Report of Fluorescence Lifetime measurements made on hydrocarbon-bearing fluid inclusions within wafers from the Porcupine Basin.

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Introduction:

In this report we present the results of fluorescence lifetime analysis of hydrocarbon bearing fluid inclusions (HCFI) obtained from three wafers i.e. PPIP5, PPIP7, and PPIP33. These samples were the same as used in a previous fluid inclusion study of the Porcupine Basin (PSG project P00/16) and their location is shown in Table 1 and Figure 1. Initial inspection was made using epifluorescence (366 nm excitation) to confirm the presence and location of HCFI, as well as capture images of individual inclusions for later work.

Measuring the fluorescence lifetime of hydrocarbon-bearing fluid inclusions (HCFI) using the frequency domain method is a new development being pioneered at NUIG. To date, fluorescence methods for the study of hydrocarbon-bearing fluid inclusions (HCFI) have been mainly based on visual observations of fluorescent colours in response to UV excitation; these methods are qualitative. Unlike other visual methods, fluorescence lifetime measurements are quantitative, non-destructive, and repeatable, and therefore offer a powerful technique for the study of petroleum charge history and exploration.

Results:

The fluorescent HCFI and were found to cover 3 lifetime ranges: 2.7-4.1 ns; 5.5-6.8 ns, and 8.1-9.4 ns. The data is summarised in Table 1.

In sample PPIP5 and PPIP7 HCFI hosted in feldspar have an apparent yellow-green fluorescence and the measured lifetimes range from 2.7-4.1 ns. Examination of the average lifetimes at discrete wavelengths shows close agreement, with an increase of average lifetimes as wavelength increases (see Figure 2). In PPIP33 some of the inclusions hosted in quartz (inclusions 3 and 4a) also exhibit lifetimes in this range. However measurements at discrete wavelengths do not correlate with inclusions in PPIP5 and PPIP7 suggesting the presence of two distinct oils.

The second group of HCFI have apparent whitish-green fluorescence, are hosted in quartz in samples PPIP5 and PPIP7 and their fluorescence lifetime range is 5.5-6.8 ns. Average lifetimes generally increase with increasing wavelength (see Figure 3).

The final group of HCFI are in PPIP33, hosted in quartz and have significantly longer lifetimes of 8.1 and 9.4 ns. Inclusion 4b has the longest recorded lifetime and analysis of the average lifetimes at discreet wavelengths indicates a decrease in lifetimes at longer emission wavelength (Figure 4). This is indicative of very light petroleum oils with a relatively small distribution of fluorophore types and contrasts with all the other inclusions studied.

Discussion:

As fluorescence lifetime measurements on HCFI are quantitative, repeatable, and independent of host mineral, this technique is considered robust and not prone to the errors associated with visual observations of fluorescence colours.

Fluorescence lifetime measurements show at least three lifetime groups. Average lifetimes for feldspar-hosted HCFI are short (2.7-4.1 ns) whereas quartz-hosted HCFI show two groups, one that is short and correlates with feldspar-hosted HCFI, and another group that has much longer average lifetimes (5.5-9.4 ns). This contrast in average lifetimes may reflect the migration of oils of different maturity in these samples, with the longer average lifetimes reflecting the trapping of more mature oils (i.e. light oils). In addition, the fluorescence response at different wavelengths from inclusion 4b in sample PPIP33 contrasts with other quartz-hosted HCFI, confirming different petroleum chemistry. The contrast of the fluorophore type between this inclusion and other inclusions in sample PPIP33 indicates that these oils were not derived from a single source.

Integration with previous fluid inclusion projects in the Porcupine Basin:

The fluorescence lifetime measurements outlined above have been combined with previous fluid inclusion data from these samples (Porcupine Basin study PSG project P00/16) in order to investigate the geological significance of this data. The fluid inclusion data recorded the presence of at least two-generations of hydrocarbons in the Porcupine Basin; early trapping of less mature relatively heavy oil with a yellow-green fluorescence colour (°API gravity ~25-35) followed by ingress of lighter more mature oil characterised by blue-white fluorescence colours (°API gravity ~ 45-50). These conclusions are confirmed by the fluorescence lifetime data, which indicates the presence of at least two populations of hydrocarbons related to multiple oil charge events of multiple compositions. Samples PPIP5 (Well 26/28-1) and PPIP7 (Well 35/8-2) contain a single population of green fluorescing inclusions, which are characterised by an increase of average lifetimes as wavelength increases (Figs. 2, 3). However when yellow-green and blue fluorescing inclusions in sample PPIP33 (Well 35/2-1) were compared there was significant variations in the average lifetimes and lifetimes at different wavelength dependence (Table 1; Fig. 4), with the response form the blue fluorescing inclusion (inclusion 4b) characteristic of very light petroleum oils.

Summary:

The fluorescence lifetime responses presented here can only be answered by a complex petroleum charge history within the Porcupine Basin and indicate that petroleum in this basin was not derived from a single source. Although the number of samples is very limited our data shows that the fluorescence lifetime methodology can enhance the study of petroleum charge history and with the importance of the Porcupine Basin to Irish energy resources we recommend expansion of the sample database.

Sample	Well Number`	Depth (m/ft)	Target	Mineral	Average Lifetime (ns)
PPIP5	26/28-1	2256.8m	Inclusion 1	feldspar	3.5
PPIP5	26/28-1	2256.8m	Inclusion 2	feldspar	4.1
PPIP5	26/28-1	2256.8m	Inclusion 3a	quartz	6.8
PPIP5	26/28-1	2256.8m	Inclusion 3b	quartz	5.5
PPIP5	26/28-1	2256.8m	Inclusion 3c	quartz	6.2
PPIP7	35/8-2	13147ft	Inclusion 1	quartz	6.4
PPIP7	35/8-2	13147ft	Inclusion 2	quartz	6.4
PPIP7	35/8-2	13147ft	Inclusion 3	feldspar	2.7
PPIP33	35/2-1	3225m	Inclusion 1	quartz	8.1
PPIP33	35/2-1	3225m	Inclusion 3	quartz	3.8
PPIP33	35/2-1	3225m	Inclusion 4a	quartz	3.7
PPIP33	35/2-1	3225m	Inclusion 4b	quartz	9.4

Table 1: Compilation of the average lifetimes (ns) measured on the Porcupine hydrocarbon-bearing fluid inclusions. The emission wavelength band sampled was from ~420 to ~835 nm, a 417 nm long-pass filter was used to attenuate the excitation laser light at 405 nm yet permit the remainder of the visible light to pass.

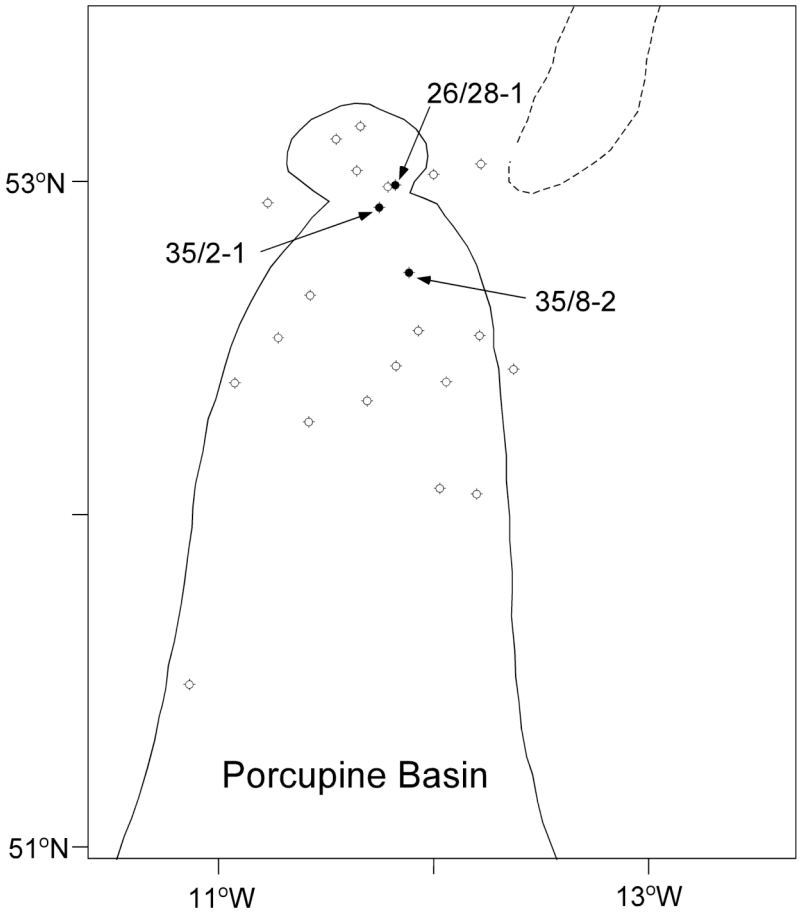

Figure 1: Map of the Porcupine Basin showing the distribution of the three wells (filled circles) studied during this project

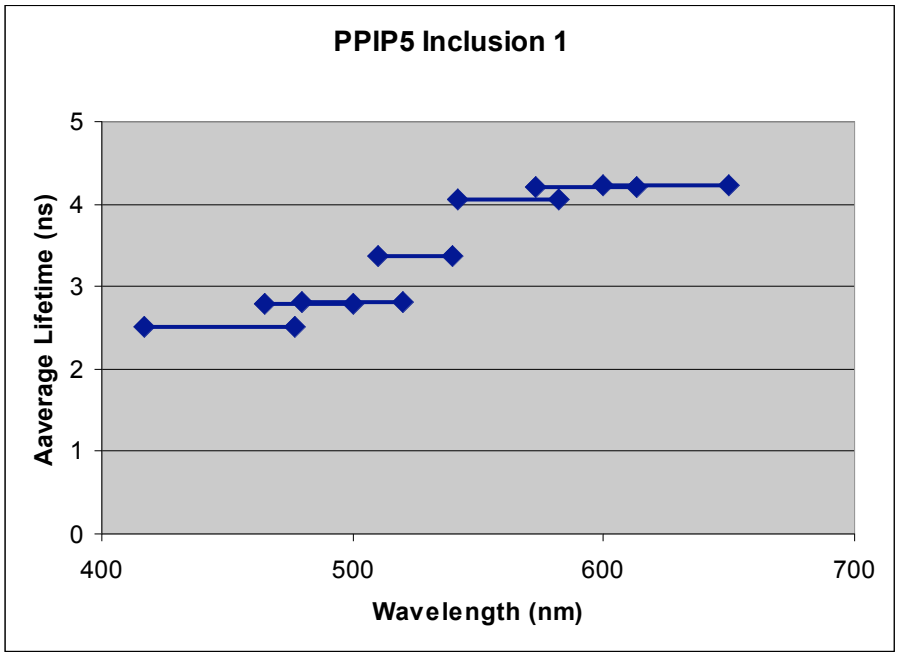

Figure 2: Graph showing average lifetime (ns) versus wavelength (nm) for sample PPIP5, inclusion 1. Although the average lifetimes increase with increasing wavelength, they are longer than in PPIP4.

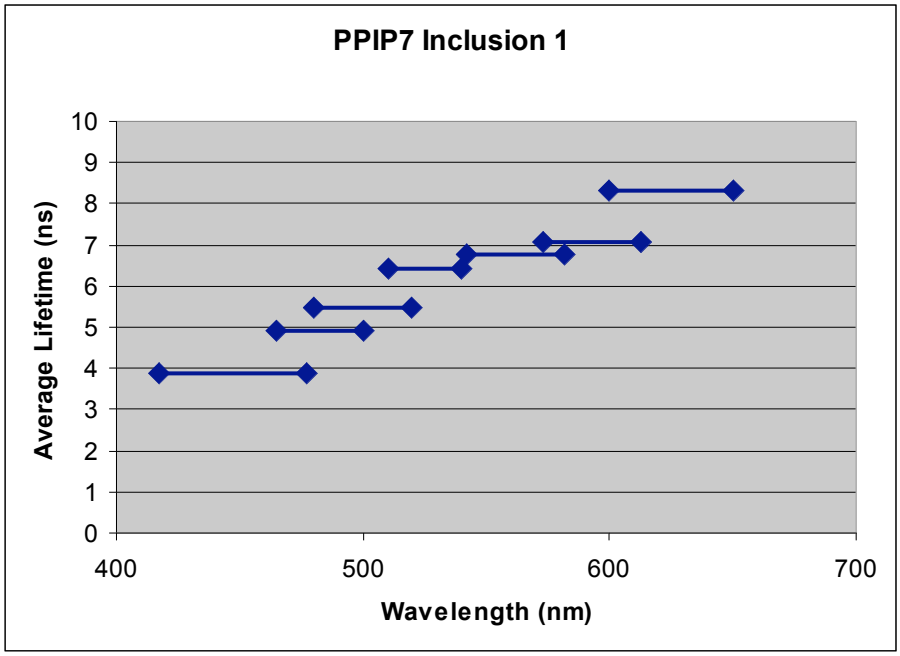

Figure 3: Graph showing average lifetime (ns) versus wavelength (nm) for sample PPIP7, inclusion 1. The average lifetimes increase with increasing wavelength but the lifetimes are longer than in PPIP5.

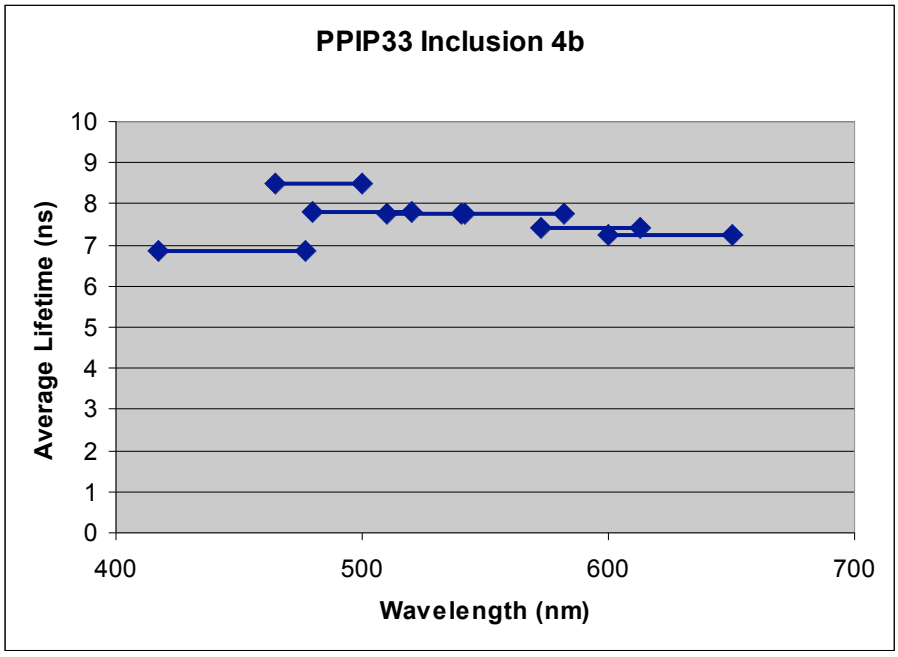

Figure 4: Graph of average lifetime (ns) versus wavelength (nm) for sample PPIP33, inclusion 4b. Unlike previous samples where lifetime increases with emission wavelength, in this inclusion there is an initial increase (to ~500 nm) followed by a slight decrease at longer emission wavelengths.

Figure 5: Upright ISS Alba system for Fluorescence Lifetime Imaging Microscopy.

Appendix 1: Principles of Fluorescence Lifetime Analysis

Fluorescence Lifetime Analysis Methodology:
The fluorescence lifetime of an individual fluorescent molecule (fluorophore) refers to the average time that a molecule spends in the excited state, after absorption of a photon of light and prior to decay to the ground state by emission of a photon of light of lower energy. Aromatic compounds in general are good fluorophores and owing to the abundance of aromatic compounds in petroleum crude oils, HCFI fluoresce when exposed to light in the UV to NIR spectral region.

For crude oils and petroleum products in general, the fluorescence lifetime is a composite value, since the observed emission at any wavelength comprises components from many different individual fluorophores. Consequently, the measured fluorescence lifetime is dependant on a range of factors including total number of fluorophores, types of fluorophores, energy transfer processes, and fluorescence quenching. All of these factors are related to the composition and chemistry of the petroleum sample [1,2,3]. Therefore one can correlate the fluorescence lifetime from a HCFI with the petroleum composition entrapped within the inclusion [4]. For light oils, fluorescence emission tends to be intense, narrow in bandwidth, close to the excitation frequency (small Stokes shift), and have a long lifetime. The opposite holds for heavy oils.

Fluorescence lifetimes can be measured in a variety of ways, one of the most common and simple (in principle) being the phase-modulation (PM) method. PM based systems measure fluorescence lifetimes by exciting the sample with a modulated laser, which in turn generates a modulated fluorescence signal. The phase difference and the demodulation ratio between the excitation and emission signals are directly related to the fluorescence lifetime. To accurately measure fluorescence lifetimes we measure the phase and modulation data for a range of excitation frequencies and then fit the data to an appropriate model to calculate an average lifetime [5].

Instrumentation:
The phase and modulation data were obtained using an Alba Fluorescence Lifetime Imaging (FLIM) system (ISS Inc, Champaign, Ill., USA) based on an upright Olympus BX51 microscope fitted with a modulated (1 to 200 MHz) 405 nm laser diode excitation source. The fluorescence emission was wavelength separated into two wavelength ranges using pairs of bandpass filters in each of four different filter cubes. The experimental setup enabled the simultaneous recording of phase and modulation data at two narrow wavelength ranges defined by the particular emission filter cube. In this work, lifetimes were either measured at discrete emission wavelengths from ~420 nm to 650 nm, or over the full visible spectrum from ~420 nm to ~835 nm. The instrument was calibrated by the determination of the phase and modulation responses over a range of frequencies for a number of different standards of known fluorescence lifetime. Lifetimes of the inclusions were calculated from phase and modulation responses relative to the phase and modulation responses from the chosen standard fluorophore. Figure 1 shows the Alba system with upright microscope. The system is capable of measuring lifetimes in the 0.7 to 100 ns range with an accuracy of better than 5%. The microscope using 405 nm excitation generates a minimum spot size of ~2 micron using a x50 objective, thereby allowing measurements to be performed on individual HCFI.

References:

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