should not be present in our residues following optimum conditions of liquefaction. It should be possible, therefore, to use the comparisons as an aid in identifying the best coals, processes or run conditions in any series of tests.

2) One of the most important applications is as a means of diagnosing problems or inefficiencies in plant or equipment operation. For example, operation at too high or too low a temperature or with too high a throughput rate may be reflected in the absolute and relative amounts of the different residue types. Excessive proportions of unreacted vitrinite, vitroplast or semi-coke (including that formed via the mesophase mechanism) could indicate that conditions were not optimal; under extreme conditions, the reactor can become plugged and inoperable by the formation of mesophase coke through retrogressive reactions. On the other hand, large proportions of fusinite, semifusinite or granular residue might be indicative of a far more efficient operation. Filtration problems are expected to be heightened when there is a preponderance of certain types of solid residue, notably vitroplast.

3) Much more needs to be known about the relative behaviours in hydrogenation of coal macerals and of coals of different rank. The study of residues from a wide range of coals should help to provide the data necessary for this understanding. Vitrinite is of particular importance a) because it is the predominant maceral in many coals and b) because there are so many fates to which it can be subjected. However, there are also questions to be answered about the roles in liquefaction of the various macerals which comprise the vitrinite group, as well as semifusinite, macrinite, micrinite and the liptinite macerals.

4) Identification and quantification of the minerals present and the state of their dispersion could provide some input into consideration of possible catalysis by the inorganic constituents. The same observations could be important in consideration of abrasion problems, filtration and magnetic separation.

5) Certain minerals can form under reaction conditions. These include forms of calcium carbonate and calcium sulphate. The tendency of the carbonate to form, especially during the processing of low-rank coal, can lead to blockage problems.

II. Problems Associated with Residue Analysis

The usual problems involved in identifying coal macerals are compounded when these materials have undergone phase changes, severe comminution and increase in the level of reflectance as a result of thermal treatment and solvolysis. A knowledge of the petrographic characteristics of the feed coal and of the behaviours of coals in thermal processes, such as coking, is helpful in understanding the origin of some of the residues of coal hydrogenation. However, most of the residue types presented in the following classification were established only after studying the residues obtained from series of hydrogenations at successively higher temperatures of carefully selected and characterized coals. In this way the reaction processes could be followed, and the ultimate fates of important coal macerals noted.

Some philosophical and procedural problems likely to be encountered include:

1) Several of the residue classes are transitional one into another, and a petrographer may have difficulty in deciding precisely where to set the thresholds between classes.

2) Only a few grains of any residue sample are needed for microscope study. The petrographer has to work on the assumption that the sample taken is representative of the solid product of the particular process conditions. However, it is possible that certain residue components may be generated within the reactor or at the filter during critical stages in the process. Consequently, some doubt is cast on the representativeness of samples as true residues (undissolved coal), and because of the small amount taken relative to the possible diversity of reactions involved.

3) The preparation of specimens of hydrogenation residues for microscopic study involves some special problems which do not arise in the course of preparation of untreated coals. These are:

    a) The residues have to be extracted with a solvent (e.g. benzene) prior to embedding in an epoxy resin binder. Does the extraction process in any way affect the composition or character of the residue?

    b) Certain residues, after extraction, tend to agglomerate. If left in the agglomerated state, the surface of the sample prepared for microscope examination would be unrepresentative. Crushing destroys the particle size and morphological characteristics. Agitation in acetone can be used to break up the agglomerates with some, but not total, success.

    c) The friable, porous, often mineral-rich nature of the residues makes polishing to a scratch-free surface difficult. The scratches, holes, pores and relief effects can then make proper identification and measurement difficult.

Finally, it must be emphasized that petrographic analyses of such residues are particularly complicated because of the diverse, often problematic nature of the components which have to be identified. Analysis of each sample can take about three hours.

III. Residues and Reactor Solids

Solids which are removed from a continuous-run product stream by filtration or other methods of solid-liquid separation are known as *liquefaction residues.* This term is also used for residual solids from batch liquefaction experiments; in such apparatus the amount of solids are small relative to pilot plants and there can therefore be no physical separation of residual and other solid materials. Thus the "residues" from such runs can include some reactor-formed particles as well as particles which represent undissolved material. In pilot plants it is sometimes possible to separately remove the *reactor solids,* which are organic or inorganic materials formed directly from liquid or gaseous phases within the reactor.

IV. Classification of Hydrogenation Residues

1. Unaltered Coal Macerals

2. Reacted Coal Macerals

    a) Partially Reacted Coal Macerals
    b) Vitroplast
    c) Cenosphere
    d) Granular Residue

3. Carbonized Residue

    a) Primary Semicoke
    b) Secondary Semicoke
    c) Pyrolytic Carbon

4. Inorganic Solids

    a) Unaltered Minerals
    b) Altered Minerals
    c) Neo-Minerals

1993 SUPPLEMENT	International Committee for Coal Petrology Commission III Classification of Hydrogenation Residues UNALTERED COAL MACERALS	Coal Product R.L.

I - ORIGIN OF TERM

The term is modified from "unreacted vitrinite" employed by Mitchell et al.[1] and "totally unaltered or unreacted coal" proposed by Ng[2].

II - DESCRIPTION

This group contains all the maceral types encountered in the feed coal. Included are those that are "inert" (e.g. fusinite), and those that are potentially "reactive" (e.g. vitrinite) but have not reacted because of unfavourable conditions. The main criteria for distinguishing this group of macerals are that there is no sign of softening, that they maintain their original microscopic textures and morphology, and that they are not dissolved by the immersion oil used for microscopy[2].

These materials are to be identified according to the ICCP terminology for individual macerals set out in the Handbook. Thus, for example, a residue component could be identified as "unaltered sporinite".

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Fig. 1

Unreacted particle of huminite (ulminite and corpohuminite) in residue from lignite; temperature-staged batch hydrogenation in recycle solvent (275°C for 30 min, then 425°C for 30 min) under H_2 atmosphere;
reflected light, oil immersion, x280

Fig.2

Intact spore exine coated with droplets of primary vitroplast; residue from batch hydrogenation of high volatile B bituminous coal at 350°C in tetralin;
reflected light, oil immersion, x1120

Fig.3

Residue particle from high volatile C bituminous coal, consisting of unreacted fusinite, the collapsed cell walls of which are cemented with reacted vitrinite (vitroplast); batch hydrogenation at 350°C in naphthalene/recycle solvent blend under N_2 atmosphere, with sulphided Fe/Mo catalyst;
reflected light, oil immersion, x420

Fig.4

Unreacted inertinite as fine-grained debris in a matrix of granular residue and iron sulphides; residue from pilot-plant hydroprocessing of Illinois bituminous coal (solvent-refined coal mode);
reflected light, oil immersion, x305

Fig.5

Unreacted macerals (inertinite and, notably, liptinite) in matrix of secondary vitroplast derived from high volatile A bituminous coal; temperature-staged batch hydrogenation in naphthalene (350°C for 1 h, then 425°C for 10 min) under H_2 atmosphere, with sulphided Mo catalyst;
reflected light, oil immersion, x410

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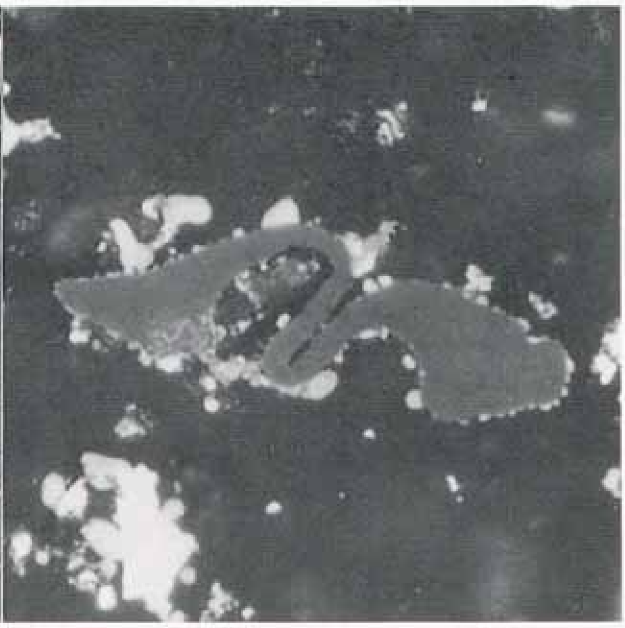

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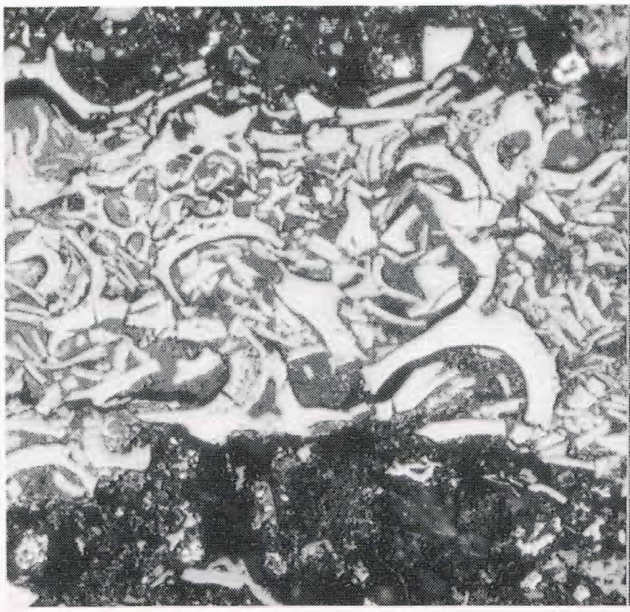

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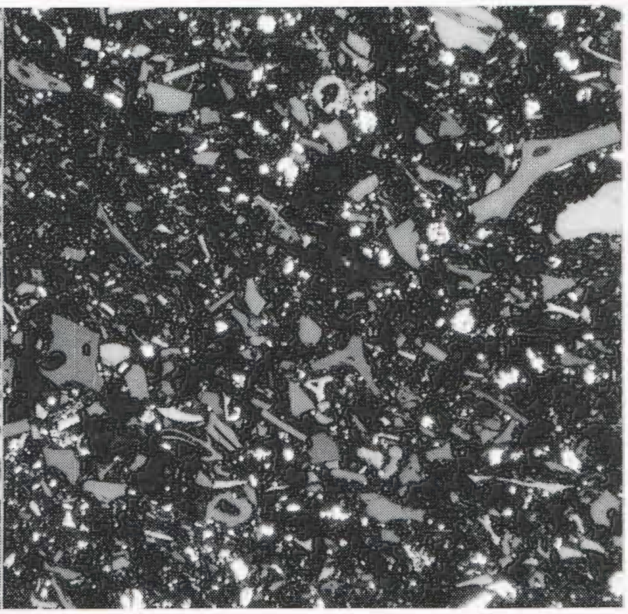

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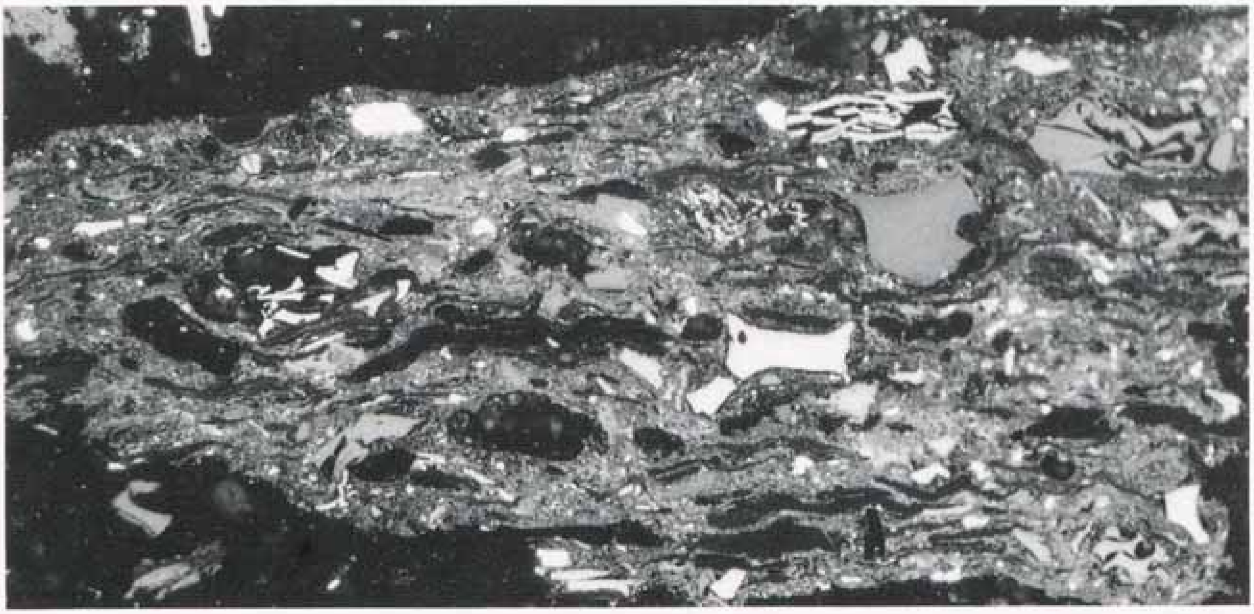

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1993

SUPPLEMENT

International Committee for Coal Petrology

Commission III

Classification of Hydrogenation Residues

PARTIALLY REACTED COAL MACERALS

Coal Product

R.L.

I. - DEFINITION

Altered organic materials in liquefaction residues that retain sufficient residual maceral structure that their maceral origin can often be identified.

Partial reaction may be indicated by change in reflectance, or change in maceral morphology, including swelling and partial dissolution. Reaction may have occurred via thermal alteration, or chemical alteration, or a combination of both. Chemical alteration includes the action of solvent and/or catalyst.

Synonyms and Analogous Terms:	Slightly altered vitrinite	(Mitchell et al.[1])
	Slightly altered coal	(Ng[2])
	Partially dissolved coal	(Diessel et al.[3])
	Partially converted coal	(Shibaoka [4,5])
		(Shibaoka et al.[6])

II - DESCRIPTION

The category of "partially reacted coal macerals" refers mostly to vitrinite (or huminite) because this maceral may exhibit the capacity to swell or contract in liquefaction. It also applies to coal particles (low-reflecting inertite and bi- or tri-macerites) which have been affected on their peripheries by heat and/or solvent.

An essential feature of residue materials in this category is that structural characteristics of the original macerals be retained at least in part. For example, a particle in which only part of the vitrinite showed evidence of plasticity would fall into the category of "partially reacted coal macerals". On the other hand, if the entire particle had clearly been rendered plastic, the appropriate category would be "vitroplast".

Thermally altered and chemically altered macerals will be described together, because the effects of the two processes are difficult to separate.

(a) Brown Coal

(i) Huminite (macerals: increase in reflectance, swelling, degasification pores, cracking and partial dissolution are common feature. Attrinite and densinite retain an "aggregate" appearance, but may exhibit an apparent loss of porosity. Humotelinite and humocollinite exhibit swelling and/or partial dissolution, as well as an increase in reflectance. Reactivity of the individual huminite macerals can vary.

(ii) Liptinite (exinite) macerals: rarely observed in residues of brown coals due to their highly reactive nature. Where liptinite occurrences have been observed in COSTEAM residues, they retain their original morphology, but lose their fluorescence characteristics.

(iii) Inertinite: usually a minor component of brown coal.

(b) Bituminous Coal

Alteration is usually at the surface or edge of the particle rather than deep-seated. If the effect is chemical, the material will usually be dissolved, at least partially, by microscope immersion oil. If it is due to heat, cracks may appear at the edge of the particle. Because the two alteration processes are difficult to separate, vitrinite or other coal grains may show signs of softening and dissolution in the peripheral zones or along cracks which radiate from the edge of the grain towards the interior. Diessel et al.[3] included the vitrinite contained in large vesicles in this category also. Macerals which have undergone a slight degree of dissolution are included. Under conditions of good hydrogen availability, fine particles of relatively low reflecting inertinite and the periphery of large particles of inertinite may undergo hydrogenation and dissolution at higher temperatures than are experienced for the corresponding vitrinite [7-9].

III - MODE OF FORMATION

Partial reaction occurs as the result of thermal alteration (due to reaction temperature), chemical alteration (due to the effects of solvents and/or catalysts), or to a combination of both thermal and chemical effects. The latter alternative is probably the most common.

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

Partially reacted coal macerals tend to occur at the low end of the range of reaction temperatures commonly used in liquefaction studies. In a continuous reactor, incomplete mixing or short residence time will also produce partially reacted coal macerals. Their presence infers less than optimum liquefaction conditions. Low oil yields may occur in hydrogenation runs that produce residues with high proportions of this residue category.

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Fig.1

Partially reacted vitrinite particle with vesicles and hydrogenation rims at margin and along bedding planes; batch hydrogenation of high volatile A bituminous coal at 380°C; reflected light, oil immersion, x300.

Fig.2

Dissolution and separation along bedding of lignite; temperature-staged batch hydrogenation with recycle solvent (275°C for 30 min, then 425°C for 30 min) under H_2 *atmosphere;*
reflected light, oil immersion, x190.

Fig.3

Transition from vitroplast into incompletely reacted cell tissue; batch hydrogenation of Sphagnum/Carex peat at 325°C under H_2/CO *atmosphere;*
reflected light, oil immersion, x350.

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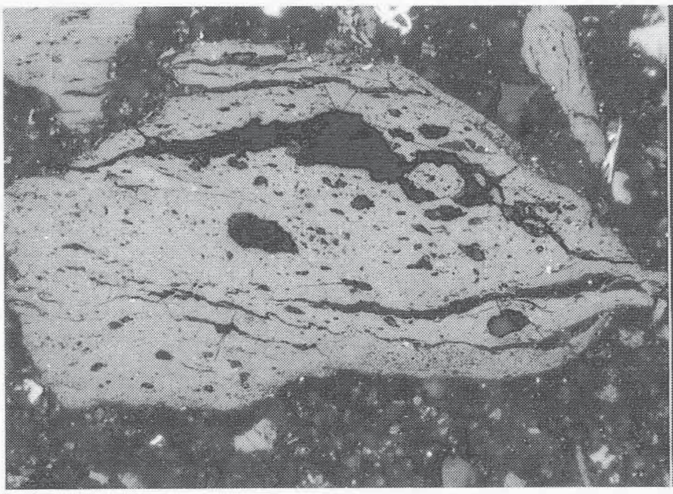

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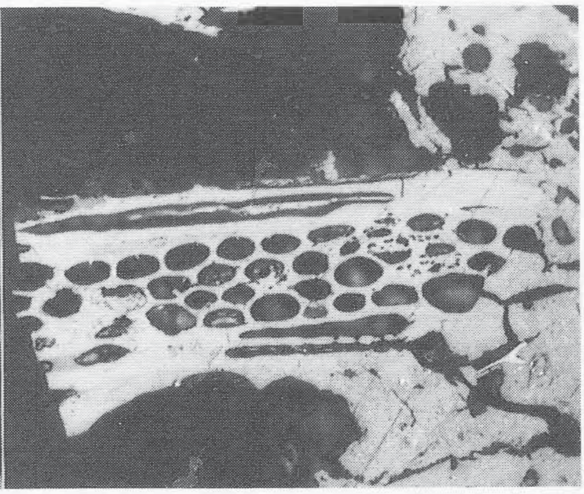

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1993	**International Committee for Coal Petrology** Commission III	Coal Product
SUPPLEMENT	**Classification of Hydrogenation Residues** **VITROPLAST**	R.L.

I - ORIGIN OF TERM

The term "vitroplast" was introduced by Mitchell et al.[1] in 1977 to describe a plastic, or once-plastic, isotropic, pitch-like material derived usually from vitrinite during hydrogenation. The material was first described, but not named, by Davis et al.[2].

Etymology:

VITRO - derived from vitrinite
PLAST - Gr. *plastos*, formed or molded

Synonyms and Analogous Terms:

Carboplast	(Shobaoka and Russell[4])
Coagulant	(Guyot and Diessel[3])
Hydroplast	(Shibaoka and Russell[4])
Plasticoal	(Shibaoka et al.[5])
Plastosphere	(Shibaoka[6])

II - DESCRIPTION

(a) *Morphography*

Vitroplast refers to isotropic, pitch-like material that occurs as spheres and agglomerates in hydrogenation residues. The spheres are usually less than approximately 10 μm in diameter, whereas broad areas (> 100 μm in any dimension) of the agglomerated vitroplast containing inclusions of other residue components can be encountered. Ng[7] recommended a lower size limit of 1 μm for the spheres, with finer grained material being included in the term "*granular residue*". Agglomerated vitroplast has been termed *coagulant* by Guyot and Diessel[3,8] who equated spherical *coagulant* with vitroplast spheres. Ng[7] described agglomerated vitroplast as *"SRC-like"* or *"pitch-like" material,* limiting the term "vitroplast" to those bodies that exhibit a spherical outline. Shibaoka[6] has used the term *"massive vitroplast"* to describe agglomerated vitroplast and *"plastosphere"* to describe isolated spheres of vitroplast.

Shibaoka[10] also has distinguished between *primary vitroplast,* being material derived directly by softening of vitrinite, and *secondary vitroplast* which is derived from the coal fraction dissolved in the vehicle solvent. It is not always possible to distinguish between these two forms of vitroplast. Much of the secondary vitroplast forms by precipitation out of the solvent in response to reduction in pressure and temperature; Shibaoka and Russell[4] have noted that fine-grained plastospheres can be formed in this way. Plastospheres not only agglomerate as a result of mutual coalescence in the plastic state, but also as a result of being cemented together by secondary vitroplast[9,10]; this secondary vitroplast cement has been termed *matrix vitroplast*[6].

Spherical vitroplast bodies containing a single vesicle resemble simple cenospheres, and vesiculated vitroplast, in general, may resemble complex cenospheres. Mitchell et al.[1] noted that simple cenospheres are often associated with spherical vitroplast.

Flow structures have been observed in vitroplast[1,10]. Residual thread-like non-plastic material associated with plastospheres has been reported[6,10,11] the term *vitrofibre* has been used to describe this material[12]. Transmission electron microscopy has revealed some of the fine structure within plastospheres[12]; in many instances the plastospheres exhibited a narrow margin of material of lower electron density than the core.

(b) Physical Properties

The physical properties of vitroplast depend upon reaction conditions, i.e. reaction time, residence time, the nature of the solvent vehicle, etc., and the solvents employed in extraction and sample preparation.

Colour: Reflected light (bright field, oil immersion) - dark grey to pale grey or, rarely, white.

Reflected light (fluorescence, oil immersion) - non-fluorescent under ultraviolet- or blue-light excitation in most instances. Any fluorescence response may reflect the degree of solvent extraction.

Reflectivity: Variable - it can be higher or lower than that of the vitrinite in the untreated feedstock coal, although the spherical vitroplast seen in residues from continuous-flow reactors generally has a reflectance well above the original coal[13]. A vitroplast reflectance value lower than that of the vitrinite from which it developed is thought to be due to a breakdown of the lamellar ordering[1]. Progressively higher vitroplast reflectances have been noted as reaction temperature has been increased. Shibaoka[10] observed an increase in plastosphere reflectance with increase in plastosphere diameter between 5 and 20-30 µm.

Vitroplast has been divided into *low-reflectance vitroplast* ($R_0 < 1.2\%$) and *high-reflectance vitroplast* ($R_0 > 1.2\%$); vitroplast with a reflectivity of 1.2% and above is usually associated with mesophase spheres and semicoke[14,15]. Vitroplast of low reflectance is considered to be amenable to further hydrogenation, whereas that of high reflectance must be regarded as being more or less unreactive[7].

Anisotropy: Isotropic in reflected light.

(c) Chemical Properties and Constitution

The chemical composition of vitroplast will depend on both reaction conditions and the scheme used to process the reaction products.

Solubility: *Vitroplast* is insoluble in n-pentane and n-hexane. It is partially soluble in benzene or toluene, and almost completely soluble in pyridine or tetrahydrofuran. It follows that vitroplast consists of a mixture of asphaltenes (benzene/toluene-soluble material) and preasphaltenes (benzene/toluene-insoluble and pyridine/tetrahydrofuran-soluble material).

Shibaoka[6] reported that plastospheres of higher reflectance are insoluble in benzene, i.e. they consist primarily of preasphaltenes. On the other hand, lower reflecting plastospheres, which in this instance were the finer grained plastospheres, were partially soluble in benzene, i.e. they consisted primarily of asphaltenes.

Under the microscope vitroplast has been observed to partially dissolve in the immersion oil used in incident-light microscopy. This may reflect incomplete solvent extraction of the residue sample. The immersion oil may react with vitroplast to impart a greenish yellow autofluorescence.

III - MODE OF FORMATION

Vitroplast is a thermoplastic, isotropic, n-pentane- or n-hexane-insoluble coal-derived material formed during hydrogenation with or without the addition of inorganic catalysts. It has been recognized by many authors that both low-reflecting inertinite and liptinite may contribute to vitroplast[1,7,10]; however, the bulk of vitroplast is derived from vitrinite directly as primary vitroplast, or indirectly, by precipitation, as secondary vitroplast. Vitroplast is produced during the hydroliquefaction of all ranks of coal below low volatile bituminous; Kalkreuth and Chornet have noted its presence in the residues of peat hydrogenolysis[16].

It is preferable that petrographic terms used for hydrogenation residues be based on optical and other physical and chemical properties, and not be dependent upon the reaction conditions employed. Therefore, vitroplast is an appropriate generic term to describe all of the isotropic, plastic material present in residues. However, Shibaoka and co-workers[4,5,6] had suggested that the term "vitroplast" should be confined to material formed from mainly vitrinite at elevated temperatures and pressures in a hydrogen atmosphere in the presence of an organic solvent. This serves to distinguish vitroplast from *hydroplast*, a material analogous to vitroplast, but which forms from vitrinite during hydrogenation in the absence of an organic solvent, and in the presence of certain metal halides as catalysts, e.g. tin^{II} chloride, zinc chloride[4,5,17]. Hydroplast is relatively low in reflectance; it is partially soluble in benzene or toluene, and completely soluble in pyridine or tetrahydrofuran, indicating that it consists of a mixture of asphaltenes and preasphaltenes. *Carboplast*[4] has a higher reflectance than hydroplast and is insoluble in benzene or toluene. When coarse-grained coal is reacted, hydroplast may form a marginal zone, with the core of the particle remaining unhydrogenated (carboplast). Carboplast also tends to form as a result of carbonization in runs made without a catalyst. In the residue classification scheme employed here, hydroplast and carboplast are sub-types of vitroplast.

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

Vitroplast, together with unaltered coal particles is likely to be a major n-pentane- or n-hexane-insoluble component of coal hydrogenation residues in which hydrogenation has been incomplete and in which the process conditions have not favoured carbonization reactions. The ratio of vitroplast to mesophase spheres and semicoke may be a guide to the balance between competing hydrogenation and carbonization reactions[4,5]. High proportions of vitroplast indicate an inefficient hydrogenation process in terms of the production of liquids and gases; however this may be the desired result if solvent refined products are sought. Concentrations of vitroplast have the potential to detrimentally affect filtration[1].

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Fig.1

Vitroplast derived by melting of vitrinite in Carboniferous high volatile A bituminous coal (primary vitroplast); batch hydrogenation at 425°C in naphthalene under H_2 atmosphere; reflected light, oil immersion, x265.

Fig.2

Vitroplast derived by melting of vitrinite in Carboniferous high volatile C bituminous coal (primary vitroplast); batch hydrogenation at 325°C in tetralin under N_2 atmosphere; reflected light, oil immersion, x 305.

Fig.3

Spheres of primary vitroplast (plastospheres) derived by melting of vitrinite and semifusinite in Australian semifusinite-rich subbituminous Callide coal; batch hydrogenation at 400°C in tetralin under N_2 atmosphere;
reflected light, oil immersion, x230.

Fig.4

Vitroplast filling cell lumina of fusinite in Sphagnum/Carex peat; batch hydrogenation at 350°C under H_2/CO atmosphere;
reflected light, oil immersion, x350.

Fig.5

Rim of low-reflecting vitroplast (hydroplast) surrounding core of anisotropic semicoke in unextracted residue of high volatile A bituminous coal; temperature-staged batch hydrogenation without solvent (275°C for 30 min, then 425°C for 30 min) under H_2 atmosphere, with sulphided Mo catalyst;
reflected light, oil immersion, x450.

Fig.6

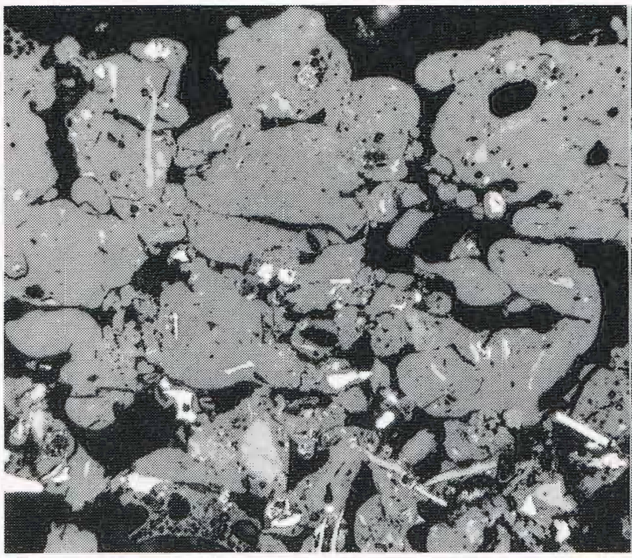
Zone of low-reflecting vitroplast (hydroplast) surrounded by high-reflecting vitroplast (carboplast) and anisotropic semicoke in unextracted residue of high volatile A bituminous coal; conditions as for Fig.5;
reflected light, oil immersion, x430.

Fig.7

Area of remnant isotropic secondary vitroplast surrounded by zone which has been converted to anisotropic secondary semicoke; reactor solid from pilot-plant processing of Illinois bituminous coal (solvent-refined coal mode);
reflected light, partially crossed polars, oil immersion, x845.

Fig.8

Vitroplast matrix with spheres of mesophase semicoke in residue from high volatile A bituminous coal; batch hydrogenation at 400°C under H_2 atmosphere;
reflected light, oil immersion, x215.



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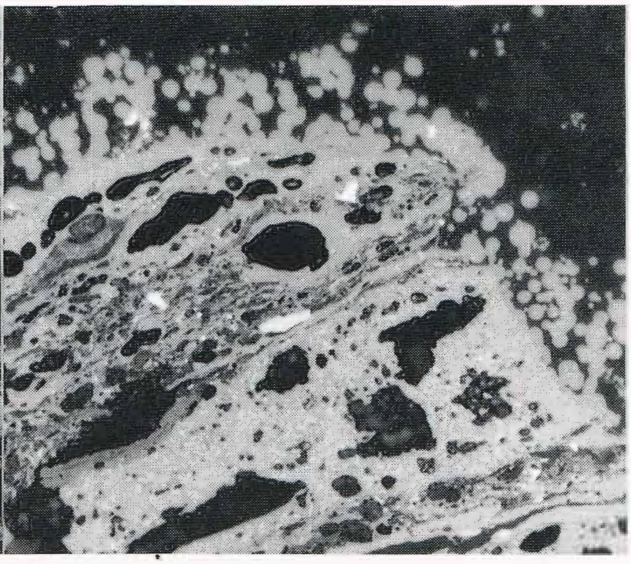

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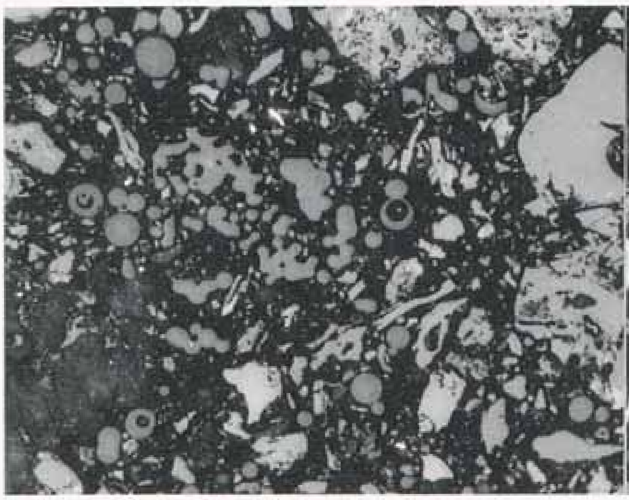

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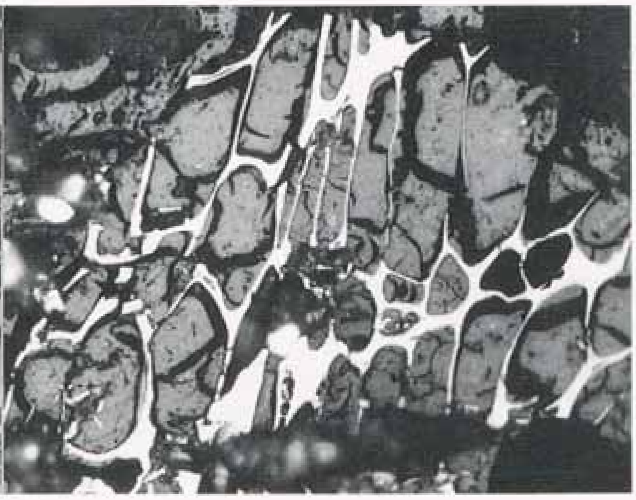

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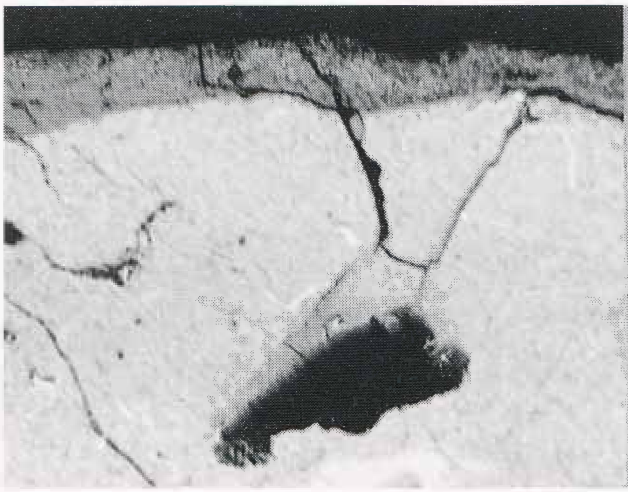

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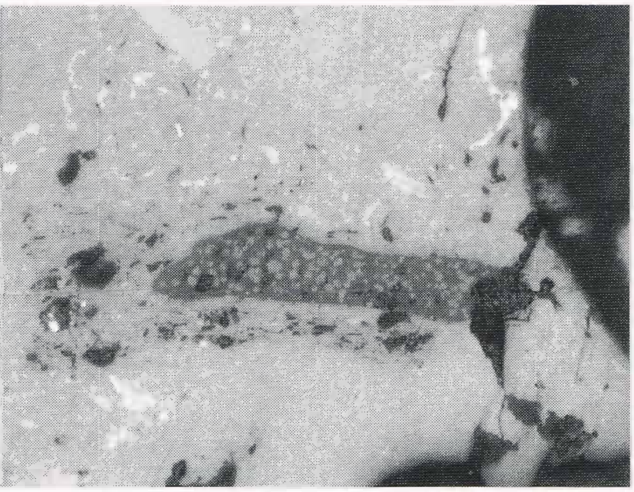

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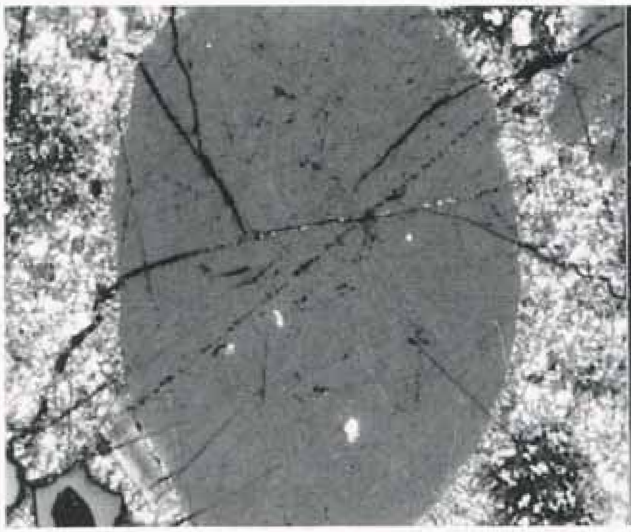

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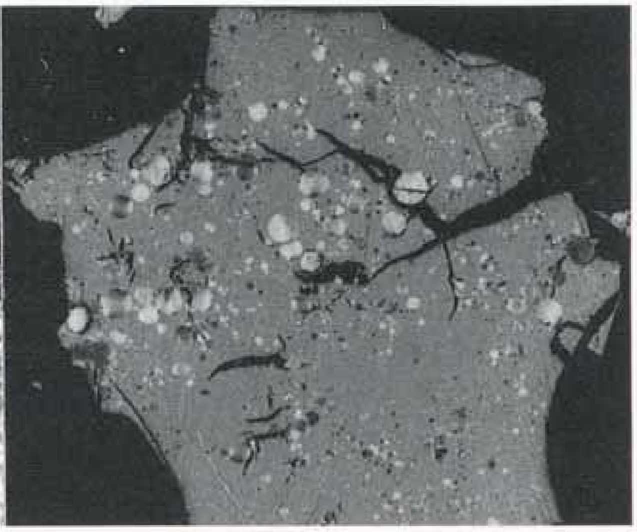

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1993	**International Committee for Coal Petrology** Commission III	Coal Product
SUPPLEMENT	**Classification of Hydrogenation Residues** **CENOSPHERE**	R.L.

I - ORIGIN OF TERM

The term "cenosphere" has been used by Davis et al.[1] to describe thin-walled, isotropic, hollow spheres of vitrinite-derived material observed in coal hydrogenation residues. It was first used as a morphological term by Newall and Sinnatt[2] to describe the products of rapid heating of coal particles in an inert atmosphere at temperatures of 600°C and above. In combustion studies the term has been used to describe structures formed from both organic and inorganic sources.

Etymology: CENOS - Gr. *cenos*, empty

II - DESCRIPTION

(a) *Morphography*

As originally employed in the description of particles produced by rapid heating of pulverized coals, cenospheres are reticulate, hollow spheres consisting of ribs, or frames, of opaque material enclosing thin films, or windows, of transparent material. Other details of their morphography are to be found in the literature[2-6]. Mitchell et al.[6] reported that hydrogenation residues could contain both *complex cenospheres* (with reticulate structures akin to the lacy cenospheres of Lightman and Street[4], or *simple cenospheres* composed of only one or a few vesicles). Attention has been drawn to the fact that simple cenospheres are often in close association with spherical *vitroplast*[6]. Problems may arise in distinguishing between vesiculated vitroplast and cenospheres, in particular when the vitroplast exhibits thin vesicle walls.

(b) Physical properties

Colour: Reflected light (bright field, oil immersion) - pale grey, white or yellow.

Reflected light (fluorescence, oil immersion) - nonfluorescent under ultraviolet- or blue-light excitation.

Reflectivity: Variable - for the most part greater than that of the vitrinite component of the untreated feedstock coal. Similar to or greater than that of associated vitroplast.

Anisotropy: Isotropic or anisotropic.

(c) Chemical Properties and Constitution

Cenospheres may represent carbonized material and, as such, are assumed to be condensed and highly aromatic. This is most likely to be the case with anisotropic cenospheres. Isotropic cenospheres may have similar structure to devolatilized vitroplast.

Solubility: Insoluble in hexane and benzene. Some cenospheres are insoluble in pyridine and tetrahydrofuran.

II - MODE OF FORMATION

Mitchell et al.[6] proposed the following mode of formation of cenospheres during hydrogenation based on examination of residues from a continuous-flow hydrogenation reactor. Vitroplast, formed by the softening of vitrinite, undergoes devolatilization and expansion at higher temperatures to form cenospheres. The rate of gas evolution, particle size and the plasticity of the vitroplast presumably influence the morphology of the resulting cenosphere. The plasticity and reflectance of the vitroplast depends on its degree of carbonization and hydrogenation. The rate of gas evolution is a function of heating rate. Cenosphere development is most evident in the liquefaction residues of coals in the rank range high volatile B to medium volatile bituminous[7].

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

Cenospheres are most likely to develop in high-temperature reactors with relatively high heating rates and, possibly, relatively short residence times. At an early stage of liquefaction, the bloating of vitroplast into highly porous cenospheres may contribute to the dissolution of coal by providing a large surface area of an intermediate plastic phase in which the molecular structure has been loosened by depolymerization. However, if reaction conditions are conducive to a recombination of thermally ruptured bonds, it is unlikely that the resulting cenospheres will be readily hydrogenated[8]. High-reflecting and anisotropic cenospheres are evidence that carbonization reactions dominated over hydrogenation reactions.

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Fig.1

Simple cenospheres derived from high volatile C bituminous coal; residue from batch hydrogenation at 425°C in tetralin N_2 atmosphere; reflected light, oil immersion, x1490.

Fig.2

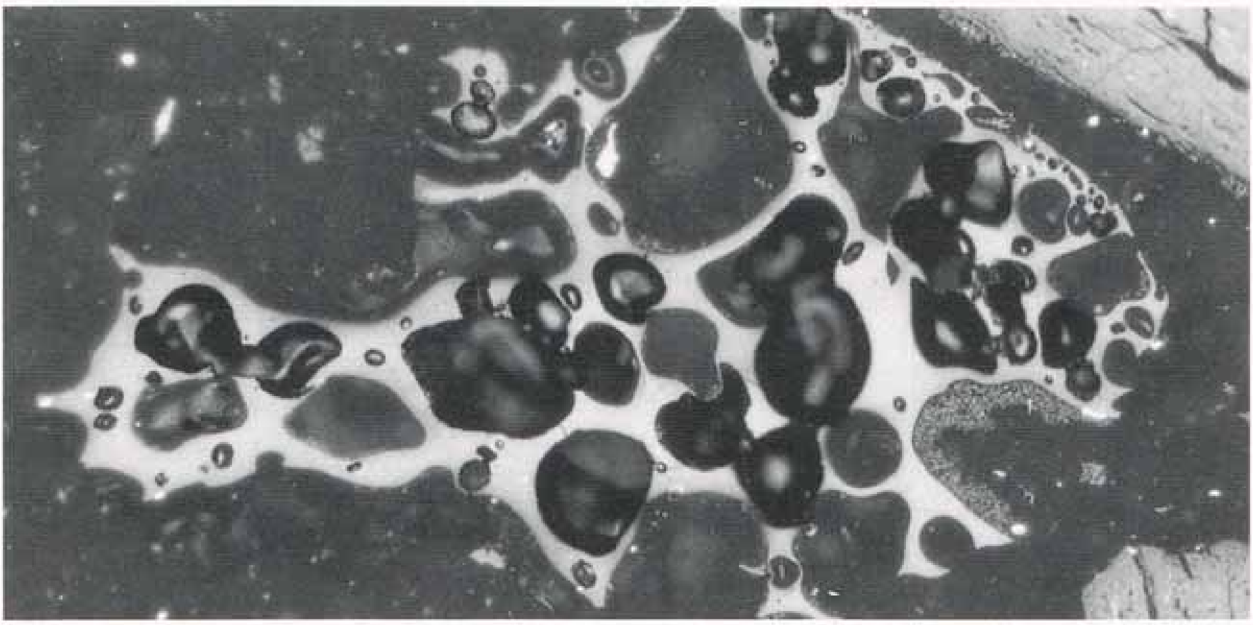
Complex cenosphere in vitroplast matrix; residue of subbituminous coal from batch hydrogenation at 400°C in tetralin; reflected light, oil immersion, x340.

Fig.3

Thin-walled complex cenosphere; residue of Illinois bituminous coal from pilot-plant hydroprocessing (solvent-refined coal mode); reflected light, oil immersion, x1015.

Fig.4

Thick-walled complex cenosphere; residue of subbituminous coal from batch hydrogenation at 400°C in tetralin; reflected light, oil immersion, x410.



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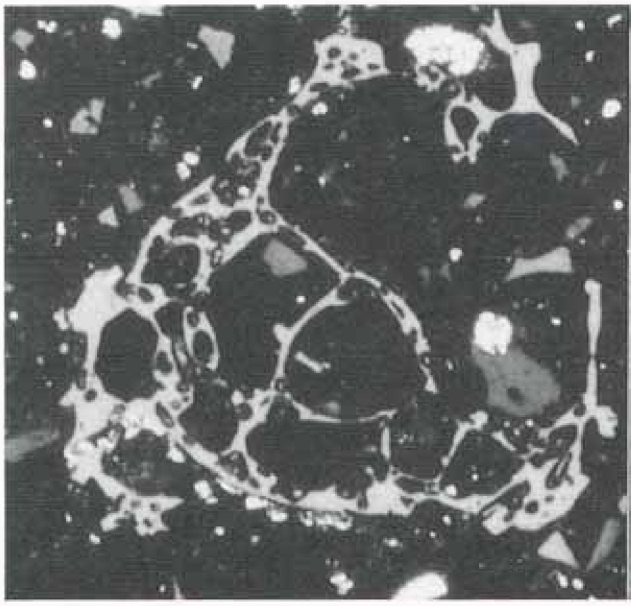

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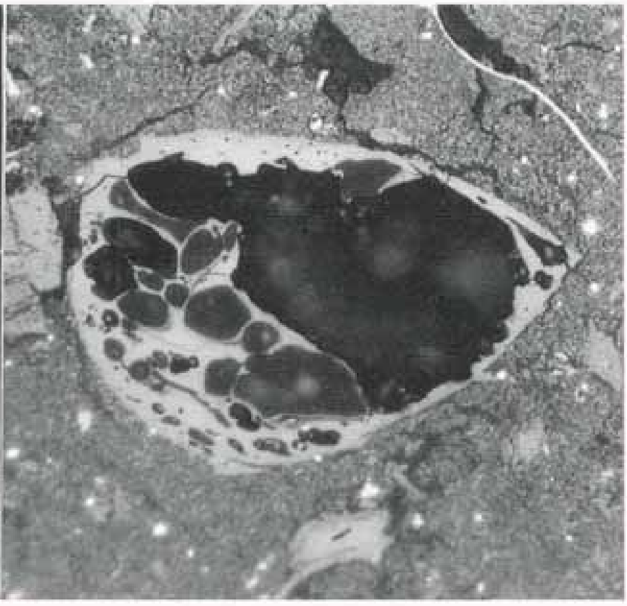

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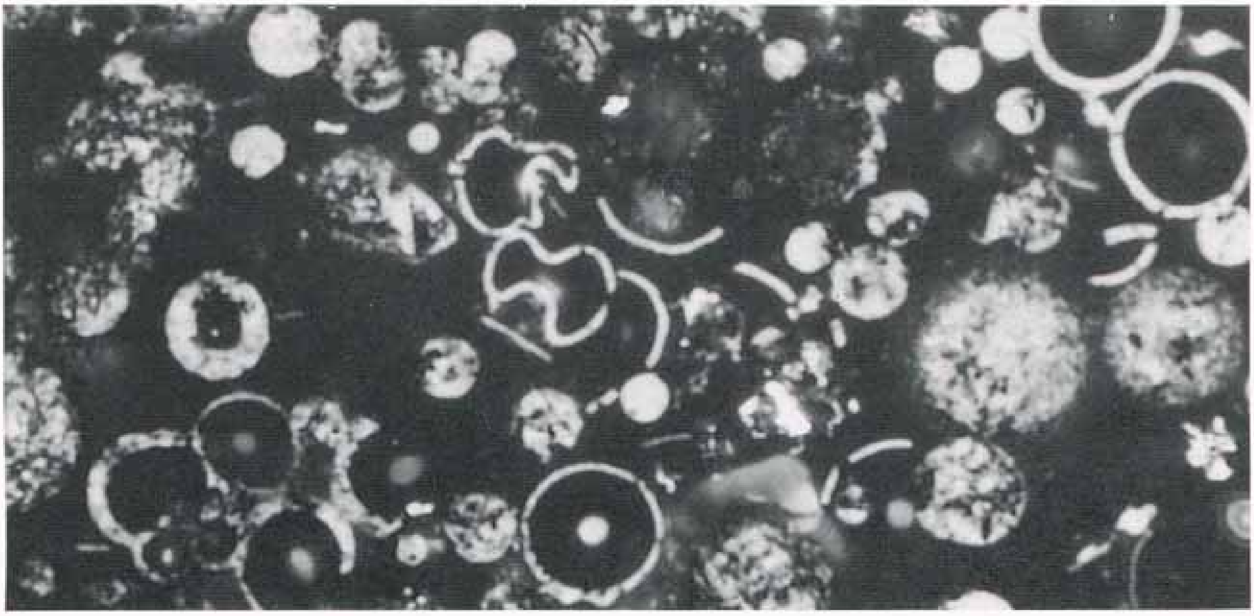

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1993	**International Committee for Coal Petrology** Commission III	Coal Product
SUPPLEMENT	**Classification of Hydrogenation Residues** **GRANULAR RESIDUE**	R.L.

I - ORIGIN OF TERM

Mitchell et al.[1] used the term to describe a mixture of finely dispersed carbonaceous material and alumino-silicate particles in coal hydrogenation residues.

II - DESCRIPTION

(a) *Morphography*

Submicrometre sized carbonaceous spheres or irregular bodies which may be interspersed with plate-like alumino-silicates. Ng[2] suggested that granular residue may be the submicrometre equivalent of vitroplast, with minerals or SRC-like material dispersed between the carbonaceous spheres.

(b) *Physical Properties*

Colour: Reflected light - ranges from grey to white. The fine size of the particles can result in their appearing coloured, especially reddish brown.

Reflectivity: The reflectance ranges from that of vitrinite to that of inertinite. However, it has been suggested that the brassy yellow coloured material (highly reflecting) be referred to as *carbon black*[2].

(c) *Chemical Properties*

Ng[2] has suggested that the dark grey coloured material which is dissolved by immersion oil (dimethyl phthalate) contains asphaltenes, whereas that which is insoluble contains preasphaltenes or carbonized material. Qualitative electron probe analysis of one residue by Mitchell et al.[1] indicated that a major component could be finely dispersed clays.

III - MODE OF FORMATION

Mitchell et al.[1] described how granular residue can have several different modes of formation including organic and inorganic sources. Where granular residue occurs in association with spherical vitroplast, a similar origin may be assumed for the submicrometre and the larger spheres. The same authors also observed granular residue resulting from the hydrogenation of sporinite and low-reflecting vitrinite; they noted the resemblance between this development and that of micrinite during coalification as discussed by Teichmüller[3]. Other granular residue appears to be finely divided inertinite which has resisted hydrogenation. Finally, a significant proportion of some granular residues appear to be clay minerals which have been dispersed as submicrometre particles.

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

In general, larger proportions of a granular residue component are likely to indicate that hydrogenation has been more effective in converting coals into liquids.

Large concentrations of any submicrometre component of hydrogenation product streams have been observed to have a detrimental effect on most of the common means of separating residues from the liquid products, i.e. filtration, centrifugation, or critical solvent deashing.

References

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Fig.1

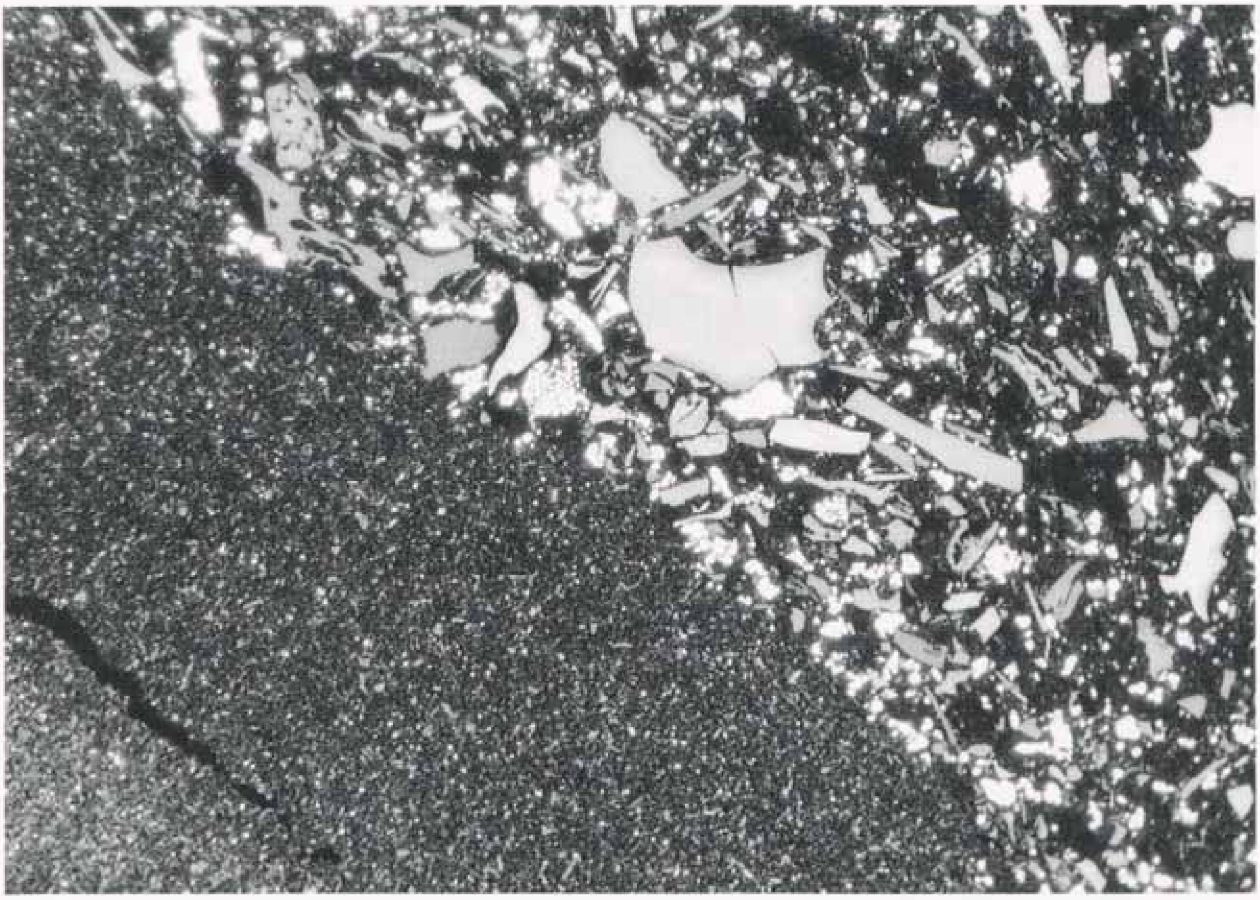
Agglomerate of granular residue (bottom left) from residue of pilot-plant hydroprocessing of West Kentucky bituminous coal (solvent-refined coal mode); apparently much of the granular residue consists of very fine vitroplast spheres;
reflected light, oil immersion, x400.

Fig.2

Granular residue from high volatile A bituminous coal; batch hydrogenation at 400°C under H_2 atmosphere;
reflected light, oil immersion, x215.

Fig.3

Inertinite and sulphide mineral particles in granular residue matrix; pilot-plant hydroprocessing of Indiana bituminous coal (solvent-refined coal mode);
reflected light, oil immersion, x290.



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1993	**International Committee for Coal Petrology** Commission III	Coal Product
SUPPLEMENT	**Classification of Hydrogenation Residues** **PRIMARY SEMICOKE**	R.L.

I - ORIGIN OF TERM

In the context of coal hydrogenation, primary semicoke is defined as carbonized material derived directly from unhydrogenated coal. It is distinct from secondary semicoke[1] which is derived largely through the mesophase mechanism from a fluid phase. Primary semicoke may be derived either from vitrinite or inertinite.

II - DESCRIPTION

(a) Morphography

Depending upon the rank of coal processed, primary semicoke derived from vitrinite may be either isotropic or exhibit a fine-grained anisotropic texture. That which has been derived from inertinite usually is isotropic[1]. The sizes of anisotropic mosaics in primary semicoke tend to be smaller than those of secondary semicoke.

(b) Physical properties

Colour: Reflected light (oil immersion) -- grey to light yellow.

Reflectivity: Greater than that of vitrinite in the feed coal.

III - MODE OF FORMATION

During the initial, thermal, stage of coal hydrogenation, the linkages between aromatic ring systems tend to be ruptured. Where hydrogen deficiency precludes the formation of vitroplast or coal liquids and gases, repolymerization is favoured, resulting in the formation of primary semicoke when temperature increases[1,2].

In direct coal liquefaction processes, hydrogenation and carbonization reactions are competing. Primary semicoke is a product and indicator of the latter process. Because hydrogen availability may be different for individual particles moving through a reactor, and even for different zones within a single particle, the overall petrographic characteristics of a residue have to be considered in evaluating the balance between competing hydrogenation and carbonization.

Because the hydrogenation of inertinite requires higher temperatures than vitrinite, it follows that some carbonization will be involved[1].

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

The presence of primary semicoke, like that of secondary semicoke, indicates that there was incomplete conversion of the coal due to lack of hydrogen availability or to excessive temperature.

References

1. Shibaoka, (M.) and Heng, (S.). Model for the coal hydrogenation process and its applications. Fuel, 63, (1984), p. 174-177.

2. Shibaoka, (M.), Russell, (N.J.) and Bodily, (D.M.). Coal liquefaction model: microscopic examination of solids from metal halide catalysed coal hydrogenation experiments. Fuel, 61, (1982), p. 201-203.

Fig.1

Particle of ulminite from subbituminous coal displays fine-grained anisotropy but has maintained its original shape and cell structure; the rim of the particle has a somewhat coarser anisotropic texture than the interior, probably reflecting a greater influence of hydrogenation; residue from pilot-plant hydrogenation process (solvent-refined coal mode); reflected light, partially crossed polars, oil immersion, x775.

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1993

SUPPLEMENT

International Committee for Coal Petrology

Commission III

Classification of Hydrogenation Residues

SECONDARY SEMICOKE

Coal Product

R.L.

I - ORIGIN OF TERM

Shibaoka and Heng[1] defined secondary semicoke produced during coal hydrogenation as being derived from mesophase or partially hydrogenated anisotropic inertinite. An earlier paper[2] had given the somewhat more restrictive definition of material derived from mesophase formed in the hydrogenated products of experiments without a liquid vehicle but with metal halide catalyst. Because of the importance of mesophase-derived semicoke formation during hydrogenation, the broader definition is adopted here.

Brooks and Taylor[3] described optically anisotropic spheres and the mosaic formed during the fluid-phase carbonization of coal tar pitch and some organic compounds. Later, the same authors[4] applied the term "mesophase"[5] to the spheres and mosaics existing before solidification into semicoke.

In 1975, Walker et al.[6] observed that "coking" in the Wilsonville, Alabama SRC-I pilot- plant had taken place by way of the mesophase mechanism. Since then mesophase-derived semicoke has been identified as an important component of residues resulting from laboratory and pilot-plant scale coal hydrogenation experiments.

It is not possible to make a microscopic distinction between mesophase which has solidified into semicoke following continued heat treatment, and that which has solidified through cooling. In fact, it has been common but incorrect practice to refer to all such anisotropic carbonaceous material in hydrogenation residues as mesophase. Nevertheless, some of the mosaic-textured material in residues appears not to be rigid semicoke; it can be liquefied or undergo molecular rearrangement leading to modification of the optical characteristics[7].

Synonyms and Analogous Terms:	Mesophase	(Brooks and Taylor[3,4])
	Secondary Semicoke	(Shibaoka et al.[2])
	Intermediate Semicoke	(Shibaoka et al.[2])

II - DESCRIPTION

(a) Morphography

Mesophase spheres that have been observed in the carbonized residues of hydrogenated coals[8] are discrete anisotropic spherical bodies ranging up to several tens of micrometres. The coalescence of spheres during the plastic phase may give rise to larger spheres or irregularly shaped coalesced mesophase. Mosaic sizes within the coalesced mesophase or the resulting semicoke may range from a fraction of a micrometre to several tens of micrometres[8,9]; however, secondary semicoke usually has a medium- coarse-grained anisotropic texture (in contrast to the fine-grained or isotropic texture of primary semicoke[1]. Flow anisotropy with isochromatic areas greater than 50 µm in length also may develop[9].

(b) Physical Properties

Colour: Reflected light (oil immersion) -- grey to yellow

Reflectivity: Can range between that of vitrinite to that of semicoke. R_0max values of 2 to 7.2 have been reported[8,10].

(c) Chemical Properties

Condensation reactions convert the more reactive hydrocarbons in the isotropic pitch phase to larger, planar polynuclear aromatic species. These compounds separate out from the pitch in partly ordered molecular assemblages, the mesophase, which, in contrast to the remnant pitch, is essentially insoluble in solvents. The mesophase is highly absorbing in the UV, visible and IR regions[4]. In general, the more aromatic the pitch, the greater is the degree of plasticity developed by the resulting mesophase; the aromatic molecules have relatively low reactivity in comparison to heterocyclic and substituted, unsaturated, non-planar molecules[11].

The highly functional components in a coal liquid display the greatest propensity to form semicoke via the mesophase mechanism[9]. More extensive hydrogenation results in the development of lesser amounts of anisotropic carbon, but larger mosaic and domain sizes[9,12].

III - MODE OF FORMATION

Mesophase is a plastic, polymeric, anisotropic stable phase intermediate between an isotropic pyrolysate, such as coal-tar pitch or solvent-refined coal (SRC), and solid anisotropic semicoke. It is structurally similar to a transient nematic liquid crystal phase in which only weak forces, such as Van der Waals, maintain the parallel orientation of the molecules. However, once chemical bonding occurs between the molecules, the possibility of dissociation is lost[11]. With increasing temperature or time, the mesophase becomes increasingly viscous through a process of polymerization until rigid semicoke results.

In coal hydrogenation processes, mesophase may form from vitroplast, material previously liquefied, or recycle solvent, beginning at temperatures about 400°C.

Secondary semicoke formation from vitroplast or the liquid reaction products represents the dominance of condensation reactions over hydrogenation reactions in the system, after an initial hydrogen-sufficient stage. The presence of anisotropic structures indicates that the coal has undergone solvation and/or hydrogenation prior to carbonization[2].

The process of mesophase formation described here is temperature and time dependent. It cannot be reversed by simply lowering the temperature. However, under certain conditions, mesophase can be reliquefied if sufficient hydrogen becomes available[1].

The development of anisotropy in inertinite during hydrogenation is different from that involved in the case of fluid materials. The differences are described in detail by Shibaoka and Heng[1].

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

In coal hydrogenation processes, the formation of mesophase-derived semicoke has the deleterious effects of:

1) lowering the yield of liquid products, and

2) interfering with or causing blockage in the flow system of hydrogenation plants.

The occurrence of mesophase-derived secondary semicoke is an indicator of hydrogen deficiency or of excessive temperatures within the reactor.

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Fig.1

Secondary semicoke consisting of coalesced mesophase spheres; batch hydrogenation at 400°C of high volatile A bituminous coal under H_2 *atmosphere;*
reflected light, oil immersion, x215

Fig.2

Secondary semicoke consisting of partially coalesced mesophase spheres; reactor solids from pilot-plant hydroprocessing of subbituminous coal (solvent-refined coal mode);
reflected light, oil immersion, x365.

Fig.3

Secondary semicoke (anisotropic) derived from vitroplast; batch hydrogenation of high volatile A bituminous coal at 475°C;
reflected light, oil immersion, x300.

Fig.4

Secondary semicoke (anisotropic) formed through the mesophase mechanism, containing areas of unconverted isotropic vitroplast; reactor solids from pilot-plant hydroprocessing of subbituminous coal (solvent-refined coal mode);
reflected light, oil immersion, x330.

Fig.5

Reactor solid of secondary semicoke nucleated on unaltered particle of calcite; note welding at margins of reactor-solid grains; pilot-plant hydroprocessing of high volatile bituminous coal (solvent-refined coal mode);
reflected light, oil immersion, x225.

Fig.6

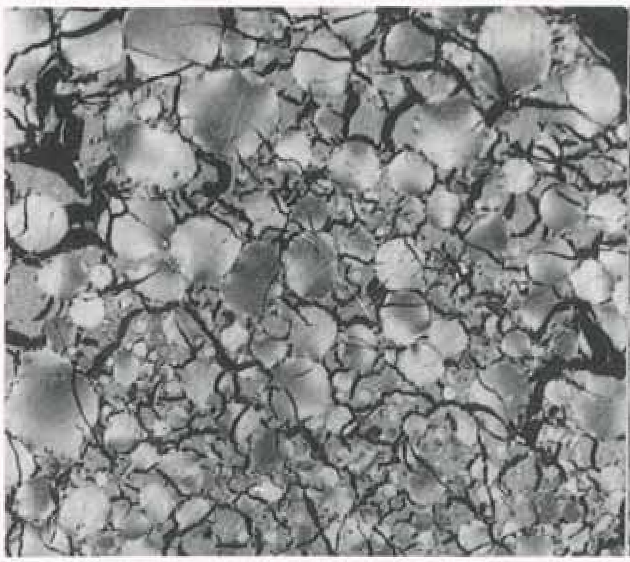
Coalesced mesophase-derived secondary semicoke cementing reactor-formed spheres of carbonate/pyrrhotite; reactor solids from pilot-plant hydroprocessing of subbituminous coal (solvent-refined coal mode);
reflected light, oil immersion, x220.

Fig.7

Secondary semicoke (anisotropic); residue from batch hydrogenation at 400°C under H_2 *atmosphere of Victorian brown coal;*
reflected light, oil immersion, x1400.

Fig.8

Reactor-solid grain showing separate phases of secondary semicoke deposition; pilot-plant hydroprocessing of subbituminous coal (solvent-refined coal mode);
reflected light, oil immersion, x180.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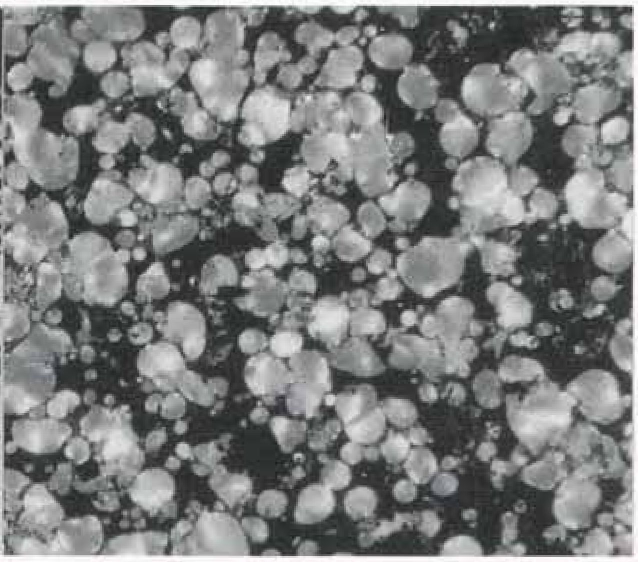
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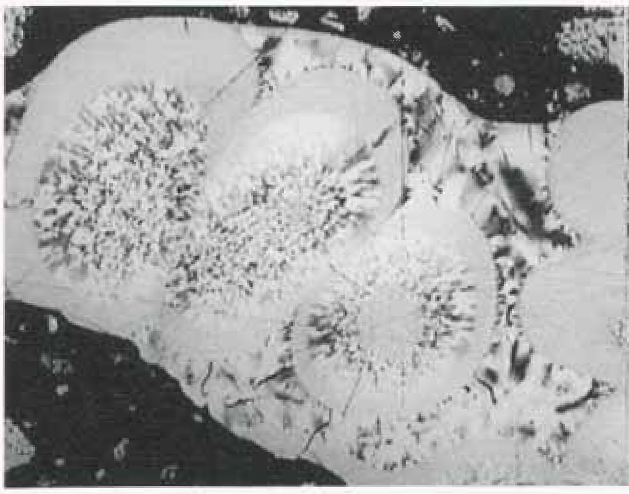
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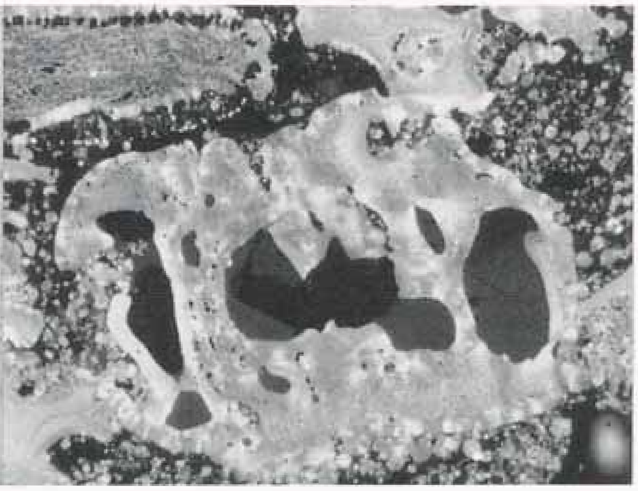
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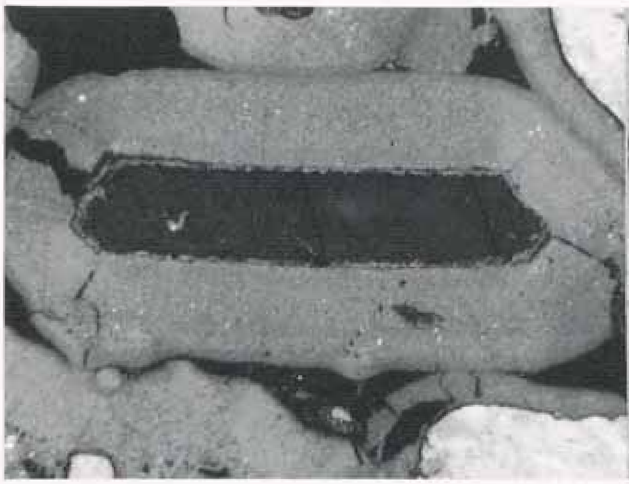
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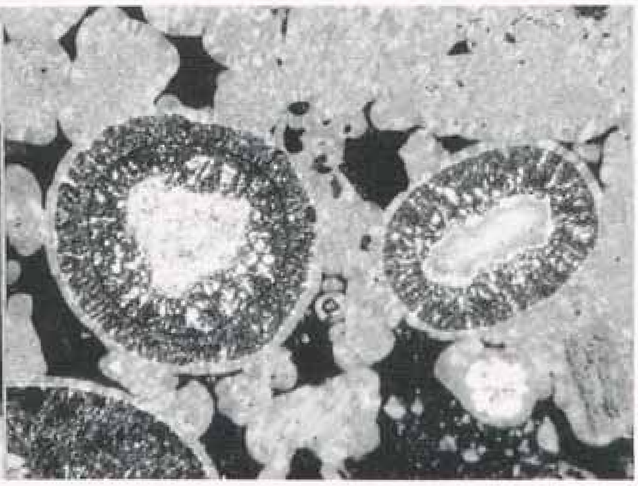
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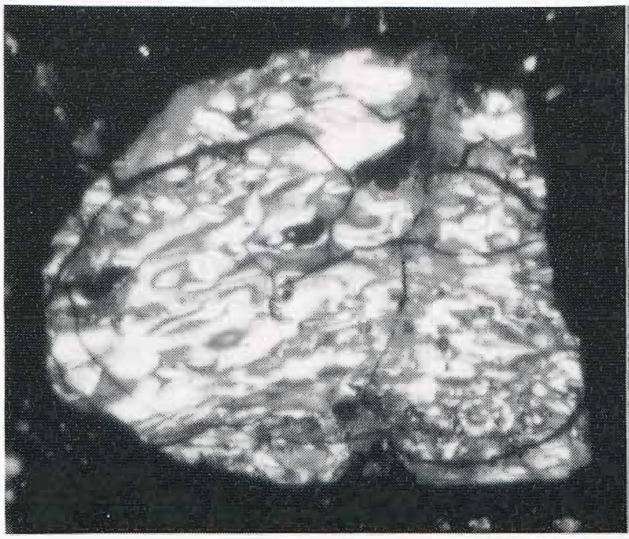
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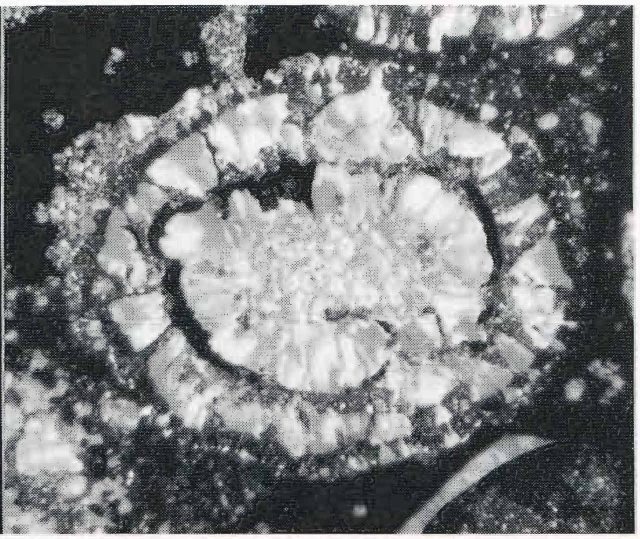
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1993 SUPPLEMENT	International Committee for Coal Petrology Commission III Classification of Hydrogenation Residues PYROLYTIC CARBON	Coal Product R.L.

I - ORIGIN OF TERM

The term has been used to describe the concentrically structured carbonaceous material deposited from the gas phase by the thermal cracking of volatile matter from coal. In the laboratory, this material has been produced at temperatures of 500°C and above[1]. The same term has been used to describe a component of liquefaction residues by Shibaoka and co-workers[2-3] and Steller et al.[4].

Etymology: PYRO - Gr. *pyr*, fire
LYTIC - Gr. *lytikos*, loosing

Synonyms and Analogous Terms:
Graphitoid Sphaerolith = gas graphite[1]
Graphite (Diessel and Guyot[5])
Carbon Black (Ng[6,7])

II - DESCRIPTION

(a) Morphography

Pyrolytic carbon can occur as concentrically structured bodies or as layers (1 to 10 µm thick), lining or filling cavities. Under crossed nicols each sphere shows a Brewster cross.

Carbon black[6,7] is a submicrometre spherical form of pyrolytic carbon which is too fine to be readily resolved by optical microscopy; its morphology may be determined by electron microscopy.

(b) Physical Properties

The reflectance and anisotropy of the pyrolytic carbon increase with temperature of formation. Shibaoka et al.[2,3] have reported pyrolytic carbon produced in laboratory hydrogenation experiments as having very high reflectances (R_0max = 8.5-17.0%).

III - MODE OF FORMATION

Pyrolytic carbon is formed from the chemical cracking of volatile matter derived from carbonaceous matter. In hydrogenation processes, both liquid and gaseous products could provide volatiles for cracking.

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

Pyrolytic carbon can be generated during hydrogenation in a manner similar to the heating of coal to temperatures above 300°C in the absence of air, when a proportion of coal is converted to volatile matter[8]. This volatile matter is thermally cracked at temperatures greater than 500°C into products which, on cooling, form pyrolytic carbon.

The presence of pyrolytic carbon in hydrogenation reactor blockage material has been reported as an indicator of excessively high temperatures and high gas hold-up. Pyrolytic carbon has been observed in the residues from a laboratory-scale continuous coal hydrogenation reactor and an autoclave even though the nominal reaction temperature was reported as only 450°C; apparently there were localized hot-spots within the reactors[2-4].

Pyrolytic carbons in the original feed probably would be non-reactive during the hydrogenation process.

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Fig.1

Pyrolytic carbon associated with debris of unaltered and altered coal fragments of high volatile bituminous coal; residue from batch hydrogenation at 450°C in recycle solvent under H_2 atmosphere;
reflected light, oil immersion, x310.

1

1993 SUPPLEMENT	International Committee for Coal Petrology Commission III	Coal Product
	Classification of Hydrogenation Residues UNALTERED MINERALS	R.L.

I - ORIGIN OF TERM

Minerals in liquefaction residues have been described extensively in reports by Walker et al.[1,2,3,4] and Ruch et al.[5]. The term includes only those minerals which were present in the feed coal and passed through the liquefaction process with little or no chemical alteration. Physical breakdown in particle size may have occurred. Neo-minerals which have formed from inorganic elements attached to the organic molecular structure of coal are excluded from this category.

II - DESCRIPTION

The principal mineral groups which contribute to unaltered minerals in liquefaction residues are those which occur in coals, namely:

1.	Clay minerals	e.g. illite
2.	Carbonates	e.g. calcite, siderite
3.	Sulphides	e.g. pyrite
4.	Silica	e.g. quartz
5.	Sulphates	e.g. barite
6.	Other minerals	e.g. oxides, phosphates, chlorides, nitrates, zircon

Comparison with the mineralogy of the feed coal should reveal whether the minerals present in the residue have passed through the liquefaction process with or without alteration[7]. Clay minerals tend to become dispersed as very fine-sized particles. Identification under the microscope may be difficult, and other techniques such as XRD and electron microprobe may be needed.

III - MODE OF FORMATION

The mode of formation of this class of inorganic solids generally is unrelated to liquefaction process conditions. Three crystal forms of calcium sulphate (gypsum, bassanite and anhydrite) have been detected in residues by XRD; this change of hydration state may be related to laboratory preparation procedures[7].

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

Because all coals contain some proportion of minerals, even after beneficiation processes such as washing, liquefaction residues will likewise contain mineral matter. The presence of hard, abrasive species such as quartz can lead to wear and abrasion of reactor units. Some minerals may act as catalysts. Others may inhibit agglomeration or the development of mesophase[8]. In combination with carbonaceous phases such as semicoke, mineral matter can contribute to blockages in reactor systems.

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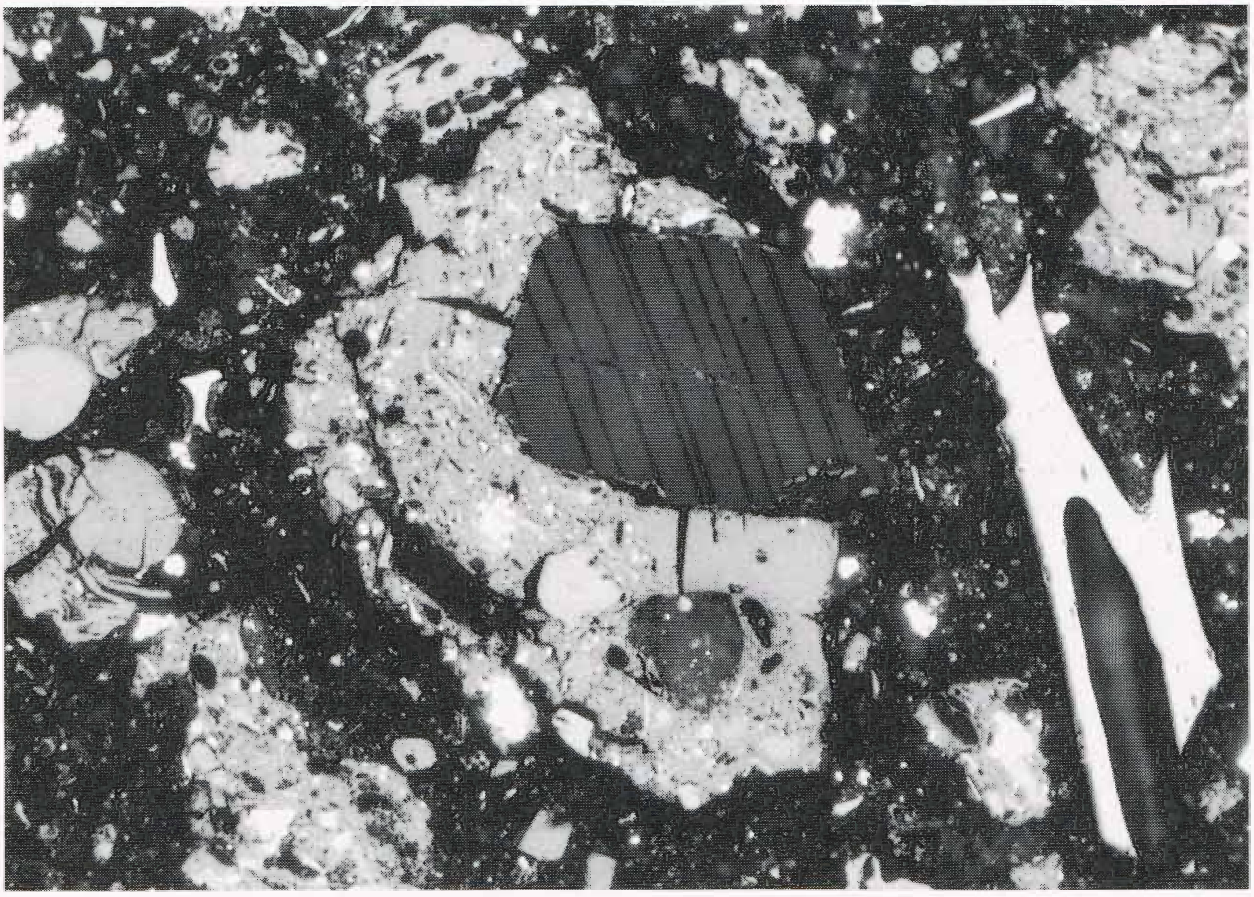
Fig.1

Central particle contains unaltered twinned calcite in matrix of vitroplast with inertinite fragments; residue from batch co-processing at 415°C of high volatile bituminous coal with fraction of natural bitumen under H_2 atmosphere; reflected light, oil immersion, x445.

Fig.2

Remnant quartz grain with inclusions; reactor solid from pilot-plant processing of Kentucky bituminous coal (solvent-refined coal mode); reflected light, oil immersion, x1250.



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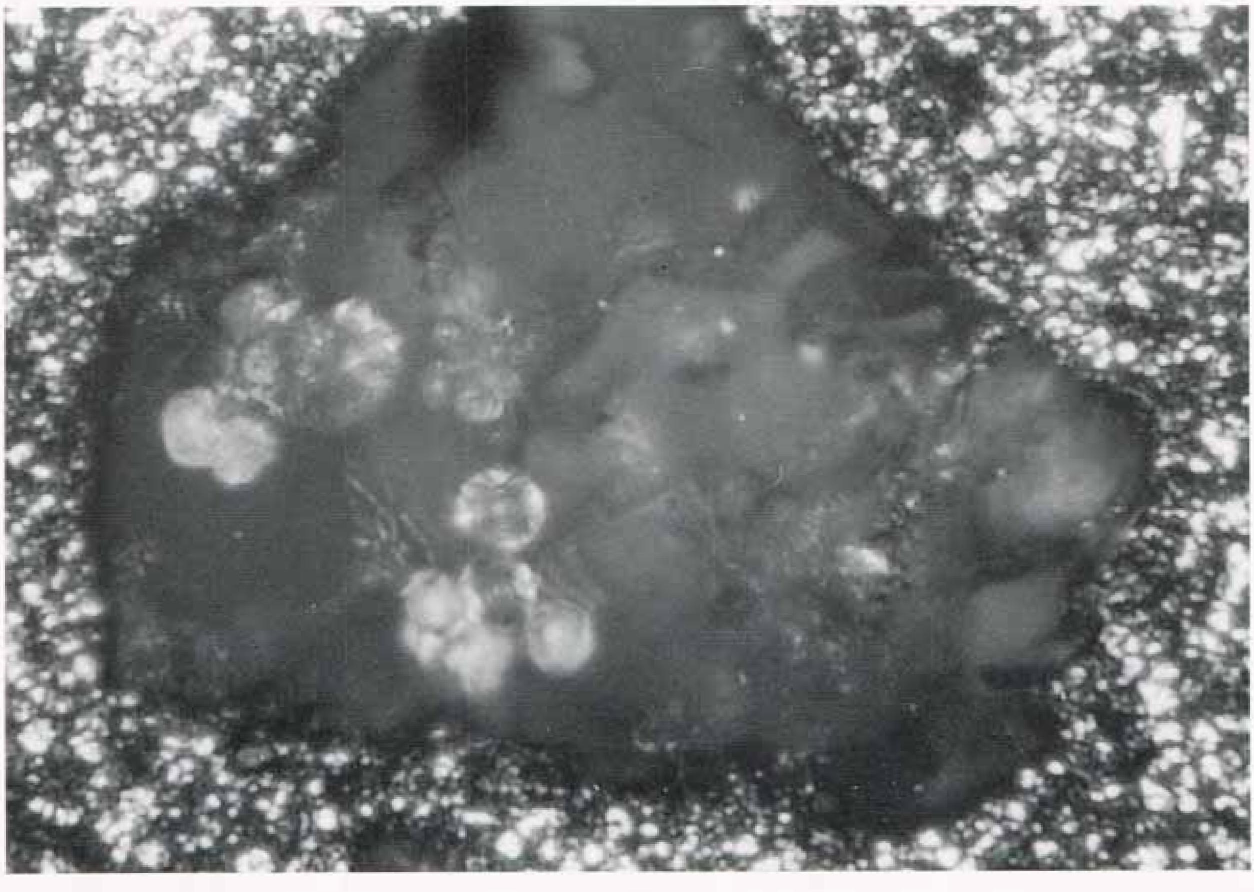

2

1993 SUPPLEMENT	International Committee for Coal Petrology Commission III	Coal Product
	Classification of Hydrogenation Residues ALTERED MINERALS	R.L.

I - ORIGIN OF TERM

Altered minerals refer to inorganic species formed during the hydrogenation of coal by the alteration of pre-existing minerals. Excluded are those minerals resulting from the reaction of carboxyl groups during the processing of low-rank coals, or from additions of organometallic catalysts (see neo-minerals). It is possible that some minor changes in the state of hydration of clays may occur during liquefaction processing[1], but these and the disaggregation of clays into finer sizes are insufficient for classification here as altered minerals.

The only notable mineral so far reported which belongs to this category is pyrrhotite; most of the subsequent information presented here refers to this mineral.

II - DESCRIPTION

Comparison with the mineralogy of the feed coal should reveal whether any of the minerals in a residue have passed through the liquefaction process with or without alteration[1].

Pyrrhotite

Pyrrhotite can be distinguished from pyrite under the optical microscope by its colour, reflectance, anisotropy, and hardness.

(a) Morphography and Crystallinity

Pyrrhotite can be either hexagonal or monoclinic. At liquefaction temperatures, and under hydrogen pressure, isometric pyrite can be expected to convert, at least partially, to hexagonal pyrrhotite and H_2S. At lower temperatures, a fraction of the hexagonal pyrrhotite can transform to monoclinic pyrrhotite, which is thermodynamically stable below about 250°C[2,3].

Common forms of pyrrhotite in reactor solids are tabular crystals, crystal aggregates and finely dispersed grains within aggregates containing other minerals and undissolved macerals. Radiating pyrrhotite crystals can occur as rims around cores of remnant pyrite[1].

(b) *Physical Properties*

Colour: Under oil immersion the colour of pyrrhotite is cream with a faint pinkish brown tint. In contrast, pyrite appears a brilliant yellow white. Pyrrhotite exhibits a very distinct reflectance pleochroism, from a darker red brown to a lighter brownish cream[4,5]. Pyrite displays no pleochroic effect.

Anisotropy: Under crossed nicols pyrrhotite displays a very strong anisotropy from grey blue to yellow grey in oil immersion[4,5]. In contrast, the anisotropy of pyrite generally is unnoticeable or indistinct.

Reflectivity[4,5]: The reflectivity is noticeably lower than that of pyrite seen in the same field of view.

R_ω (air) = 34%; R_ε (air) 0 39%. Compare to R (air) = 54% for pyrite

R_ω(oil) = 21.5%. Compare to R (oil) = 46% for pyrite

Hardness: The polishing hardness of pyrrhotite is medium high, but considerably less than that of pyrite.

	Vickers Hardness number[6]	*Talmage Hardness*[5]
Pyrrhotite	230-318 kg/mm^2	D
Pyrite	1027-1240 kg/mm^2	F

(c) *Chemical Properties*

The composition of pyrrhotite is non-stoichiometric, $Fe_{1-x}S$. The hexagonal form is reported to have 47.8-48.1% of iron (or other metals), whereas the monoclinic is reported to have 46.5% of metals[4].

III - MODE OF FORMATION

Under elevated temperatures and with a hydrogen source (either hydrogen gas or a hydrogen donor solvent such as tetralin) pyrite can be reduced to pyrrhotite. The precise mechanism involved is unclear, but the growth of radiating crystals, indicates that more than simple replacement of the pyrite morphologies is involved.

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

Pyrrhotite is a ubiquitous component of liquefaction residues and reactor solids. Considerable attention has focussed on the possibility that this mineral, because of its defect structure, may behave as a catalyst, increasing conversion to liquids and gases, and improving the product distribution by enhanced generation of hexane-soluble components. Paradoxically, it has also been reported that pyrite or pyrrhotite may catalyse desulphurization of the products[7]. An alternative explanation to the presumed catalytic activity of pyrrhotite in liquefaction is the concept that H_2S, generated through the pyrite-pyrrhotite transformation, acts as the catalyst[8,9].

The significance of the formation of the ferromagnetic monoclinic form of pyrrhotite has been considered in regard to potential magnetic separation of iron-sulfur compounds from liquefaction residual products[3].

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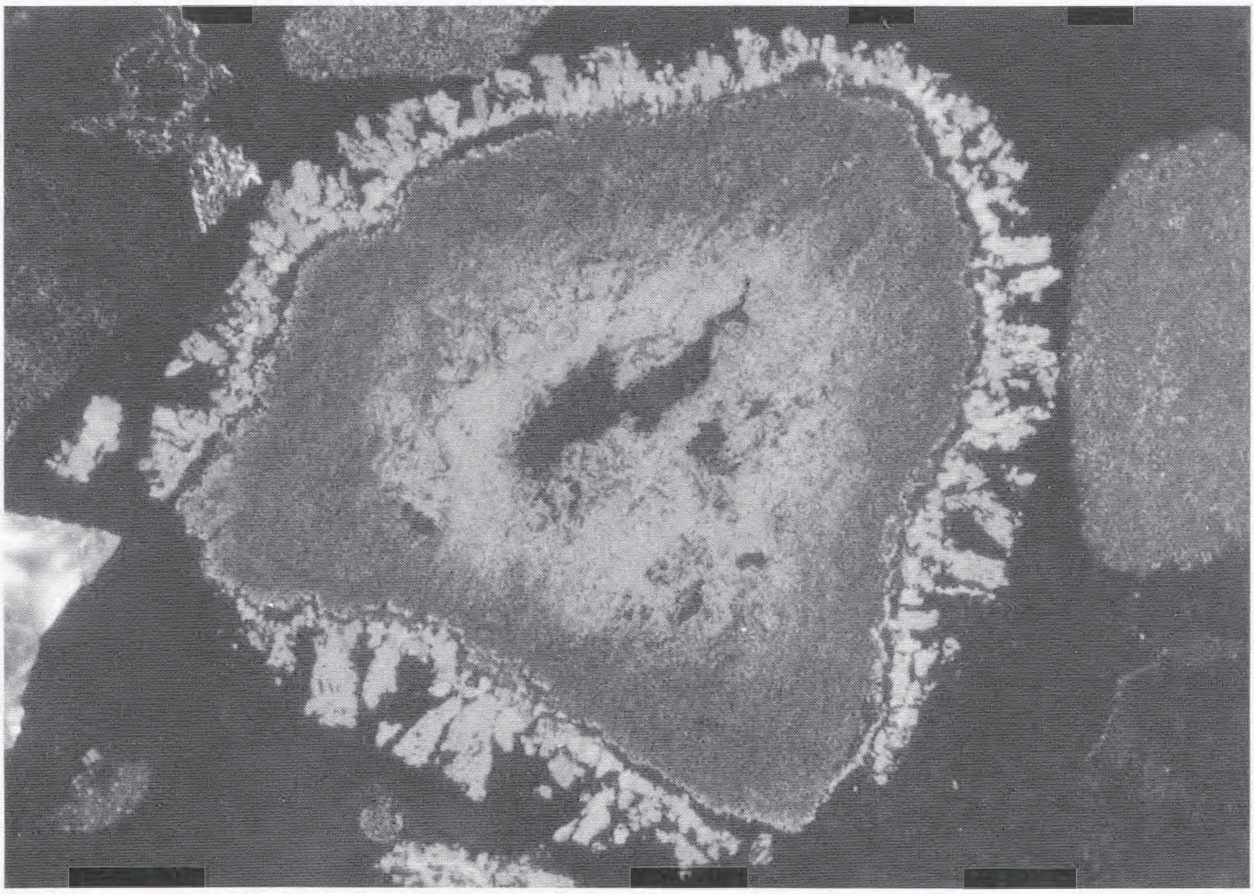
Fig.1

Overgrowth of anisotropic pyrrhotite on isotropic pyrite; reactor solids from pilot-plant processing of Indiana bituminous coal (solvent-refined coal mode); reflected light, partially crossed polars, oil immersion, x480.

Fig.2

Core and radial alignment of pyrrhotite within spherical carbonate reactor solid; pilot-plant hydroprocessing of bituminous coal (solvent-refined coal mode); reflected light, oil immersion, x420.



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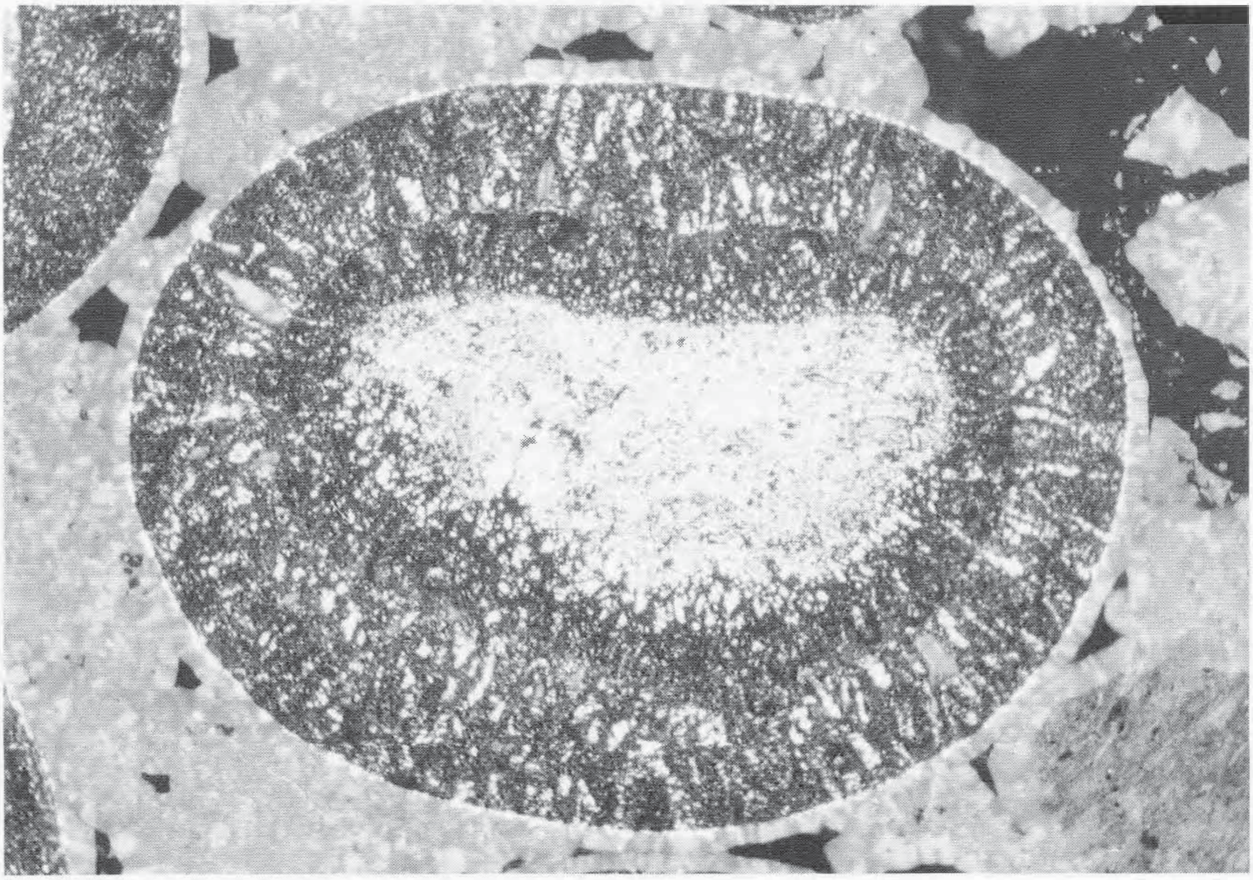

2

1993	**International Committee for Coal Petrology** Commission III	Coal Product
SUPPLEMENT	**Classification of Hydrogenation Residues** **NEO-MINERALS**	R.L.

I - ORIGIN OF TERM

Neo-minerals refer to inorganic mineral species which are formed within the reactor during hydrogenation. They specifically include those minerals formed by the reaction of carboxyl groups during the processing of low-rank coals, but exclude those formed by alteration of previously existing minerals. Neo-minerals also may be formed following the addition of organometallic catalyst materials.

The formation of new minerals during liquefaction has been well documented[1-6]. In addition to optical microscopy, other analytical techniques have been used to determine the nature of neo-minerals in liquefaction residues[1-5].

Neo-minerals are particularly important components in the residues derived from the processing of lignites and subbituminous coals, whose cations associated with carboxylate groups are available to form new carbonate mineral species[1,7-8]. Some calcium sulfate minerals may also be generated during the processing of low-rank coals[1].

Etymology: Neo - Gr; new, recent

II - DESCRIPTION

(a) *Morphography and Crystallography*

Neo-minerals may have readily recognisable crystal form, but frequently carbonate and sulphate species occur as aggregates of fine-grained material (frequently < 1 µm) combined with carbonaceous matter. Identification under the microscope may be difficult, and other techniques such as XRD and electron microprobe may be necessary.

Reactor-formed calcium carbonate has been found to be either calcite or the metastable form vaterite[1]. The sodium-magnesium carbonate mineral eitelite has also been found in deposits[8]. Layers of granular calcium carbonate have been observed as concentric zones in spherical reactor solids particles, and in wall-scale deposits[1].

In laboratory liquefaction experiments, the use of an organometallic salt of iron as a catalyst in the presence of elemental sulphur has led to the formation of pyrrhotite as a neo-mineral[9].

(b) Physical Properties

Reflectivity: Carbonate and sulfate minerals have low reflectances. The overall reflectance of the fine-grained aggregates of intimately mixed neo-minerals and unaltered clays is very low.

III - MODE OF FORMATION

The mechanism which produces carbonates from low-rank coals is not completely understood[6], although decomposition of carboxylates under the conditions in the reactor is involved.

IV - OCCURRENCE AND PRACTICAL IMPORTANCE

The formation of neo-mineral species during coal liquefaction processes is of particular importance in the case of low-rank coals, which contain much of their inorganic matter as carboxylate cations. The formation of new minerals, especially carbonates, has led to blockages in hydrogenation plants. Minerals may also combine with carbonaceous phases, particularly mesophase semicoke, in the creation of blockages.

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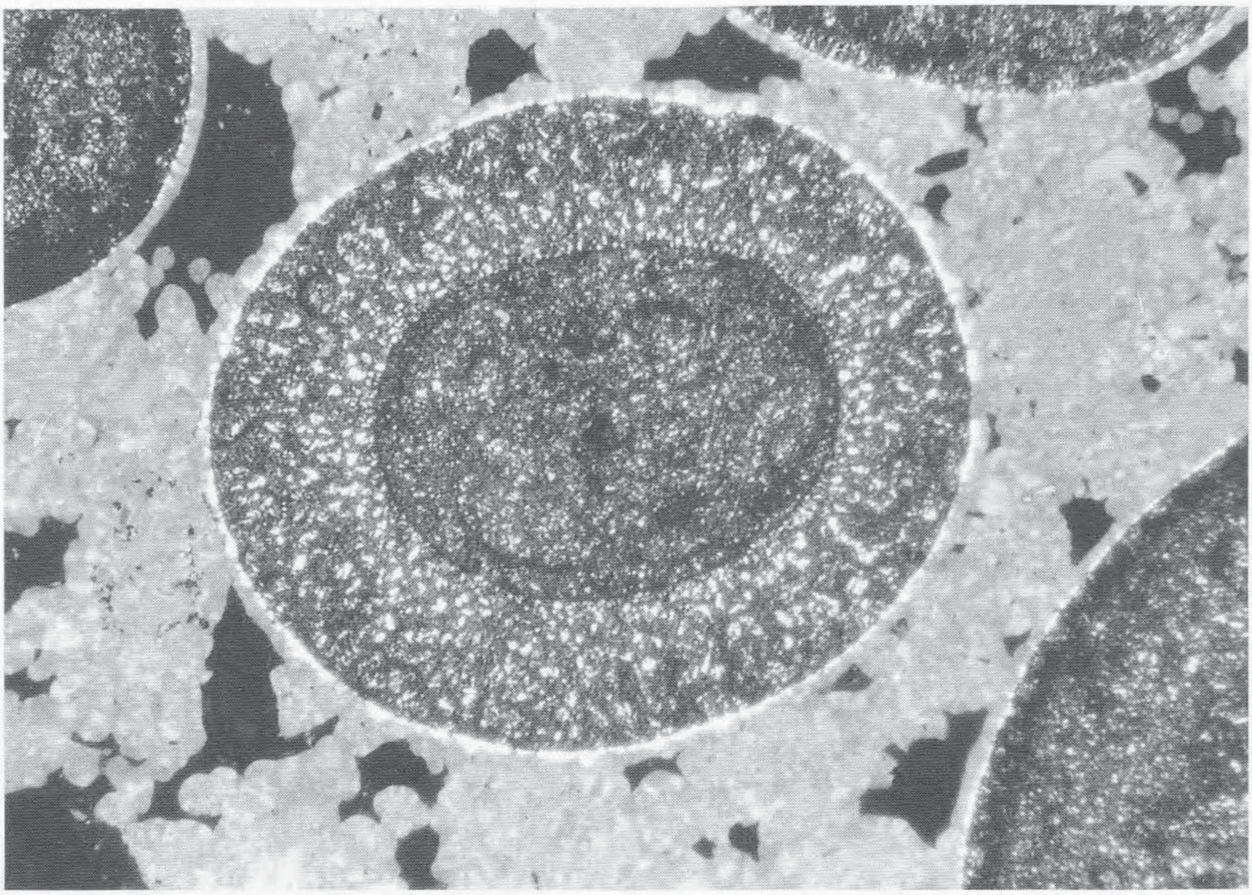
Fig.1

Spheres of calcium carbonate neo-mineral (calcite and/or vaterite) with pyrrhotite rim and inclusions, embedded in mesophase-derived secondary semicoke; reactor solids from pilot-plant hydroprocessing of subbituminous coal (solvent-refined coal mode); reflected light, oil immersion, x410.



1

1993 SUPPLEMENT	**International Committee for Coal Petrology** Commission I **LITHOTYPE GROUP** **(Stopes-Heerlen System)**	Soft Brown Coal Dull Brown Coal

I - ORIGIN OF TERM

The term was introduced by Seifert and Rascher[1]: "the lithotype group is characterized by the quantity of its major component without consideration of its qualitative variations".

Commission I (General Coal and Organic Petrology) in 1982 adopted the term in a somewhat altered form to describe major groupings of petrographic units:

Analogous terms:	lithotype class	(Hagemann and Hollerbach[2])
	supralithotype	(Brzyski[3])

II - DEFINITION

The lithotype groups serve to characterise the major macropetrographic units of coal that are visible in coal faces, borehole cores or hand specimens. They can be distinguished in moist as well as dried faces of samples. For their definition, the genetic and technically important components of coal - xylite, groundmass and mineral - are used. It is not necessary that xylite and minerals be major components of the coal, but they must be a component determining one of its properties. (For the subdivision of individual lithotype groups see individual sheets). The following lithotypes are distinguished:

xylite-rich coal,
charcoal-rich coal,
matrix coal, and
mineral-rich coal.

The sheets relating to lithotype groups always contain the following information in the sequence:

I	origin of the term
II	description
III	origin and genesis
IV	practical importance
V	literature

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Lithotype Classification System for Soft Brown Coals

Lithotype Group (Constituent Elements)	Lithotype (Structure)	Lithotype Variety * (Colour: Gelification)
MATRIX COAL	STRATIFIED COAL	Brown (weakly gelified) Coal Black (gelified) Coal
	UNSTRATIFIED COAL	Yellow (ungelified) Coal Brown (weakly gelified) Coal Black (gelified) Coal
XYLITE-RICH COAL		
CHARCOAL-RICH COAL		
MINERAL-RICH COAL		

* not yet defined

1993 SUPPLEMENT	**International Committee for Coal Petrology** Commission I **LITHOTYPE** **(Stopes-Heerlen System)**	Soft Brown Coal

I - ORIGIN OF TERM

The term lithotype was first introduced by C.A. Seyler[1] for the macroscopically distinguishable layers of hard coal (Stopes-Heerlen System).

H. Jacob[2] and M. Süss[3] were the first to apply the term lithotype to the petrographic characterization of brown coals.

Analogous terms:	rock type, ingredient, banded ingredient, banded constituents, coal type, petrographic type (partly)
Etymology :	lithos (Greek) - rock typos (Greek) - character, type

II - GENERAL OBSERVATIONS

The definition of lithotype, adopted from hard-coal nomenclature, must be expanded if it is to be used to describe macroscopically recognisable petrographic units of soft brown coals. In comparison with hard coals, because of the lower coalification of soft brown coals more details of the original plant materials can be recognised. In principle, the macropetrographic logging of lithotypes (or lithotype varieties) is undertaken on fractured surfaces of coal perpendicular to the bedding. Structure can be recognised in fresh conditions, but the colour of soft brown coal can only be established with certainty after air drying, i.e. after about two days, or freeze-drying.

III - DEFINITION

The lithotypes of soft brown coal are recognisable with the naked eye in fresh conditions by their constituent elements and structure. They form petrographically distinct units of seams. They can form large lenses or appear in a seam as persistent bands from a few centimetres to a meter or more in thickness.

The lithotypes are combined into lithotype groups on the basis of their constituent materials. Lithotype varieties can be differentiated by their degree of gelification and colour.

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1993	International Committee for Coal Petrology Commission I	Soft Brown Coal
SUPPLEMENT	**MATRIX COAL** **(Stopes-Heerlen System)**	Dull Brown Coal

I - ORIGIN OF TERM

The term matrix coal was introduced by Commission I (General Coal and Organic Petrology) in 1990.

Analogous term:	groundmass texture coal	(Seifert and Rascher[1])
	pure coal, non-xylitic	(Hagemann and Hollerbach[2])
	humodurain, humoclarain, liptain	(Bulgarian standard)

II - DESCRIPTION

The lithotype group, matrix coal, consists predominantly of a fine detrital humic groundmass, homogeneous in appearance and yellow to dark brown in colour. Tissue fragments (plant debris), e.g. fragments of leaves, needles, conducting vessels etc. and resin grains, may be embedded in the groundmass. Xylite and charcoal may constitute 10% at most of the components in matrix coal. Gelified nodules, in the form of dopplerite, can occur in matrix coal, which may be stratified or unstratified. The stratification is determined by the nature and amount of included tissue fragments.

Lithotypes and lithotype varieties may be distinguished by the intensity of banding, degree of gelification, colour and/or characteristic inclusions.

III - ORIGIN AND GENESIS

Matrix coal is particularly common in Tertiary soft brown coals. In general, matrix coals are a normal component of all brown coals. According to Teichmüller and Thomson[3] some matrix coals originate from peats formed in treeless, low-lying swamps, others from angiosperm-marsh coals. Matrix coal can also originate through strong decomposition of a variety of forest-swamp peats (Hagemann and Hollerbach[2] ; von der Brelie and Wolf[4]). Finely banded matrix coal indicates a subaquatic origin in an open-water swamp environment.

IV - PRACTICAL IMPORTANCE

Matrix coals are the most valuable brown coals for briquetting, coking and liquefaction. Matrix coals provide high yields of tax and bituminous extracts and are therefore an important raw material for the chemical industry. Briquettes with very high strength may be produced from little gelified, not very bitumen-rich, brown matrix coals. For this reason matrix coals are specially valuable in the production of form coke. (Jacob[5]; Suss and Sontag[6]).

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1993	**International Committee for Coal Petrology** Commission I	Soft Brown Coal
SUPPLEMENT	**XYLITE-RICH COAL** **(Stopes-Heerlen System)**	Dull Brown Coal

I - ORIGIN OF TERM

The term xylite-rich coal was introduced by Commission I (General Coal and Organic Petrology) in 1990.

Analogous terms:	marsh-forest coal	(Teichmüller and Thomson[1]) in part
	xylite coal	(Seifert and Rascher[2]) pure
	coal, xylitic	(Hagemann and Hollerbach[3])
	xylitic coal	(Jacob and Süss[4])
	xylain, humovitrain	(Bulgarian standard)

II - DESCRIPTION

The lithotype group, xylite-rich coal, includes light-brown to dark-brown coals, in which xylite* constitutes more than 10% of the coal. The groundmass of this coal is detrital. Depending on the amount of tissue present (e.g. fragments of leaves, needles, conducting vessels), it can be unstratified to stratified. The xylite should be more or less regularly distributed through the coal. Groundmass-rich coals with scattered inclusions of isolated stumps or large stems are not included in this lithotype group. The xylite may be present in different forms (eg fibrous tissue etc.) and can also be mineralised. With increase in the amount of mineralised xylite, this lithotype group becomes the lithotype group, "mineral-rich coal" (see the sheet "mineral-rich coal"). Other inclusions in xylite-rich coal can be large resin grains or charcoal but they must constitute less than 10% of the coal. Gelified nodules (e.g. in the form of dopplerite), can also occur in xylite-rich coal. Dried coal faces or hand specimens of xylite-rich coal, depending on the degree of gelification, appear more or less coarsely fissured.

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* Coalified wood fragments (stems, stumps etc) and their broken pieces still with clearly visible structure.

Further lithotypes or lithotype varieties may be distinguished on the basis of the development of stratification, degree of gelification, colour and/or characteristic inclusions.

III - OCCURRENCE AND GENESIS

Xylite-rich coal occurs in all brown coals: frequently it is the predominant lithotype.

Xylite-rich coal originates under predominantly anaerobic conditions from forest and shrub moors (Teichmüller and Thomson[1]; Hagemann and Hollerbach[3]; von der Brelie and Wolf[5]).

IV - PRACTICAL IMPORTANCE

The industrial properties of xylite-rich coal depend predominantly on the nature and amount of xylite because xylite can interfere with crushing processes.

Briquetting behaviour is variable. Little gelified, xylite-rich coal produces briquettes with high strength (Jacob[6]). Xylite-rich coal is not suitable for the production of form coke. Xylite-rich coal which does not have too high a xylite content is usable as a boiler fuel (see crushing processes above).

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1993 SUPPLEMENT	International Committee for Coal Petrology Commission I **CHARCOAL-RICH COAL** **(Stopes-Heerlen System)**	Soft Brown Coal

I - ORIGIN OF TERM

The term charcoal-rich coal was introduced by Commission I (General Coal and Organic Petrology) in 1990.

II - DESCRIPTION

The lithotype group charcoal-rich coal includes coal that is composed of considerable quantities (> 10%) of fossil charcoal. The groundmass of the coal can be variable in composition (humic-detrital to tissue-rich). Depending on the type of fusinitised inclusions and the amount of tissue (e.g. fragments of leaves and needles, conducting vessels) the coal can be weakly to strongly stratified. Other inclusions, such as xylite or resin grains, may appear, but only in minor amounts in charcoal-rich coal.

Gelified nodules may also occur in charcoal-rich coal. On dried coal faces, charcoal-rich coal has a coke-like appearance: the surface is rough, the colour is brownish-black with occasional silvery lustre.

Lithotypes and lithotype varieties can be distinguished based on the development of stratification, degree of gelification and additional inclusions.

III - ORIGIN AND GENESIS

Charcoal-rich coal appears mainly in lenses and occasionally also in persistent horizons. Quantitatively this lithotype is only a minor constituent of all soft brown coals. Most components of charcoal-rich coal originate from the remains of burned forest moors. More or less unstratified charcoal-rich coal is autochthonous and developed on the site of burned forest-moor peat. Stratified charcoal-rich coal indicates water or wind-aided accumulation of charcoal relicts in an open-water swamp environment.

IV - PRACTICAL IMPORTANCE

The technical properties of pure charcoal-rich coal are poor because charcoal fragments behave inertly during briquetting and coking. Because the amounts of charcoal-rich coal in bulk production are small, they do not affect technical processes.

1993 SUPPLEMENT	**International Committee for Coal Petrology** Commission I	Soft Brown Coal
	MINERAL-RICH COAL **(Stopes-Heerlen System)**	Dull Brown Coal

I - ORIGIN OF TERM

The term mineral-rich coal was introduced by Commission I (General Coal and Organic Petrology) in 1990.

Analogous terms:	mineral coal	(Seifert and Rascher[1])
	clayey-sandy coal	(Jacob and Süss[2]) in part

II - DESCRIPTION

The lithotype group includes all kinds of mineral intergrowths with the different brown-coal lithotype groups. The mineral components in the coal should be clearly recognizable in hand specimen or at the coal face, through properties such as brightness, colour, density, salty taste, grittiness between the teeth for silty quartz, HCl test for calcium carbonate, Geiger-counter tests etc. The following inorganic components may occur in mineral-rich coal:

clay minerals
quartz
carbonates (predominantly $CaCO_3$)
sulphides (predominantly pyrite)
sulphates (predominantly gypsum)
chlorides (predominantly NaCl)
oxides (limonite, haematite)
radioactive minerals

Individual lithotypes may be distinguished by the predominant mineral in the coal.

III - OCCURRENCE AND GENESIS

Coal-mineral associations are rare in Central-European Miocene brown coals, for example, while they occur more frequently in Eocene coals (e.g. pyrite-rich coal in the Helmstedt mining district). Coal-mineral associations can often be found in the soft brown coals of the Balkan Peninsula (Ercegovac[3]; Mincev[4]) and in the Pliocene lignites of Greece and Turkey.

The frequency and nature of coal-mineral associations depend above all on the conditions of formation in the swamp (water cover, water movement, PH value, redox potential) and on the local geographic and meteorological conditions (topographic relief of surroundings, rainfall, strength and direction of wind) i.e. coal-mineral intergrowths, especially those with quartz, clay minerals and pyrite are mainly synsedimentary. Dolomitization of brown coals and silicification or pyritization of wood may be syngenetic to early epigenetic (Gothan and Bennhold[5]; Gothan[6]). Occurrences of gypsum, limonite, and haematite, mostly as oxidation products of pyrite, are the result of oxidation of brown coal (Jacob[7]).

IV - PRACTICAL IMPORTANCE

Coal-mineral associations, because of their ballast effect, generally reduce coal quality and, for this reason, are undesirable in nearly all upgrading processes. Mineral-matter enrichment in individual grain fractions during beneficiation have an adverse effect on the briquetting process (wear of pressing equipment) and on briquette quality. Subsequent processing steps, such as "form-coke" production, are also affected adversely.

When brown coal is burned in large boilers, quartz and silicate minerals, in combination with alkalies (Na, K), produce badly fouled heating surfaces because the alkalies lower the ash-fusion temperature. An increased calcium content reduces this fouling tendency, as well as SO_2 emission, by the formation of calcium sulphate (Pietzner and Schiffers[8], Jacob[9]).

Pyrite-rich coals, sulphidic additions or organic sulphur compounds in coals in general have an impact on the environment due to the sulphur dioxide emissions generated by the combustion process.

"Salt coals", i.e. coals with high NaCl contents and/or alkalies (Na, K) in humate compounds, have a corrosive effect that causes problems in all processes. (In Australia coals with >0.3% wf Na are called "salt coals".)

Pyrite or marcasite has a catalytic and therefore a partially beneficial influence on brown-coal hydrogenation (Lenz et al[10]).

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1993 SUPPLEMENT	**International Committee for Coal Petrology** Commission I **STRATIFIED MATRIX COAL** **(Stopes-Heerlen System)**	Soft Brown Coal

I - ORIGIN OF TERM

The term stratified matrix coal was introduced by the Commission I (General Coal and Organic Petrology) in 1990.

Analogous terms:	banded coal	(Jacob[1])
	xylite-free bedded coal, xylite free textured coal, xylite-free textured groundmass coal	(Vogt[2])
	weakly banded coal, banded coal	(Sontag and Süss[3])
	weakly banded coal, banded coal, strongly banded coal	(Hagemann[4])

II - DESCRIPTION

The lithotype, stratified matrix coal, is composed predominantly of a detrital humic groundmass and inclusions of plant organs or parts of organs, e.g. fragments of leaves, needles and conducting vessels. Resin grains and charcoal fragments can also occur in minor amounts. The degree of stratification is determined by the nature and type of enclosures.

Stratified matrix coal breaks into platy pieces. The more tissue fragments that are included in the coal the platier the fracture.

Lithotype varieties can be distinguished on colour and degree of gelification.

III - ORIGIN AND GENESIS

See the lithotype-group, "matrix coal".

IV - PRACTICAL IMPORTANCE

Ungelified varieties are in general the most valuable brown coal for all currently used processing methods. Strongly stratified ungelified varieties generally produce good briquettes but do not make good coke (Jacob[5]). Gelified varieties are not suitable for briquetting and thus they are also not suitable for the production of BHT coke. They can be used as boiler fuel.

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1993 SUPPLEMENT	International Committee for Coal Petrology Commission I **UNSTRATIFIED MATRIX COAL** **(Stopes-Heerlen System)**	Soft Brown Coal

I - ORIGIN OF TERM

The term unstratified matrix coal was introduced by Commission I (General Coal and Organic Petrology) in 1990.

Analogous terms:	unbanded coal	(Jacob[1])
	xylite-free groundmass coal	(Vogt[2])
	unbanded coal	(Sontag and Süss[3])
	unbanded coal	(Hagemann[4])

II - DESCRIPTION

The lithotype, unstratified matrix coal, is composed of a fine detrital humic groundmass that is homogeneous in appearance. Except for resin grains it contains practically no inclusions. The gelification (if it has occurred) has uniformly affected the humic groundmass. Gelified nodules are therefore relatively rare. They appear especially in the light lithotype varieties in root tubes.

The coal in general has a compact appearance and breaks into irregular pieces of different sizes.

Lithotypes and lithotype varieties can be distinguished on the basis of colour and degree of gelification.

III - ORIGIN AND GENESIS

See the lithotype-group, "matrix coal".

IV - PRACTICAL IMPORTANCE

Ungelified varieties are suitable for beneficiation by all current methods. Gelified varieties can - like other lithotypes or lithotype varieties - be used as boiler coal.

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1993 SUPPLEMENT	International Committee for Coal Petrology Commission II	Bitumen
	MIGRABITUMEN	R.L.

I - ORIGIN OF THE TERM

The term migrabitumen was introduced by Alpern[1] and signifies bituminous material that has migrated. This term was adopted by the International Committee for Coal Petrology in 1986.

Etymology:
Migrare (Lat.) = to migrate
Bitumen = asphalt

Analogous terms:

exsudatinite (in part)	(M. Teichmüller[2])
solid bitumen	(Jacob[3])
dispersed bitumen	(Jacob[4])
epibituminite	(Malan[5])

II - DEFINITION

The term migrabitumen signifies secondary bitumen generated from fossil organic material during diagenesis and catagenesis. Migrabitumen may range from a fraction of a millimeter to several kilometers. In contrast to most macerals migrabitumens are amorphous; their shape adapts to the form of the cavities they occupy (e.g. interstices, fissures, cavities in microfossils, diffuse disseminations). Hence it follows that vitrodetrinite and inertodetrinite can mainly be distinguished from migrabitumen in original undisturbed samples; organoclast concentrates are unsuitable for the indentification of migrabitumen.

The terms defined in the International Handbook are constituent units (macerals) of the solid organic matter found in coals and other sedimentary rocks. Macerals are defined by their appearance under the microscope (morphology, reflectance), regardless of other physical properties and their chemical composition. Migrabitumen can be partly analyzed by the same methods as macerals, but unlike macerals these substances cannot be characterized unequivocally by their optical properties; besides reflectance and fluorescence, microsolubility is an essential feature in the identification of the individual constituents of migrabitumen. Migrabitumen is therefore not a maceral term and cannot be included in the Stopes-Heerlen system.

III - CLASSIFICATION

The micro-classification for migrabitumens (Jacob[6,7]) is based on the technically oriented macro-classification of Abraham[8]. The parameters are reflectance, intensity of fluorescence, microsolubility (and microflowpoint). As far as possible, these parameters are related to the macro-classification. On this basis the migrabitumens are differentiated as follows:

group	subgroup	type
migrabitumen	———	ozocerite
	———	asphalt
	asphaltite	gilsonite glance pitch grahamite
	———	wurtzilite albertite
	impsonite	epi-impsonite meso-impsonite cata-impsonite

IV - DESCRIPTION

a) Physical properties

a) *Colour:* Transmitted light- almost colourless (ozocerite, in most cases) to red-brown (e.g. asphaltite) to opaque (cata-impsonite).

Incident light, bright field, oil immersion- dark grey with yellow interior reflectance (ozocerite) to medium light grey (e.g. epi-impsonite) to yellowish white (cata-impsonite).

Incident light, fluorescence- strong yellow-green fluorescence (ozocerite) to moderate or weak, brownish fluorescence (e.g. asphaltite) to complete lack of fluorescence (e.g. meso- and cata-impsonite).

b) *Reflectance, fluorescence intensity, microsolubility and micro-flowpoint:* see table from Jacob and Wehner[9].

c) *Anisotropy:* Ozocerite, asphalt, gilsonite, glance pitch, grahamite, wurtzilite, and albertite are, in general, optically isotropic. Ozocerites that contain no oil may sometimes form fine crystalline aggregates and show mosaic anisotropy. The impsonites may be optically isotropic or anisotropic; there is no clear interrelationship with degree of metamorphism. Some impsonites have a mosaic texture which resembles a mesophase (Jacob and Wehner[9)]).

d) *Solubility:* The solubility in organic solvents, especially in carbon disulfide (Abraham[10)]), is an essential parameter for differentiating between various migrabitumens. Asphalt and asphaltites are nearly 100% soluble; wurtzilite, albertite, and impsonite are almost 100% insoluble. Consequently, asphaltites, on the one hand, and wurtzilite and albertite, on the other, are basically different although they show the same reflectance and fluorescence.

e) *Softening point:* The softening point can be determined using the "ring and ball" method or the method of Kraemer and Sarnow (Abraham[10]). The softening points determined by the two methods differ little. Asphalt and asphaltites soften when heated but wurtzilite, albertite and impsonite have no measurable softening points. Using the method of Kraemer and Sarnow, asphalt and asphaltites have the following softening point ranges:

asphalt	up to 110°C
gilsonite	110 - 177°C
glance pitch	110 - 177°C
grahamite	177 - 316°C

Gilsonite and glance pitch cannot be differentiated using this method.

f) *Density:* In general, density is measured at a temperature of 25°C using the pyknometer method or the density is corrected to this temperature. The density values of the migrabitumens range from about 0.8 (ozocerite) to approximately 1.7 (cata-impsonite); thus, the values give information about the degree of catagenesis or metamorphism or the original type of organic matter from which the sample is derived. According to Abraham[8] and Jacob and Wehner[9], the individual migrabitumens have the following density ranges:

	g/mm^3
ozocerite	c. 0.8 - 0.9
asphalt	c. 1.0 - 1.1
gilsonite	c. 1.0 - 1.1
glance pitch	c. 1.1 - 1.15
grahamite	c. 1.15 - 1.25
wurtzilite	c. 1.0 - 1.1
albertite	c. 1.1 - 1.2
impsonite	c. 1.2 - 1.7

To obtain reliable density values, it is imperative that the migrabitumens are almost free of mineral matter but regrettably, this is seldom achieved. Density is therefore only of minor practical importance.

Microhardness: analyses by Robert[11] suggested that the Vickers microhardness number of migrabitumen was generally lower than that of vitrinite of the same rank.

b) *Chemical Properties*

a) *Moisture and ash:* The migrabitumens are almost moisture-free; only weathered migrabitumens (oxybitumens) may contain some water. Their ash content varies considerably. In general, vein-like migrabitumen contains little ash, while migrabitumen from seeps usually contains a large amount of ash.

b) *Volatile matter:* The volatile-matter yield is determined in an oven, as for coal. The content of volatile matter is the most important chemical parameter for the classification of solid fossil bitumen. This parameter is used primarily to determine the degree of diagenesis, catagenesis or metamorphism of a migrabitumen. The values range from about 2% to nearly 100%. According to Abraham[8] and Jacob and Wehner[9] the migrabitumens are defined as follows:

Migrabitumens: Volatile-Matter Yields

	% VM (daf)
ozocerite	>99
asphalt	>90
gilsonite	90 - 80
glance pitch	80 - 65
grahamite	65 - 45
wurtzilite	95 - 75
albertite	75 - 45
epi-impsonite	45 - 19
meso-impsonite	19 - 8
cata-impsonite	<8

As can be seen from this table, asphalt and asphaltites, on the one hand, and wurtzilite and albertite, on the other, show similar contents of volatile matter. Differentiations cannot be made solely on the basis of their contents of volatile matter. At least one other parameter (physical) is necessary, e.g. the solubility or the softening point.

c) *Ultimate analysis:* Ultimate analyses can be carried out by different methods, as for coals, which is necessary for genetic analysis (e.g. identification of weathered migrabitumens on the basis of the oxygen content). The results of ultimate analyses range between the following values (after Abraham[8] and Jacob and Wehner[9]):

Migrabitumens: Ultimate Analyses

	C % daf	H % daf	0* % daf	N % daf	S % daf
ozocerite	84-89	11-17	<0.1-0.8	<0.1-0.5	<0.1-1.5
asphalt	75-86	11-13	<0.1-1.0	1.0-3.0	0.2-6.0
gilsonite	85-86	9-11	<0.1-1.0	2.0-4.0	0.1-3.0
glance pitch	80-85	7-11	<0.1-1.0	<0.1-2.0	0.1-8.0
grahamite	83-90	6- 9	0.5-1.0	0.1-2.0	1.0-8.0
wurtzilite	72-84	8-13	0.7-1.0	2.0-5.0	1.0-6.0
albertite	83-92	6-13	0.1-1.0	0.1-3.0	<0.1-7.0
impsonite	88-93	2- 6	0.7-2.0	0.7-2.0	1.0-4.0

The analyses were made on a large number of samples and thus may be considered sufficiently representative. With further analyses the ranges given above may be extended.

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*) The oxygen content of weathered samples may be as much as 13% or even higher.

d) *Hydrocarbon analysis:* After soxhlet extraction with dichloromethane and deasphaltization with petroleum benzene, samples are fractionated by column chromatography into the following groups of compounds: saturated hydrocarbons, aromatic hydrocarbons, heterocyclic hydrocarbons and asphaltenes. The following ranges have been obtained for migrabitumens on the basis of 90 samples (Jacob and Wehner[9]):

Migrabitumens: Hydrocarbon Analyses

	saturated hydrocarbons %	aromatic hydrocarbons %	heterocyclic compounds %	asphaltenes %
ozocerite	58-80	7-14	1- 7	1- 8
asphalt	9-18	18-31	13-38	7-38
gilsonite + glance pitch	1- 7	2-18	15-38	12-68
grahamite	<1- 3	2-13	5-25	50-90
wurtzilite	2- 9	1- 9	6-41	22-55
albertite	1-12	9-28	15-53	15-54

Since only approximately 2 - 25% of wurtzilite and albertite is soluble in dichloromethane, the analyses of these extracts cannot be considered with certainty to be representative for all migrabitumens of this type. Less than 2% of the impsonites are soluble; such analyses are thus hardly representative for all impsonite migrabitumens and they are not presented here.

V - GENESIS

The development of migrabitumens begins below the "oil window" at a vitrinite reflectance of c. R_{oil} = 0.35-0.55%. Micro-organisms, e.g. algae, are a possible source material. No details are known about the particular conditions of formation of the first member of each of the three different groups of migrabitumens (asphalt, wurtzilite, and ozocerite). Hunt, Stewart and Dickey[12] and Hunt[13] believed facies differentiation to be responsible for the development of different bitumen groups. More recent studies by Jacob[7] and Jacob and Wehner[9] cast doubt on the influence of the geological facies in determining the different chemical and physical properties of individual migrabitumens. Certain properties of asphalt, on the one hand, and of wurtzilite, on the other, indicate the important role disproportionation plays, but details are unknown at present.

VI - ALTERATION DURING DIAGENESIS, CATAGENESIS AND METAGENESIS

Temperature is the most important parameter for the maturation of migrabitumens; in some cases, analogous to coal, time can also be an important factor.

Asphalt develops to gilsonite then to glance pitch, then to grahamite. Only grahamite requires elevated temperatures and/or long periods of time for its formation.

Wurtzilite develops - evidently under elevated temperature - to albertite.

Nothing is known about the diagenetic, catagenetic and anchimetamorphic behaviour of *ozocerite.*

Above a reflectance of ca. R_{oil} = 0.7%, the migrabitumens above cannot be distinguished by present methods. Grahamite and albertite can develop to epi- and meta-impsonite and then to cata-impsonite. During this process reflectance increases and, in some cases, a more or less intense optical anisotropy (very often with mosaic texture) may develop.

VII - ALTERATIONS CAUSED BY WEATHERING

In principle, all migrabitumens can be altered by weathering. Increase in oxygen content is the most reliable indicator of weathering (Jacob and Wehner[9]). The oxygen content can reach 10% without any visible change. Heavy weathering, particularly of impsonites, may cause typical weathering fissures (cf. coal). Some weathered migrabitumens show complex properties, i.e. assignment to a special type of bitumen cannot be made on the basis of microscopical, chemical and physical parameters. The solubility of asphaltites decreases with weathering and the softening point particularly is raised, which is of special interest for technical applications. Heavily weathered migrabitumen has been shown to be a mixture of more or less optically unaltered migrabitumen, minerals and bitumen coke (Jacob[7]).

VIII - SCOPE OF APPLICATION

Migrabitumen can occur in rocks either massively - possibly as a workable deposit - or dispersed. There are thus very different applications for migrabitumens.

a) *Technical applications:* Under this heading, only migrabitumens in workable deposits are considered. Numerous deposits of this kind were mined around the turn of the century, but the oil boom stopped mining of most deposits. In particular, asphalt is used for road construction, in civil engineering, and in building construction. Oil and petroleum coke can be obtained from ozocerite and asphaltites by pyrolysis. Impsonite was temporarily mined as "coal". In addition, vanadium was obtained from the ashes of some impsonites for use in steel alloys.

b) *Petroleum / natural gas indicator:* Where asphalt seeps occur (e.g. in California) petroleum most probably exists in the subsurface. Numerous occurrences of dispersed, non-metamorphic migrabitumen in a small area may indicate petroleum. Dispersed metamorphic migrabitumen, particularly impsonites, may imply that little petroleum can be expected; if suitable trap structures are present, natural gas or condensate might occur.

c) *Migrabitumens as parameters for maturity*

Carbonate rocks usually contain little or no vitrinite particles for microphotometric measurement of maturation when prospecting for petroleum and natural gas. Carbonate sediments that are prospects for oil or gas usually contain dispersed migrabitumen. There is a stochastic relationship between the reflectance of vitrinite and migrabitumen which is linear between $<0.1\%$ and about R_{oil} = c. 3.0% migrabitumen reflectance (Jacob[14]). If several migrabitumen generations occur, it is likely that the generation with the lowest reflectance represents the correct level of organic-matter maturity (it is assumed that the migrabitumen generations do not belong to migrations that occurred at greatly different times, e.g. one generation in the Palaeozoic and another in the Cainozoic).

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Properties of Migrabitumens *

	random reflectance % (oil)	fluorescence (special, masked uranyl glass standard = 1%)	microsolubility in immersion oil and petroleum ether 40 - 80°C	microflowpoint °C
ozocerite	< 0.01 - c. 0.02	c. 9.0 - > 50	soluble	c. 30 - c. 90
wurtzilite	< 0.01 - c. 0.1	ca. 0.1 - > 2.0	insoluble	does not flow
albertite	c. 0.1 - c. 0.7	≦ 0.1	insoluble	does not flow
asphalt	c. 0.02 - c. 0.07	c. 0.4 - > 4.0	soluble	<104
gilsonite	c. 0.07 - c. 0.11	c. 0.05 - c. 0.4	soluble	c. 104 - c. 164
glance pitch	c. 0.11 - c. 0.3	c. 0.05 - c. 0.2	soluble	c. 104 - c. 164
grahamite	c. 0.3 - c. 0.7	≦ 0.05	slightly soluble or insoluble	> 164 - c. 287
epi-impsonite	c. 0.7 - 2.0	≦ 0.02	insoluble	does not flow
meso-impsonite	2.0 - 3.5	< 0.01	insoluble	does not flow
cata-impsonite	3.5 - ca.10	< 0.01	insoluble	does not flow

* These four parameters are grouped here since a combination of these values is used in the optical identification of bitumen

Fig. 1

Fine porous glance pitch / grahamite
Sadkinskij Colliery near Bugurustan, Orenburg district, USSR

Fig. 2

Wurtzilite / albertite filling a microfissure
Etzel borehole, Germany

Fig. 3

Epi-Meso-impsonite forming a porous spheroid with a calcite nucleus
Nammen Colliery, Germany

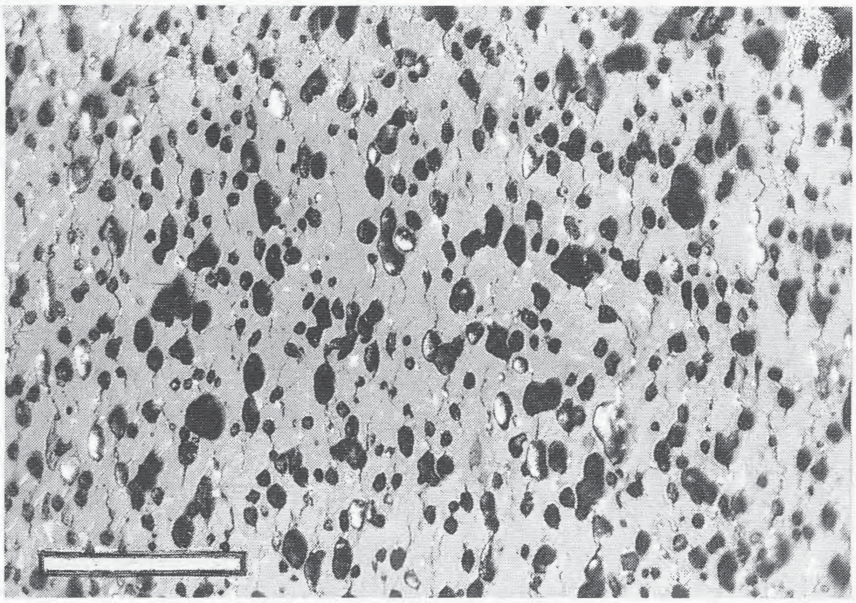
Fig. 4

Asphaltite containing gilsonite splinters
blue-light excitation
Bonanza Colliery, Utah, USA

Fig. 5

Mylonitic wurtzilite showing several generations of different fluorescence intensity
blue-light excitation
Ingram Colliery, Utah, USA

Horizontal bar is 0.1 mm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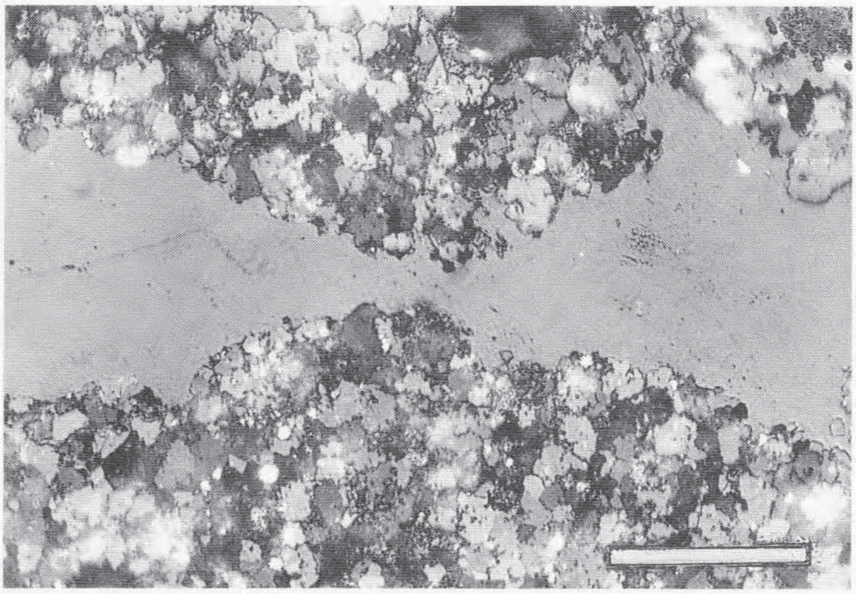
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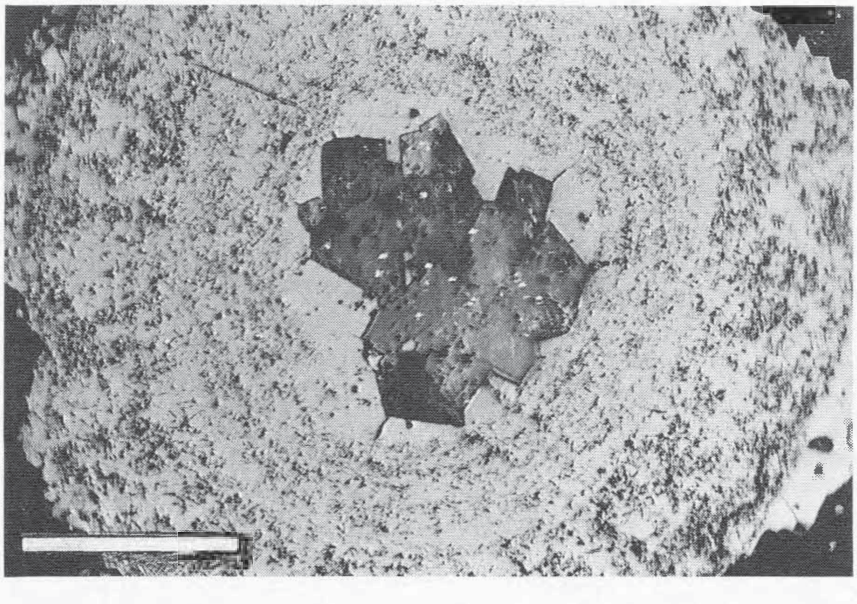
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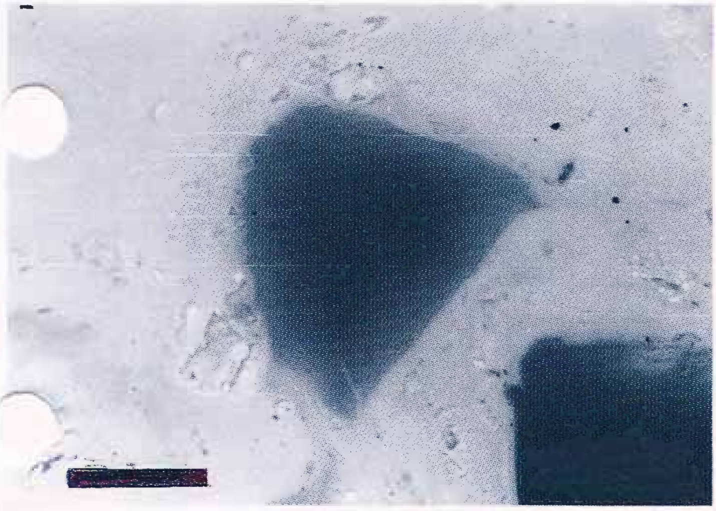

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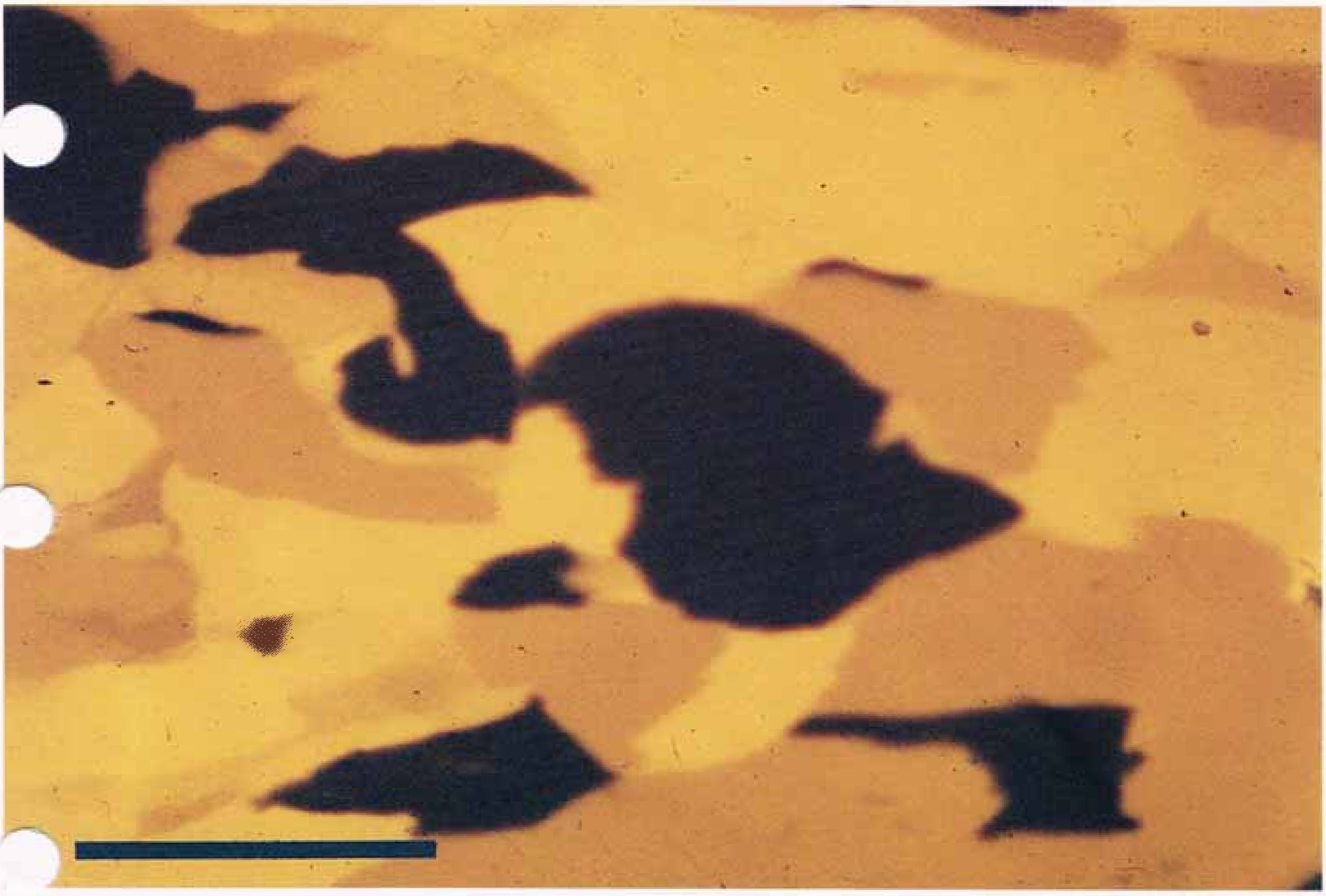

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