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Study of genetic evolution of oil inclusion and density of surface oil by measurement of fluorescence lifetime of crude oil and oil inclusion

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Abstract By using fluorescence lifetime image microscope (FLIM) and time-correlated single photon counting (TCSPC) technique, we measured fluorescence lifetime of crude oils with density of 0.9521–0.7606 g/cm^3 and multiple petroleum inclusions from Tazhong uplift of Tarim Basin. As indicated by the test results, crude oil density is closely correlated with average fluorescence lifetime following the regression equation Y=–0.0319X+0.9411, which can thus be used to calculate density of oil inclusions in relation to fluorescence lifetime and density of corresponding surface crude. For type A oil inclusions showing brown-yellow fluorescence from Tazhong 1 well in Tarim Basin, their average fluorescence lifetime was found to be 2.144–2.765 ns, so the density of surface crude corresponding to crude trapping these oil inclusions is 0.852–0.873 g/cm^3, indicating that they are matured oil inclusions trapped at earlier stage of oil formation. For type B oil inclusions with light yellow-white fluorescence, their average fluorescence lifetime was found to be 4.029–4.919 ns, so the density of surface crude corresponding to crude trapping these oil inclusions is 0.784–0.812 g/cm^3, indicating that they are higher matured oil inclusions trapped at the second stage of oil formation. For type C oil inclusions showing light blue-green fluorescence, their average fluorescence lifetime was found to be 5.063–6.168 ns, so the density of surface crude corresponding to crude trapping these oil inclusions is 0.743–0.779 g/cm^3, indicating that they are highly-matured light oil inclusions trapped at the third stage of oil formation.

Keywords Oil inclusion, Fluorescence lifetime, Tarim Basin, Crude density, Crude charging episode

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1. Introduction

Fluid inclusions are primitive fluid enclosed in minerals and rocks. They are recording abundant information, such as fluid composition, trapping temperature and pressure in geological evolution history. (Liu et al., 1995; Lu et al., 2004; Liu, 1988; Liu et al., 2006, 2007). Generally, occurrence of hydrocarbon inclusions in strata can yield evidence of hydrocarbon activity, as color and spectra of fluorescence of oil inclusions can provide key evidence of formation episodes and maturation of oil and gas (Liu et al., 2009). Liu et al., (2003) studied fluorescence color, homogenization temperature, trapping pressure of oil inclusions in crude, and charging episodes and maturation of crude from Ordovician strata in Tarim Basin. Fluorescence lifetime of crude and oil inclusion data refers to nanometer scale time between ground state electrons in luminescent group being excited to first single line excitation state after absorbing energy and going back from excitation state to ground state. Here fluorescence lifetime is closely related not only to molecular structure of luminescent substance but also to microenvironment of the substance, so being the frontier of petroleum geology and geochemistry (Fang

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*Corresponding author (email: liudh@gig.ac.cn) et al., 2001). Blamey et al., (2009) used Frequency-Domain (FD) method to systematically measure distribution of fluorescence lifetime of multiple oil inclusions from North Atlantic Basins, Porcupin Basin and Kangerlussuaq Basin, to explore formation episodes and evolution of hydrocarbon; Owens et al. (2008) used FD technique and TCSPC technique for fluorescence lifetime measurement and three data processing methods, compared and studied the relationships between average fluorescence lifetime and API value as well as polar composition of crude oils (Ryder et al., 2002; Owens et al., 2008). Their results indicate smaller API value (heavy oil) and higher polar composition correspond to shorter average fluorescence lifetime of crude oil, otherwise, higher API value (light oil) corresponds to longer average fluorescence lifetime of crude, in other words, API value is linearly correlated with fluorescence lifetime of crude oil. In addition, some large petroleum companies have established database for average fluorescence lifetime of crude oils from different regions, as required by appraisal, storage and transportation of crude oil. However, available literature on fluorescence lifetime shows significant difference exist in relation to average fluorescence lifetime for oil inclusions from different basins and of different ages, therefore, the relationship between oil inclusions and their host crude oils cannot be ascertained. Tarim Basin is abundant in hydrocarbon resources, as it hosts multiple oil reservoirs and undergoes complicated hydrocarbon evolution history. In particular, Tazhong uplift hosts multiple stages of hydrocarbon migration and accumulation ever since Paleozoic time, its strata contain abundant information on hydrocarbon occurrence, and its carbonate reservoirs host multiple fluorescence types of oil inclusions. However, density of oil inclusions cannot be measured directly. In this paper, we would use new techniques and new methods to measure precisely fluorescence lifetime of multiple surface crude oils and multiple oil inclusions from Tazhong uplift under identical experimental conditions. By comparative analysis, we would be able to yield evidences for effectively predicting density of oil inclusion-trapping crudes corresponding to surface crudes. We believe that the results would be meaningful for exploring genetic evolution of oil inclusions and for exploring and assessing hydrocarbon resources deep down the crust.

2. Samples and geological background

The Tarim Basin is a hydrocarbon resource-rich compound basin resulted from multiple cycles of structural activity; our research was focused on the central uplift of Tarim Basin, which was formed at early Hercynian and reconstructed at late Hercynian and Himalayan. For this uplift anticline, its axis is composed of Ordovician strata, while its two limbs are composed of Silurian and Devonian strata, which are overlain by structurally subdued Carboniferous-Cretaceous strata upon a plane of unconformity. This uplift extends in an area of ca. 11×10^4 km^2, with the west section of its north boundary being adjacent to Awati depression, the east section of its north boundary being adjacent to Manjiaer depression, the west section of its south boundary being linked with Maigaiti slope, the east section of its south boundary being linked with Tangguzibasi depression. Anyway, Tazhong uplift extending from east to west is a favorable zone for hydrocarbon migration and accumulation in geological history, as multiple types of crude and oil inclusions were found to occur in this region (Jia et al., 1992; Zhang et al., 1992; Liu et al., 2003). Crude samples for fluorescence lifetime study were collected from 8 boreholes, including heavy oil, intermediate oil, light oil and condensate oil with density ranging from 0.9521 g/cm^3 to 0.7606 g/cm^3 as listed in Table 1.

Samples for oil inclusion study were collected from the Ordovician carbonate reservoir that mainly occurs around the plane of unconformity in Tazhong region. As plane of stratigraphic unconformity and carbonate pressure solution stylolite structure are key channels for migration of oil, gas and water, fluid inclusions are well developed during its diagenesis and evolution, and information regarding hydrocarbon migration and accumulation in geological history can very possibly be preserved in mineral inclusions or fluid inclusions formed at different formation stages. Therefore, these key strata are important for study of hydrocarbon formation, migration and accumulation in petroleum geology. Particularly, in carbonate minerals occurring around the Ordovician carbonate suture at Tazhong 1 well in the anticline axis, three fluorescent types of oil inclusions were found to be in paragenetic association with one another. In this study we would measure fluorescence lifetime of these oil inclusions under identical experimental conditions, calculate the density of crudes that trap these oil inclusions, so as to explore the formation and evolution of these oil and gas resources.

Figure 1a1 shows dense distribution of oil inclusions of

Table 1 Crude samples from Tazhong region for fluorescence lifetime measurement

Borehole	Crude code	Density (g/cm^3)	Type
TZ-122	CB-037	0.9521	Heavy oil
TZ-69	CB-053	0.9349	Heavy oil
TZ-161	CB-104	0.8774	Medium oil
TZ-168	CB-096	0.8575	Medium oil
TZ-122	CB-033	0.8522	Medium oil
TZ-242	CB-260	0.8065	Light oil
TZ-261	CB-204	0.7899	Light oil
TZ-244	CB-102	0.7606	Condensate oil

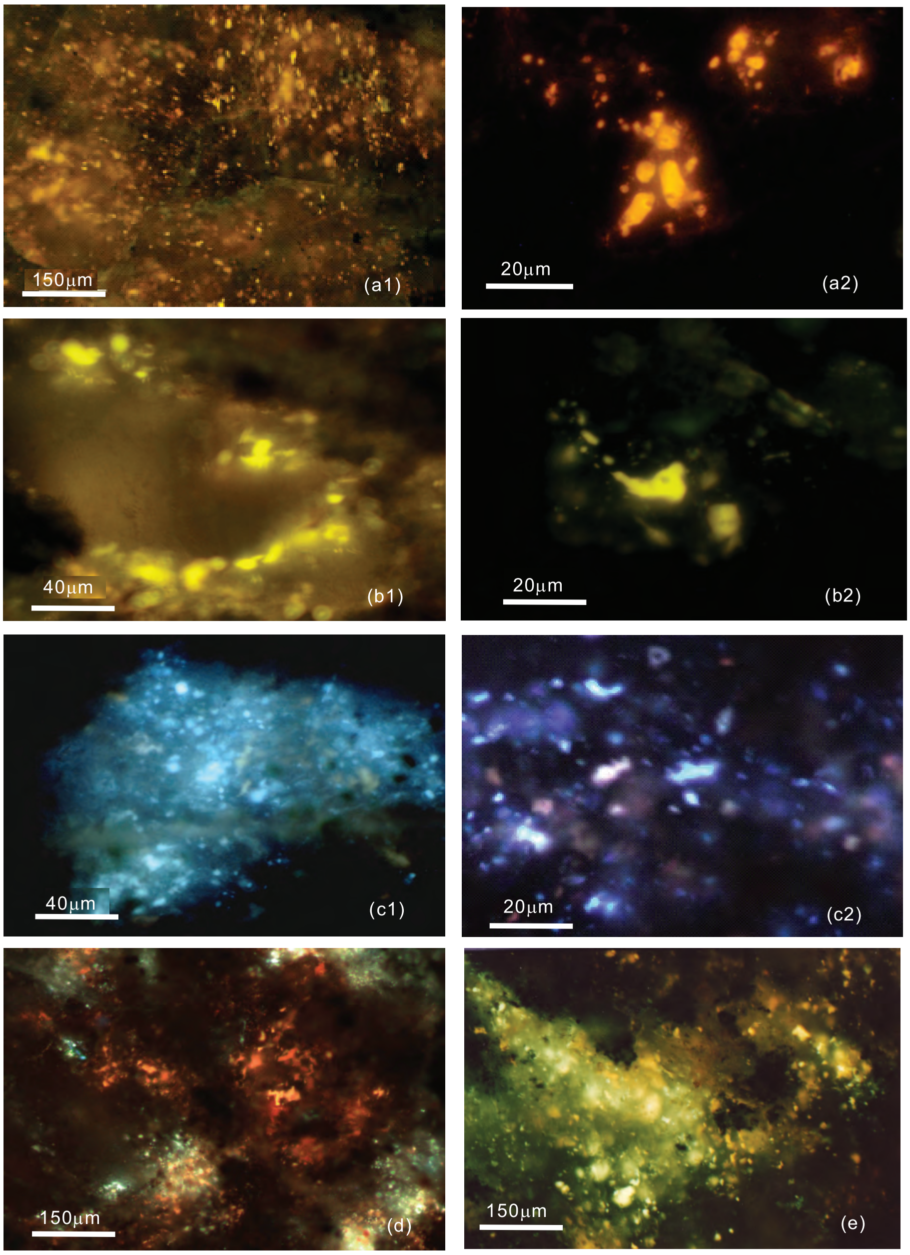

Figure 1 Occurrence of oil inclusions of multiple fluorescence colors at around Ordovician carbonate reservoir pressure solution stylolite structure in Tazhong 1 well. (a1) and (a2) are type-A oil inclusions; (b1) and (b2) are type-B oil inclusions; (c1) and (c2) are type-C oil inclusions; (d) and (e) are multiple fluorescence colors of oil inclusions in sample.

brown fluorescence colors, being mainly distributed in authigenic carbonate minerals formed at earlier stage; Figure 1a2 shows oil inclusions with brown fluorescence bubbles under higher magnification. Figure 1b1 shows oil inclusions with light yellow fluorescence distributed in rings and bands, these are secondary inclusions occurring in carbonate minerals. Figure 1b2 shows higher magnification of oil inclusions exhibiting occurrence of small bubbles. Figure 1c1 and Figure 1c2 are photomicrographs under different magnifications of oil inclusions with light blue-green fluorescence, these are also secondary inclusions occurring in carbonate minerals, but no conspicuous bubbles were seen, which may be due to too strong light blue-green fluorescence of oil inclusion under microscope. Figure 1d and Figure 1e basically reflect occurrence and distribution of oil inclusions, with multiple fluorescence colors in samples around the carbonate suture of Tazhong 1 well.

3. Test methods and technology

As the experimental conditions for fluorescence lifetime measurement of crude oils should be basically identical to those for oil inclusions, we directly sealed crude oils between object slide and cover glass for fluorescence lifetime measurement. While for fluorescence lifetime measurement of oil inclusions, we used polished thin-section of mineral inclusions. For measurement of fluorescence lifetime of single oil inclusion, under fluorescence lifetime image microscope we selected oil inclusions with > 3−5 µm size according to fluorescence type and 50−100 magnification objectives based on sizes of inclusions.

Currently three basic methods are available for fluorescence lifetime measurement of samples. The first uses phase modulation method (FD), the second uses TCSPC, the third uses stroboscopic technique developed by PTI Inc., with the TCSPC method being most extensively used due to its high sensitivity (Fang et al., 2001). As a result, TCSPC method was utilized in this study for fluorescence lifetime measurement of both crude oils and oil inclusions. We used HORIBA DeltaMyc fluorescence lifetime microscopic imaging system, and calibrated it with standard europium chloride ($EuCL_3$) with known fluorescence lifetime. Available literature indicates that crude fluorescence lifetime is related not only to crude composition but also to excitation wavelength for fluorescence lifetime measurement (Ryder, 2002; Owens et al, 2008; Blamey et al., 2009). Therefore, identical experimental conditions and identical single excitation wavelength were employed for fluorescence lifetime measurement of crude oils and oil inclusions and related data processing, and to calculate density of oil inclusion trapping crude, and for contrast and application of test results. Here the experimental conditions can be listed as follows: sample excitation light source wavelength 377 nm, emission filter wavelength 400 nm, measurement pinhole 200 µm, and 50−100 magnification objectives. The practical measurement scope of samples is related to magnification under microscope, and is generally 3−5 µm under higher magnification. Laser intensity can be modulated with 5-level adjustable attenuation filter to detect signal < 2.00, professional instrument software “Date Station” will be used for “decay” and “prompt” measurement of fluorescence lifetime attenuation curve for samples, and test results will be fit and calculated using instrument software DAS6 and multiple parameters for fluorescence lifetime attenuation curve. When curve fitting parameter is close to 1, fluorescence lifetime data T_1, T_2, T_3 and their percentage B_1, B_2, B_3 can be derived from sample fluorescence lifetime attenuation curve, and finally the average fluorescence lifetime data can be calculated from all test points for the sample (Table 2).

4. Results and discussion

For crude from Tazhong uplift, a series of crude samples with density in the range of 0.952–0.7606 g/cm^3 (Table 1) were

Table 2 Datasheet of fluorescence lifetime and formation episodes for three types of oil inclusions from Tazhong 1 well[a)]

Oil inclusion type	T_1 (ns)	B_1 (%)	T_2 (ns)	B_2 (%)	T_3 (ns)	B_3 (%)	Average fluorescence lifetime (ns)	Calculated density for corresponding surface crude (g/cm^3)	Fluorescence color	Formation episodes
Type A1	1.493	84	6.013	16			2.144	0.873	Brown-yellow	Stage 1
Type A2	1.447	82	6.473	18			2.743	0.854	Brown-yellow	Stage 1
Type A3	1.490	85	6.418	15			2.235	0.869	Brown-yellow	Stage 1
Type A4	1.536	84	6.651	16			2.339	0.865	Brown-yellow	Stage 1
Type A5	1.585	84	6.499	16			2.764	0.852	Brown-yellow	Stage 1
Type A6	1.487	86	6.482	14			2.210	0.871	Brown-yellow	Stage 1
Type B1	3.351	82	11.874	18			4.919	0.784	Light yellow	Stage 2
Type B2	3.347	83	12.971	17			4.910	0.784	Light yellow	Stage 2
Type B3	2.773	84	10.406	16			4.209	0.812	Light yellow	Stage 2
Type B4	3.033	81	11.900	19			4.739	0.790	Light yellow	Stage 2
Type B5	3.239	84	12.158	16			4.649	0.793	Light yellow	Stage 2
Type B6	3.181	85	12.210	15			4.517	0.797	Light yellow	Stage 2
Type B7	2.930	83	12.058	17			4.490	0.798	Light yellow	Stage 2
Type C1	6.886	36	2.221	58	21.99	6	5.063	0.779	blue-green	Stage 3
Type C2	6.725	43	1.959	50	21.66	6	5.273	0.773	blue-green	Stage 3
Type C3	7.450	45	2.392	48	22.52	8	6.168	0.744	blue-green	Stage 3
Type C4	6.856	39	2.026	55	23.22	6	5.106	0.778	blue-green	Stage 3
Type C5	6.056	44	1.900	49	21.12	7	5.090	0.779	blue-green	Stage 3
Type C6	6.479	42	1.964	52	21.96	6	5.158	0.776	blue-green	Stage 3

a) T_1, T_2 and T_3 represent representative time on fluorescence lifetime attenuation curves; B_1, B_2 and B_3 represent representative proportions occupied by T_1, T_2 and T_3 on fluorescence lifetime attenuation curves.

collected for fluorescence lifetime measurement and multiple parameters fitting and calculation, and the finally derived average fluorescence lifetime data and known density data of crude were analyzed with regression equation. As the main results listed in Figure 2 illustrate, crude density is correlated with average fluorescence lifetime through linear regression equation $Y = -0.0319X + 0.9411$, where Y equals crude oil density, X equals average fluorescence lifetime of crude. Figure 2 also indicates that lowly matured crude shows higher contents of asphaltene and polar composition, higher density and shorter average fluorescence lifetime, highly matured light oil shows lower contents of asphaltene and polar composition, higher content of saturated component, lower density and longer average fluorescence lifetime (Ryder et al., 2002; Owens et al., 2008). For example, lowly matured crude with density 0.9521 g/cm^3 shows average fluorescence lifetime 0.8339 ns (Figure 2), intermediate crude with density 0.8522 g/cm^3 shows average fluorescence lifetime ca.1.773 ns, light crude-condensate crude with density 0.789–0.761 g/cm^3 shows average fluorescence lifetime 5.299−5.993 ns. Therefore, the above-listed regression equation can be effectively used to calculate density of surface crude corresponding to oil inclusions with different fluorescence lifetime in the study region.

For three types (A, B, C) of oil inclusions with different fluorescence colors from reservoirs around the Ordovician carbonate suture in Tazhong 1 well (ZT-1), their fluorescence lifetime test results are listed in Table 2, while their representative fluorescence lifetime attenuation curves are shown in Figure 3. Table 2 summarizes main results for fluorescence lifetime testing of three types of oil inclusions. From fluorescence lifetime data for six type A oil inclusions with brown-yellow fluorescence, T_1=1.506 ns (1.447–1.587 ns), T_2=6.423 ns (6.013–6.499 ns), average fluorescence lifetime =2.315 ns (2.210–2.764). From fluorescence lifetime data for seven type B oil inclusions with light yellow fluorescence, T_1=3.148 ns (2.773–3.351 ns), T_2=11.939 ns (10.406–12.971 ns), average fluorescence lifetime=4.5413 ns (4.029–4.991 ns). From fluorescence lifetime data for six type C oil inclusions with light blue-green fluorescence, T_1=6.742 ns (6.056–7.450 ns), T_2=2.026 ns (1.900–2.592 ns), T_3=22.079 ns (21.117–23.223 ns), average fluorescence lifetime=5.199 ns (4.956–6.168 ns). Figure 3 shows fluorescence lifetime attenuation curve morphology and fitting calculation results of fluorescence lifetime for three types of oil inclusions. For example, type A coil inclusions with brown yellow fluorescence show steep fluorescence attenuation curve morphology due to strong absorption of fluorescence molecules by high contents of asphaltene and polar components, requiring generally two parameters T_1 and T_2 for curve fitting and showing short average fluorescence lifetime; type-C oil inclusions with light blue-green fluorescence show flat fluorescence attenuation curve morphology due to weak absorption of fluorescence molecules by low contents of asphaltene and polar components, requiring generally parameters T_1, T_2 and T_3 for curve fitting and showing longer average fluorescence lifetime.

In order to study the relationship between oil inclusion fluorescence lifetime and crude density as well as crude maturation, linear regression equation for average fluorescence lifetime and density of crude as shown in Figure 2 was used to calculate the density of surface crudes corresponding to the three types of oil inclusions. It was found that type A oil inclusions of brown-yellow fluorescence show density of 0.852–0.873 g/cm^3, indicating that these are matured oil

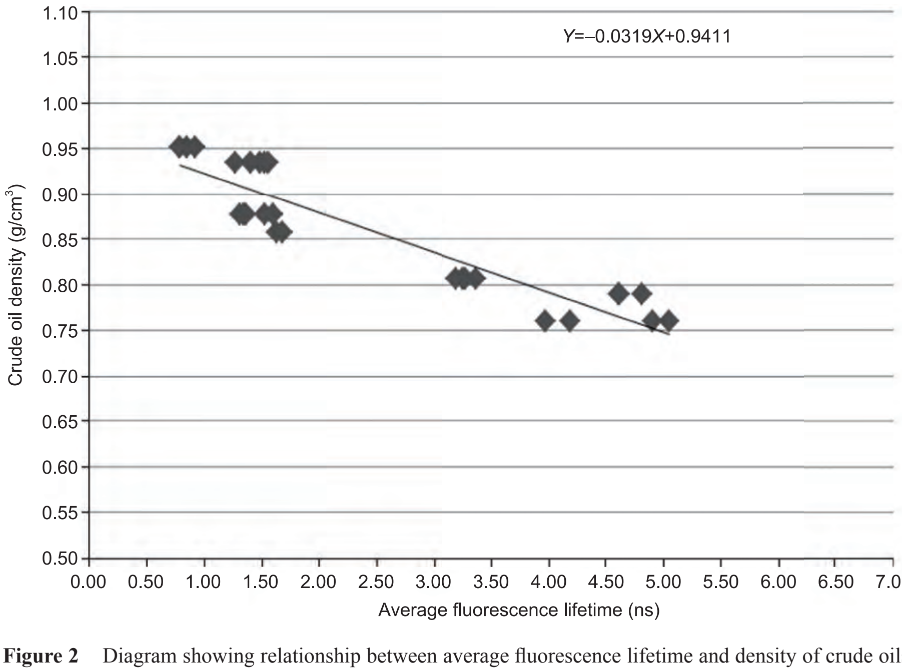

Figure 2 Diagram showing relationship between average fluorescence lifetime and density of crude oils.

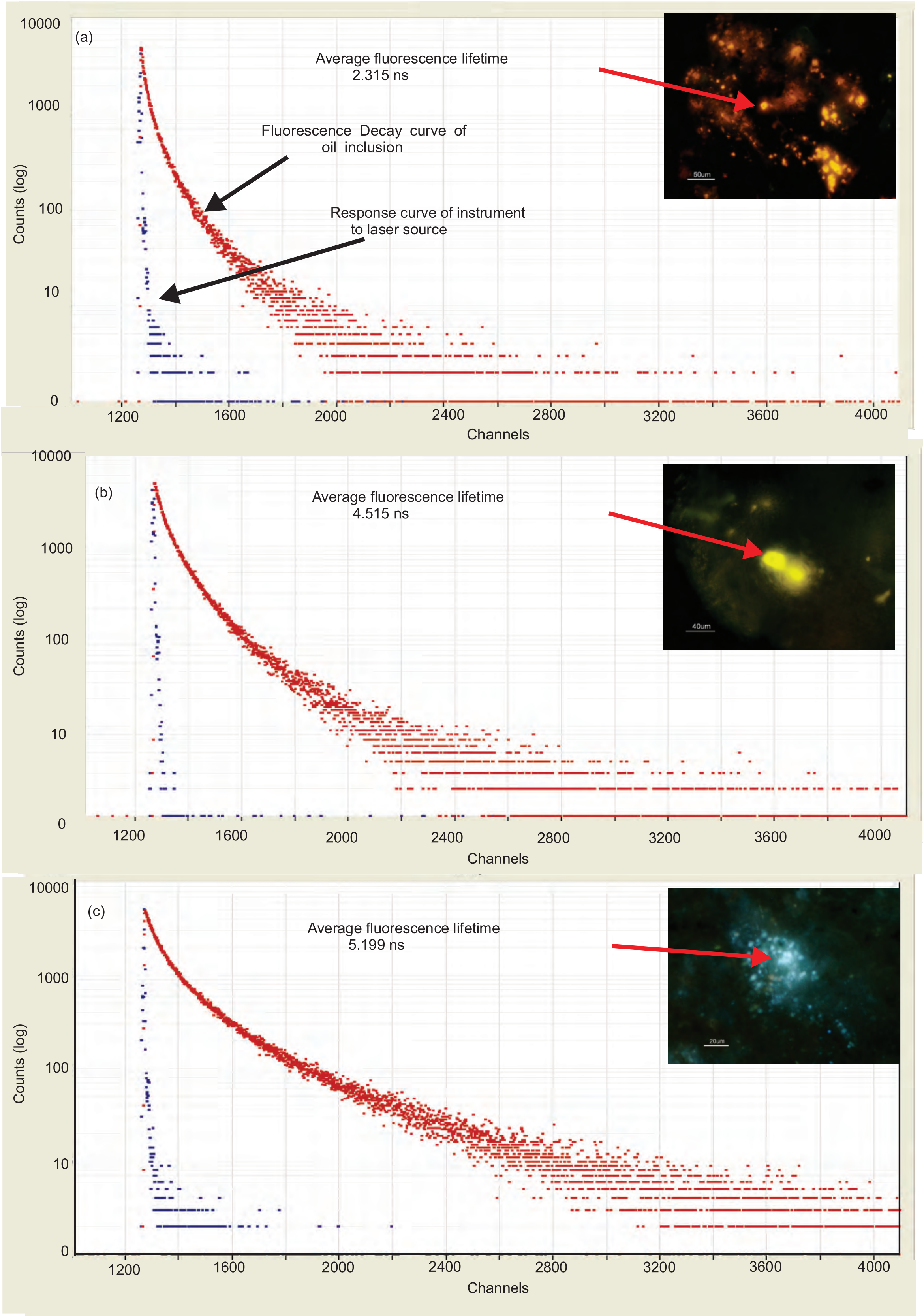

Figure 3 Diagrams showing morphology of fluorescence lifetime attenuation curves for type A, B and C oil inclusions in samples. (a) Type A oil inclusions with brown-yellow fluorescence (average fluorescence lifetime 2.315 ns); (b) type B oil inclusions with light yellow fluorescence (average fluorescence lifetime 4.515 ns); (c) type C oil inclusions with light blue-green fluorescence (average fluorescence lifetime 5.199 ns). Red signals fluorescence attenuation curve for samples; blue signals curve of response of instrument to laser source.

inclusions trapped by authigenic mineral calcite at earlier stage; type B oil inclusions of light yellow fluorescence show density of 0.784–0.812 g/cm^3, indicating that these are matured light oil inclusions trapped by calcite overgrowth at the second stage; type C oil inclusions of light blue-green fluorescence show density of 0.774–0.779 g/cm^3, indicating that these are highly matured light oil or condensate oil inclusions trapped in carbonate-sealed fissures at the third stage.

5. Conclusions

For crude oils from Tazhong uplift, average fluorescence lifetime is linearly correlated with density of crude, heavy oil with big density shows shorter fluorescence lifetime, light crude with small density shows longer fluorescence lifetime, and their relationships can be described with linear regression equation Y=–0.0319X+0.9411, which can thus be used for calculation of density of oil inclusion-trapping crude oil. Among samples of oil inclusions from Tazhong 1 well for fluorescence lifetime study, type A oil inclusions with brown-yellow fluorescence show calculated density of 0.852–0.873 g/cm^3 for corresponding surface crude oil based on average fluorescence lifetime, indicating that these are matured oil inclusions trapped at the stage 1; type B oil inclusions with light yellow fluorescence show calculated density of 0.784–0.812 g/cm^3 for corresponding surface crude oil based on average fluorescence lifetime, indicating that these are higher matured light oil inclusions formed at the stage 2; type C oil inclusions with light blue-green fluorescence show calculated density of 0.743–0.779 g/cm^3 for corresponding surface crude oil based on average fluorescence lifetime, indicating that these are highly matured light oil inclusions trapped at the stage 3.

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