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Optical Morphology of Hydrocarbons and Oil Progenitors in Sedimentary Rocks – Relations with Geochemical Parameters

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Front cover: Black matrices strongly producing during fluorescence excitation. X 1600. (Angola)

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Optical Morphology of Hydrocarbons and Oil Progenitors in Sedimentary Rocks – Relations with Geochemical Parameters

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Contents

ABSTRACT

The objective of the present research is geared to systematize and to validate optical analyses of Hydrocarbons in sedimentary rocks through the use of simple routine methods applicable to polished sections either of crushed rocks or of washed but non-extracted cuttings.

The work herewith presented has been developed in two directions:

A. Through the compilation of a catalogue on morphology and optical properties of hydrocarbons in sedimentary rocks, in course of maturation, mainly in source rocks, and secondly in reservoirs.

In this catalogue the following main categories have been established:

1. Liquid hydrocarbons: Drops, Films, Exsudates, Dissolved oil (in resin), Non-spherical hydrocarbons (intercrystal fillings).
2. Solid hydrocarbons (Migrabitumen): Dark, Grey and White migrabitumens.
3. Productive mature source rocks classified in function of the apparently dominant oil progenitor: Sporinite, Bituminite, Alginite, Acritarchs, Microfauna, and organic matrices without visible progenitors.
4. Reservoirs: clasts, carbonates.

B. The optical properties of hydrocarbons were, at a first stage, used to detect their presence, and subsequently to estimate their abundance, their quality and the position of mature zones and of reservoirs in boreholes. For this purpose two parameters were used:

1. The fluorescence intensity of the embedding resin (λ = 546 nm, related to U-glass standard) which has acted as a chemical extractor by dissolving a part of the free hydrocarbon present in a sample.
2. The Q_{UV} 650/500 nm established, on one hand, on the embedding resin in the polished block samples and, on the other, on free crude oils directly mounted on slides.

It has been clearly established that these fluorescence parameters are correlative (all correlation coefficients equal to about 0.9) both to quantity (S_1 from Rock-Eval) and to quality of oils in terms of chemical composition. The variations of optical properties and geochemistry of oils with depth was also established, and examples of real case studies are presented.

<u>Key words</u>: crude oil, fluorescence, geochemistry, hydrocarbon, maturation, oil progenitor, optical analysis, reservoir, source rock.

RESUMO

O presente trabalho tem por objectivo sistematizar e valorizar as análises ópticas, efectuadas nos hidrocarbonetos presentes nas rochas sedimentares, a partir de métodos simples e de rotina, aplicáveis a amostras preparadas em superfície polida, tanto de rochas trituradas como de cuttings lavados mas nao submetidos a extracçao.

O trabalho foi desenvolvido segundo as duas seguintes componentes:

A.Compilaçao de um catálogo da morfologia e das propriedades ópticas dos hidrocarbonetos presentes nas rochas sedimentares no decurso da maturaçao, principalmente em rochas-mae e, secundariamente, em rochas-reservatório.

Estabeleceram-se as seguintes categorias:

1. Hidrocarbonetos líquidos: Gotas, Filmes, Exudatos, Petróleo bruto dissolvido (na resina), Hidrocarbonetos nao-esféricos (enchimentos intercristalinos).
2. Hidrocarbonetos sólidos (Migrabetumes): Migrabetumes negros, cinzentos e brancos.
3. Rochas-mae productivas, em funçao do progenitor do petróleo aparentemente dominante: Esporinite, Betuminite, Alginite, Acritarcas, Microfauna e Matrizes orgânicas sem progenitores visíveis.
4. Rochas-reservatório: Clastos, Carbonatos.

B.As propriedades ópticas dos hidrocarbonetos foram utilizadas, em sondagens, primeiro para identificar a sua presença e, depois, para estimar a abundância e a qualidade dos mesmos hidrocarbonetos e, bem assim, a posiçao das zonas maduras e dos reservatórios. Utilizaram-se dois parâmetros para o efeito:

1. Intensidade de fluorescência (λ = 546 nm e padrao de vidro de uranilo) da resina de aglutinaçao, a qual actua como extractor químico por dissoluçao de uma parte dos hidrocarbonetos livres presentes na amostra.
2. Q_{UV} 650/500 nm medido, por um lado, na resina de aglutinaçao e, por outro lado, em petróleos brutos directamente montados entre lâmina e lamela.

Concluiu-se que os citados parâmetros de fluorescência se correlacionam (coeficientes de correlaçao da ordem de 0,9) tanto com a quantidade (S_1 do Rock-Eval) como com a qualidade dos petróleos brutos, em termos de composiçao química. Estabeleceram-se, outrossim, as variaçoes das propriedades, tanto ópticas como geoquímicas, dos petróleos brutos com a profundidade, fornecendo-se exemplos de casos reais estudados.

<u>Descritores</u>: análise óptica, fluorescência, geoquímica, hidrocarboneto, maturaçao, petróleo bruto, progenitor de petróleo, reservatório, rocha-mae.

RESUME

L'objectif de notre travail est de collecter, de systématiser puis de valoriser l'analyse optique des hydrocarbures inclus dans les roches sédimentaires au moyen de méthodes de routine simples, applicables aux sections polies de roches broyées, ou aux cuttings lavés mais non-extraits.

Les travaux présentés ci-dessous ont été développés dans deux directions:

A. Par la constitution d'un catalogue des propriétés optiques et de la morphologie des hydrocarbures des roches sédimentaires en cours de maturation, principalement les roches-mères et accessoirement les réservoirs.

Dans ce catalogue les principales catégories suivantes ont été établies:

1. Hydrocarbures liquides: Gouttes, Films, Exsudats, Huile dissoute (dans la résine), Hydrocarbures non sphériques (remplissages inter-cristallins).
2. Hydrocarbures solides (Migrabitumes): Migrabitumes noirâtres, gris, blancs.
3. Roches-mères productives classées en fonction du progéniteur d'huile apparent: Sporinite, Bituminite, Alginite, Acritarches, Microfaunes et matrices organiques sans progéniteurs visibles.

B. Dans une première étape les propriétés optiques des hydrocarbures ont été utilisées pour détecter leur présence, puis ensuite pour estimer leur abondance, leur qualité et la position des zones matures et des réservoirs dans les forages. A cet effet deux paramètres ont été sélectionnés:

1. L'intensité de fluorescence de la résine d'enrobage mesurée à λ = 546 nm et rapportée à un étalon de verre-uranyl. La résine agit comme un extracteur chimique en dissolvant une partie des hydrocarbures libres présents dans l'échantillon.
2. Le rapport Q_{UV} 650/500 nm établi, d'une part, sur la résine d'enrobage des blocs polis et, d'autre part, sur des huiles brutes directement montées entre lame et lamelle.

Il a été clairement établi que ces paramètres de fluorescence sont liés (avec des coefficients de corrélation d'environ 0,9) à la fois à la quantité d'huile (corrélation avec S_1 du Rock-Eval) et à leur qualité chimique. Les variations des propriétés optiques et de la géochimie des huiles en fonction de la profondeur ont été établies sur la base d'exemples réels.

<u>Mots clefs</u>: analyse optique, fluorescence, géochimie, hydrocarbure, maturation, pétrole, progéniteur d'huile, roche-mère, reservoir.

1. INTRODUCTION AND OBJECTIVES

Oil is present in many sedimentary rocks, mainly in mature source rocks and reservoirs. Although oil is easy to detect in fluorescent reflected light, it has never been introduced as a normal constituent of sedimentary rocks, either in coal petrology (macerals), or in palynological classifications (palynomorphs). The reasons are that oil is more or less liquid, by definition, and also often migrated; therefore not belonging to the rocks in which it is discovered. Nevertheless, Oil droplets in coals have been described since a long time by Teichmüller (1974) and by many others.
The detection of oil in sedimentary rocks by optical methods have been investigated among others by Laggoun-Defarge et al. (1992), Martinez & Connan (1989), Mukhopadhyay et al. (1985), Pradier et al. (1990), Robert (1979), Teichmüller (1986) and Teichmüller & Ottenjann (1977).
Furthermore, the fluorescence properties of extracted oils have been studied, among others, by Bertrand et al. (1986) and Hagemann & Hollerbach (1986).
On the other hand, some hydrocarbons are solid; the maceral Exsudatinite, created by Teichmüller (1974), corresponds to the solid fluorescent hydrocarbons present in coal fractures.
Solid hydrocarbons present in sedimentary rocks have been grouped in a specific classification worked by Jacob (1989) and accepted by the International Committee for Coal and Organic Petrology-ICCP, since 1986, under the general term of Migrabitumen.

The aim of our research is to systematise and to validate optical analysis through the use of **simple routine methods** applied to polished sections of crushed whole rock washed samples. The research has been developed in two directions:

a. Through the compilation of a catalogue on morphology and optical properties of hydrocarbons in sedimentary rocks on polished, embedded in resin, granular samples.

b. Through the use of hydrocarbon optical properties as a tool to estimate their abundance, their quality and the position of the mature zones and reservoirs in sedimentary basins.

Samples used in the investigation were borehole cuttings supplied by Oil Companies, namely, Chevron Overseas Petroleum Inc., Total, and Gabinete para a Pesquisa e Exploraçao de Petróleo-GPEP. The oil samples were supplied by Total, and Institut Français du Pétrole-IFP, and GPEP. All geochemical data were provided by the above cited entities.

2. METHODOLOGY

2.1. Sample preparation

a. Most of the samples studied were whole rock cuttings already in a granular form. Mild crushing (< 2 mm) is only necessary when the size is too big or

irregular. The cuttings were cleaned, washed and relieved from visible contaminations (nuts, pigments, etc). When mud-oil has been used for drilling, a chloroform extration is often practised by geochemists, thus reducing an unknown portion of free hydrocarbons. This procedure may alter the evaluation of hydrocarbon quantities but will apparently not affect the quality estimation.
The clean granular samples of whole rocks are then embedded in a epoxy resin (EPOFIX) and polished according to classical methods.

b. Oil samples studied were mounted on a slide (single drop) and covered with a lamella, and also mixed with embedding resin in various proportions ranging from 0.5% to 4%.

2.2. Optical analysis

a. Firstly, a specific sheet is completed in which the nature of the samples (shale matrix or clast), the morphology, color, and abundance of detected hydrocarbons are reported. The colors indicated correspond to blue light excitation (BG12, λ=408 nm). When possible, the reflectance of autochthonous vitrinite is also verified.

b. Secondly, the fluorescence intensity of the embedding resin, which acts as a chemical extractor, is measured at λ=546 nm, using a uranyl-glass as standard and a UG1 (λ=365 nm) as excitation filter. The size of the field measured is $100\mu^2$.

Laboratories not equipped with photometry, but disposing of a mercury lamp for qualitative fluorescence examination, can validly estimate the fluorescence intensity by simply using the inverse of exposure time reported by the photographic equipment. The correlation with the preceding photometric method is satisfactory.

c. In complement, the ratio of Q=650/500 in UV light (UG1, λ=365 nm) is calculated, both for the hydrocarbons (films, drops), when present, and for embedding resin.

For both data, I_{546} and Q_{UV}, no corrections are necessary as all measurements are made with monochromatic filters (not by spectral fluorescence) and are related to the uranyl-glass standard.

3. OPTICAL MORPHOLOGY OF HYDROCARBONS (HC) AND OIL PROGENITORS IN SEDIMENTARY ROCKS

The description is according to the classification presented in Table 1, and it is based on the various aspects obtained from analysing more than one thousand samples.
In fact, the various HC morphologies correspond to those aspects detected in the sedimentary rocks and around the rock particles where a specific relation between generated oil and the embedding resin exists.

Table 1 - Optical Morphology of Hydrocarbons (HC) and Oil Progenitors

1. Liquid Hydrocarbons
    1.1. Drops
        a. green (saturated HC)
        b. yellow (aromatic HC)
    1.2. Films
        a. green (saturated HC)
        b. yellow (aromatic HC)
    1.3. Exsudates
    1.4. Dissolved (in resin)
        a. green (saturated HC)
        b. yellow (aromatic HC)
    1.5. Non-spherical HC (intercrystal fillings)

2. Solid Hydrocarbons: Migrabitumen (MB)
    2.1. Dark MB ($R \leq 0.2\%$)
        a. fluorescent
        b. non-fluorescent
    2.2. Grey MB ($0.2 < R \leq 0.7\%$)
        a. fluorescent
        b. non-fluorescent
    2.3. White MB ($R > 0.7\%$)
        a. isotropic
        b. anisotropic
        c. bitumen coke

3. Mature Source Rocks (SR) and HC progenitors (coal excluded)
    3.1. SR with Sporinite
    3.2. SR with Bituminite
    3.3. SR with Alginite
        a. Telalginite
        b. Lamalginite
    3.4. Source rocks with Acritarchs and/or Dinoflagellates
    3.5. Source rocks with Fauna
    3.6. Source rocks with mixed progenitors
    3.7. Source rocks without Organoclasts
        a. green matrices
        b. brown matrices
        c. black matrices

4. Reservoirs
    4.1. Clasts
    4.2. Carbonates

3.1. Liquid hydrocarbons (Pl.1 to 7)

Five categories have been distinguished:

3.1.1. Drops (Pl.1 and 2)

They are clearly spherical and could be divided by size: from few microns (Pl.2, ph.4) to hundreds of microns (Pl.1, ph.3). However, as the color is related to the oil quality, it is more interesting to classify them by color from yellow-brown (Pl.1, ph.1) to green (Pl.1, ph.2). Drops are generally isolated, but they can be grouped or packed. They look empty, some show a central cavity or are multivacuolate (gas bubbles). Furthermore, their proportion is related to oil quantity and, as mentioned, their color is related to oil quality (see 4.1). Drops may also increase in size during fluorescence excitation (with oil immersion objectives) and may show a strong negative fading.

3.1.2. Films (Pl.3 and 4)

Films appear as coatings, stuck or inflated (transition with droplets), short (Pl.3, ph.2) or long (Pl.4, ph.3), thin (Pl.3, ph.3) or thick (Pl.3, ph.4). The color can vary from green to yellow-brown with the same chemical significance as for the drops. Under blue light they may react as the drops do, and some with negative fading. Thick yellow films are more stable.

3.1.3. Exsudates (Pl.5)

Exsudates are difficult to describe. Their size is greater than for films, they are irregular and complex, with waves (Pl.5, ph.1), networks (Pl.5, ph.2), corona (Pl.5, ph.3), thickenings (Pl.5, ph.4).
This category is the one which, perhaps, could be related or affected by mud-oil contamination, but we have no specific argument to present.

3.1.4. Dissolved hydrocarbons in resin (Pl.6)

Some oils seem to be quasi-totally extracted by the embedding resin (saturated oils). In such cases, no drops nor films are visible. In other cases drops and films can co-exist. The latter correspond to the best source rocks.
In such cases when drops and films do not mix with the resin (aromatic oils) their presence is inversely proportional to the amount of HC dissolved by the resin.
The resin color is related to the oil quality: greenish for saturated oils (Pl.6, ph.1), and yellow for aromatic ones (Pl.6, ph.2 to 4).
The fluorescence intensity is more related to oil quantity and is the subject of a specific fluorescence scale (see 4.1).

3.1.5. Non-spherical hydrocarbons (intercrystal fillings) (Pl.7)

Some HC fill cavities and fractures, and may be present between and in the minerals. This is typical for many clastic aggregates (see also Pl.15, ph.1). Therefore the shapes of these HC are totally irregular and angular in form. They are most frequent in reservoirs. This category is transitional with solid HC. Contrary to drops and films, they do not change with fluorescence excitation.

3.2. Solid hydrocarbons: Migrabitumen (Pl.8 to 10)

As mentioned in the introduction, solid hydrocarbons are treated in a specific classification (Fig.1) worked by Jacob (1989), then accepted and improved by the ICCP under the concept of Migrabitumen (MB) (Table 2). Microsolubility and micro-flow point are difficult to use routinely, thus we have simplified the classification by only using the reflectance and fluorescence properties. Migrabitumen have been divided into three categories according to their aspect in reflected light: dark, grey and white.

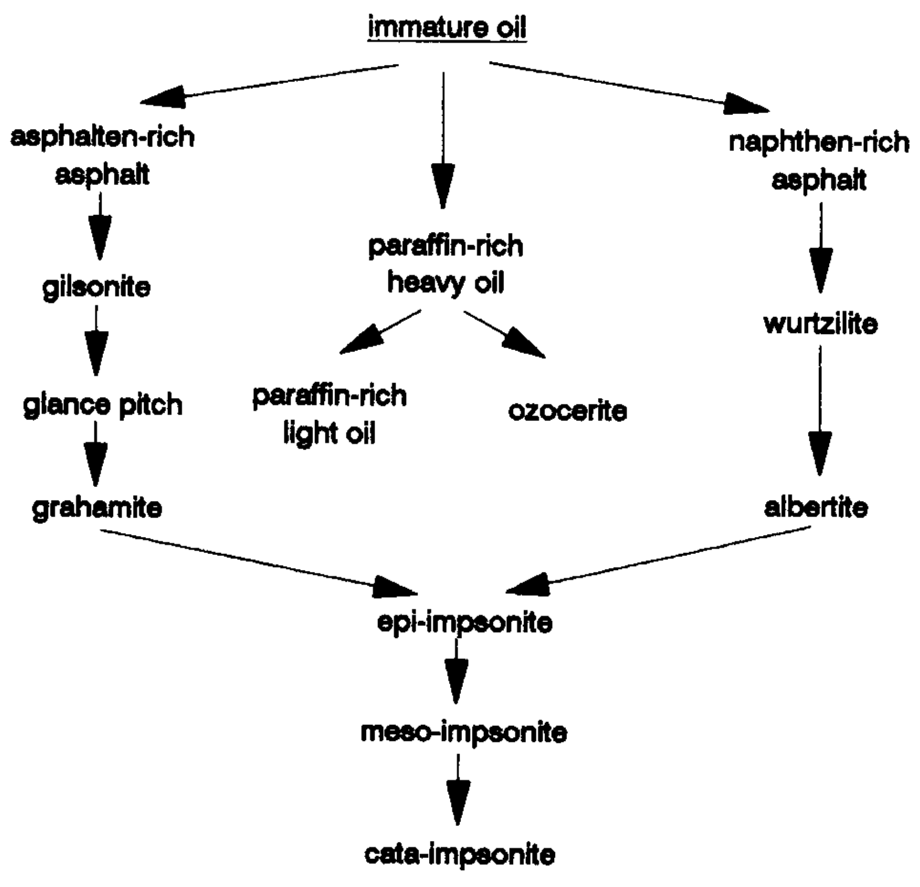

Fig 1 - Genetic relation between oil and bitumen, after Jacob (1989).

Table 2 - Classification and properties of Migrabitumen, after Jacob (1989).

	Random Reflectance (oil) %	Fluorescence (special masked uranyl glass standard = 1 %)	Micro-solubility in immersion oil and petroleum ether	Micro-flowpoint °C
ozocerite	< 0.01 - ca. 0.02	ca. 9.0 - > 50	soluble	ca. 30 - ca. 90
wurtzilite albertite	< 0.01 - ca. 0.1 ca. 0.1 - ca. 0.7	ca. 0.1 - > 2.0 ≤ 0.1	insoluble insoluble	does not flow does not flow
asphalt gilsonite glance pitch grahamite	ca. 0.02 - ca. 0.07 ca. 0.07 - ca. 0.11 ca. 0.11 - ca. 0.3 ca. 0.3 - ca. 0.7	ca. 0.4 - > 4.0 ca. 0.05 - ca. 0.4 ca. 0.05 - ca. 0.2 ≤ 0.05	soluble soluble soluble slightly soluble or insoluble	< 104 ca. 104 - ca. 164 ca. 104 - ca. 164 > 164 - ca. 287
epi-impsonite meso-impsonite cata-impsonite	ca. 0.7 - 2.0 2.0 - 3.5 3.5 - ca. 10	≤ 0.02 < 0.01 < 0.01	insoluble insoluble insoluble	does not flow does not flow does not flow

3.2.1. Dark Migrabitumen (Pl.8 and 9)

This category includes all low reflecting black-reddish MB whose reflectance is less than 0.2%. The surface is smooth and homogeneous (Pl.8, ph.3) or scratched (Pl.8, ph.1). Sometimes the aspect is granular (Pl.9, ph.5).
They generally fluoresce yellow-brown, very often with peripherical differentiation in which fluorescence is of lower intensity and more brown (Pl.8, ph.4; Pl.9, ph.4).
This dark MB family includes the following categories from Jacob's classification: asphalt, ozocerite, wurtzilite, gilsonite, glance-pitch and, perhaps, a small proportion of albertite.
Under fluorescence excitation they can react and produce liquid hydrocarbons (Pl.8, ph.2).

3.2.2. Grey Migrabitumen (Pl.10)

This category corresponds to grey MB of reflectivity between o.2% and 0.7%. Some are fluorescent (Pl.10, ph.5) and others not. This group corresponds to grahamite, albertite (in part) and perhaps a part of glance-pitch of Jacob's chart.

3.2.3. White Migrabitumen (Pl.10)

They correspond to MB having a reflectivity higher than 0.7% (Jacob's impsonites). The color is light grey and white till yellowish.
They are divided in three classes: isotropic (Pl.10, ph.1), anisotropic (global anisotropy (pl.10, ph.2)) and bitumen or petroleum cokes. This last category shows clear mosaic or fibrous textures after complete fusion and mesophase formation. Spherobitumen are classified according to their reflectivity and fluorescence properties.

3.3. Mature Source Rocks (SR) and hydrocarbon progenitors (Pl.11 to 14)

We do not intend to describe all sedimentary rocks in reflected light, nor the various macerals dispersed in matrices. We concentrate our descriptions only on mature source rocks in course of oil production.
The main subdivisions introduced are a function of the **supposed dominant** oil **progenitors** which have been detected in fluorescent light.
In some cases oil progenitors can be mixed. Moreover, even if the supposed oil progenitor is detected, the organo-mineral matrices play a significant role and their fluorescence intensity, color and fading should always be considered.

3.3.1. Source rocks with Sporinite (Pl.11)

Due to its richness in hydrogen, Liptinite has long been considered a good oil progenitor. The most frequent Liptinite maceral, mainly when it is associated with coals, is Sporinite (including spores and pollen).
When spores are passing from yellow to golden-brown and orange or red (so-called "red-shifted") they are indicative of significantly mature rocks, and can show a visible oil production under fluorescence light (Pl.11, ph.1,2). Nevertheless, it is difficult to acertain if the oil is coming specifically from spores or

from fissures in the organo-mineral matrix (Pl.11, ph.2). These fissures may correspond to spores already cracked and almost totally disappeared. It should be mentioned that exinite, in coals, can produce more than 80% of volatile matters. The residue should therefore be very small in volume.
Sometimes spore populations are mixed (Pl.11, ph.3) one being red-shifted and mature, the other yellow-brown (early mature). Different oils could therefore be produced.

3.3.2. Source rocks with Bituminite (Pl.12)

Bituminite is a common matrix in generally immature oil shales and sapropelic coals. When mature, bituminite is difficult to recognize because its fluorescence disappears and the reflectivity passes to medium grey similar to vitrinite. The bituminite presented in Pl.12 (ph.1,2) is supposed to be early mature. Although oil generation is not evident, it could come from intermixed algodetrinite included in the bituminite matrix.

3.3.3. Source rocks with Alginite (Pl.12)

a. Telalginite, as Botryococci (Pl.12, ph.3) or Tasmanaceae, are easy to recognize. When Botryococci are mature they are reddish and poorly fluorescent.

b. Lamalginite, including algodetrinite and mixed with organo-mineral matrices (Pl.12, ph.4), also progresses towards orange color with increase in maturity. It differs from bituminite by its higher fluorescence.

3.3.4. Source rocks with Acritarchs-Dinoflagellates (Pl.13)

These are probably the best source rocks when mature, and they can contain a great mass of micro-algal fragments and ornaments. Sometimes bigger specimen are conserved permitting to measure some parameters in fluorescent light (Pl.13, ph.1). They generally look less mature than the other corresponding liptinitic rocks.

3.3.5. Source rocks with fauna (Pl.13)

Foraminifera are frequent in many limestones and often easy to recognize (Pl.13, ph.4). Very often the cavities are filled with yellow HC, generally stable under fluorescent light. Many other faunal relicts can be present but are difficult to recognize, either due to submicroscopic size or to strong destruction.

3.3.6. Source rocks with mixed progenitors

Various oil progenitors can be associated in matrices and may be significant for palaeoenvironmental interpretations:

a. mixing of micro-megaspores, cuticles, resins are clearly of continental origin;

b. spores and Botryococci mixed with Bituminite are more lacustrine. Fish remains are often present with the same sapropelic associations in rich oil shales;

c. Dinoflagellates and Acritarchs, often associated to lamalginite, belong to a clearly different milieu with a marine character.

3.3.7. Source rocks without visible organoclasts (Pl.14)

Many sedimentary rocks do not reveal any visible organic automorph inclusions. One can suppose that they are absent since the beginning or that they have disappeared by cracking (overmature rocks). The first hypothesis is the most probable one, and thus the matrices have been divided according to their fluorescence color which varies from greenish (Pl.14, ph.1) to brown (Pl.14, ph.2), dark brown (Pl.14, ph.3) and black (Pl.14, ph.4). Nevertheless, high producing black matrices (as Pl.14, ph.4) can be considered as probably being totally cracked.

3.4. Reservoirs (Pl.15)

Reservoirs have not been the subject of intense studies as they are easily detected by other techniques. However, they can simply be divided into:

3.4.1. Clasts (Pl.15, ph.1,2) characterized by their non-spherical intercrystal HC fillings (ph.1) or films (ph.2).

3.4.2. Carbonates. They are visible as oolites or rhombohedric crystals and may include fluorescent organic matter. The fluorescence can be green, yellow, orange or red (Pl.15, ph.4) in relation with the quality of the HC captured. The same crystal can contain various HC generations (Pl.15, ph.3). Sometimes, in the same field, yellow and green crystals coexist, the latter being always a second posterior generation. Most of these carbonates are probably of biological origin.

4. APPLICATION OF THE OPTICAL PROPERTIES OF HYDROCARBONS IN SEDIMENTARY ROCKS

This part is presented in greater detail by Alpern et al. (1992).

4.1. Relations with oil quality and quantity

The fluorescence properties of oils were determined:

a. directly, on a free crude oil drop simply mounted on a glass slide and covered by a lamella;
b. on hydrocarbons mixed with the embedding resin, thus changing all its fluorescence properties;
c. on automorphic hydrocarbons (films, drops) in polished block.

The work herewith presented is concerned with the first two methods.

a. Relations with free oil (on slide)

Based on ten selected oils of variable compositions, a very good correlation ($r = 0.951$) was obtained between Q_{UV} 650/500 and the percentage of aromatic HC (ARO) plus heavy products (HP) expressed as ARO + HP % (Fig.2). Heavy products comprise resins + asphaltenes.

b. Relations with oil mixed with embedding resin

b.1. Oil quality

In comparing the same oils in slides and mixed with embedding resin, it appears that the corresponding Q_{UV} values obtained are very different (Fig.3).
Free oils are more reddish (Q up to 0.8) than embedded oils (Q up to 0.4); the correlation is good ($r = 0.877$). During routine work, all HC optical properties are established on polished embedded granular particles,and thus, most of the correlations with geochemical data have been established with the embedding resin.
A good correlation between Q_{UV} and the amount of saturated HC (SAT) has been obtained ($r = -0.854$) (Fig.4). The correlation improves ($r = -0.922$) when the relation between Q_{UV} and the SAT/ARO ratio is established (Fig.5). However, the best correlation is obtained when the relation between Q_{UV} and SAT/ARO + HP is considered ($r = -0.963$) (Fig.6). The Q values obtained on each one of the different concentrations of oil mixed with the embedding resin were so similar that an average Q value is considered representative and is the one used in Figs 3 to 6.
This latter point was a strong and valid reason to consider Q as an optically detectable quality parameter.

b.2. Oil quantities

For most boreholes investigated during routine analyses, the correlations obtained between I_{546} and S_1 from Rock-Eval are rather good.
In borehole CA1 (Fig.7) the correlation is excellent ($r = 0.934$). It is lower, but still good, in borehole CA2 (Fig.8).
It is evident that this type of correlation is affected when cuttings have been subjected to a chloroform extraction. Furthermore, these correlations improve with increasing rank: when the maturation is low, the HC are heavier and a part of them will report to S_2 (+C30) and not to S_1; when maturation is high, HC are lighter and will report to S_1, thus giving better correlations.

c. Artificial blends: oils and resin

In order to obtain a better understanding and an improved valorisation of the optical properties, seven selected oils have been mixed, in increasing proportions (0.5% to 4%), with the EPOFIX embedding resin.

Results indicate that, when the percentage of oil mixed with the embedding resin is higher than 4-5%, some problems arise. Aromatic oils (ARO) do not mix with resin, whilst saturated oils (SAT) mix well even up to 10% or 15%. The I_{546}, measured on embedding resin, correlates with oil quantities for SAT oils but not for ARO oils probably due to mixing and quenching effects in the latter. Therefore, the best relations are obtained for oil proportions below 5% (Fig.9). It is clear from Fig.9 that for a fixed oil quality obtained by its Q_{UV} value (for example, 0.4), I_{546} of the embedding resin is validly correlated to the percentage of oil mixed with the resin. All correlation coefficients are higher than 0.9.
If we consider now the relation between I_{546} and oil quality obtained by SAT/ARO+HP, it is clear (Fig.10) that for a given I_{546} value (for example 100) the corresponding percentage of oil varies from 0.5% for ARO oil, to 4% for SAT oil, that means eight times more.

4.2. Variation of optical properties and geochemistry of oils with depth

Two examples are given.
One for borehole TC on which S_1, S_2, and S_1+S_2 are correlated with I_{546} (Fig.11). The correlation between I_{546} and S_1 can be considered as good (r=0.89).
The second case refers to the Paris basin, considered as a basic reference. Geochemical data from Institut Français du Pétrole (IFP) have been correlated with I_{546} (Fig.12).
The variations of both parameters, I_{546} and S_1/TOC, with depth are presented on Fig.12a. The crossing of mature Toarcien oil shales at about 2400m is clearly detected by optical data. The correlation between I_{546} and S_1/TOC (Fig.12b) can be considered as excellent (r=0.954). Moreover, experience has shown that better correlations are obtained with S_1/TOC instead of S_1 alone.
As a point of interest, the correlation with the chloroform extracts provides the same results.

5. CONCLUSIONS

With the use of unsophisticated equipment (monochromatic filters) it is possible to detect oil during simple routine optical fluorescence examination of whole rock polished samples, mounted on an epoxy embedding resin.
Source rocks, main oil progenitors, and reservoirs can also be recognized.
Good correlations were established between optical indices measured on embedding resin (I_{546} and Q_{uv} 650/500) and the quality of free crude oils in terms of chemical composition (saturated (SAT) versus aromatic (ARO) + heavy products (HP)).
In borehole sequences, good relations have been established between optical index (I_{546}) and the quantity of the oil present in the sedimentary rocks in terms of Rock-Eval data (S_1 and S_1/TOC).

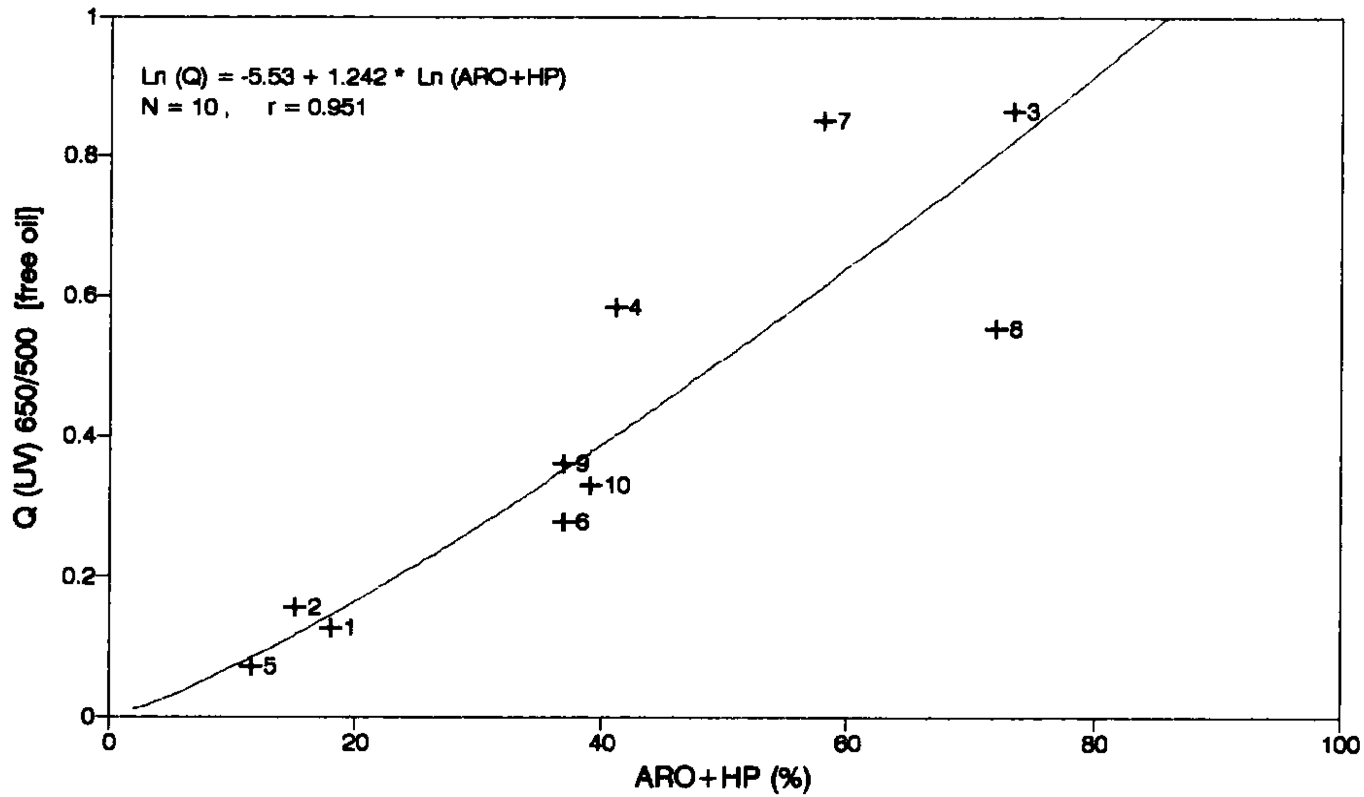

Fig. 2 - Correlation between optical parameter Q(UV) on free oil (slide) and oil quality (ARO+HP %) for 10 selected oils.

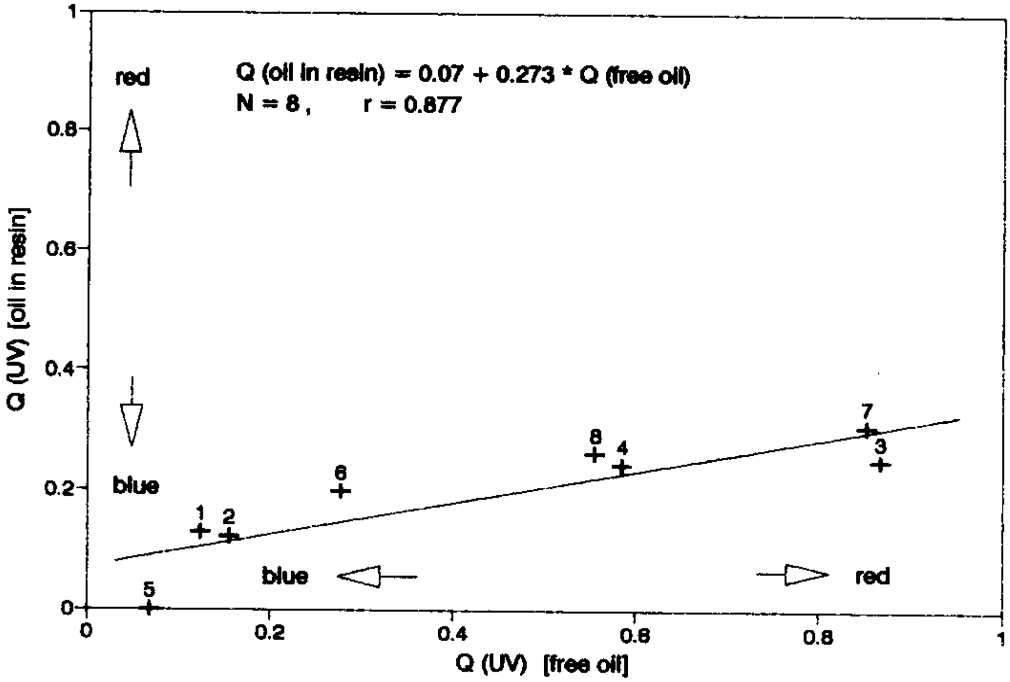

Fig. 3 - Correlation between Q(UV) measured on free oil (slide) and on oil mixed with embedding resin (polished block). Free oils (slide) are more reddish (Q up to 0.8) than oils mixed with resin (Q up to 0.4).

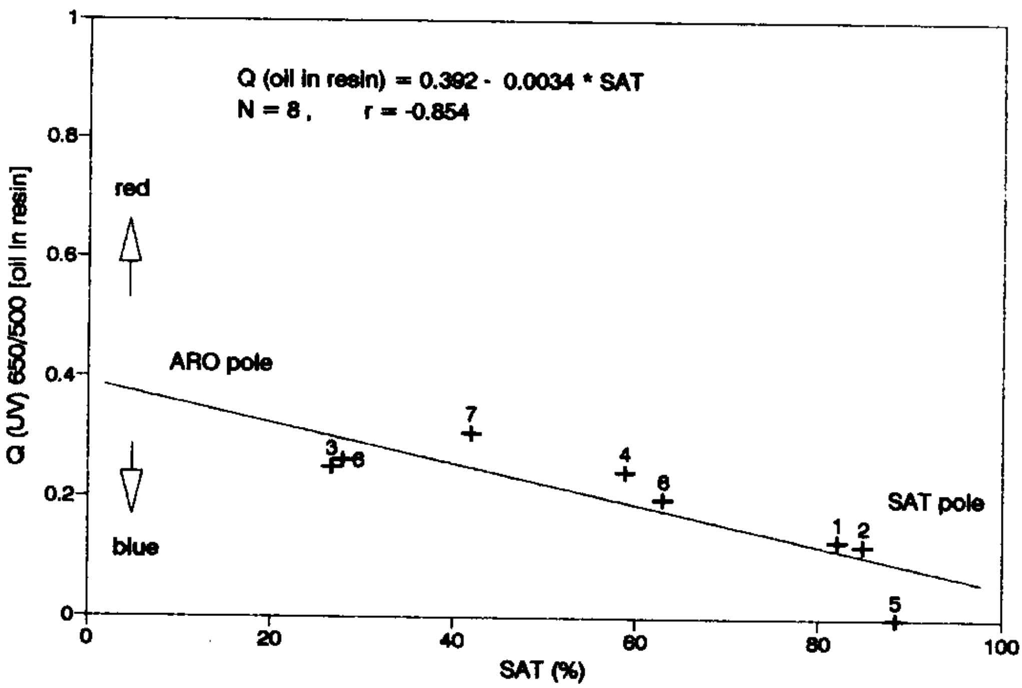

Fig. 4 - Correlation between Q(UV) of oil mixed with embedding resin (polished block) and oil quality (SAT %). Saturated oils fluoresce in lower wavelengths than aromatic ones.

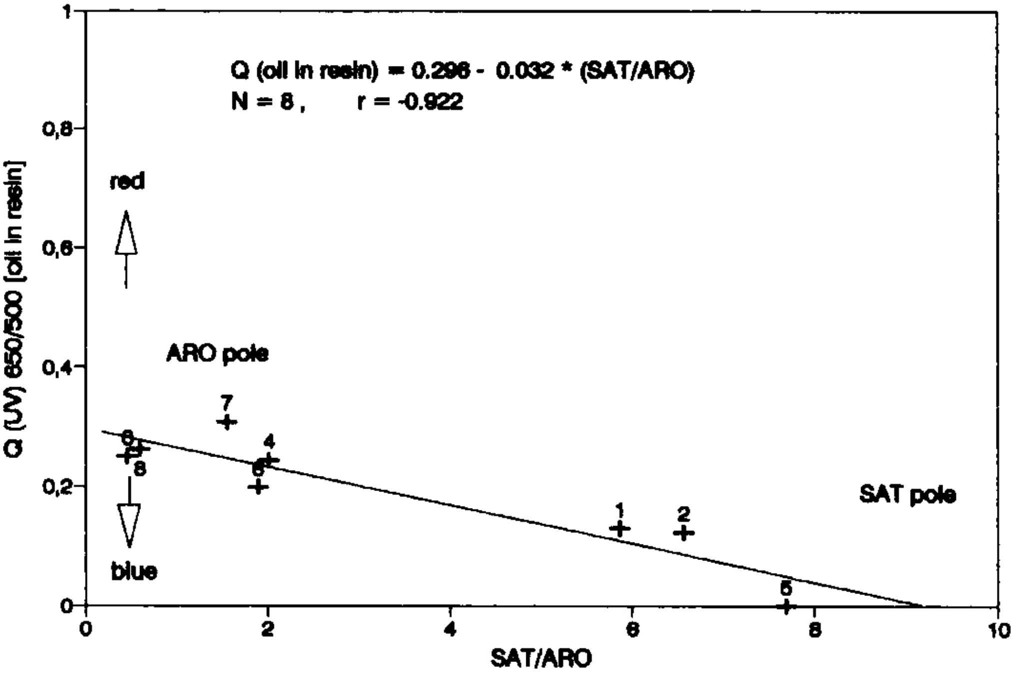

Fig. 5 - Correlation between Q(UV) of oil mixed with embedding resin (polished block) and oil quality (SAT/ARO).

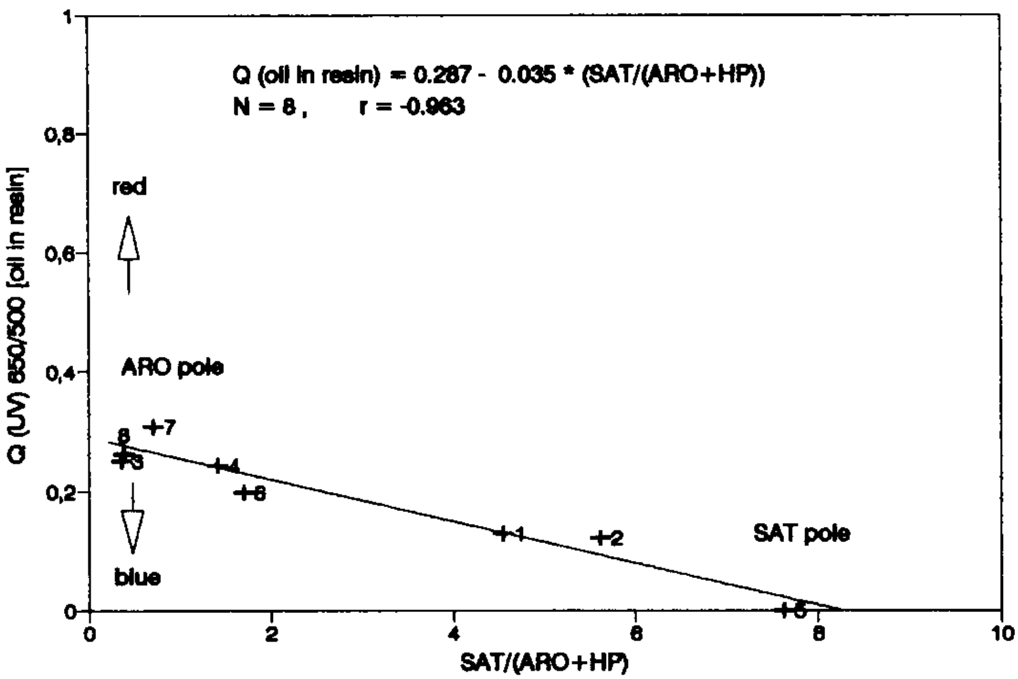

Fig. 6 - Correlation between Q(UV) of oil mixed with embedding resin (polished block) and oil quality (SAT/(ARO+HP)).

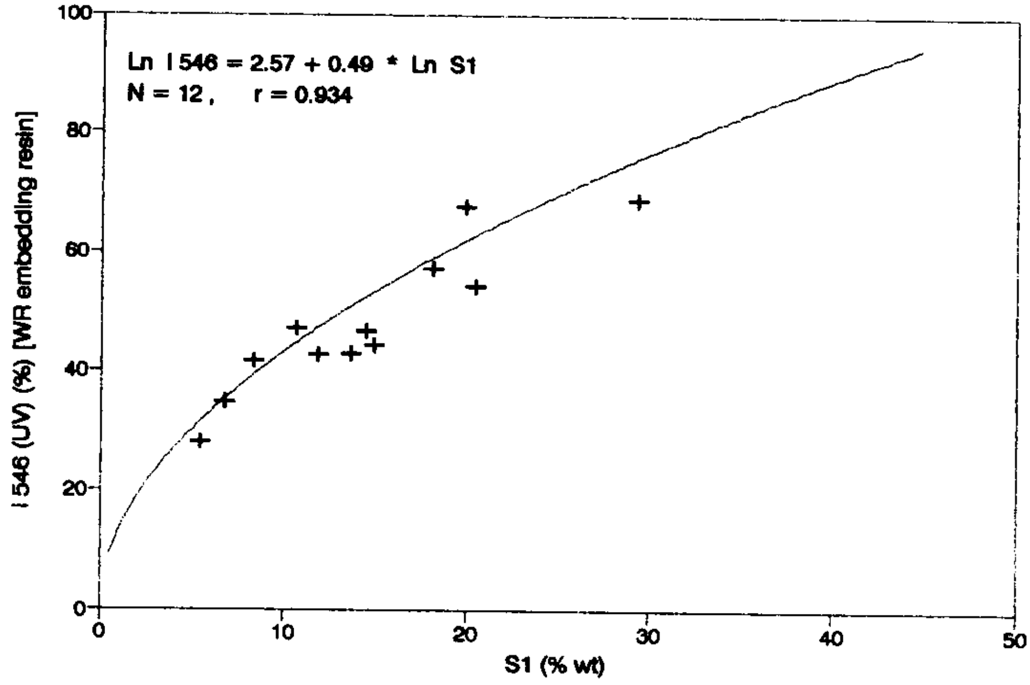

Fig. 7 - Borehole CA 1: Correlation between I 546 of the whole rock (WR) embedding resin (polished block) and S1 from Rock Eval.

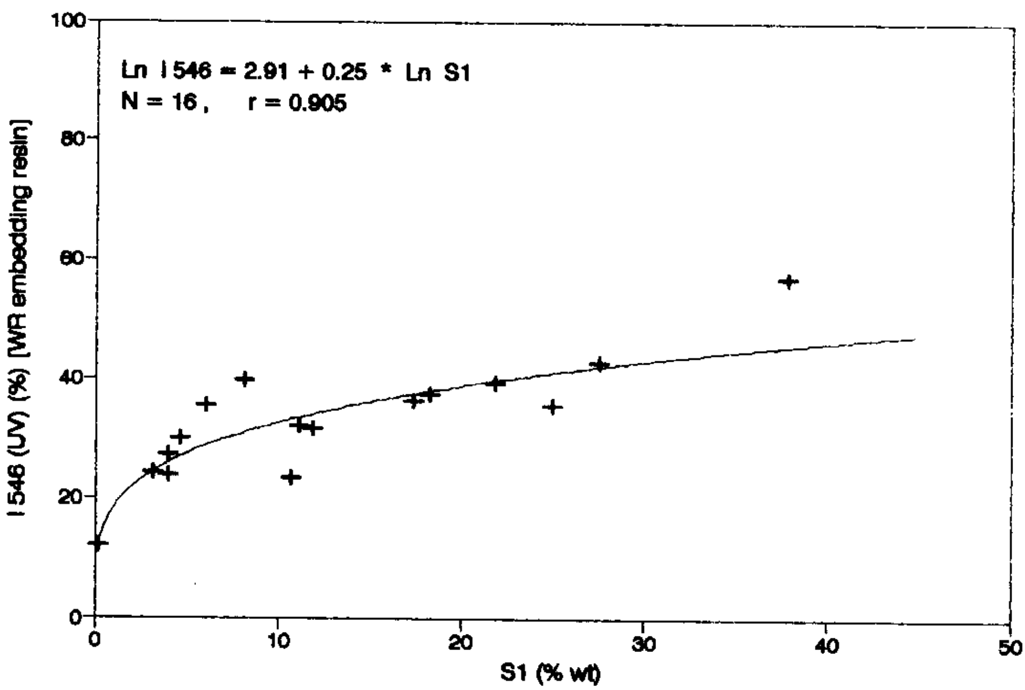

Fig. 8 - Borehole CA 2: Correlation between I 546 of the whole rock (WR) embedding resin (polished block) and S1 from Rock Eval.

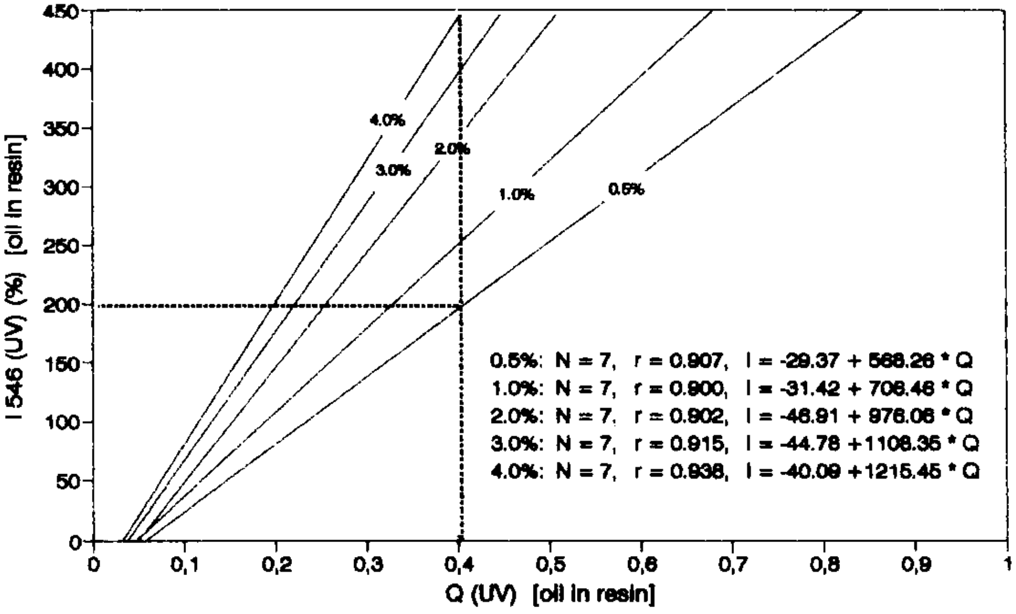

Fig. 9 - Correlation between optical parameters (Q (UV) and I 546 (UV)), oil qualities and increasing percentages (0.5-4.0 %) of oil mixed with embedding resin (polished blocks). If the quality is fixed, then I 546 is proportional to hydrocarbon percent.

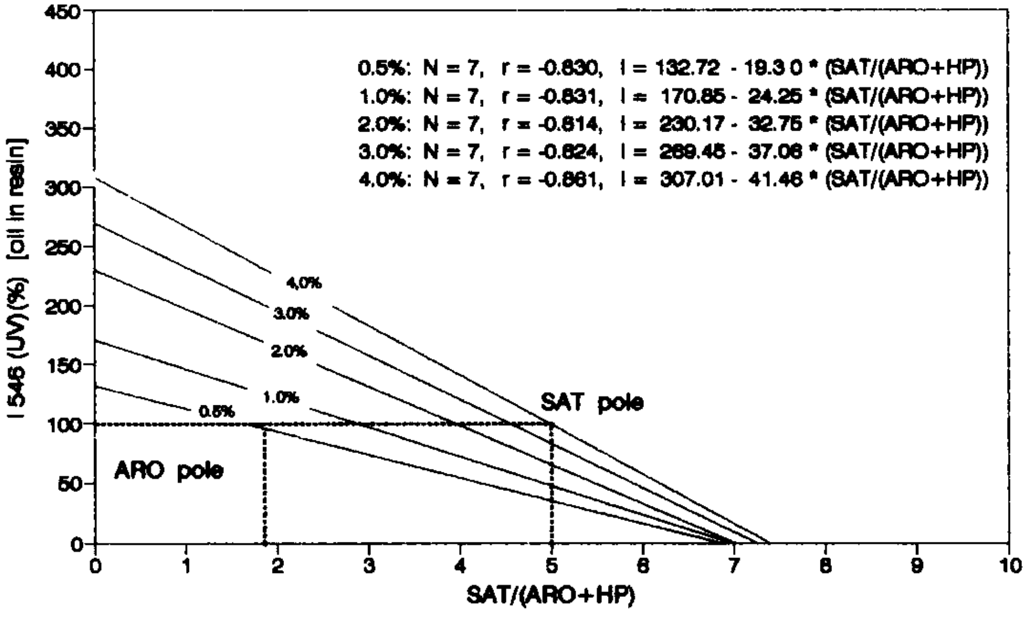

Fig. 10 - Correlation between I 546 (UV) oil qualities (SAT/(ARO+HP)) and increasing percentages of oil mixed with embedding resin (polished blocks). SAT oils need 8x more concentration than ARO oil in order to have the same I 546 value.

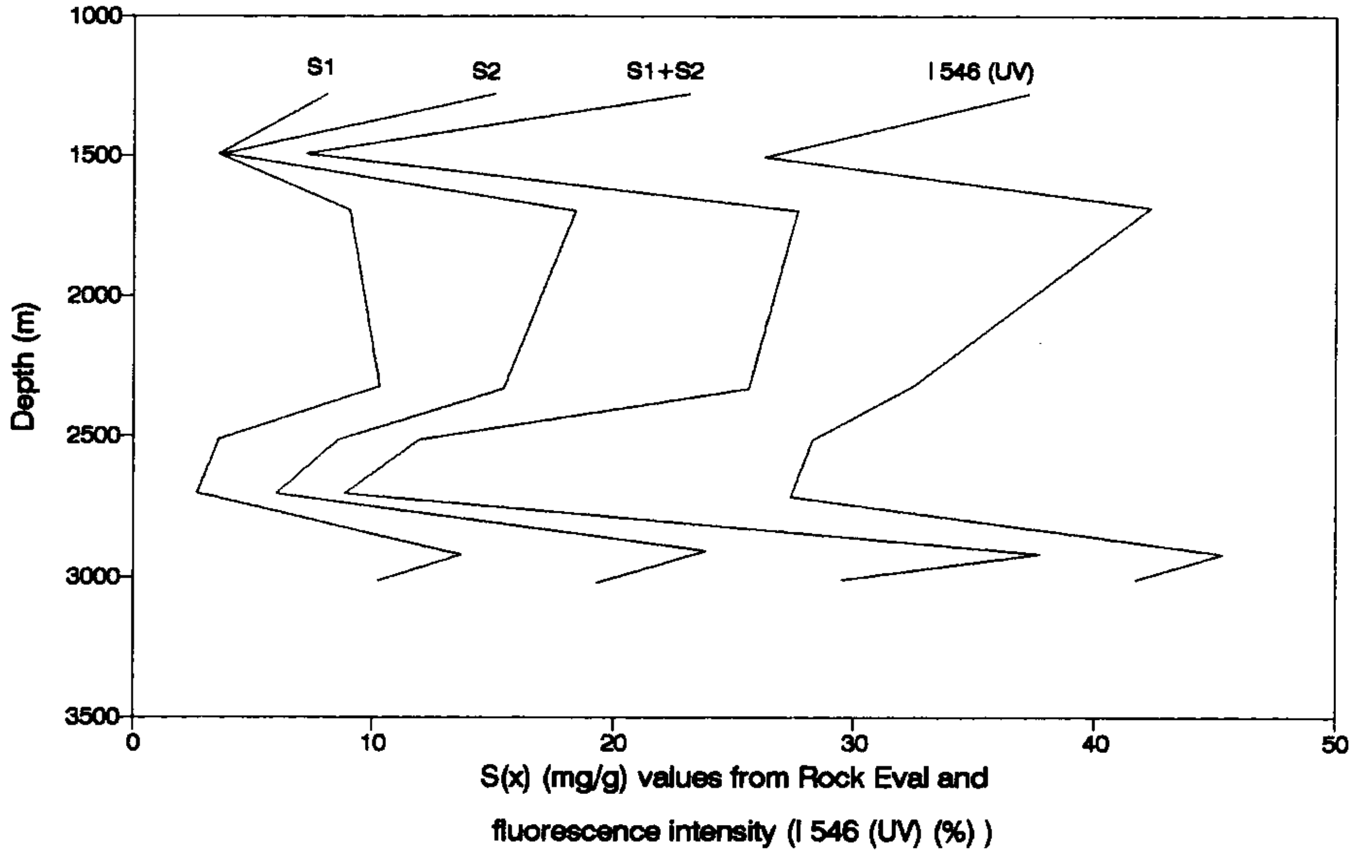

Fig. 11 - Borehole TC: An example of the relation between selected Rock Eval geochemical data (S1 and S2) and embedding resin fluorescence intensity (I 546 (UV)). In this case the correlation coefficient between I 546 and S1 is 0.89.

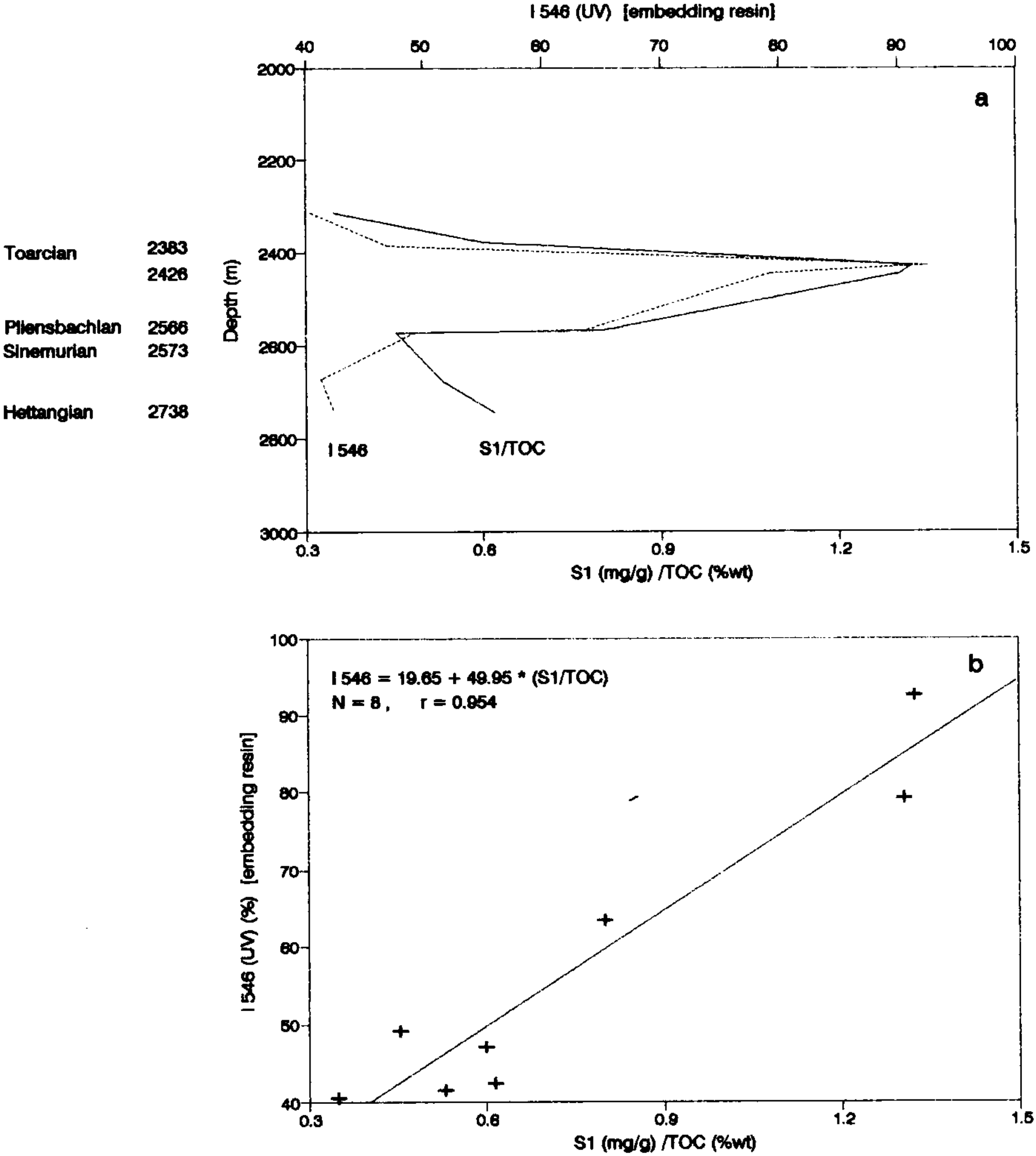

Fig. 12 a, b - Variations with depth and correlation between optical (I 546 (UV)) and geochemical parameters (S1/TOC) for the Paris Basin.

Acknowledgements

The authors are indebted to Chevron Overseas Petroleum Inc., Total, Institut Français du Pétrole - IFP, and Gabinete para a Pesquisa e Exploraçao de Petróleo - GPEP for supplying borehole cuttings, oils and geochemical data, and for permission to publish corresponding information. In particular, Mr G. Demaison and Miss M.R. Cassa (Chevron), Mr J.-L. Oudin (Total), Mssrs B. Durand and J. Espitalié (IFP), and Mssrs J. Agnelo Fernandes, R. Vieira, and F. Laima (GPEP) are acknowledged for the assistance provided during this investigation.
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PLATES

All photographs have been taken with a Leitz Orthoplan microscope equipped with fluorescence and a Photoautomat MPS 55.

Blue light fluorescence was obtained with BG 12 excitation filter (λ = 408 nm), K 510 barrier filter and TK 510 dichroic mirror.

Ultraviolet fluorescence was obtained with UG 1 excitation filter (λ = 365 nm), K 430 barrier filter and TK 400 dichroic mirror.

Magnification is provided in each plate in the form of a graphic scale.

Plate 1 - DROPS

1. Small to medium yellow oil drops issuing from dark brown matrices and trapped in high yellow embedding resin.

   Type of sample: cuttings
   Depth: 13740-13750 ft
   Region: Angola

2. Medium green drops related to greenish matrix. Low green embedding resin.

   Type of sample: cuttings
   Depth: 5640-5670 ft
   Region: India

3. Big greenish oil drop issuing from black matrix with orange Liptinite.

   Type of sample: cuttings
   Depth: 7740-7770 ft
   Region: India

Plate 1

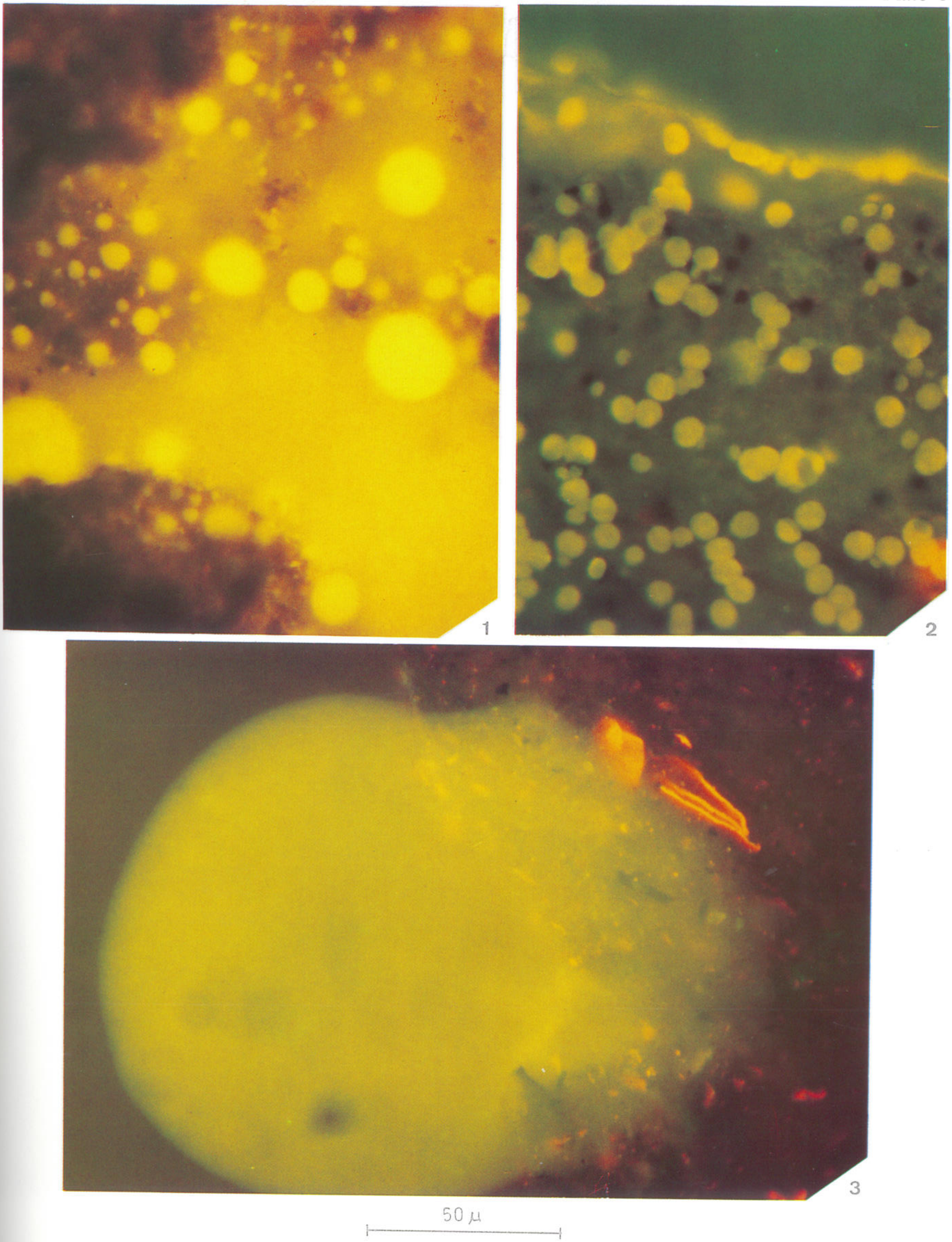


Plate 2 - DROPS

1. Yellow-green irregular drop partly covering a dark brown shale matrix containing pale minute Liptodetrinite (visible under the drop).

   Type of sample: cuttings
   Depth: 7140-7170 ft
   Region: India

2, 3. Big isolated oil drops seen in UV light (2) and in blue light (3).

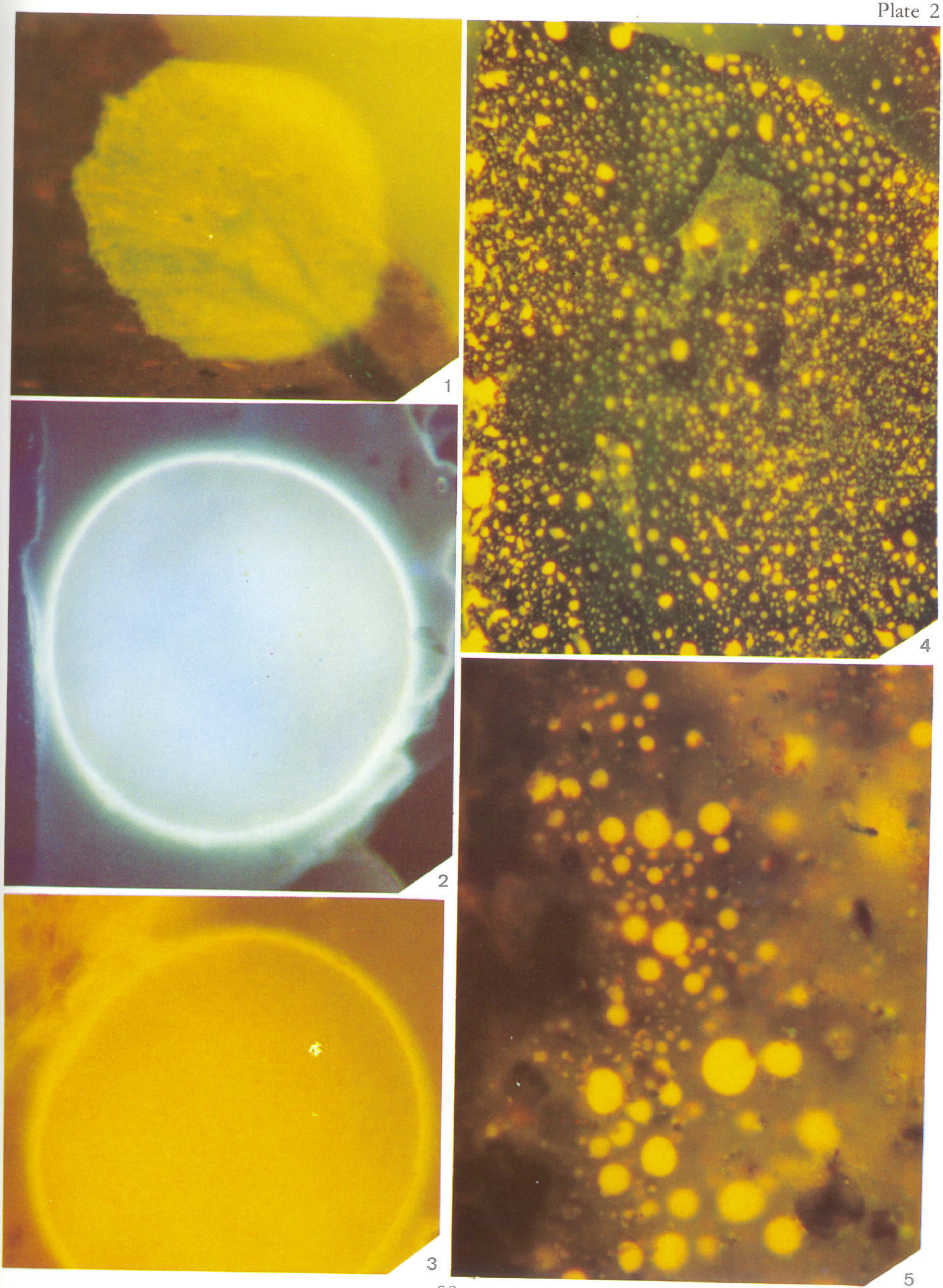
   Type of sample: cuttings
   Depth: 5750 ft
   Region: Papua-New Guinea

4. Abundant population of small to medium yellow drops related to a black particle.

   Type of sample: cuttings
   Depth: 7000 ft
   Region: Colombia

5. Medium yellow drops associated to dark brown matrices.

   Type of sample: cuttings
   Depth: 14320-14330 ft
   Region: Angola



50 μ

Plate 3 - FILMS

1. Medium brown matrix, without Liptinite, impregnated (in fissures) and covered by a thin yellow film. Weak green embedding resin.

   Type of sample: cuttings
   Depth: 6670-6690 ft
   Region: Angola

2. Irregular yellowish film, inflated (top) and coating a dark brown matrix (bottom) containing a weak brown Sporinite. Weak green embedding resin.

   Type of sample:cuttings
   Depth: 7870-7890 ft
   Region: Angola

3. Thin inflated green-yellow film related to a dark brown matrix with no visible Liptinite. Weak greenish embedding resin.

   Type of sample: cuttings
   Depth: 8200 ft
   Region: Papua-New Guinea

4. Thick yellow film covering a black matrix. Medium yellowish embedding resin.

   Type of sample: cuttings
   Depth: 9650-9670 ft
   Region: Angola

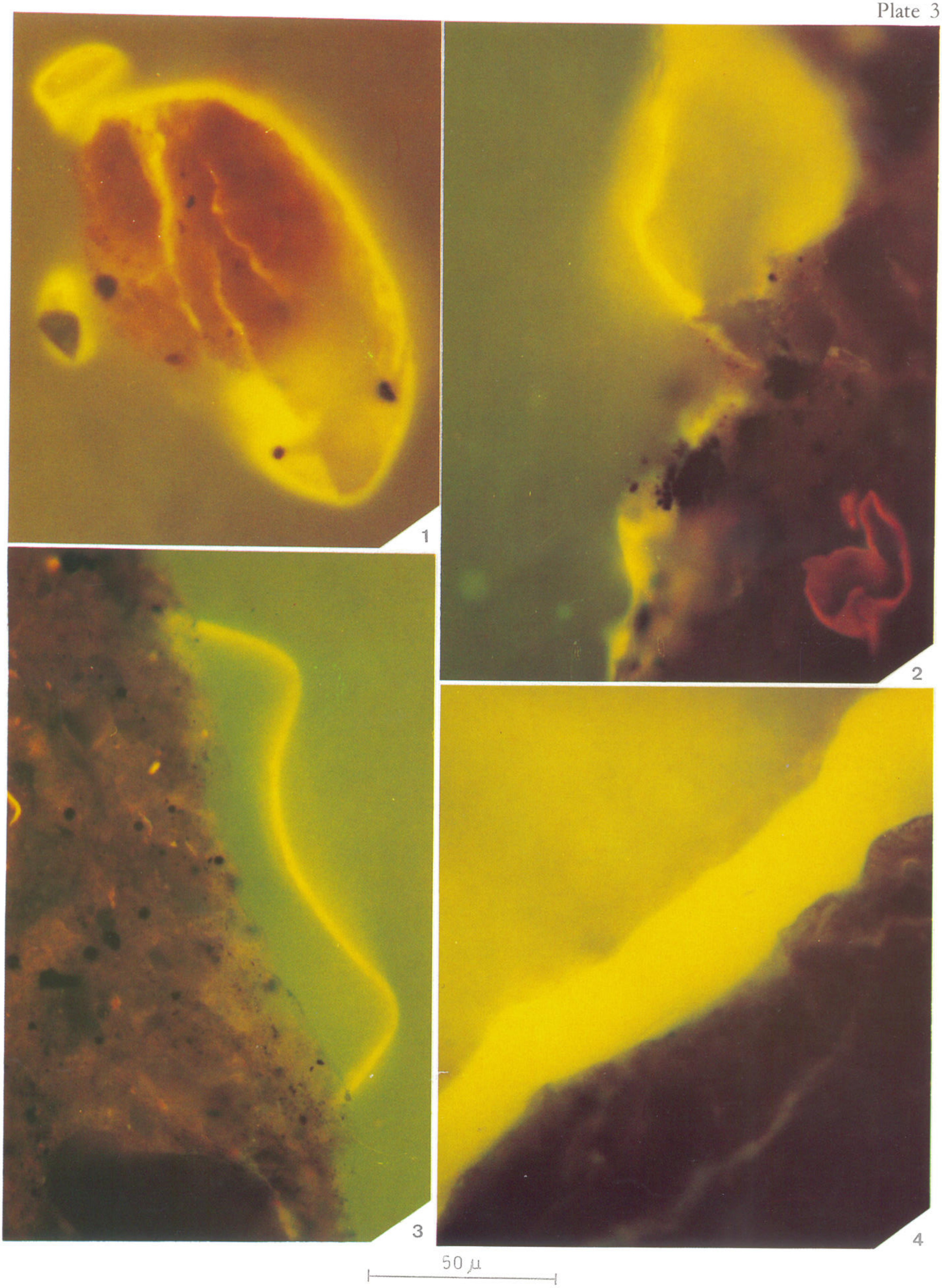

1
2
3
4
50 μ

Plate 4 - FILMS

1. Inflated thick yellow film related to a medium brown organo-mineral matrix containing light brown Sporinite.

   Type of sample: cuttings
   Depth: 7740-7770 ft
   Region: India

2. Green film issuing from a well stratified shale containing Lamalginite (top) and minute yellow Algodetrinite (bottom). Weak green embedding resin.

   Type of sample: cuttings
   Depth: 7740-7770 ft
   Region: India

3. Thin yellow inflated film related to a weak brown matrix with rare orange Liptinite. Weak green embedding resin.

   Type of sample: cuttings
   Depth: 3500 m
   Region: Romania

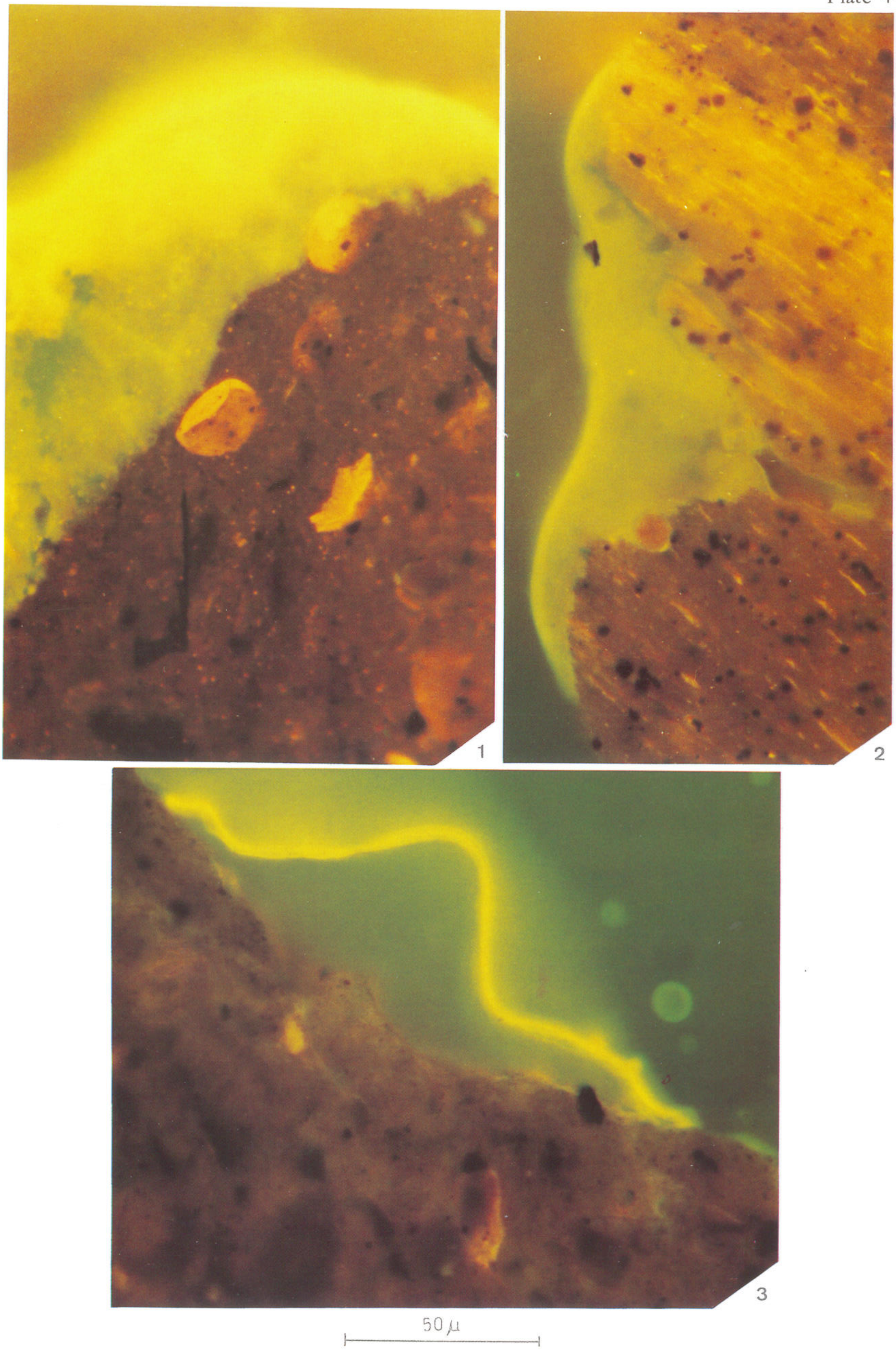

1
2
3
50 μ

Plate 5 - EXSUDATES

Various irregular aspects of oil exsudates associated to black particles.

1. Wavy

   Type of sample: cuttings
   Depth: 5750 ft
   Region: Papua-New Guinea

2. Network

   Type of sample: cuttings
   Depth: 7000 ft
   Region: Colombia

3. Corona

   Type of sample: cuttings
   Depth: 3500 m
   Region: Romania

4. Thickenings

   Type of sample: cuttings
   Depth: 5640-5670 ft
   Region: India

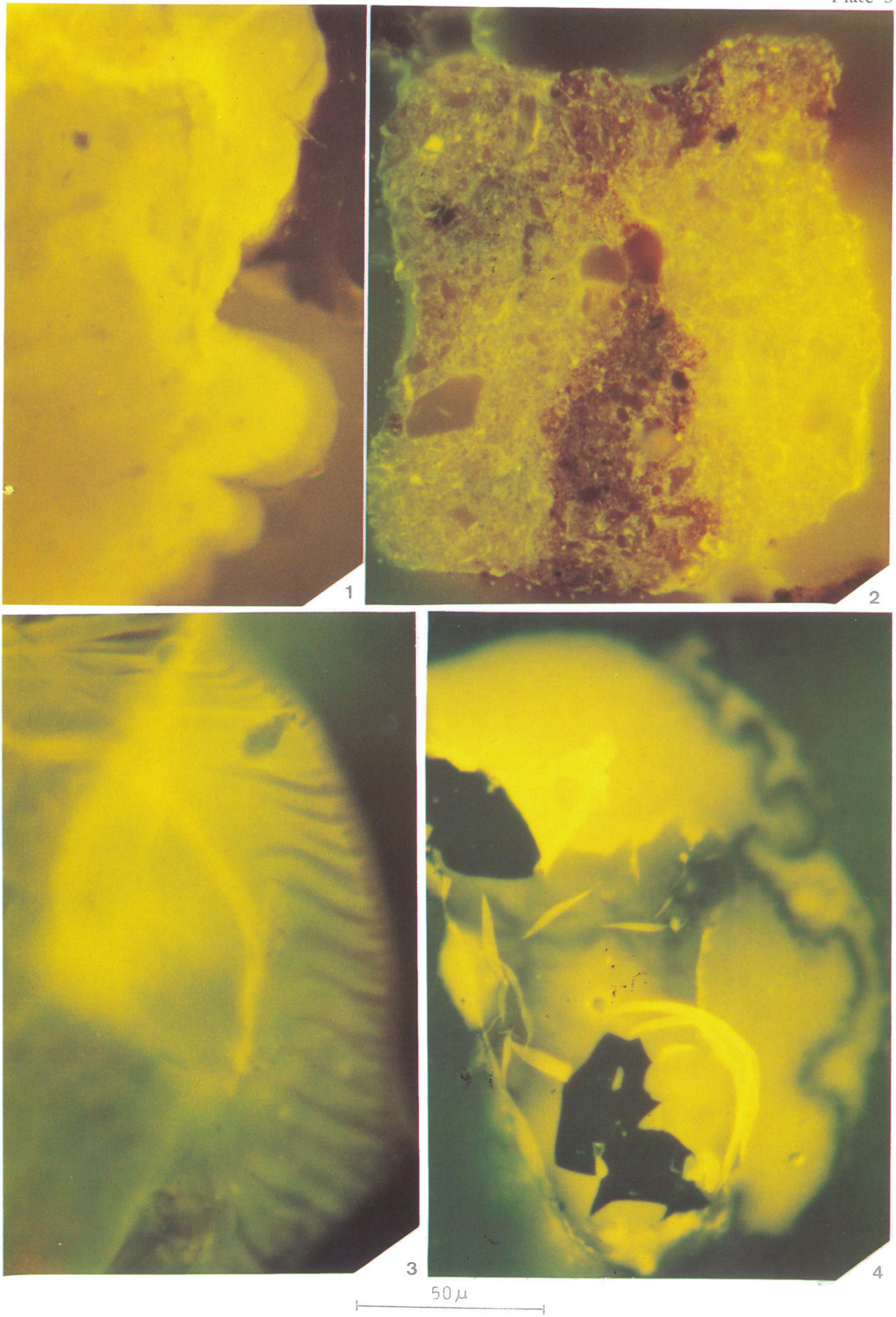

1
2
3
4
50 μ

Plate 6 - DISSOLVED HYDROCARBONS

1. Medium green embedding resin having dissolved green hydrocarbons produced by a dark brown matrix containing orange shifted Sporinite.

   Type of sample: core
   Depth: 2068.9-2079.4 m
   Region: Commonwealth of Independent States (CIS)

2. Intense yellow hydrocarbons impregnating embedding resin around a black massive matrix. A fracture is impregnated with a yellow drop in formation, as well as at the periphery.

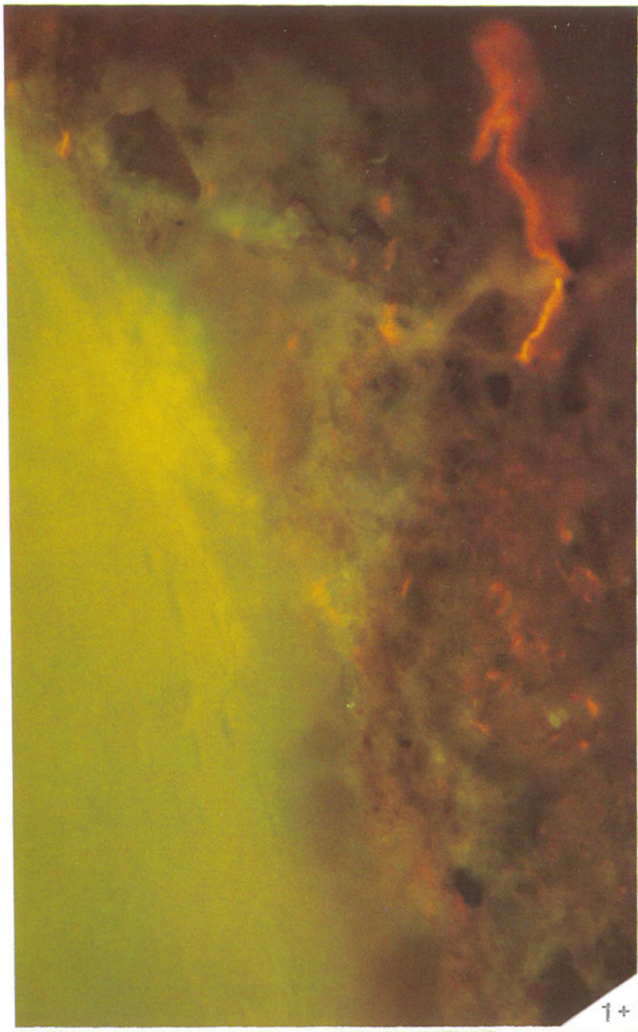
   Type of sample: cuttings
   Depth: 8940-8980 ft
   Region: Angola

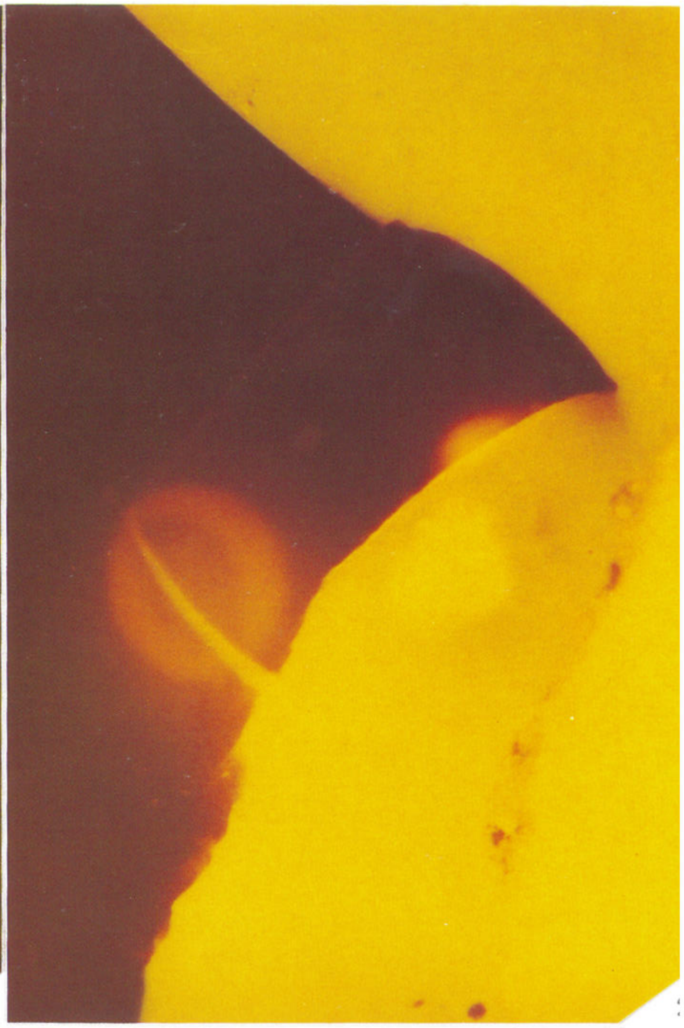
3. Productive black matrix containing Liptinite. Both matrix and high yellow embedding resin are hydrocarbon impregnated.

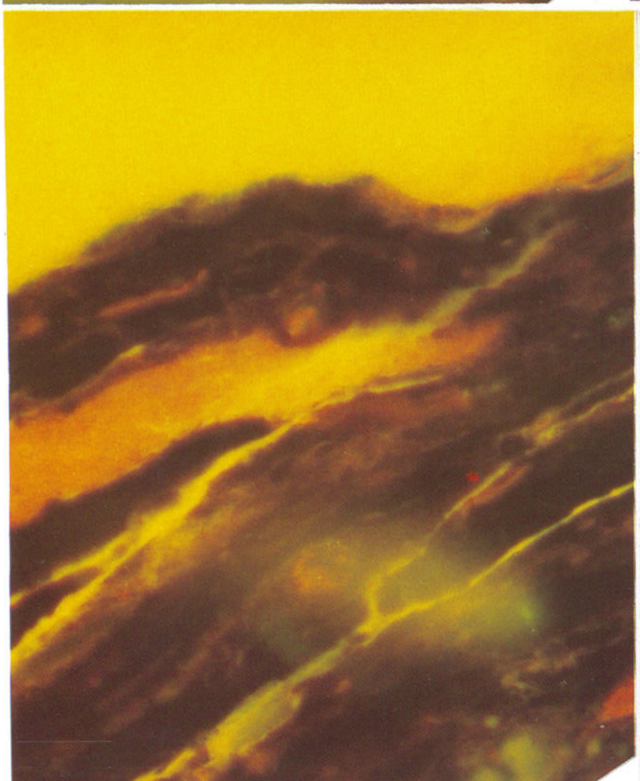
   Type of sample: cuttings
   Depth: 11070 ft
   Region: North Sea

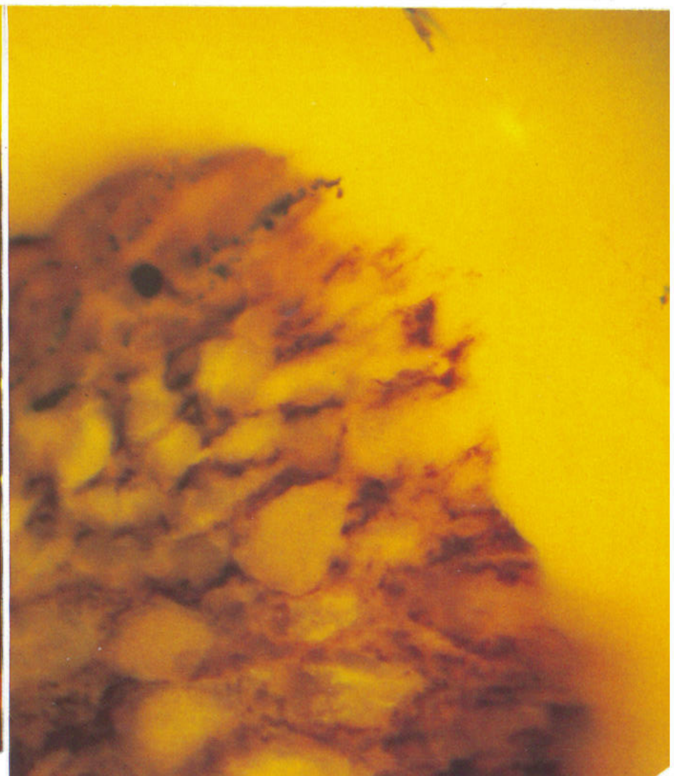
4. Matrix rich in carbonates in a high yellow hydrocarbon impregnated embedding resin.

   Type of sample: cuttings
   Depth: 8970-9000 ft
   Region: Papua-New Guinea









50 μ

\+ 50 μ

Plate 7 - NON-SPHERICAL HYDROCARBONS

1. Isolated mineral particle surrounded by various coatings and non-spherical irregular yellowish hydrocarbons (compare with plate 15, photo 1, in which hydrocarbons are still between minerals and have not been liberated by crushing).

   Type of sample: cuttings
   Depth: 2520-2550 ft
   Region: Angola

2. Irregular greenish, non-spherical hydrocarbons around a black massive particle.

   Type of sample: cuttings
   Depth: 6670-6690 ft
   Region: Angola

3. Irregular, non-spherical yellow hydrocarbons (left) related to a small stratified complex particle with a brown organo-mineral matrix containing minute Liptodetrinite. More greenish exsudates are visible between particles (right).

   Type of sample: cuttings
   Depth: 9110 ft
   Region: Papua-New Guinea

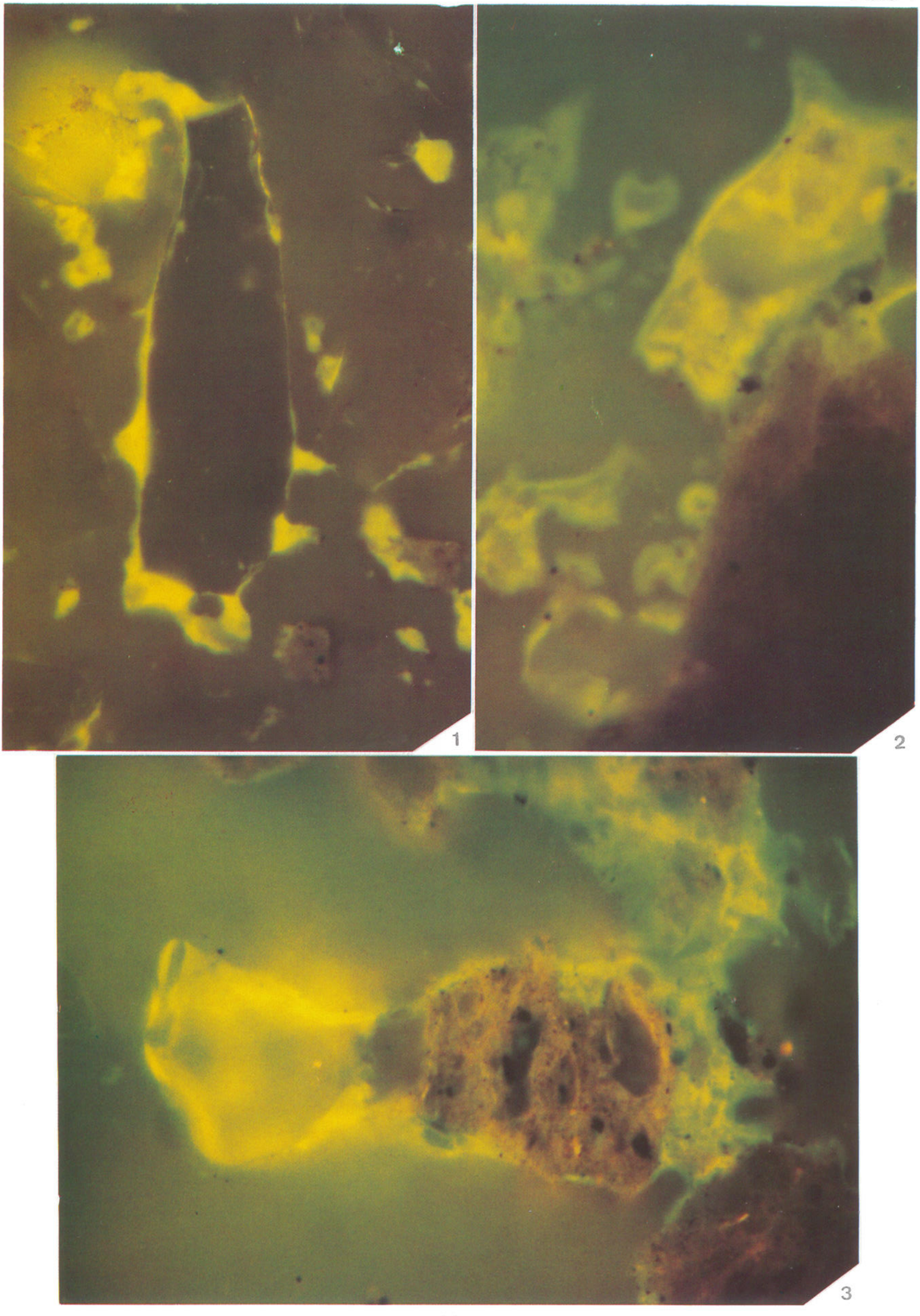

1
2
3
50 μ

Plate 8 - ASPHALTITES

1. Dark Migrabitumen (Gilsonite-type) in reflected light. Note the presence of many scratches due to the softness of the material, and the differentiated periphery (often typical).

   Type of sample: cuttings
   Depth: 5810 ft
   Region: Korea

2. As in photo 1, in fluorescence, showing hydrocarbon production from the central part during blue light excitation. High yellow intensity of the embedding resin.

3. Dark Migrabitumen inclusions (Asphaltite-type) in the matrix seen in reflected light. White Inertodetrinite particles are present.

   Type of sample: cuttings
   Depth: 2470-2490 m
   Region: Turkey

4. As in photo 3, in fluorescence (blue light), showing medium brown color of the Migrabitumen, with a distinct peri-differentiation. The mineral matrix contains Inertodetrinite particles (black) and light brown Liptinite.

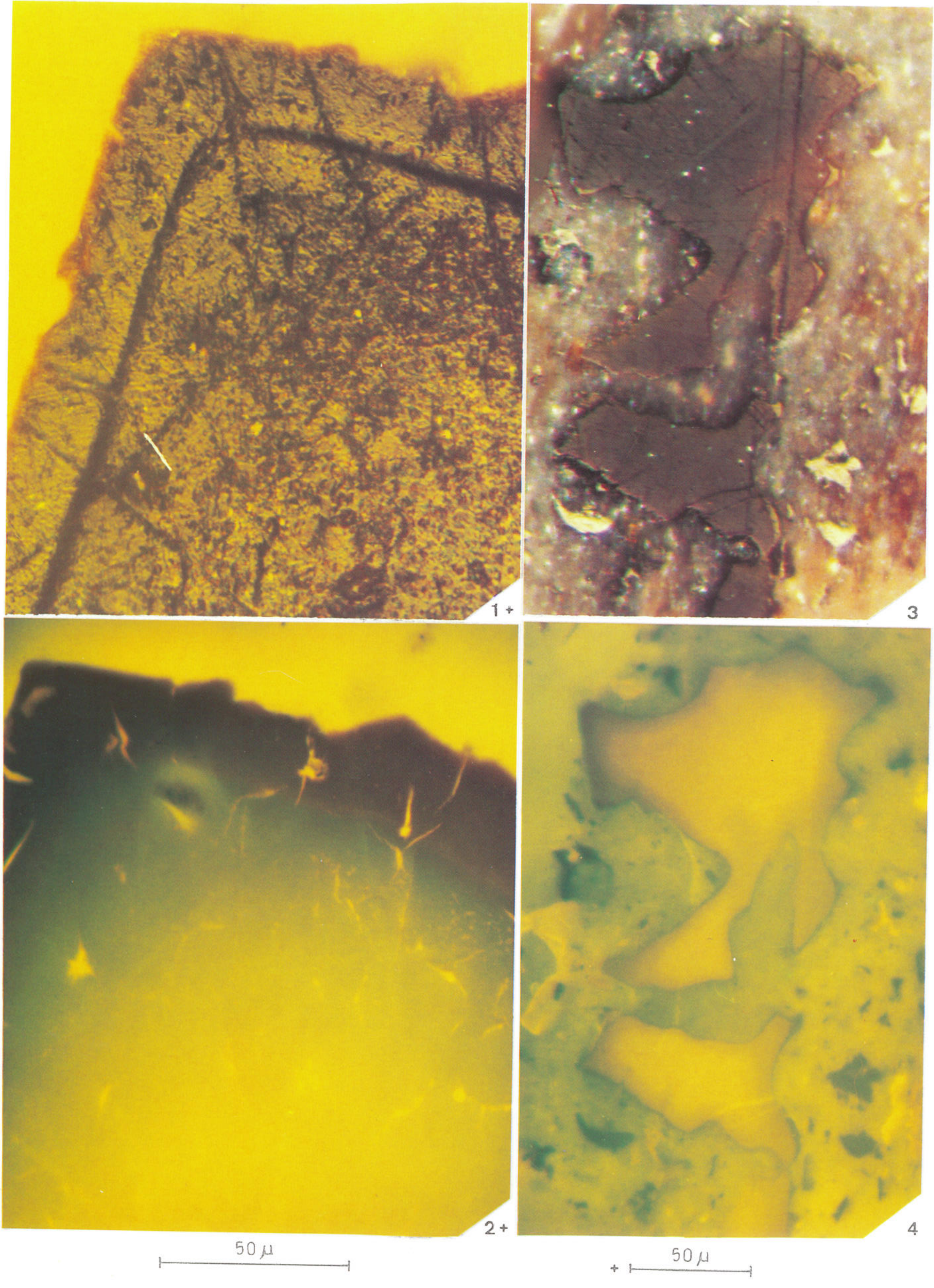

1 +
3
2 +
4
50 µ
+ 50 µ

Plate 9 - ASPHALTITES

1, 2. Dark reddish Migrabitumen (Gilsonite-like) seen in fluorescence (blue light) (1) and in reflected light (2). Peri-differentiation (in fluorescence) and black reddish reflectance are clearly visible.

Type of sample: cuttings
Depth: 2749-2752 m
Region: South Africa

3. Dark Migrabitumen (Asphaltite) big particle with orthogonal oxidation marks and rims.

Type of sample: cuttings
Depth: 6519-6550 ft
Region: Malaysia

4. Same aspect as in photo 1.

Type of sample: cuttings
Depth: 2749-2752 m
Region: South Africa

5. Black granulate Migrabitumen infilling carbonate minerals spaces.

Type of sample: cuttings
Depth: 13080-13085 ft
Region: Angola

Plate 9

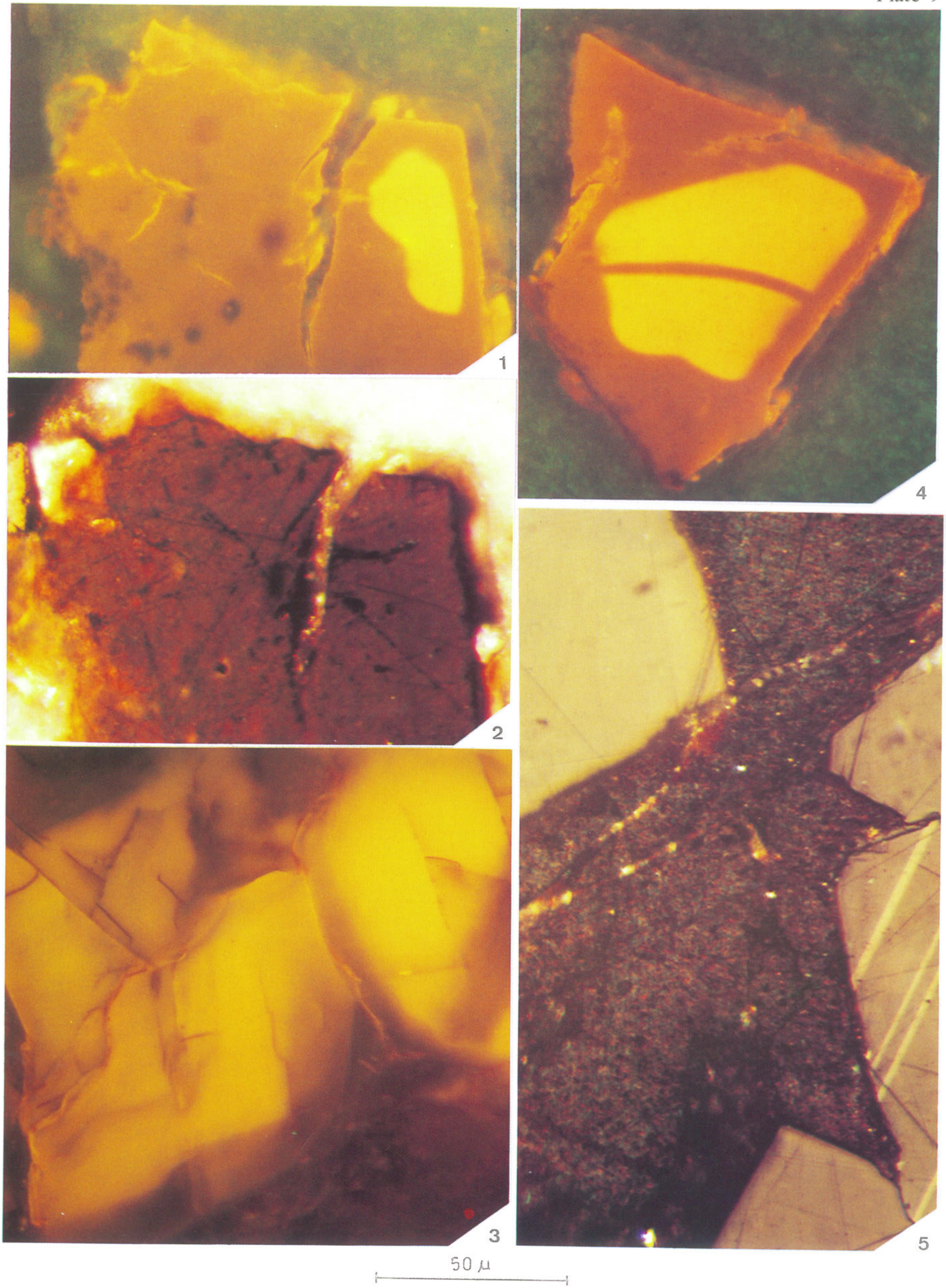


Plate 10 - IMPSONITES

1. White isotropic Migrabitumen (Cata-impsonite) infilling inter-mineral spaces, giving an aspect of pseudo-botanical fusinitic-like structures.

Type of sample: cuttings
Depth: 7890 ft
Region: Papua-New Guinea

2. Grey isotropic heterogeneous Migrabitumen (Meso-impsonite), non-fluorescing, in inter-mineral spaces.

Type of sample: cuttings
Depth: 8010-8020 ft
Region: Papua-New Guinea

3. Association of white Migrabitumen inclusions (Cata-impsonite), probably resulting from faunal destruction, in relation with carbonates.

Type of sample: cuttings
Depth: 2070 m
Region: Portugal

4. Grey fractured Migrabitumen (R=0.5%) surrounding a mineral particle (centre).

Type of sample: Uraniferous oil shale
Locality: Seam 6, Lodève, France

5. As in photo 4, in fluorescence, showing yellow to brown Migrabitumen zones.

Plate 6 - DISSOLVED HYDROCARBONS

1. Medium green embedding resin having dissolved green hydrocarbons produced by a dark brown matrix containing orange shifted Sporinite.

   Type of sample: core
   Depth: 2068.9-2079.4 m
   Region: Commonwealth of Independent States (CIS)

2. Intense yellow hydrocarbons impregnating embedding resin around a black massive matrix. A fracture is impregnated with a yellow drop in formation, as well as at the periphery.

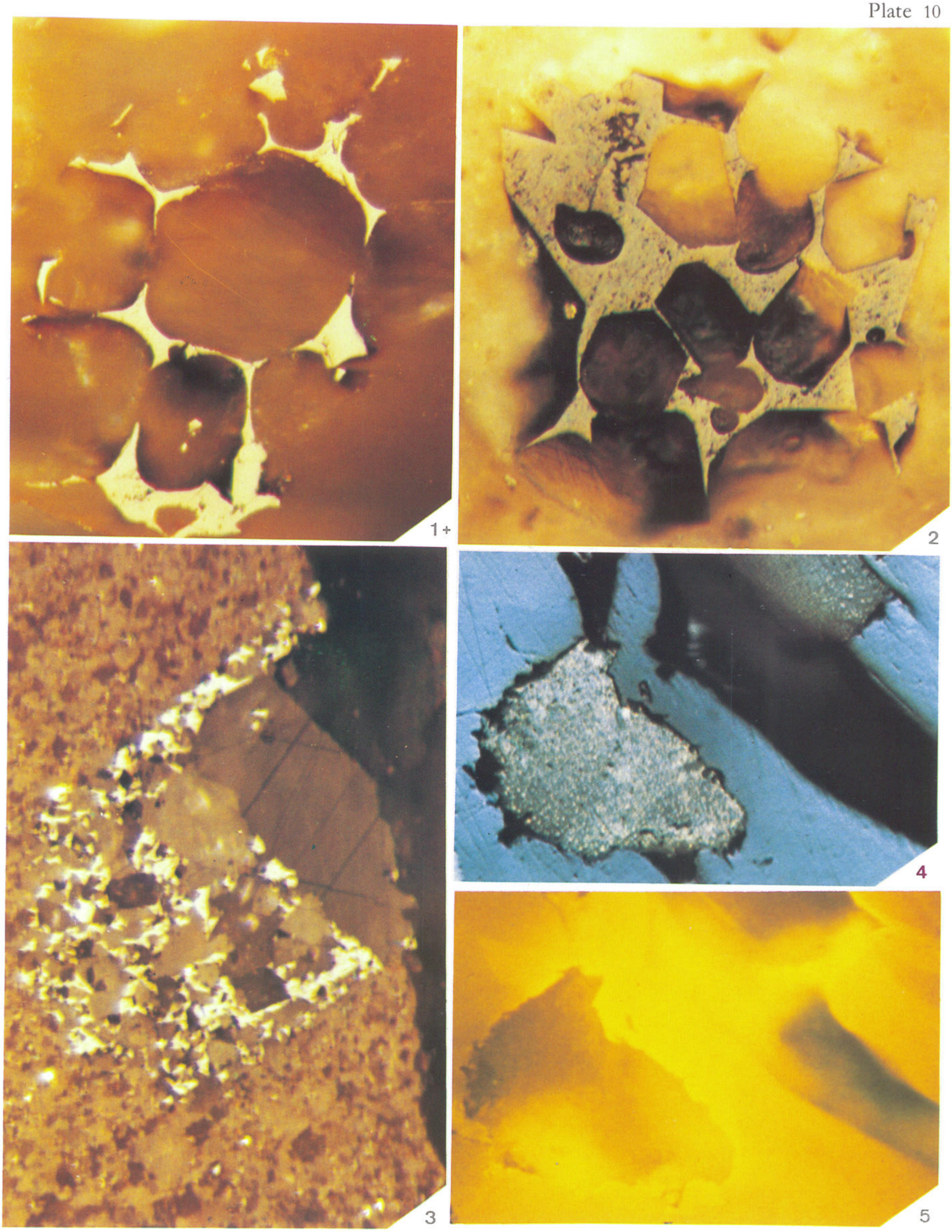
   Type of sample: cuttings
   Depth: 8940-8980 ft
   Region: Angola

3. Productive black matrix containing Liptinite. Both matrix and high yellow embedding resin are hydrocarbon impregnated.

   Type of sample: cuttings
   Depth: 11070 ft
   Region: North Sea

4. Matrix rich in carbonates in a high yellow hydrocarbon impregnated embedding resin.

   Type of sample: cuttings
   Depth: 8970-9000 ft
   Region: Papua-New Guinea



50 μ

\+ 50 μ

Plate 11 - PRODUCTIVE SOURCE ROCKS WITH SPORINITE

1. Highly productive dark brown matrix with impregnated fissures containing orange-reddish, clearly shifted, liptinitic inclusions. Hydrocarbons generated during fluorescence excitation are yellowish.

   Type of sample: cuttings
   Depth: 14030-14040 ft
   Region: Angola

2. Productive, medium brown, rather massive organo-mineral matrix, containing orange-reddish shifted spores. Greenish hydrocarbons generated from neoformed microcracks during fluorescence excitation. Both probably result from thermal cracking of already disappeared liptinitic progenitors.

   Type of sample: cuttings
   Depth: 660 m
   Region: Portugal

3. Weakly producing brown-reddish organo-mineral matrix containing two spore populations: one orange-reddish, clearly shifted and mature, the other yellow-brown, probably still immature.

   Type of sample: cuttings
   Depth: 9630-9660 ft
   Region: Papua-New Guinea

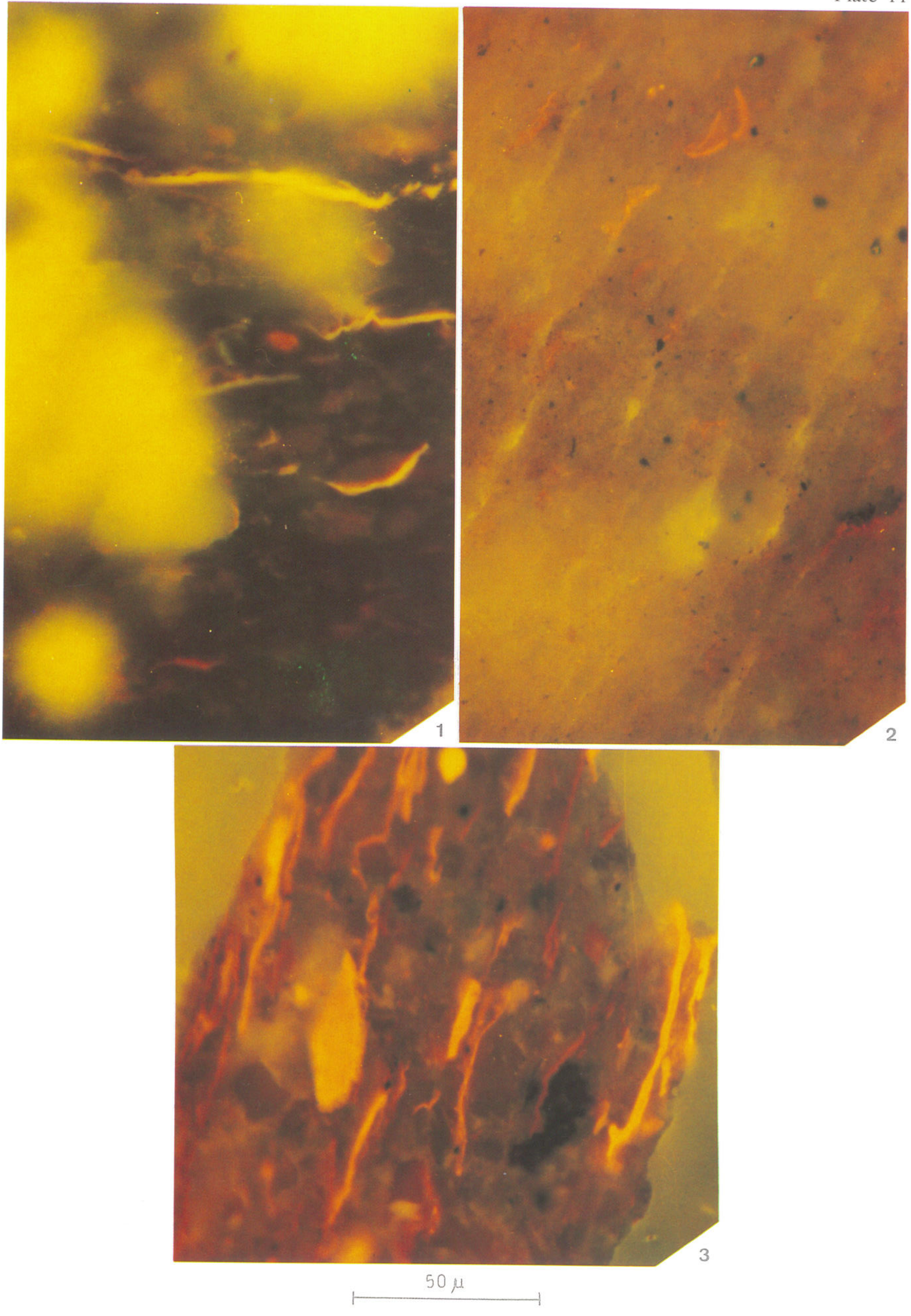

1
2
3
50 μ

Plate 12 - **PRODUCTIVE SOURCE ROCKS**

1. Source rock (slightly immature) with black-reddish Bituminite, in reflected light.

   Type of sample: cuttings
   Depth: 8100 ft
   Region: Angola

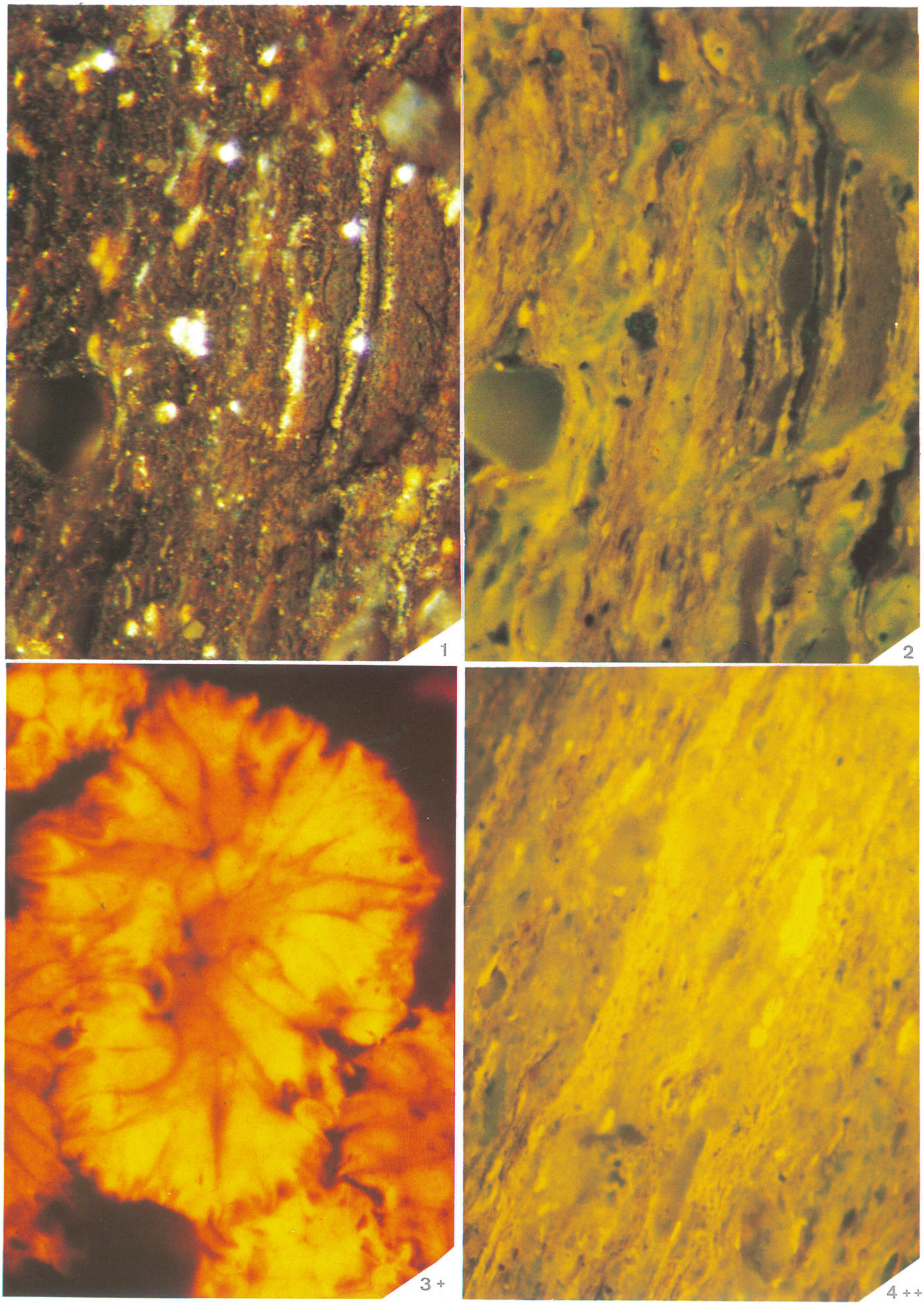
2. As in photo 1, in fluorescence (blue light), showing the heterogeneity of most Bituminite streaks.

3. Orange-red typical *Botryococci* colonies.

   Type of sample: Oil shale
   Locality: Reyran, France

4. Shale rich in golden-brown Lamalginite.

   Locality: Jouy aux Arches, France



+ 50 μ   50 μ   ++ 50 μ

Plate 13 - PRODUCTIVE SOURCE ROCKS

1, 2. Medium brown matrices containing minute and big ornamented Dinoflagellates.

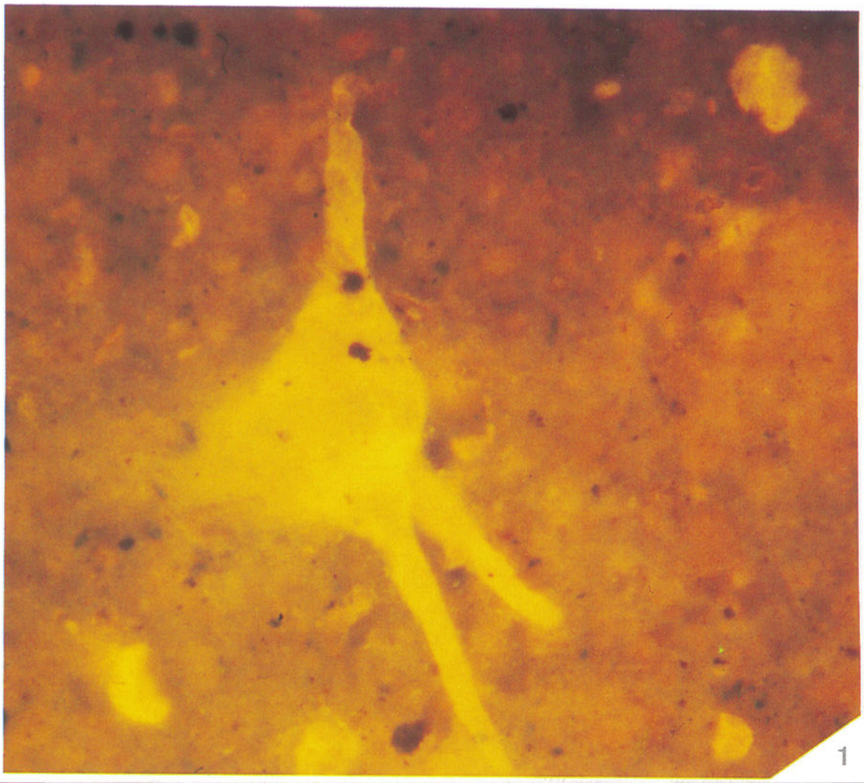
1. Type of sample: cuttings
   Depth: 660 m
   Region: Bolivia

2. Type of sample: cuttings
   Depth: 2926-2934 m
   Region: Turkey

3, 4. Microfaunal population whose internal cavities are filled with yellowish hydrocarbons.

3. Type of sample: cuttings
   Depth: 6060-6080 ft
   Region: Angola

4. Type of sample: cuttings
   Depth: 1560-1590 ft
   Region: Turkey



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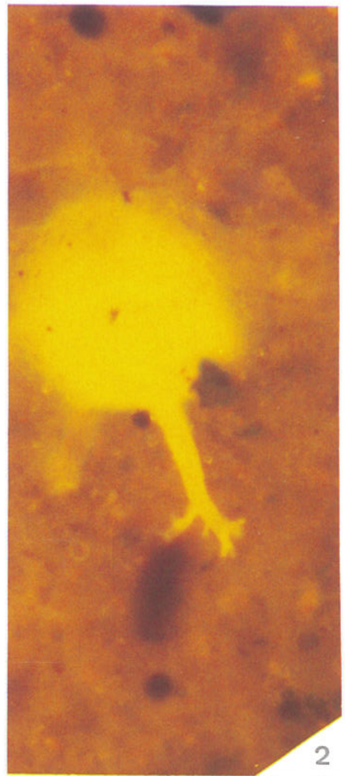

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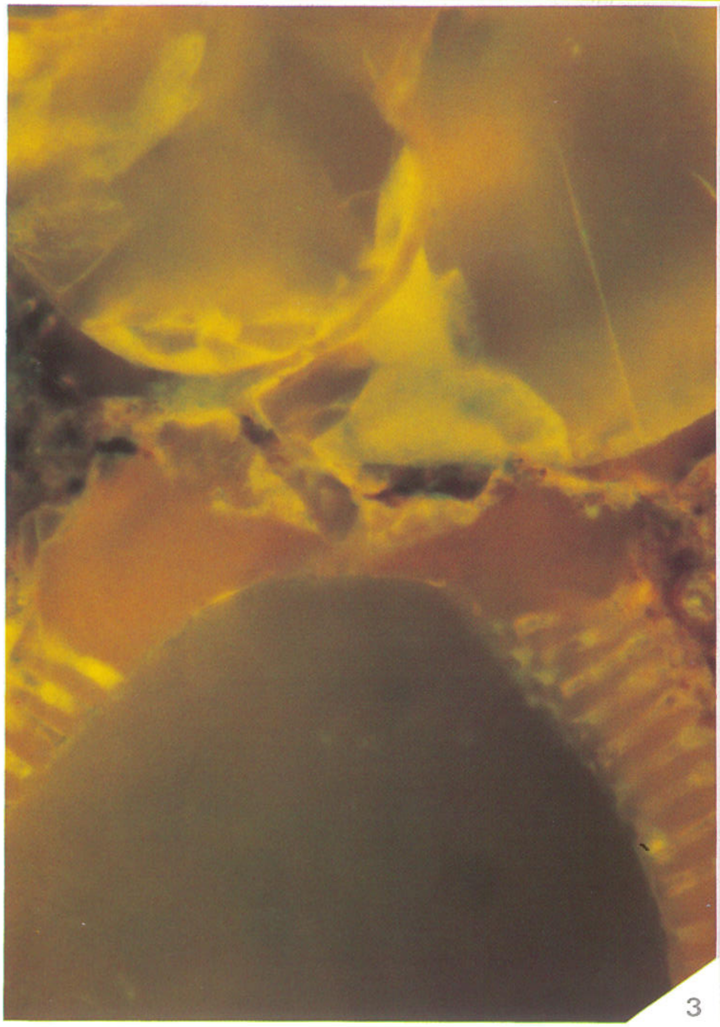

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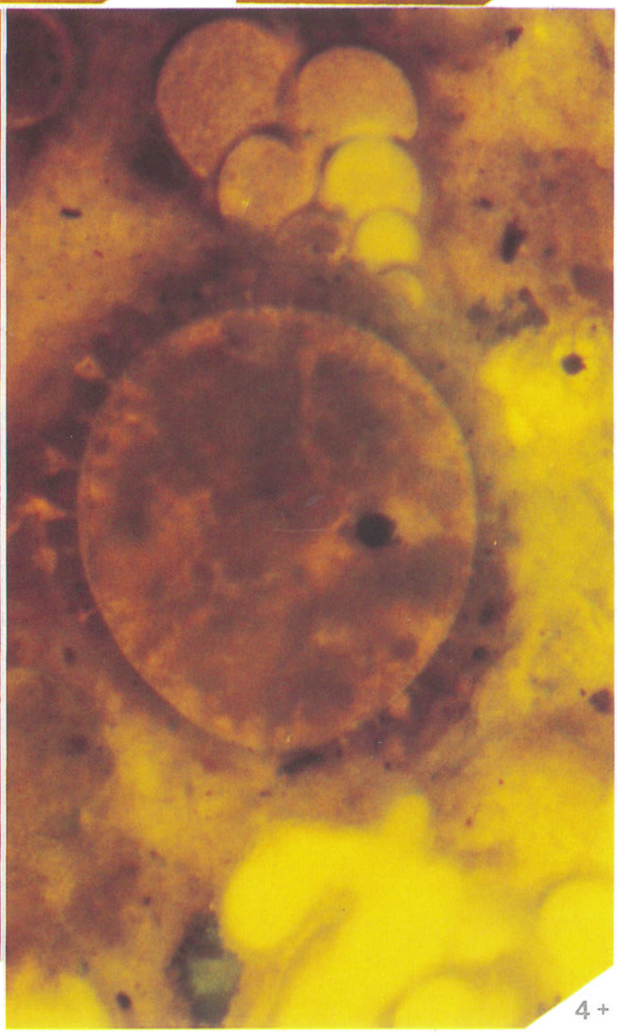


4 +

50 μ

+ 50 μ

Plate 14 - SOURCE ROCKS WITHOUT ORGANOCLASTS

1. Rather compact greenish matrix surrounded by intense yellow hydrocarbon impregnated embedding resin.

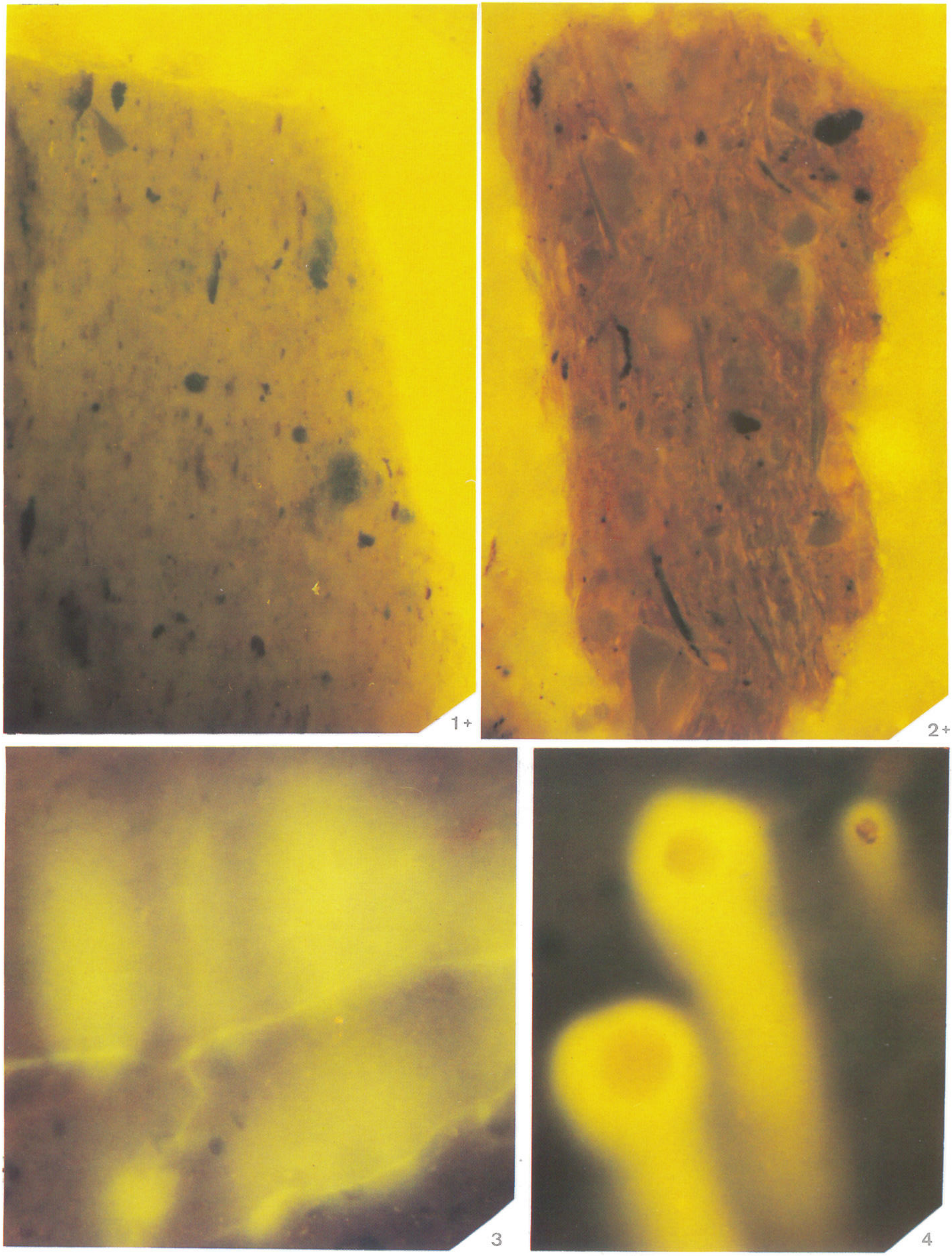
   Type of sample: cuttings
   Depth: 12800-12810 ft
   Region: Angola

2. Dark brown organo-mineral matrix surrounded by orange-yellow drops in course of being dissolved by the embedding resin.

   Type of sample: cuttings
   Depth: 11200-11210 ft
   Region: Angola

3, 4. Black matrices strongly producing during fluorescence excitation.

   Type of sample: cuttings
   Depth: 6950-6970 ft
   Region: Angola



1+ 2+

3 4

50 μ

+ 50 μ

Plate 15 - RESERVOIRS

1. Clastic aggregate with non-spherical hydrocarbons filling inter-mineral spaces.

   Type of sample: cuttings
   Depth: 798-800 m
   Region: Argentina

2. Hydrocarbon fillings in the form of inter-mineral films.

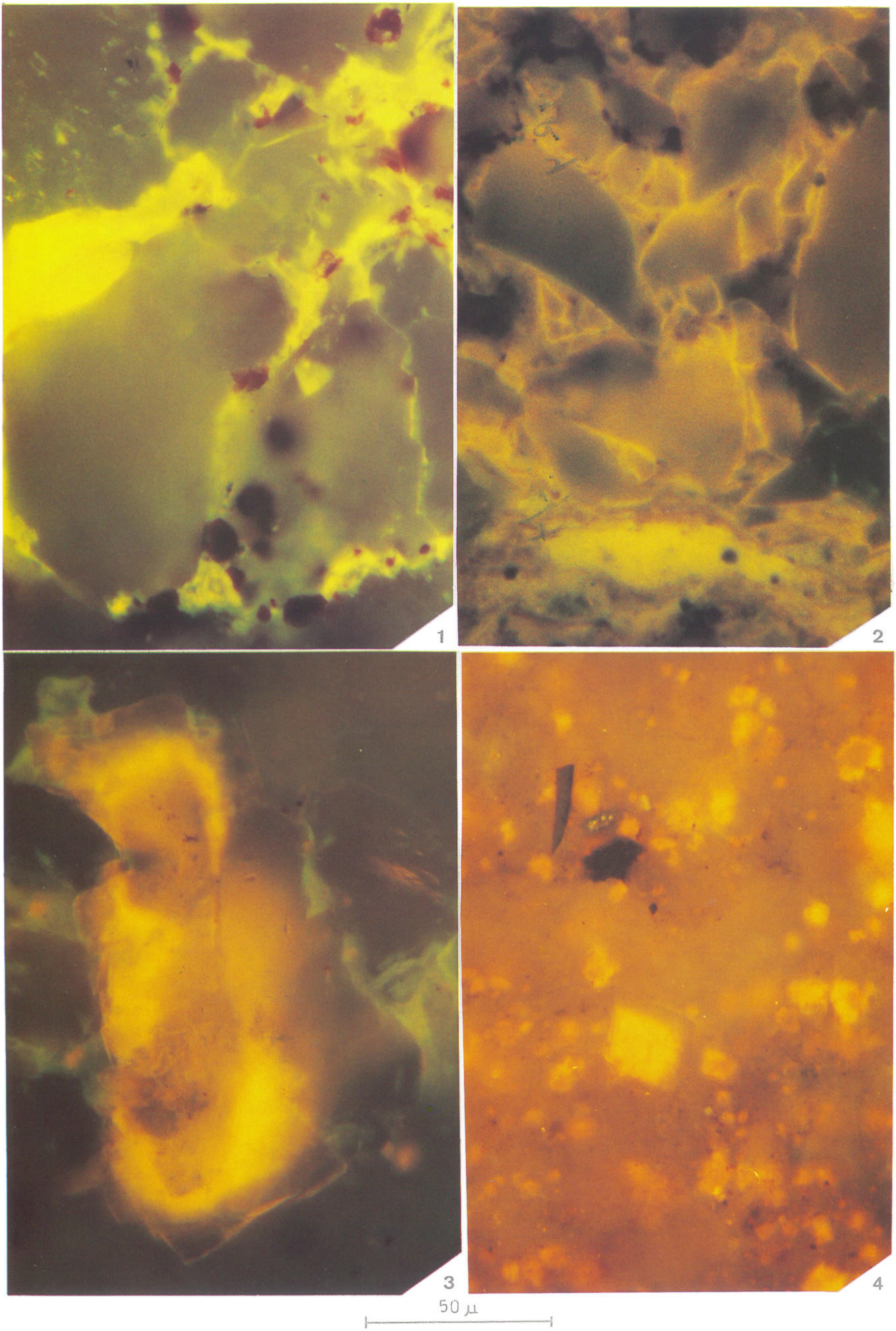
   Type of sample: cuttings
   Depth: 10810-10840 ft
   Region: Zaire

3. Big carbonate crystal containing golden-orange hydrocarbon inclusions surrounded by a green secondary phase.

   Type of sample: cuttings
   Depth: 7200 ft
   Region: Angola

4. Orange-reddish carbonate rhombohedres probably of biological origin.

   Type of sample: cuttings
   Depth: 1700 m
   Region: Portugal


1
2
3
4
50 μ