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Observation of hydrocarbon generation and migration of highly-matured carbonates by means of laser-induced fluorescence microscopy

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Abstract Some important information on hydrocarbon generation, inclusion and migration in highly-matured carbonates of lower Palaeozoic age from the Ordos Basin and Tarim Basin has been analyzed by a newly-combined laser-induced fluorescence microscope (LFM) designed by our laboratory. The following information has been obtained from the lower Ordovician lamellar carbonates with equivalent vitrinite reflectance (R_o) as high as 1.6%—1.7% and residual TOC of 0.14%—0.35% from the Ordos Basin: wide occurrences of oil and source macerals with strong fluorescence, including *G.Prisca* alginite, lamalginite, telalginite and algae-detrinite; fluorescing asphalt among mineral crystals; some groundmass and spheroid-like reservoir bitumen with high maturation levels in the pores of dolomites. Various kinds of fluorescing organic inclusions and asphalt have been found in the carbonates, calcareous shales and silt-shales with high maturation levels from the Cambrian-Ordovician strata in the Tarim Basin. All this helps us find and evaluate significant and excellent source rocks for large- and middle-scale gas fields. The net and micro-net systems for hydrocarbon generation, expulsion and migration in carbonates have been revealed by the highly-powered laser-induced fluorescence microscopy.

Keywords: laser-induced fluorescence microscopy, highly-matured carbonate, hydrocarbon generation and migration, organic inclusions.

The fluorescence microscopy is an important tool for determining the organic matter of source rocks, and for investigating hydrocarbon generation and migration in strata for petroleum geology. It has been widely applied in oil and gas exploration[1—3]. However, great difficulties have been met for the lower Palaeozoic carbonates in basins such as Ordos, Tarim and Sichuan where much fluorescence information of the strata was lost because of the high maturity for most of the strata. In this paper, a newly combined laser-induced fluorescence microscope (LFM) is used to investigate the hydrocarbon generation and migration of the highly-matured carbonates in early Palaeozoic strata, and to identify and evaluate significant source rocks.

1 Distribution and characteristics of the studied samples

Large- and middle-scale oil and gas fields related to lower Palaeozoic carbonate strata have been discovered recently in the Tarim, Ordos and other basins. However, there are different opinions about the hydrocarbon potential of the lower Palaeozoic Majiagou carbonates in the Ordos Basin since it has a high maturation level and a low residual total organic carbon (TOC). Thus, quite a few of Ordovician samples, including limestone, dolomite and lamellar argillaceous carbonates that formed in a shallow marine platform facies were selected. These samples have a relatively strong hydrocarbon potential, with TOC of 0.14%—0.45%, and equivalent vitrinite reflectance (R_o) of 1.6%—1.74%, but little fluorescence information is available (samples HC1—HC3).

The Ordovician carbonates in the Tarim Basin have a lower maturity than that in the Ordos Basin, so they have abundant fluorescence information in petroleum-producing sections, but the Cambrian carbonates and calcareous black shales and the other strata with higher maturation levels have very weak fluorescence information. The residual TOC for these samples varies widely, and different opinions exist about the discrimination between a significant source rock and an excellent source rock. In order to study the information of hydrocarbon generation and hydrocarbon inclusion, some samples of the Cambrian and Ordovician ages were selected, from high-mature to over-mature with equivalent

R_o of 1.30%—3.69%. Samples HC-5 and HC-6 in table 1 are from the Keping outcrop. They are upper Ordovician Saergun calcareous shale and limestone, formed in a closed bay environment, with TOC of 3.65% and 1.09%, respectively. Samples HC-7 and HC-9 are the Ordovician micrite and limestone formed in hillock depression and lime-mud mound facies of shallow marine environment, with residual TOC of 1.40%—0.23% and equivalent R_o of 1.30%—1.47%. Samples HC-10, HC-11, and HC-12 are black lime-dolomite and calcareous shale and silicic limestone, formed in a hungry basin environment in the Manjiaer Depression, with residual TOC of 1.40%—1.87% and equivalent R_o of 1.76%—1.94%. Sample HC-13 is a highly-matured Cambrian recrystallized dolomite from the well TZ-1 containing reservoir bitumen whose measured reflectance is as high as 2.60%, corresponding with an equivalent R_o of 2.40%. Samples HC-14 and HC-15 are an over-mature Cambrian carbonate from the well TD-1 and a lower Permian thinly-plated bituminous limestone from Nayong, respectively, with corresponding residual TOC of 0.16% and 1.86%. Table 1 presents some basically analytical data of these samples.

2 Experimental

The fluorescence of macerals in a source rock mainly depends on the reaction between macro molecular solid phase consisting of three-dimensional aromatic network system and micro-molecular liquid phase trapped in this network. When the active π electrons absorb the energy from an exciting light, and jump to an excitation state with a high energy and then go back to the ground state, it will emit fluorescence. If the intensity of the exciting light was low, fluorescing groups would produce a too small amount of fluorescing particles to emit an obvious fluorescence. Only when the intensity of the exciting light was increased to the absorbed saturation of fluorescing group and made the amount of the jumping atoms constant, would the increase of the fluorescence intensity be independent of the intensity of the exciting light. Therefore when the intensity of the exciting light does not reach the saturated absorption of fluorescence-producing groups, to increase its intensity and efficiency can increase the brightness and sensitivity of the fluorescence of the studied samples. Since the fluorescence-producing groups of macerals in the highly-matured source rocks have a low fluorescence-producing efficiency, we have tried to use a laser-inducing fluorescence microscopy system with a high power and excellent monochromatic light to investigate the fluorescence information of hydrocarbon and inclusion in highly-matured carbonates.

The laser-induced fluorescence microscope designed by our laboratory was equipped with an argon ion laser generator as its laser source emitting a light with waves of 488 nm and 514 nm. The used laser power for general use will be more than 100 mW. It should be regulated according to the conditions of the studying samples to obtain an obvious fluorescence but not to destroy the samples. The Leitz MPV3 micro-photometer has been modified for the use of this microscopy system. The objectives for use are 25/0.6, 40/0.75, 50/1.0 and other FLUORESZNZ types, depending on the size of macerals measured in the samples.

3 Main results

(i) Range and determination for micro-fluorescence observation of the samples. The fluorescing macerals in source rocks, observed under a fluorescence microscope equipped with a high pressure mercury lamp with a power of 50—100 W are usually confined to R_o less than 1.30%[4, 5] (a little higher R_o for fluorescing carbonate bituminous groundmass). With the increasing maturity, the fluorescence intensity of macerals will be too weak to measure their fluorescence spectra and take a photograph[6,7]. In this paper, the highly-matured samples in table 1 have been investigated by the above laser inducing fluorescence microscopy system under the above conditions. The results show that various fluorescence information for some macerals which can hardly be observed by a conventional microscope was found, which provides new criteria for discriminating different types of source rocks and to evaluate their petroleum potential. For instance, yellow fluorescence macerals including a type of algae which is similar to *Gloeocapsomorpha Prisca* alginite, lamalginite, telalginite, algae-detrinite and fluo-amorphinite were found in the lower Ordovician carbonate and lamellar carbonates with equivalent R_o of 1.65%—1.74% from the Ordos Basin. This reveals that the organic matters in these source rocks were mainly derived from algae and other similar precursors, and that these fluorescing macerals are abundant in lamellar carbonates and sutured textures (Plate I-3, 4, 6). A type of fluorescing asphalt occurs widely among mineral crystal grains in some of the source rocks, and it indicates that these carbonates are significant source rocks in which hydrocarbon generation and expulsion happened (Plate II 3—8). Various fluorescing macerals have also been observed in the upper Ordovician Saergun black calcareous shale and a lensoid carbonate with an equivalent R_o of 1.4%—1.6% from the Tarim Basin. Alginite and other original macerals are relatively abundant in the calcareous shale, and fluorescing asphalt and fluorescing mineral bituminous groundmass abundant in the lensoid carbonate. All the fluorescence information is the important features of an excellent source rock (Plate I-1, 2). Organic inclusions and yellow fluorescence asphalt with the micro-grain, irregular band and star-like shape were found in a silicic carbonate with an equivalent R_o of 1.70%—1.94% in the well KN-1 (Plate I-7). Various mineral asphalt with fluorescence occurs widely in a dolomite with an equivalent R_o of 2.40% from the well TZ1 (Plate I-8). However, very little fluorescence information for the lower Permian plated bituminous limestone with an equivalent R_o of 3.20% from Nayong and the Cambrian carbonate with an equivalent R_o of 3.69% from the well TD1 could be obtained. Therefore, the range of visible fluorescence for macerals and mineral bituminous groundmass in a rock have been believed to be extended to equivalent R_o 1.80% and 3.20%, respectively.

(ii) Information of hydrocarbon generation and inclusion for a significant source rock. A significant source rock is regarded as a type of source rock contributing to the formation of an oil and gas pool in geological history. If it was evaluated by means of the relationship of the present oil and gas pools with the distribution of source rocks, and the residual TOC of the source rocks, it would depend on a lot of analytical work related to oil-source correlation as well as a big collection of experiences for petroleum exploration. However, the method of the laser-induced fluorescence microscopy and organic petrology can investigate the hydrocarbon generation and inclusion for various rocks, helping to find and forecast a significant source rock.

According to the results for the samples in table 1, the Ordovician samples in the Tarim Basin such as HC-7 and HC-9 are significant source rocks for the oil and gas pools in this area because of the wide occurrences of alginite, algae-detrinite, graptolite (Plate I-1, 5), fluorescing asphalt and fluorescing organic inclusions (Plate II-1,2). The Cambrian silicic limestone and calcareous shale with equivalent R_o of 1.74% from the well KN1 in the Tarim Basin are believed to be an excellent source rock since some star-like organic inclusions with a size of 1 μm are distributed widely in them (Plate I-7). It should be noticed that the lower Ordovician carbonates with residual TOC of 0.14%—0.35% and equivalent R_o of 1.65%—1.74% from the well Yi25 and Er-5 contain a lot of macerals with fluorescence, including *G. Prisca* alginite, lamalginite and telalginite, algae-detrinite, fluorescing mineral bituminous groundmass (Plate I-2,3,4,6) which shows that these rocks have hydrocarbon potential and underwent a hydrocarbon generation process. In particular, some reservoir bitumen was found in a dolomite which, with a burial depth of 4 516 m, occurs below a salt seam (O_{1m}) from the well Yi25 located in the west of the Ordos Basin (Plate II-7,8), which shows that hydrocarbon accumulation happened in this section. Since the section was away from the unconformity surface existing at the top of Ordovician strata with a distance of 425 m, and was sealed by quite a few gypsum seams, the hydrocarbon generated from the upper Palaeozoic strata could not migrate downward. Moreover, since the upper Palaeozoic strata, dominated by a coal measure, formed mainly gas hydrocarbon, it is hard to believe there was liquid hydrocarbon to migrate downward. Thus, this reservoir bitumen originated from the lower Palaeozoic carbonates. The above results show that the hydrocarbon generation of the carbonates in some sections of the Majiagou formation (O_{1m}) and their contribution to oil and gas pools could not be neglected in geological history.

(iii) Net system for hydrocarbon expulsion and migration in carbonates. A carbonate is a type of rocks with rapid diagenesis and active chemical properties. So, it is different from mudstone source rocks in hydrocarbon expulsion and migration. It is well known that the hydrocarbon generation and expulsion of organic matter in mudstone source rocks is completed by the dehydration of clay minerals during their burial, compaction and diagenetic evolution. However there is no general idea for the processes and mechanism of hydrocarbon expulsion and migration in carbonates. In this paper, the following four net systems for hydrocarbon expulsion and migration in carbonates are given on the basis of the results obtained by the laser-induced fluorescence microscopy system.

Table 1 Occurrences and basic characteristics of the studied samples

No.	Occurrence	Well and depth /m	Age	Lithology	Maturity R_o(%)	TOC (%)	S_1 /mg • g^{-1}	S_2 /mg • g^{-1}	HI /mg • g^{-1}(TOC)
HC-1	Ordos	Yi25 4435	O_{1m}	lime-dolomite	1.68	0.14	0.24	0.11	79
HC-2	Ordos	Yi25 4516	O_{1m}	dolomite	1.74	0.35	0.08	0.02	6
HC-3	Ordos	Er5 2961	O_{1m}	limestone	1.65	0.30	0.06	0.04	13
HC-4	Ordos	Xiangling outcrop	O_{1m}	limestone		0.19	0.14	0.05	28
HC-5	Tarim	Keping outcrop	O_2	calcareous shale	1.61[a)]	3.65	2.65	4.56	110
HC-6	Tarim	Keping outcrop	O_2	limestone	1.4	1.09	0.39	1.08	99
HC-7	Tarim	He3 4040	O	micrite	1.49	0.23	0.54	0.36	157
HC-8	Tarim	Qk1 3531	O	mudstone	1.3	0.20	0.17	0.06	30
HC-9	Tarim	LN46 6106	O_{2+3}	limestone	1.26	0.14	0.66	0.17	121
HC-10	Tarim	He4 5341	Є	lime-dolomite	2.07	0.37	1.74	0.35	95
HC-11	Tarim	KN1 4995	Є	silicic limestone	1.76	1.87	0.63	0.19	10
HC-12	Tarim	KN1 5189	Є	silicic limestone	1.94	1.41	0.17	0.01	1
HC-13	Tarim	TZ1 6505	Є	dolomite	2.4	0.40	0.47	0.63	158
HC-14	Tarim	TD1 4060	Є	limestone	3.69	0.16			
HC-15	Guizhou	Nayong	P_1	bituminous limestone	3.2	1.86	0.43	0.22	12

a) Data after Wang Feiyu.

(1) Micro-net system among carbonate mineral grains. On the basis of the investigation of the samples: HC-1,4; HC-6,7,9,10,12 and the presentation of Plates I-2,7 and II-4, a micro-net system that consists of fluorescing asphalt between carbonate mineral grains was found in some carbonates with good hydrocarbon potential. The width of the micro-nets varies widely, from <0.20 to >2.0 μm, sometimes filled with clay minerals, pyrite grain and pyrobitumen, or with micro-inclusions distributed in a dotted line around edges of mineral grains. This is in fact the trace of micro-net system for hydrocarbon generation and migration of carbonate source rocks during diagenetic evolution.

(2) The grain-sequence bedding and lamellar surfaces for hydrocarbon expulsion and migration in carbonates. Yellow fluorescing asphalt with line or band distribution showing hydrocarbon migration was observed in the grain-sequence bedding and lamellar surfaces in lamellar carbonates in the Ordos Basin (HC-3) and carbonates in the Tarim Basin (HC-7,9,10). This shows that various grain sequence bedding and lamellar surfaces are not only the important site for the accumulation of original organic matter, but also the important channels for hydrocarbon expulsion and migration and to connect micro-nets among crystals in carbonate source rocks. These are an important system to complete hydrocarbon migration in the cross direction.

(3) Sutured textures for hydrocarbon expulsion and migration in carbonates. Suture is a common texture formed in carbonates by pressure solution during diagenesis. There are many factors to have an influence on the development of the pressure solution and suture. The chemical properties of source rocks and physical-chemical conditions of water in strata, together with the formation of organic acids with hydrocarbon generation of organic matter and the increasing partial pressure of CO_2 owing to the action of temperature and pressure in a burial depth of 2 000—4 000 m, will promote the development of suture textures and the cross migration of the hydrocarbon. Many observed results show that the

suture texture develops well in a significant source rock and various bitumen and organic inclusion occurs near the suture. So, the suture is an important channel for hydrocarbon migration and accumulation [5]. Plate II-6 shows the residual of hydrocarbon, bitumen, pyrite and their matrix with various fluorescence nearby sutures (HC-2), which reflects the information of petroleum migration along the sutures. Because a suture is a fissure which could be closed, and some hydrocarbon, bitumen and organic inclusions that formed in different phases could be kept in these fissures, it plays an important part in investigating hydrocarbon-generating phases of an oil and gas pool.

(4) The combined system composed of fissures, suture textures and unconformity surfaces for the vertical migration of hydrocarbon in carbonates. The oil and gas exploration practice of carbonate strata, carried out in Sichuan, Tarim, Ordos and other basins show that various fissures and faults are important channels that connect source rocks with oil and gas pools. This is why some oil and gas pools formed nearby the fissures and fault belts. The solid bitumen and a large amount of organic inclusions filling the fissures are not only evidence for petroleum migration and accumulation, but also the source matter to regenerate gas in these strata[5]. Plate II-2 (HC-7) is the photograph showing a calcite vein with a vast amount of organic inclusions formed by thermal fluid containing hydrocarbon.

4 Conclusion

Since the fluorescence intensity of organic matter in source rocks decreases rapidly up to disappearance with increasing maturity, this will render it difficult to observe and measure the fluorescence of lower Palaeozoic carbonates with high maturation levels, and to evaluate their hydrocarbon potential. The laser-induced fluorescence microscope designed by our laboratory enables the range of visible fluorescence of macerals to be extended from R_o about 1.30% to 1.80%. The investigation from a series of representative highly-matured carbonates with TOC of 0.14%—1.90% from the Ordos Basin and the Tarim Basin has revealed a wide occurrence of fluorescing macerals such as *G. Prsca* alginite, telalginite and algae-detrinite and fluorescing bitumen and organic inclusions. This helps us to discriminate various types of significant source rocks and evaluate their hydrocarbon potential. Reservoir bitumen was found in a dolomite section, which is away from the unconformity surface between Ordovician and Carboniferous by a vertical distance of 425 m, from the well Yi25 located in the west of the Ordos Basin. Therefore, its source rocks should be the lower Palaeozoic strata. This result has also shown that the oil and gas generation of some carbonates in the Majiagou formation in the Ordos Basin could not be neglected.

The results obtained by the highly-powered laser-induced fluorescence microscopy show the micro-net system composed of fluorescing asphalt occurring among mineral crystal grains and inclusions for hydrocarbon expulsion and migration in carbonate source rocks, and the systematic system composed of bedding surfaces, sutures, fissures and unconformity surfaces for petroleum migration.

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References

1. Allan, B., Lemos de Sousa, M. J., Pinheiro, H. J. et al., Detection and evaluation of hydrocarbons in source rocks by fluorescence microscopy, Org. Geochem., 1993, 20(6): 789.
2. Xia Xinyu, Zhuo Ling, Li Zuanfeng et al., The geochemical characteristics of natural gas and the origin of the gas pools in the Ordovician strata in Changchen gas field, Chinese Science Bulletin, 1999, 44(9): 1116.
3. Teichmuller, M., Organic petrology of source rocks, history and state of the art advance in organic geochemistry, Org. Geochem., 1986, 10: 581.
4. Zhao Changyi, The fluorescence mechanism of macerals and its application, Oil and Gas Exploration and Development, 1996, 23(2): 8.
5. Liu Dehan, Shi Jiyang, Zhen Xuming, The geochemical characteristics and unconventional evaluation method for highly-matured carbonates, Natural Gas Industry, 1994 (Supp.): 67.
6. Jin Kuili, Qiu Nansheng, Application of laser-induced fluorescence of coal extracts for determining rank, Org. Geochem., 1993, 20(6): 687.
7. Jin Kuili, The New Method of Coal and Organic Petrology (in Chinese), Beijing: Geological Press, 1977, 55—61.
8. Stasiok, L. D., Kybett, S, L., Bend, S. L., Reflected light microscopy and micro-FTIR of Upper Ordovician *Gloeocapsomorpha prisca* alginite in relation to paleoenvironment and petroleum generation, Saskatchewan, Canada, Org. Geochem., 1993, 20(6): 707.

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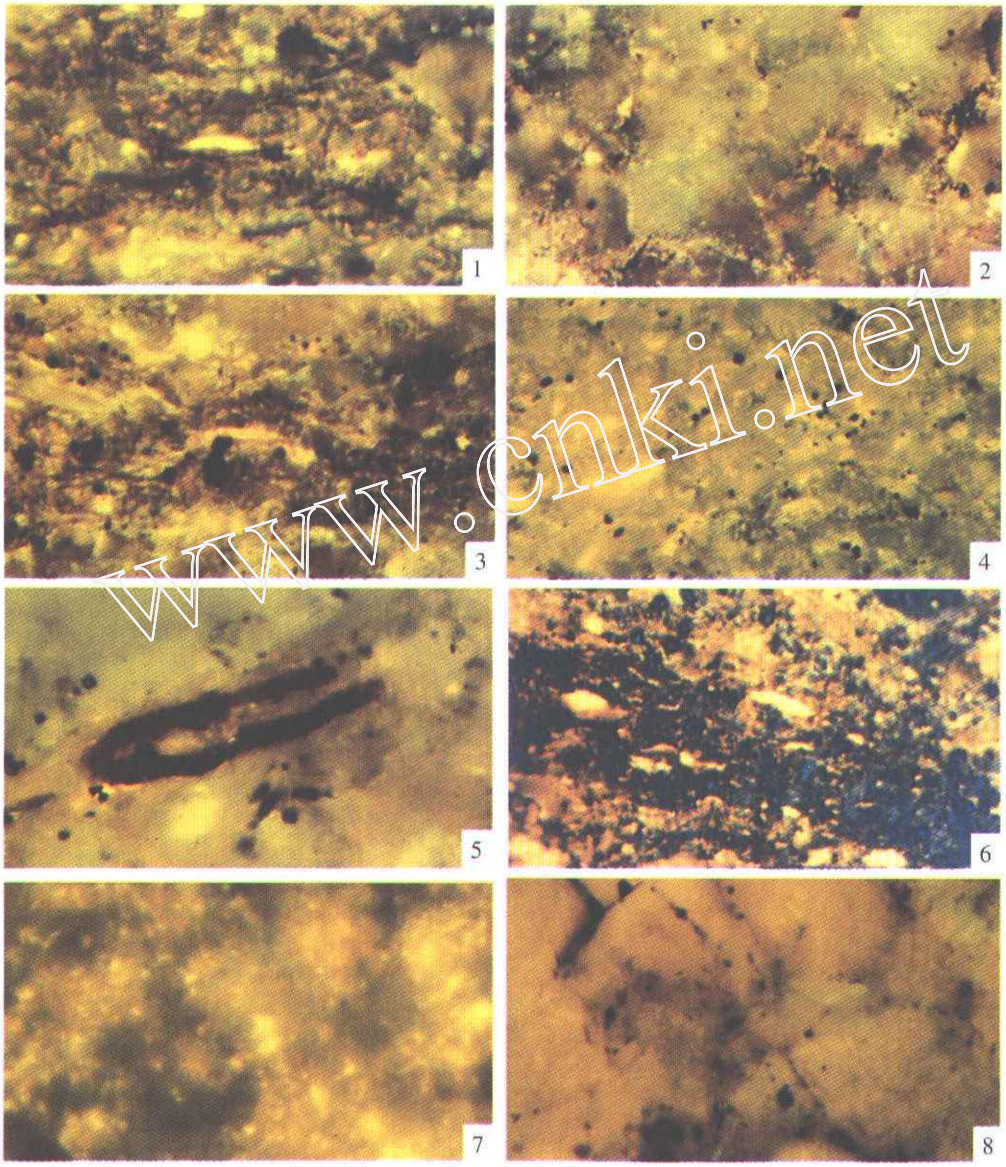
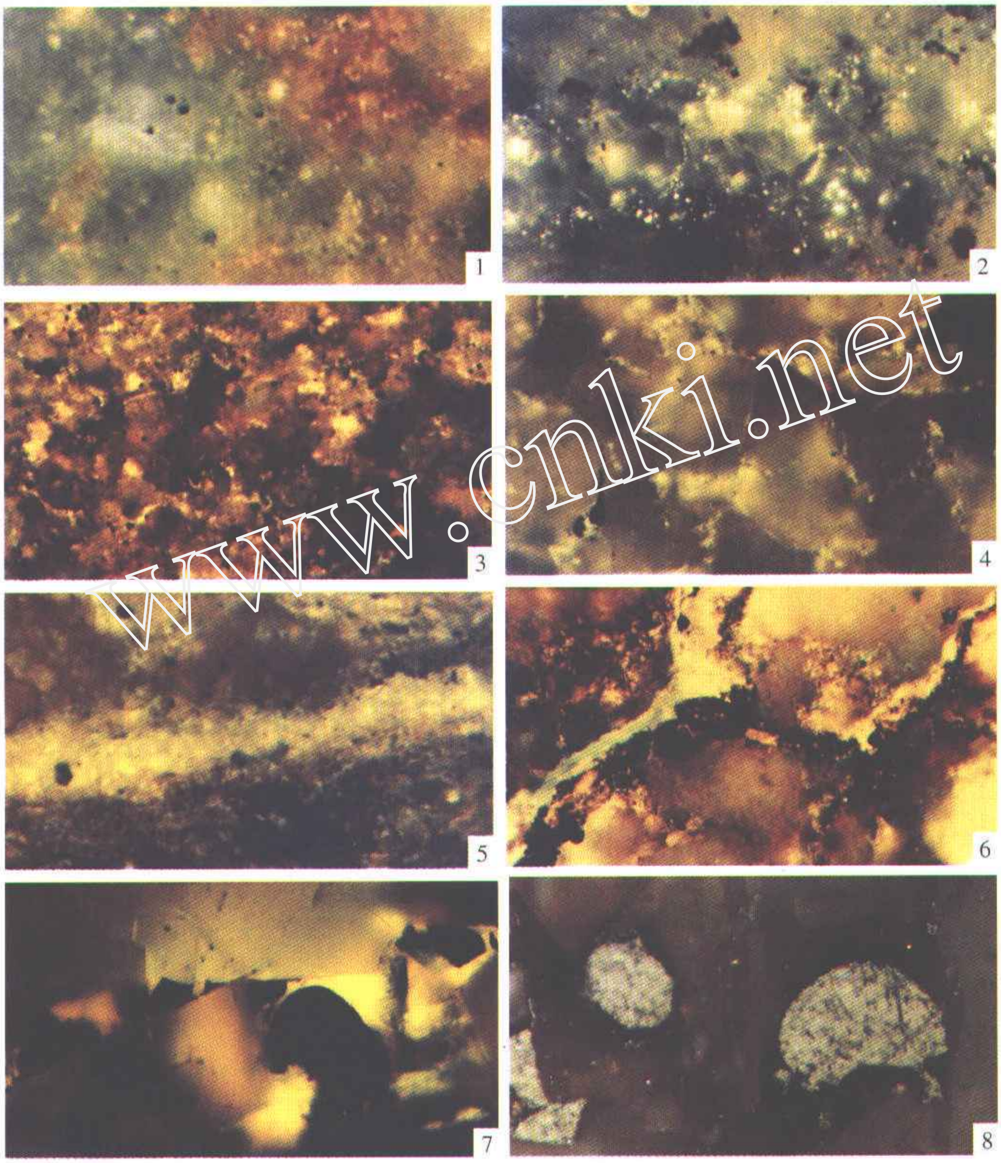


1. *G. prisca* alginite, telalginite, and algae-detrinite with yellow fluorescence, Saergun black calcareous shale, HC-5, laser-induced fluorescence microscopy (LFM), ×250. 2. Net-like asphalt and matrix with fluorescence, distributed among carbonate mineral crystals. Saergun lensoid limestone, HC-6, LFM, × 250. 3. A carbonate with mudstone band, containing lamalginite and algae-detrinite, O_{1m}, 2 961 m, Er-5, HC-5, LFM, × 250. 4. Algae-detrinite and fine dispersed asphalt among mineral crystals with yellow fluorescence, carbonate from Huixiangling section in the Ordos Basin, O_{1m}, HC-4, LFM, × 250. 5. Black brown graptolite and mineral bituminous groundmass with yellow fluorescence in the argillaceous limestone, LN-46, $O_{2\text{-}3}$, 6 106 m, Tarim Basin, HC-9, LFM, × 250. 6. Various kinds of telalginite and algae-detrinite with yellow fluorescence, a dolomite containing mudstone band, Yi-35, O_{1m}, 4 516 m, Ordos Basin, LFM, × 250. 7. Asphalt with yellow-green fluorescence, distributed among crystals, and organic inclusions with a size of about 1 μm, limestone, KN-1, Cambrian age, 5 189 m, Tarim Basin, LFM, × 250. 8. Solid bitumen without fluorescence, distributed among dolomite grains, dolomite, TZ-1, Cambrian age, 6 505 m, HC-13, Tarim Basin, LFM, × 250.



1. Lots of micro-organic inclusions with yellow to yellow-green fluorescence, limestone, Ordovician, 4 040 m, He-3, HC-7, Tarim Basin, LFM, × 250. 2. Lots of organic inclusions with bright yellow fluorescence, occurring along the wall of a calcite vein, limestone, Ordovician, 4 040 m, He-3, HC-7, Tarim Basin, LFM, × 250. 3. Wide occurrences of yellow fluorescence bituminous matter and algae-detrinite among mineral grains in an argillaceous and silt limestone, 2 961 m, Er-5, HC-3, LFM, × 250. 4. Bituminous net veins with fluorescence, occurring among calicite grains, showing the micro-net system for hydrocarbon expulsion and migration in the carbonate, O_{1m}, 4 435 m, Yi-25, HC-1, LFM, × 250. 5. Asphalt with yellow fluorescence, occurring in the grain sequence bedding, showing the information for hydrocarbon expulsion and cross migration, carbonate source rock, O_{1m}, 2 961m, Er-5, Ordos Basin, HC-3, LFM, × 250. 6. Asphalt with strong yellow fluorescence, filling the fissures nearby sutures, dolomite, O_{1m}, Yi-25, 4 516 m, Ordos Basin, HC-2, LFM, × 250. 7. Groundmass and spheroid-like pyrobitumen without fluorescence, filling in pores among dolomite grains, and an associated mineral bituminous groundmass with yellow fluorescence, O_{1m}, 4 516 m, Yi-25, HC-2, LFM, × 250. 8. Spheriod-like pyrobitumen with R_o of 2.04% and an inhomogeneous texture, the same field with Plate II-7, reflected light, HC-2, × 640.