

Characterization of hydrocarbon fluid inclusions by infra-red and fluorescence microspectrometry

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Abstract

Liquid-hydrocarbon-bearing fluid inclusions have often been described associated with petroleum occurrences and diagenetic sediments. Infra-red microspectrometry allows characterization of fluid inclusions greater than 20 μm by establishing the presence of aliphatic and aromatic hydrocarbons as well as associated H_2O , CO_2 and CH_4 . Semi-quantitative analyses have been made by focussing on gaseous and liquid phases separately. Some CH_2/CH_3 and CO_2/CH_4 ratios have been determined by this method.

Fluorescence microspectrometry permits precise measurements of the fluorescence emission spectrum of chromophore-bearing organic phases (essentially aromatic hydrocarbons) in fluid inclusions greater than 10 μm . Such a spectrum is a function of both the gross composition of the trapped oil and its thermal history.

Both of these methods lead to the *in situ* characterization of hydrocarbon fluid inclusions. They are useful in providing a quantifiable distinction between different oil generations trapped during mineral growth in diagenetic and epigenetic minerals.

KEYWORDS: fluid inclusions, hydrocarbon, infra-red, ultra-violet, fluorescence microspectrometry.

Introduction

As described earlier by Murray (1957), hydrocarbon fluid inclusions have often been found associated with petroleum occurrences (Burruss, 1981) or with diagenetic and epimetamorphic events (Touray and Yajima, 1967). They are often entrapped during different stages of mineral growth during the thermal evolution of the sediments and/or oil migrations. A knowledge of both the relative chronology and composition of individual inclusions can yield valuable information about the thermal evolution and migration of organic matter (Roedder, 1984). Very little work has been carried out to date on the composition of these types of inclusions, partly because precise

analytical non-destructive methods have not been available.

The Raman microprobe allows the semi-quantitative analysis of organic gaseous components. For example, CH_4 - H_2S - CO_2 fluids have been characterized in calcareous overgrowth from a depth of 6 km in the Smakover formation from Perry County (Mississippi) (Guilhaumou *et al.*, 1984): various CH_4 - C_2H_6 - C_3H_8 ratios were determined in newly-formed minerals of the 'Terres Noires' following shallow diagenesis and low-grade metamorphism in the pre-alpine basin. Although liquid hydrocarbons have occasionally been characterized (Guilhaumou, 1982) by Raman analysis, it is usual for the strong fluores-

cence under a laser beam (514.5 and 488.5 nm wavelength) to render such a determination impossible.

However, ultra-violet (UV) microfluorimetry and infra-red (IR) absorption microspectroscopy provide an alternative method for the analysis of such inclusions. The aim of this paper is to illustrate, using examples, how these analytical methods can help to characterize the included organic phases in fluid inclusions.

IR absorption microspectrometry allows the detection of aromatic, olefinic (C=C vibrations) and aliphatic (CH₂ and CH₃ vibrations) molecules as well as CO₂, CH₄ and H₂O in the liquid and vapour phases of fluid inclusions (Barres *et al.*, 1987). However, spectra of the vapour phases include signals from the surrounding liquid. Detection limits of CO₂ and H₂O are very low, so they can be characterized, even in inclusions where they cannot be microthermometrically detected. Semi-quantitative measurements of CO₂/CH₄ and CH₂/CH₃ ratios can be made from the peak area measurements.

Organic petrologists mainly use microfluorimetry for thermal evolution assessments of the organic content of sedimentary rocks. The variation of fluorescence properties of organic particles (microspores, algae, etc.) with the thermal evolution of the embedding sediments has been described in previous works (e.g. Ottenjann *et al.*, 1974; Techemüller and Durand, 1983). Recently, the relationship between the fluorescence properties of organic particles and their maturation state has been established (Pradier, 1988; Pradier *et al.*, 1989).

The method applied to the study of oil inclusions is aimed at quantifying the spectral parameters of different generations of oil inclusions in a given mineral. In the case of oil inclusions, such a relationship has to be tested because the thermal evolution of these oils occurred in a closed system and at constant volume. These conditions differ drastically from those in which the minerals undergo their thermal alteration.

Here we report some preliminary results on both the measurements of fluorescence emission parameters and approximate compositions determined by IR spectroscopy on some individual organic fluid inclusions hosted by diagenetic and epigenetic minerals (fluorite, baryte and quartz), and discuss the potential of this approach.

Origin of the samples

The specimens studied are from two different localities.

The samples from the first occurrence are liquid

hydrocarbon fluid inclusions contained within quartz and barytocelesteite, formed during diagenesis and epimetamorphic events in the 'Terres Noires' Jurassic shales and calcareous sediments in the pre-alpine basin of southeast France. The fluid inclusions were first studied by Barlier and others (Barlier, 1974; Barlier *et al.*, 1973; Touray and Barlier, 1974). The results of microthermometric measurements on aqueous and hydrocarbon syngenetic inclusions, as well as vitrinite reflectance and illite/smectite crystallinity, show an evolution from the western part to the eastern part, with temperatures of 150 to 240 °C, and pressure 0.5 to 2 kbar. Raman analyses of the gaseous phases entrapped as primary FI show the presence of wet gas in the west part and of dry gas with some amount of CO₂ in the east part (Fig. 1; Guilhaumou *et al.*, 1988). Liquid hydrocarbons were observed but they could not be analysed by Raman microprobe because of strong fluorescence.

The samples from the second occurrence are liquid hydrocarbon fluid inclusions entrapped during an episodic crystallization of fluorites and barytocelesteites in the F-Ba-Pb-Zn deposits from northern and central Tunisia. Hydrocarbons are frequently associated with ore concentrations in particular paleogeographic structures where they have probably migrated with the fluid responsible for mineralization in such Mississippi-Valley-Type (M.V.T.) deposits (Richardson and Pinckney, 1984). In Tunisia, these minerals are encountered in stratabound deposits lying in unconformity gaps in calcareous sediments (Jurassic-Cretaceous). Samples were collected at Djebel Kohol and Hammam Zriba-Guebli along the Zaghouan fault (Florida, 1973; Bouhleb, 1982) and in Boujaber near Tagerouine (Fig. 2; Bouhleb, 1986). Fluid inclusions containing oil have been described in geodic fluorites from Hammam Zriba and Djebel Kohol by Touray *et al.* (1967) and Hammam Zriba-Guebli by Bouhleb *et al.* (1988).

Experimental

UV microfluorometry

Theory. The phenomenon of fluorescence in organic matter consists of the emission of photons by chemical entities (fluorophores) when excited by electromagnetic radiation. Fluorophores are able to absorb part of the incident energy, rising from a fundamental energy state to an excited state of higher energy. The return to the ground state may then produce a luminescence phenomenon such as fluorescence (Hercules, 1965; Mousseron *et al.*, 1969). This de-excitation mechanism is not the only possible emission, and its efficiency

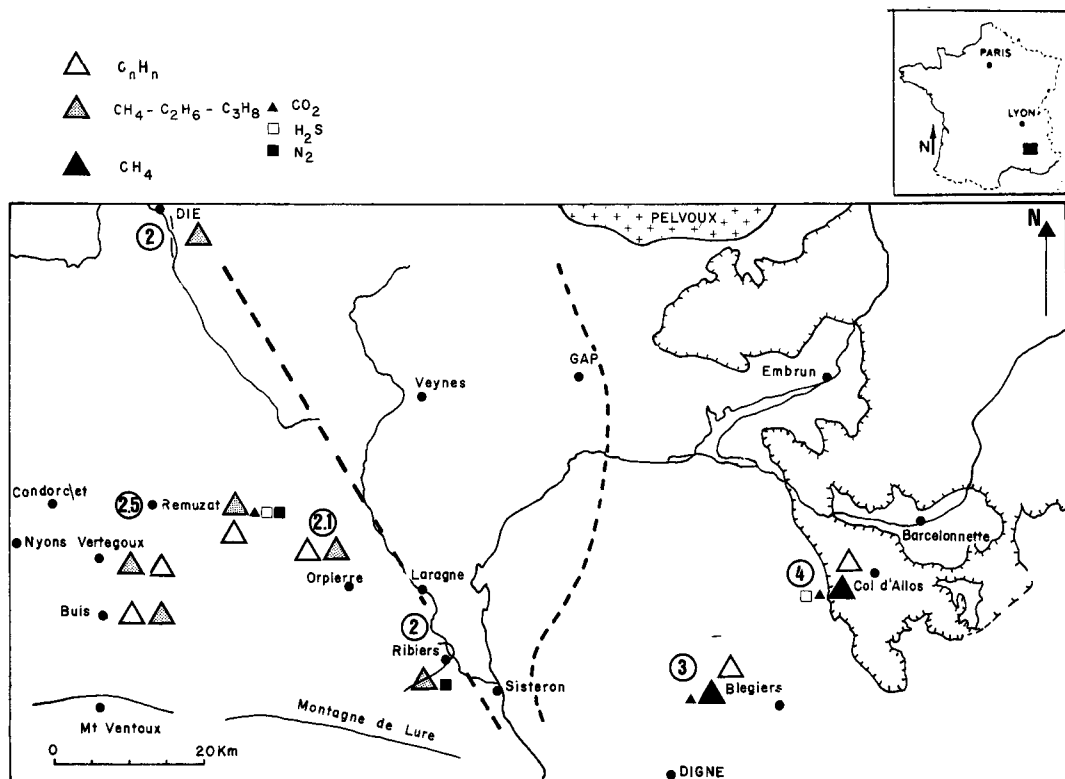


Fig. 1. Geological setting of the 'Terres Noires' in pre-alpine basin (south east France); Composition of the organic fluid inclusions associated with PR measurements of vitrinite reflectance and illite crystallinity (after Guilhaumou *et al.*, 1988).

depends both on the organic compound and on its structural environment.

Essentially the fluorescence of organic molecules is related to the energy transition phenomena in the π orbital of C=C bonds. The two energy levels of π bonds are too far apart to give any fluorescence emission without breaking the bonds themselves. Moreover, the conjugated system requires a lower excitation energy than isolated bonds, and is therefore more readily activated by electromagnetic radiation. Thus, aromatic and polyaromatic compounds are mainly responsible for the fluorescence properties of sedimentary organic matter.

Inter- and intra-molecular interactions considerably influence the fluorescence emission (Wehry, 1967). Intra-molecular energy transfers can reduce and even annihilate the fluorescence emission of a given molecule.

The intermolecular interactions explain the quenching effect of fluorescence emission induced by increasing concentration of an organic com-

pound in a given medium. This can be explained by photochemical reactions such as excimerization (excited chromophore recombination), leading to a weaker fluorescence emission, shifted towards the higher wavelengths. It can also be mentioned here that the dipolar interaction phenomenon may lead to fluorescence alteration by lowering the electronic delocalization. Some of these aspects have been studied in relation to organic petrology by Bertrand *et al.* (1986) and Lin and Davis (1988).

Methodology and spectral parameters. The analytical procedures used here were developed at URPO (Unité de Recherche en pétrologie organique, CNRS, URA 724, Orléans, France).

The principle of this method consists of the excitation of organic matter by an incident UV beam, through the optical system of a photonic microscope (LEITZ MPV III). A classical UV microscope configuration (calibrated excitation beam on 365 nm) with a dry 50 \times objective have been used for this study. The analysis diaphragm has

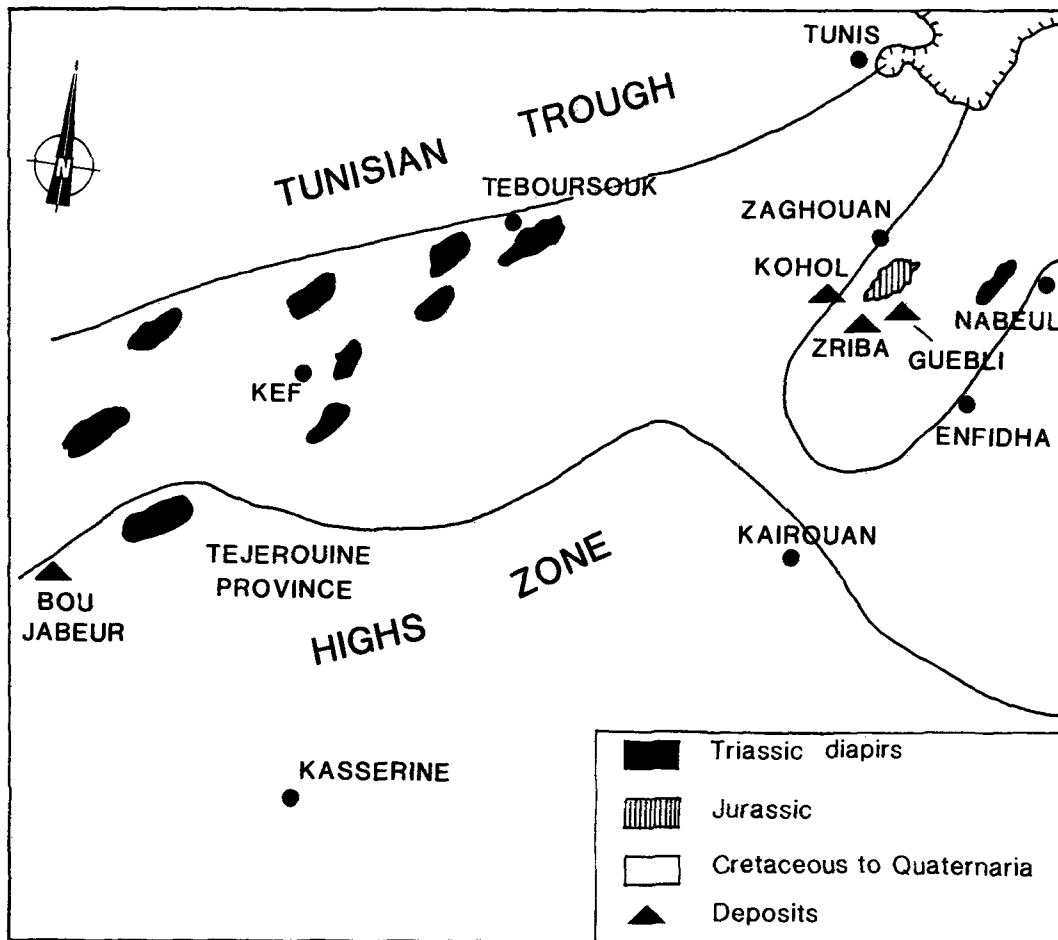


Fig. 2. Geological setting of the F-Ba ore deposits studied in northern Tunisia.

been set to $100 \mu\text{m}^2$. Further details on analytical procedures and apparatus are given elsewhere (Martinez *et al.*, 1987).

The fluorescence emission is measured at one nanometer intervals between 430 and 750 nm, and after raw data correction, spectral parameters are calculated as shown in Fig. 3. F stands for the total emission flux, normalized with respect to a standard; L max is the maximum intensity wavelength; QF-535 is the ratio of the 535–750 nm flux to the 430–535 nm flux. It stands for the 'red-green' ratio and describes the colour of the fluorescence emission.

The F parameter has not been used in this study because its value depends on the excited volume (i.e. geometry of the inclusion) and on the depth of the inclusion in the mineral sample. Con-

versely, L max and QF-535 do not depend on these constraints.

The fluorescence emission of the mineral matrix in each analysis was found to be equivalent to the background spectrum. In the case of oil-bearing inclusion analyses, the fluorescence is strong and the signal/noise ratio was greater than 400 and most of the time near 4000. The variation of L max from one inclusion to another of same generation is generally less than 5 nm.

IR absorption microspectrometry

This technique was first used by Calas *et al.* (1976) with a conventional microspectrometer; but this apparatus had a poor spatial resolution (1mm^2) which did not allow the individual analysis of fluid inclusions.

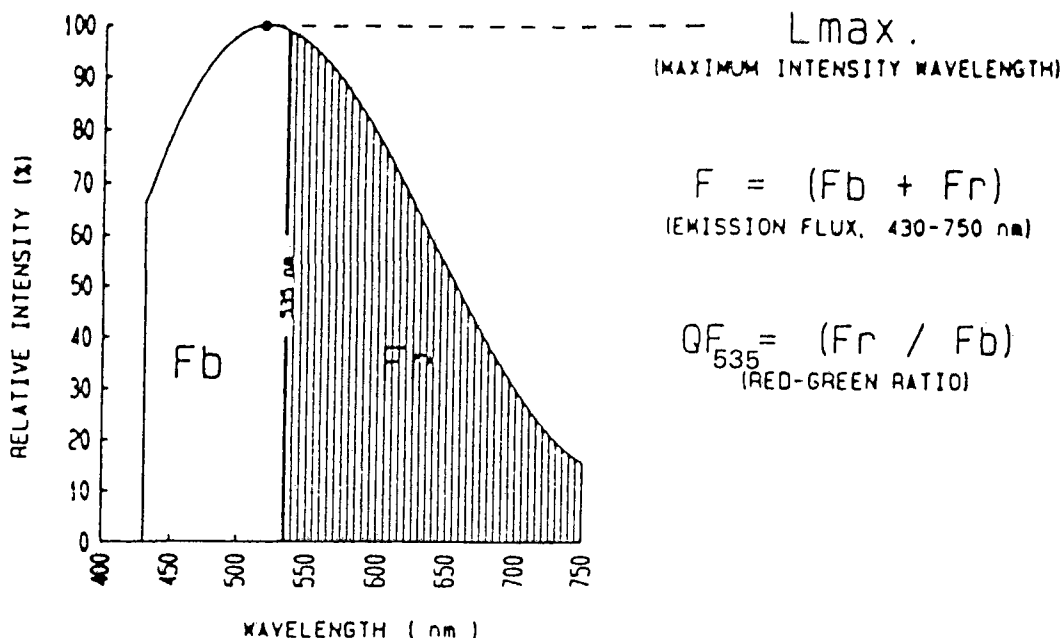


Fig. 3. Description of the spectral parameters.

The first valuable analytical results were obtained by Barres *et al.* (1987) with a Bruker IFS 88 equipped with a microscope, who discussed the analytical potential and limits of the method. They reported analyses of alkanes, aromatic esters, liquid H₂O and CO₂ and CH₄ in inclusions greater than 30 μm, and have developed a method to make semi-quantitative measurements of CO₂/CH₄ and CH₂/CH₃ ratios.

The results presented here have been obtained at the 'Institut Français du Pétrole' on an interferometer DIGILAB FTS 40 with a microscope type UMA 300 equipped with a MCT detector using an objective cassegrain ×36. A circular diaphragm restricts the field to the size of the inclusion. The spectra were registered in transmission mode with 8 cm⁻¹ resolution and 1024 accumulated scans, which are convenient conditions to obtain good signal/noise ratios. The system was purged with dry nitrogen and the air between the objective and the sample purged by a special adaptation to the objective.

The inclusions analysed are hosted in doubly-polished slides of quartz fluorite and baryte having a thickness of about 1 mm. The matrix absorption allows the detection of bands in the 800–4000 cm⁻¹

region for fluorite, in the 2000–4000 cm⁻¹ for quartz, and in the 2500–4000 cm⁻¹ region for baryte. The spectrum of the matrix was systematically recorded before each analysis and subtracted to obtain the required information. However this spectrum often partly includes signals from other numerous, smaller inclusions in the mineral; in these cases, the atmosphere was taken as a reference and the matrix spectrum obtained for comparison (see for example Fig. 10b).

Aliphatic hydrocarbons have been characterized (Table 1) by their symmetric and antisymmetric stretching vibrations bands of the CH₂ and CH₃ molecules respectively at 2856 cm⁻¹ (ν_s CH₂), 2875 cm⁻¹ (ν_s CH₃), 2930 cm⁻¹ (ν_a CH₂), and 2960 cm⁻¹ (ν_a CH₃). The angular deformation bands around 1380, 1450 and 1459 cm⁻¹, (δ_s C–CH₃, δ_a C–CH₃, δ CH₂) are used on fluorite spectra only because of matrix absorption in quartz and baryte.

Aromatic components can be identified by the bands of the CH in the 3000 to 3200 cm⁻¹ region and the deformation (C=C) band around 1610 cm⁻¹. The latter has not been used because in this case it was unfortunately overprinted by a broad water deformation band at 1640 cm⁻¹ in

BANDS ASSIGNMENT IN THE INCLUSION SPECTRA			
Vibrations	ν (cm ⁻¹)	Vibrations	$\tilde{\nu}$ (cm ⁻¹)
δ (CH ₃) ₂ -C	1170	ν_s -CH ₂	2856
δ (CH ₃) ₃ -C-R.	1250	ν_s -CH ₃	2875
ν_s -CH ₄	1304	ν_a -CH ₂	2930
δ -CH ₂	1460	ν_a -CH ₃	2960
δ_s C-CH ₃	1380	ν_3 -CH ₄	3010-3080 (R)
δ_a C-CH ₃	1450	ν = CH Aro	near 3030
ν C = C Aro Sk. near	1610		3122-3159-3214
δ -OH	1650	ν -OH	3000-3600
ν -CO ₂ near	2345	ν Combination-CO ₂	3603
		ν Combination-CO ₂	3711

TABLE 1. Peak assignments of the IR spectra in the fluid inclusions analysed. SK = Skeletal vibrations, Aro = Aromatic components. From Herzberg, 1951, II, IR and Raman microspectra, in *Molecular spectra and molecular structures*, p. 632, and from Colthup, N. B., *J. Opt. Soc. Amer.* **40**, 397 (1950), revised 1967.

fluorite, and because of matrix absorption in quartz and baryte.

CO₂ has been characterized by the antisymmetric vibrations (ν CO₂) around 2336 and 2345 cm⁻¹ depending on the pressure and state of the fluids. When absorbance is strong, the combination of bands at 3606 and 3711 cm⁻¹ is used. In some cases the spectrum of the matrix shows a weak contribution of atmospheric CO₂ (0.002 absorbance) that could be responsible for recording a double band (see for example Fig. 8). The real peak position is then measured at the maximum of the band.

The CH₄ component has been characterized by two bands at 3013 and 3084 cm⁻¹ (ν_3 CH₄) and at 1304 cm⁻¹ (ν_4 CH₄). The broad band near 3400 cm⁻¹ and the band near 1640 cm⁻¹ have been attributed to liquid H₂O, (respectively ν OH and δ OH).

Some analyses have been made by focussing separately on the liquid phase and on the vapour phase, but with respect to inclusion shape there is often a contribution of the liquid phase when spectra of the vapour phase are recorded. However, it is possible to detect light components such as CH₄ which are partitioned mainly into the vapour phase.

Quantitative measurements have been made of the CO₂/CH₄ molecular ratios in the gaseous phases from relative area measurements of the absorption bands around 2336 and 3013 cm⁻¹. A corrective coefficient of 9.3 has been used which represents the ratio of the relevant extinction coefficients (Barres *et al.*, 1987). It was applied to the corresponding surfaces to obtain the mole-

cular ratio. The corresponding surfaces were calculated as follows:

- (i) For CH₄, by decomposition of the bands at 3013 and 3084 cm⁻¹ which are overlapped by symmetric and antisymmetric stretching of CH₂ and CH₃, using a computer programme established by Alliot (1985).
- (ii) For CO₂, by measuring directly the band around 2336 cm⁻¹ for the spectra with integration boundaries defined by the baseline.

The CH₂-CH₃ ratios were calculated from the bands in the 3000 cm⁻¹ region by measurements of the peak areas of the symmetric stretching only, to avoid perturbations by CH₄ on antisymmetric stretching.

Results

Heating experiments

Primary liquid and vapour hydrocarbon-bearing cavities from Hammam Zriba-Guebli are hosted in geodic fluorite. They have a typically rounded shape and yellow colour with some brown areas (Bouhleb *et al.*, 1988).

Some of them were overheated in a pressure cell at 300 °C under 40 MPa confining pressure to study the effect of stretching in such hydrocarbon fluid inclusions in comparison with water-bearing inclusions (Guilhaumou *et al.*, 1986, 1988). To detect eventual modifications of the compositions by heating, IR microanalysis and measurements of UV fluorescence have been made out of the cell, by focussing on liquid and vapour phases before and after the heating runs (Guilhaumou and Szydowski, 1989).

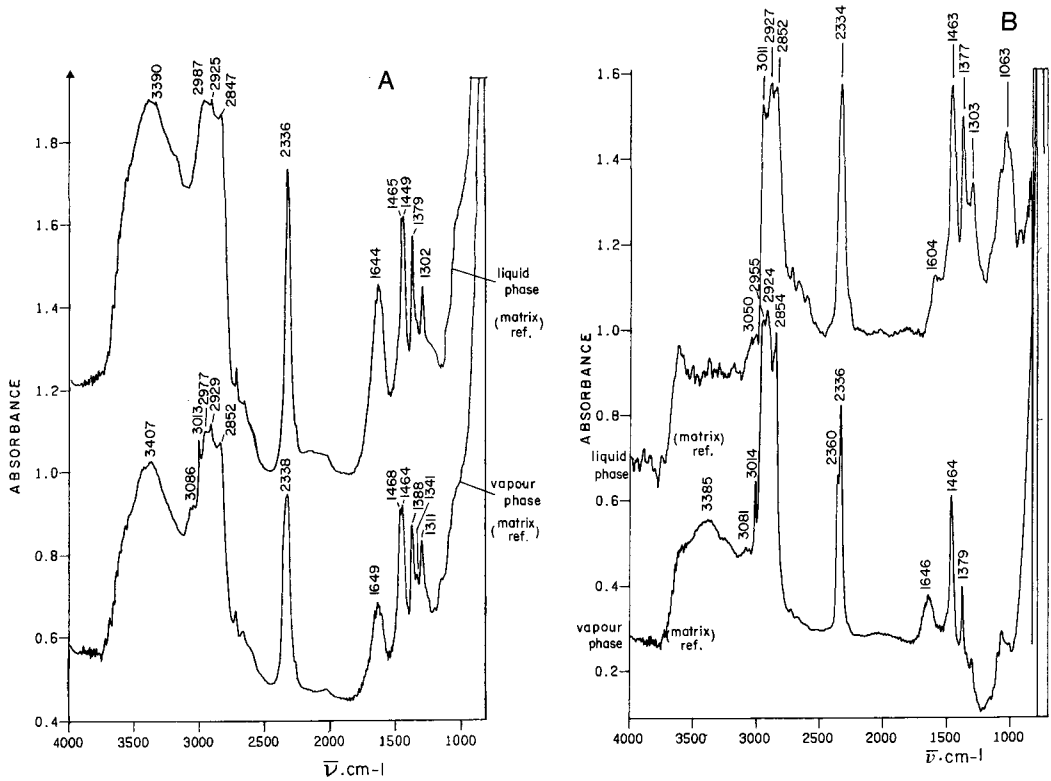


Fig. 4. IR spectra of fluid inclusions from Guebli. A, before overheating; B, after overheating.

In unheated cavities (Fig. 4a), the IR spectra show essentially aliphatic hydrocarbons with H₂O and CO₂ in the liquid phase. Absorption of CO₂ with a single band at 2336 cm⁻¹ is characteristic of CO₂ dissolved in liquid hydrocarbons (Berreby, 1983). In the vapour phase the same components are detected with additional bands characteristic of CH₄ (1304, 3013, 3080 cm⁻¹). Saturation effects do not allow the precise measurement of the position of the CO₂ peak. The CO₂/CH₄ ratio is not measurable due to the weakness of the 3013 cm⁻¹ CH₄ band. The CH₂/CH₃ ratio is about 4. Fluorescence emission occurs in the blue green region with a mean value of L max = 482 and a relatively low QF value of 0.456 (Fig. 5a, Table 2).

In overheated cavities, IR spectra (Fig. 4b) show an increase in the CH₂/CH₃ ratio to 6.2 which would indicate an increase in the alkyl chain length. The CH₄ absorbs with a greater intensity which now allows the measurement of a CO₂/CH₄ ratio. This ratio is close to 0.32. In the gaseous phase CO₂ appears with a double band at 2336 and 2361 cm⁻¹ which would correspond to gaseous CO₂ at lower pressure. A possible increase in aro-

maticity is suggested by the development of a weak, broad band from 3000 to 3100 cm⁻¹, but some interferences with the CH₄ band at 3083 do not permit confirmation of this. In the same cavities a slight shift in fluorescence towards the red region with a mean value of L max = 493 and an increase in QF to 0.701 was observed (Fig. 5b, Table 2).

Because IR spectroscopy and complementary gas chromatographic analyses of these components after individual extraction under a microscope (Guilhaumou *et al.*, 1989) have shown that the hydrocarbon components of the inclusions are mostly aliphatic, and the fluorescence emission is probably caused by the presence of very small quantities of aromatic compounds undetected by gas chromatography. Khorashani (1986) has shown that fluorescence emissions in the blue-green region are more likely when aromatic compounds are detected in paraffinic oils. He also established that, for extracted hydrocarbons the L max value would shift toward the red end of the spectrum with increasing thermal maturation and increasing aromaticity. We observed

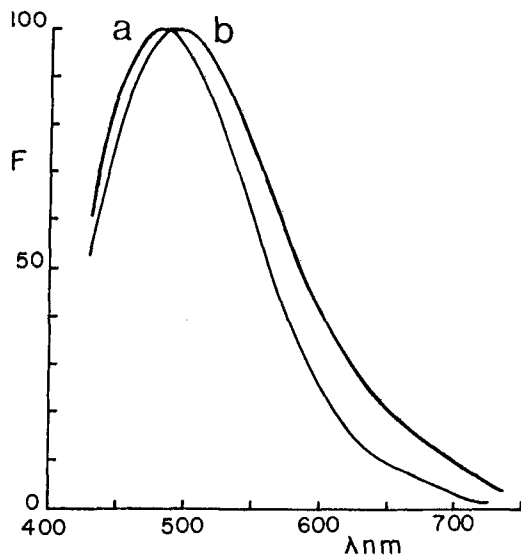


Fig. 5. Fluorescence spectra of fluid inclusions from H. Zriba Guebli. *a*, before, and *b*, after overheating.

comparable changes in overheated cavities where the hydrocarbons have had an artificial maturation.

It should be emphasised that the comparison of fluorescence parameters has been restricted to the *same* hydrocarbon inclusions. In the absence of a complete chemical characterization, the use of fluorescence parameters in assessing oil maturity in *different* generations of fluid inclusions containing hydrocarbon of an unknown origin, needs further experiments. Thus, in the studies reported below, we have used them only to *distinguish* and *characterize* different families of hydrocarbon fluid inclusions.

Fluid inclusions from 'Terres Noires'

Liquid-hydrocarbon-bearing fluid inclusions were identified as primary (type I), only in the western part but as secondary trails throughout the whole basin (type II). Type I are large (50 to 500 μm), colourless with a degree of filling from 20 to 90%. Visible H_2O is absent. Type II inclusions are of smaller size (10 to 50 μm) and yellow-coloured. They are either monophasic liquid or possess a degree of filling of about 20%.

For type I inclusions, fluorescence emission is in the blue-green region with QF values between 0.234 and 0.275, and L max values between 440 and 461 (Table 1, Fig. 6a). Such characteristics may be attributed to very low quantities of aromatic components (not detected even by gas chromatography) diluted in aliphatic components. This

is confirmed by the IR spectra, which are characteristic of aliphatic components with CO_2 and CH_4 in the gas phase, (Fig. 7a). Water was not detected.

Type V (vapour only inclusions) also occur as primary in the eastern part of the basin. These have been analysed (Fig. 8) and the results compared with those obtained by Raman analysis. There is a good correlation between the two methods that confirms a fluid composed of 4% CO_2 and 96% CH_4 . These inclusions are not fluorescent in UV light.

In the second generation (type II), fluorescence emission displays L max values between 500 and 520, and QF values between 0.825 and 0.961 (Table 2, Fig. 6). IR spectra (Fig. 7b) show the presence of aromatic components along with aliphatic ones. In the eastern part of the basin CO_2 and CH_4 have not been detected, H_2O is systematically present. In the western part (Remuzat), a slight difference seems to appear as CO_2 was also detected. A special mention should be made of the samples of barytocelestites from Vertegoux where fluorescence distinguishes two generations of type II inclusions (Fig. 9). Unfortunately, they could not be analysed by IR because of the small size and flatness of the cavities.

In summary, the above results show that it is possible to distinguish two main generations of oils:

- (i) Hydrocarbons, mainly aliphatic associated with CO_2 and CH_4 , which were often entrapped as a complete immiscible phase with respect to H_2O , as primary fluid inclusions having L max values around 450 and QF values around 0.250.
- (ii) Hydrocarbons, more aromatic in character which were trapped from an heterogeneous aqueous fluid. These inclusions were trapped as secondary trails. The hydrocarbon components show L max values around 500 and QF values around 0.9. CO_2 and CH_4 were generally absent.

The first generation of hydrocarbon-bearing inclusions were trapped during the crystallization of the host minerals and are likely to be associated with diagenetic evolution of organic matter in the western part of the basin. The second are probably representative of more evolved organic matter which migrated throughout the area.

Hydrocarbon fluid inclusions from Tunisian locations

In fluorite from Djebel Kohol organic phases were trapped as fluid inclusions only in the outer blue-violet area of cubic, geodic fluorite crystals during late stages of crystallization. The inclusions are yellow-coloured, large-sized (500 μm), intra-

Reference	Type	Microfluorometry		IR Microspectrometry				
		Lmax.	QF.535	Aliph.	Aro.	CO ₂	CH ₄	H ₂ O
Orpierre	I	448	0.275	+	-	+	+	-
Remuzat	I	456	0.276	+	-	+	+	-
	II	520	0.961	+	+	+	-	-
Cornillac	I	440	0.234	+	-	+	+	-
Blégier	II	501	0.825	+	+	-	-	+
Laragne	II	496	0.832	+	+	-	-	+
	I	461	0.402	nd	nd	nd	nd	nd
Allos	II	500	0.914	+	+	-	-	+
	V	nf				+	+	-

TABLE 2. Results from fluorescence and IR microspectrometry in samples from 'Terres Noires'. See text for inclusions references; Type I = primary inclusions, type II = secondary inclusions, (V) = vapour phase to 80%, type V = gaseous inclusions only. QF 535 = red/green ratio, L max = maximum intensity wavelength.

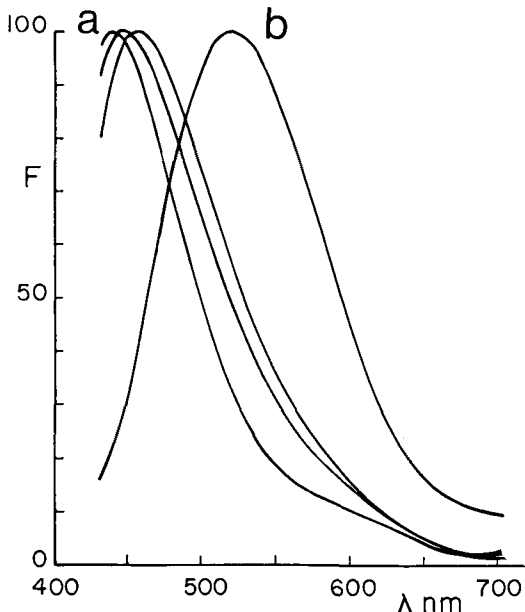


FIG. 6. Fluorescence emission spectra of fluid inclusions from the 'Terres Noires' samples. *a* = type I of three different occurrences in the western part, Orpierre, Remuzat and Vertégoux, *b* = type II in all areas (Orpierre, Remuzat, Blégier, Col d'Allos). Deviation between inclusions of these last different occurrences is less than 5 nm.

crystalline cavities, distributed irregularly or along growth zones.

Values obtained for fluorescence parameters are in the blue region with QF = 0.465 and L max = 442 (Table 3, Fig. 10).

IR spectra show the presence of aliphatic com-

ponents associated with liquid H₂O and CO₂ in liquid phase. CH₄ was detected in the 'vapour phase'.

In fluorite from Hammam Zriba only primary inclusions comprising hydrocarbon droplets in liquid were observed. Fluorescence emission is also in the blue region with L max = 497 and QF = 0.652 (Table 3). IR spectra show only aliphatic components and CO₂ in the liquid and gas phases. CH₄ was not detected.

In the Boujaber mine, hydrocarbons are frequently trapped as an immiscible brown phase with visible water in syngenetic fluid inclusions hosted by prismatic crystals of baryte and geodic crystals of fluorite (Fig. 10). From fluorescence measurements, we obtained the highest values of all our measurements, with QF and L max around 2.14 and 535 (Fig. 10*b*, Table 3) for inclusions in baryte. IR spectra also show the presence of aliphatic components, but with the addition of more aromatic components as suggested by the bands at 3025, 3122, 3159, and 3214 cm⁻¹. CO₂ and CH₄ were not detected.

Strong absorption of H₂O in the matrix is caused by numerous microscopic and sub-microscopic aqueous inclusions. CO₂ and CH₄ were not detected.

Geodic crystals of fluorite contain yellow-brown primary inclusions in the external parts of the crystals. Fluorescence emission is in the red region with QF = 2.3 and L max = 548. From the IR spectra aromatic compounds are detected together with aliphatic components as in the baryte sample discussed above.

From these results we can clearly distinguish two different hydrocarbon components representing two different evolution states. In fluorites from the Zaghouan area, they are only aliphatic

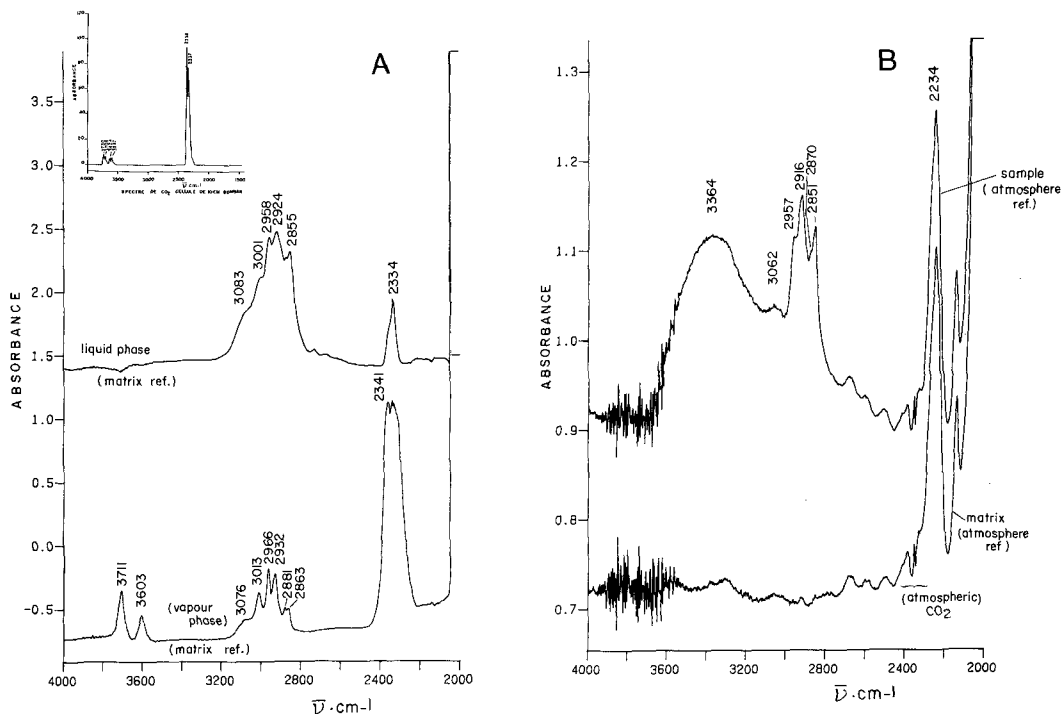


FIG. 7. (a) IR spectrum of type I fluid inclusion from the 'Terres Noires'. Inset, spectrum of gaseous CO₂ under pressure for reference. (b) IR spectrum of type II inclusions from the 'Terres Noires' (liquid + vapour).

Reference	Type	Microfluorometry		IR Microspectrometry				
		Lmax.	QF.535	Aliph.	Aro.	CO ₂	CH ₄	H ₂ O
Gueb 1	I	482	0.456	+	-		+	+
Gueb 3/4	I	493	0.701	+	?	+	+	+
H. Zriba	I	497	0.652	+	-	+	-	+
DJ. Kohol	I	442	0.465	+	?	+	+	-
Boujabeur.								
9533 ba	I	535	2.14	+	++	-	-	+
9533 fl	I	548	2.3	+	++	-	-	+

TABLE 3. Results from fluorescence and IR microspectrometry in samples from Northern Tunisia. Same legend as Table 1. Ba = baryte, Fl = fluorite.

and are associated with CO₂ and CH₄. In minerals from the Tajerouine area they are more aromatic in character and probably of a different level of maturity.

Discussion and conclusions

Correlation between approximate composition determined by IR microspectrometry and the

fluorescence parameters, QF and Lmax, measured on the same hydrocarbon fluid inclusions, permit one to distinguish and characterize the different generations of hydrocarbons trapped in a given mineral or in the various crystallization episodes during diagenesis or ore deposition. These fluids could be related to different thermal events or migrations of organic matter in the associated sediments.

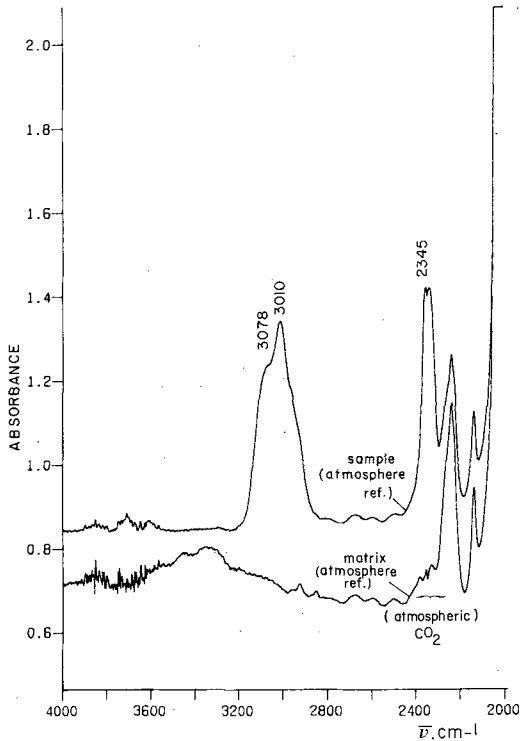


Fig. 8. IR spectra of type V inclusion from Eastern part (Col d'Allos). A slight contribution of atmospheric CO_2 can be seen on the matrix spectra. See text for discussion.

Pradier (1988) and Pradier *et al.* (1988) have established a relationship between fluorescence emission parameters of organic particles (kerogen) and their maturation stage. Khorashani (1986) has further shown that fluorescence characteristically develops in the blue region when aromatics are diluted in paraffinic oils. He also demonstrated a correlation between the evolution towards the red region of spectral ranges of fluorescence emission obtained from extracted paraffinic oils and the increase of aromatic character during thermal maturation.

Preliminary experimental studies presented here on natural fluid inclusions show that for the same trapped hydrocarbon (mainly the aliphatic component), maturation resulting from *in situ* heating under confining pressure causes a slight shift toward the red region of the fluorescence emission spectrum. From IR data, we identified an increase in the alkane chain length, although aromatization of the hydrocarbons is not well supported by our results to date. However, a relationship might be established using different

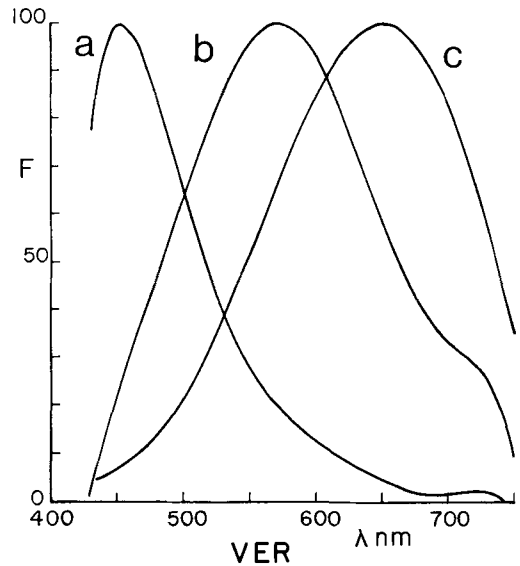


Fig. 9. Fluorescence emission spectra of fluid inclusions from Vertegoux. *a* = type I, *b* and *c* = type II.

analytical conditions, at a later date, that would enable maturation stages of hydrocarbon entrapped as fluid inclusions to be defined from fluorescence parameters.

From our work it is apparent that the highest values of QF and L max in samples from two very different geological settings are obtained from the more aromatic components. However, some authors have found a different evolution (McLimans, 1987) on series of oil inclusions from various petroleum reservoirs. We therefore have to consider that in hydrocarbon maturation the light aliphatic fraction will separate from the heavy aromatic fraction and often migrate subsequently. The former will evolve by cracking of lighter aliphatic components into CH_4 and the fluorescence emission will be then shifted toward the blue region. The latter will become more aromatic and the emission will be shifted towards the red region. This phenomenon should be taken into account when interpreting the measured fluorescence parameters.

Because the controls on the fluorescence parameters the present data has not yet been used to determine maturation level of organic matter trapped in fluid inclusions. However, further experiments involving the evolution of fluorescence parameters with temperature, coupled with more precise semi-quantitative characterization by IR spectrometry, gas chromatography and mass spectrometry, would provide important

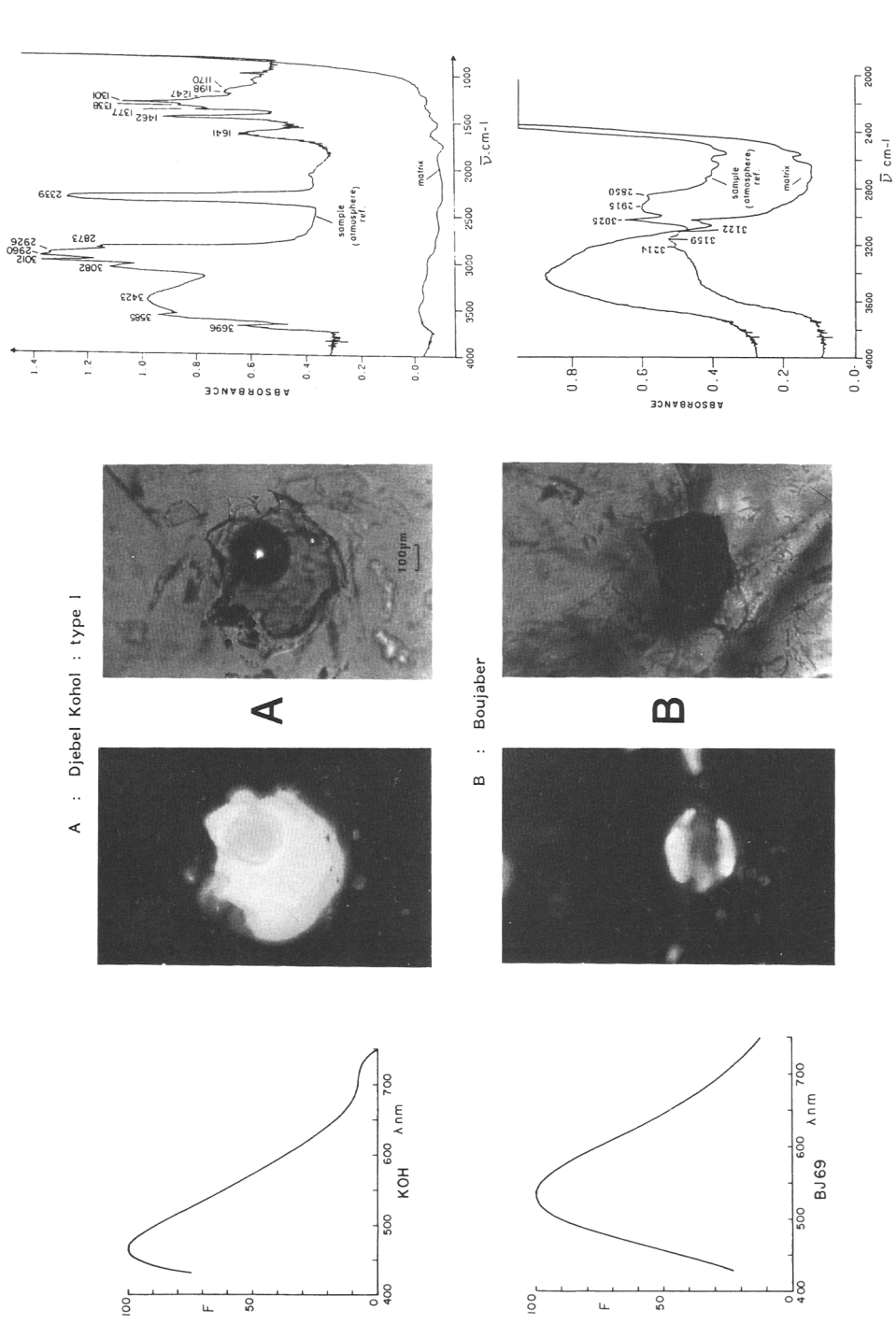


Fig. 10. Fluid inclusions from Djebel Kohol (A, fluorite) and Bou Jabeur (B, baryte) associated with their fluorescence spectra (on left) and IR spectra (on right) [liquid + vapour].

information from hydrocarbon-bearing fluid inclusions, as valuable as that obtained from comparable analyses of kerogen in rocks.

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