P275-WE

FLUORESCENCE LIFETIME ANALYSIS OF SINGLE HYDROCARBON-BEARING FLUID INCLUSIONS – A PARAGENETIC PERSPECTIVE

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UV fluorescence is commonly used as a first-pass visualisation tool for the study of Hydrocarbon bearing Fluid Inclusions (HCFI). Fluorescence colour is commonly used as a guide to estimate API gravity (Bodnar, 1990) and allow visual discrimination of single or multiple HCFI generations into a paragenetic context. Bulk HCFI crushing with GC analysis has also been compared in an effort to link fluorescent colour and petroleum chemistry (George et al, 2001). However, the human eye is easily deceived by colours and thus observing fluorescent colours is at best a semi-qualitative technique. In contrast, fluorescence lifetimes provide quantitative measurements that are: repeatable, unaffected by host mineral colour, inclusion size, or inclusion dimensions. Fluorescence lifetime measurements correlate with crude oil composition (Ryder, 2004) and lifetime measurements on HCFI have previously been measured by single-photon counting technology (Ryder et al., 2004).

In this work we present new data based on frequency-domain (FD) lifetime measurements and full Fluorescence Lifetime Imaging Microscopy (FLIM) imagery. The FD method uses a modulated (1-300 MHz) 405 nm laser excitation source and calculates the fluorescence lifetime by measuring the phase delay and demodulation ratio of the fluorescence signal relative to the modulated excitation source. The FLIM system we use has an optical resolution of <1 micron, a motorised XYZ stage, and is capable of generating 3D FLIM images of HCFI in the low micron size range. The fluorescence lifetime data is generated via a variety of data fitting models which can be correlated to crude oil composition. Using single modulation frequency measurements we are able to produce FLIM images rapidly that can discriminate different HCFI generations very clearly. Using the more time consuming multi-frequency single-point average lifetime measurements we get very accurate and reproducible lifetime data that can be used to estimate oil composition. The variation in average lifetime of HCFI or crude oils is attributed to the interplay between energy transfer and quenching, which is a function of the oil composition.

To date we have collected data from a diverse selection of HCFI's and measured lifetimes in 0.6 to 25 ns range, with most measurements being between 1.8 and 10 ns with a precision that is better than 5%. Measurements also confirm that lifetimes are homogeneous within individual HCFI and are independent of fluorescence intensity. HCFI's that fluoresce red or orange during UV excitation generally have the shortest lifetime measurements whereas the longest lifetimes are associated with HCFI's that fluoresce blue in colour (by visual observation). For groups of HCFI that have the same apparent fluorescence colour, we are also able to discriminate HCFI groups on the basis of lifetime. The opposite is also true, and for one sample of a single HCFI generation, the large inclusions fluoresced white whereas very thin inclusions had an apparent blue fluoresce, but lifetime measurements gave the same average lifetime indicating that the composition is the same.

Petroleum-related samples are commonly host to multiple HCFI generations. The average lifetimes for an individual generation are the same whereas other generations invariably have different average lifetime measurements. By establishing the paragenetic relationships between each HCFI generation from careful studies under plain and UV fluorescent light we have documented that lifetime measurements generally increase with each successive inclusion generation. An exception to this rule resulted from a secondary petroleum fluid being captured as an additional HCFI generation.

In conclusion, FLIM on HCFI's provide repeatable measurements and are unaffected by signal intensity, inclusion size or shape, or host mineral colour. Fluorescent lifetimes are quantitative, allowing us to both discriminate HCFI populations and improve paragenetic studies. Unlike the human eye which is deceived by fluorescent colour and intensity, FLIM is definitive, providing a valuable tool to enhance the study of HCFI.

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