

## **REVIEW OF FLUID INCLUSION STUDIES: IMPLICATIONS FOR HYDROCARBON MIGRATION, CHARACTERIZATION AND UNDERSTANDING PROCESSES IN THE GEOLOGIC SYSTEM**

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### **ABSTRACT**

Geological fluid inclusions are small voids that can contain a variety of fluids which are often found in natural minerals and rocks. Typically they are less than 50micrometres in size that host fossil fluids which existed when the minerals grew or healed after fracture. Of particular interest to the petroleum industry are inclusions that contain hydrocarbon fluids, which originated from petroleum that once migrated through the rocks before becoming trapped. These hydrocarbon bearing fluid inclusions (HCFI) are useful for learning about the processes, fluid compositions, temperatures and pressure conditions in geologic systems such as the migration of hydrocarbon fluids in petroleum basins. The accurate characterization of the petroleum fluid entrapped in inclusions presents the analyst with considerable challenges. HCFI samples are very valuable (usually obtained from core drilling) and thus a non-contact, non-destructive analytical method is required. The small size of HCFI necessitates the use of microscopy based techniques, while spectroscopic methods are needed to characterize the chemical composition. Fluorescence based methods offer the best combination of high sensitivity, diagnostic potential and relatively uncomplicated instrumentation. Significant variables which affect exploration success, such as (1) evidence for migration, (2) product type, quality and volumetrics, (3) timing of migration with respect to porosity evolution, and (4) effectiveness of petroleum seals over geologic time can be addressed, to some extent, by fluid inclusion studies.

## **INTRODUCTION**

When a crystal grows in the presence of a fluid phase, some of the fluid may be trapped as imperfections in the growing crystal to form fluid inclusions. The trapped fluid may be liquid, vapor, or supercritical fluid, and the composition of the trapped fluid may include essentially pure water, brines of various salinity, gas or gas-bearing liquids, and silicate, sulfide or carbonate melts, among others.

Fluid inclusion represents any inclusion that trapped a phase that was a fluid at the temperature and pressure of formation, regardless of the phase state of the inclusion as observed at laboratory conditions (Bodnar, 2003).

Generally, these inclusions are localized by imperfections in the growing or healing crystals, including actual crystallographic defects, growth-poisoned grain surfaces and mismatches across fracture apertures. Additionally, old fluid inclusion cavities can be ruptured and refilled with new fluids, and the drilling process itself can create "drilling-induced" fluid inclusions. Generally, fluid inclusions in sedimentary rocks are in the 2-50 micron range and are classically studied with polished thin section preparations (Burrus, 1999).

Fluid inclusions, despite their small size, are highly valuable to understanding many geological processes. When these cavities within the rock were sealed, they trapped the original fluid at these fossil pressure-volume-temperature (PVT) conditions. This PVT data can be used for modelling fluid phase behaviour and give an indication of the "oil window" at which oil formation occurs (Blamey and Ryder, 2007). Geologists can learn much about the fluid compositions, temperatures, and pressure conditions in geologic systems from fluid inclusions that form at a key time, such as during ore formation in base-metal or gold deposits, or from the migration of hydrocarbon fluids in petroleum basins.

## **WHY FLUID INCLUSION?**

Standard geochemical techniques that analyze residual pore fluids are often inadequate for determining where petroleum fluids have been, and are typically hampered by contamination, fractionation and alteration issues. Fortunately, subsurface fluid processes, such as migration of petroleum and charging of reservoirs, leave resolvable chemical traces in the form of crystallographically trapped fluids in diagenetic cements and healed microfractures. These fluid inclusions are generally faithful recorders of pore fluid chemistry and are not subject to evaporation during sample storage or loss of light ends during sampling from depth. They persist in the geologic record long after the parent fluids have moved on, but are continuously formed even up to the very recent past.

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).

Accurate analysis of the chemical composition of the entrapped hydrocarbons in Hydrocarbon Fluid Inclusion (HCFI) can yield vital information about the history, evolution, and migration of petroleum fluids, and is thus crucial data for the petroleum exploration industry. Studying HCFI is advantageous because the trapped fluids are representative of the actual hydrocarbon fluids that existed when the inclusions were sealed in the mineral. This sealing in process preserves the petroleum fluid, thus isolating it from subsequent infiltration of petroleum fluids and events in oil reservoirs such as loss of charge, water washing or biodegradation. It also preserves the fluid from contamination during the drilling processes used to extract samples from the ground (Blamey and Ryder, 2007).

Critical to the determination of the timing of oil migration is the relationship between the fluid inclusions and diagenetic processes occurring in the sediments, as the entrapped oil/gas in fluid inclusions is found within diagenetic cements formed during sediment burial. Thus, an important part of the analysis of fluid inclusions relates to the diagenetic history of the host sediment itself.

## **TEMPORAL CLASSIFICATION OF FLUID INCLUSION**

There are many ways to classify fluid inclusions (Roedder, 1984; Goldstein, 2003), but one of the most useful classification schemes relates the timing of formation of the inclusion relative to that of the host mineral namely:

- Primary Fluid Inclusion
- Secondary Fluid Inclusion and
- Pseudo-secondary/Tertiary Fluid Inclusion.

Accordingly, **primary fluid inclusions** (*fig 1*) are formed during, and as a direct result of growth of the surrounding host crystal.

Primary inclusions form when fluid is trapped on the active growing surface of a crystal. In mineralogy class, the face of a growing crystal is often portrayed as a perfect surface, with atoms being added to the surface in a very regular fashion. While this is true in the broadest sense, at the atomic scale the growing surface shows considerable topography (Zhang & Nancollas, 1990). Recent advances in analytical techniques, such as Transmission Electron Microscopy (TEM) and Atomic-Force Microscopy (AFM), now permit these surfaces to be viewed at the atomic scale, revealing the many irregularities that occur (Hochella *et al.* 1990). Growth spirals may develop if the growing crystal contains screw dislocations. In addition, etch pits and etch hillocks may develop on the crystal surface in response to changing degrees of saturation of the fluid - these features provide ideal sites for entrapment of fluid. Texturally, primary inclusions tend to

be solitary or isolated, and are best identified by being trapped parallel to a growth zone or crystal face.

If a crystal fractures after it has been formed, some fluid may enter the fracture and become trapped as **secondary fluid inclusions** (fig 1) as the fracture heals. Thus, secondary inclusions are trapped after crystal growth is complete.

Texturally, secondary inclusions can be recognized by their occurrence in trails or clusters that often cut across grain boundaries. If fracturing occurs during growth of the crystal, **pseudo-secondary fluid inclusions** may be trapped during continued crystal growth.

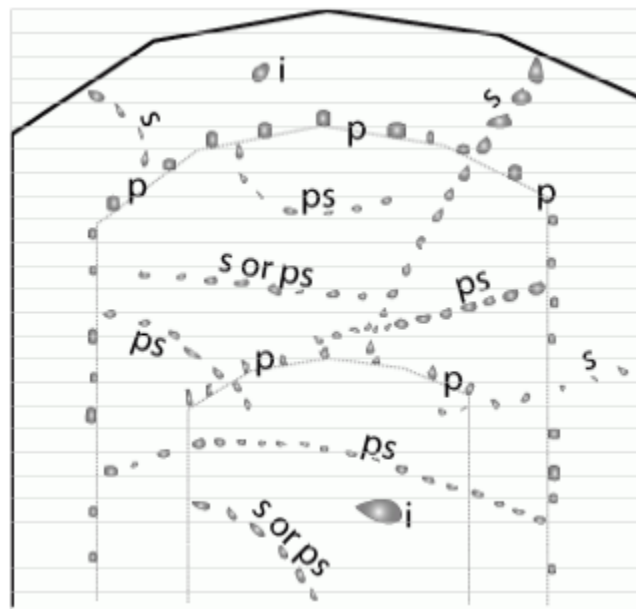


Fig. 1: Fluid inclusion morphology: i= indeterminate; origin unknown; p: primary; ps: pseudo-secondary; s: secondary

## ANALYTICAL METHODS

### Fluid Inclusion Petrography and Ultra Violet Microfluorimetry

This involves preparation of transparent, polished slabs of rock materials which are studied optically with a petrographic microscope. Samples are then examined under epi-ultra violet illumination to check for fluorescence.

The principle of UV fluorimetry consists of the excitation of organic matter by an incident UV beam, through the optical system of a photonic microscope. Fluorescence spectra of the petroleum inclusions can be acquired in epi-illumination by a Leitz™ MPVII spectrometer mounted on a Leitz microscope. The spectral response is automatically calibrated using a halogen lamp. To facilitate comparison between different inclusion generations, each spectrum is transformed using Leitz™ software into coordinates that can be plotted in the CIE-1931

chromaticity diagram. This transformation (e.g. Wyszecki and Stiles, 2000) involved multiplying the spectrum independently by three colour-matching functions which describe the non-linear perception of the human eye to red, green and blue hues.

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).

### **Infra Red Absorption Microspectrometry (IR)**

IR absorption microspectrometry allows the detection of aromatic, olefinic (C = C vibrations) and aliphatic (CH<sub>2</sub> and CH<sub>3</sub> vibrations) molecules as well as CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O in the liquid and vapour phases of fluid inclusions (Barres *et al.*, 1987).

Analysis can be carried out on an interferometer DIGILAB FTS 40 with a microscope type UMA 300 equipped with a MCT detector using an objective cassegrain X36. A circular diaphragm restricts the field to the size of the inclusion.

The spectra is registered in transmission mode with 8cm<sup>-1</sup> resolution and 1024 accumulated scans, which are convenient conditions to obtain good signal/noise ratios. The system is purged with dry nitrogen and the air between the objective and the sample purged by a special adaptation to the objective.

### **Fluid Inclusion Microthermometry (FIM)**

The principle governing FIM is that fluids trapped at a certain pressure (P) and temperature (T) will undergo phase changes when their uplift path intersects a phase boundary. To study phase transitions in fluid inclusions, a doubly polished thin section is prepared, then broken into small chips that are mounted on a special heating and freezing stage. These chips are then observed while the stage is either heated or cooled, and the phase changes which take place during a heating or cooling cycle are carefully recorded along with the temperatures at which such changes occur.

Fluid Inclusion Microthermometry can be carried out using Linkam<sup>TM</sup> MDS-600 and THMS-600 heating-freezing stages mounted on Olympus TM BXX-60 microscopes equipped with 40X and 100X long-working-distance objectives. Phase equilibria within the trapped fluids reflect their composition and bulk density, which in turn are related to trapping temperature, pressure and fluid composition.

## **SOME IMPLICATIONS OF FLUID INCLUSION STUDY**

### **Timing of Fluid emplacement and migration history**

The very presence of fluid inclusion (oil) clearly indicates that entrapment and migration has taken place. Oil inclusions contained in authigenic grains suggest insitu entrapment within the current basin of deposition whereas inclusion contained in detrital grains may be pointing to an inherited inclusion from a neighbouring basin.

Also the range of API oil gravity of inclusion provides information on the history of the oil. Low gravity oil most likely points to early expulsion or biodegradation which occur when oil migrates at a relatively low migration-path temperature and shallow overburden (Burrus, 1999).

Crack-seal texture are important for constraining the timing of migration of fluids because the repetitive, sequential cracking and sealing of fracture filling cements, traps fluid that are present during deformation. If the time of deformation is well constrained by structural, stratigraphic and chronological studies, then the time of migration is well constrained.

### **Qualitative API Gravity Estimation and hydrocarbon Maturation**

The fluorescence colour of petroleum fluid inclusion provides a general indication of the API gravity of fluid trapped in the inclusion (Burrus, 1991; Goldstein and Reynolds, 1994).

Very bright blue fluorescence is characteristics of high API gravity gas-rich oil with no biodegradation (fig 2).

A dull blue-white fluorescence is suggestive for a limited amount of biodegradation prior to entrapment. Yellowish fluorescence is usually shown by low API gravity oil that has undergone significant biodegradation.

Very aromatic hydrocarbon inclusions tend to have reddish fluorescence.

Aqueous inclusions (including brine) and bubbles of methane are non-fluorescent.

Studies have shown that during hydrocarbon maturation, the light aliphatic fraction will separate from the heavy aromatic fraction and often migrate subsequently. The former will evolve by cracking of the lighter aliphatic components into methane and the fluorescence emission will be then shifted towards the blue region. The latter will become more aromatic and emission will be shifted towards the red region (McLiman, 1987; Pradier, 1988).

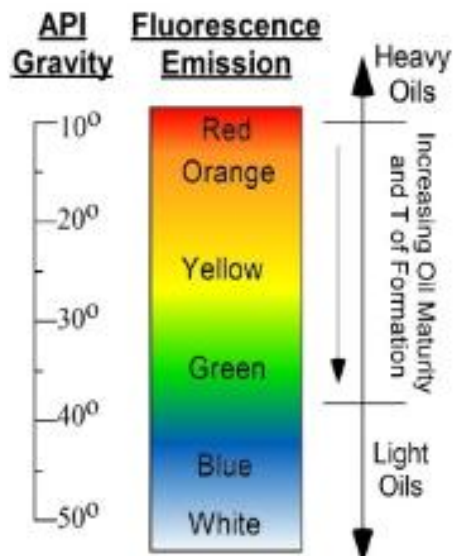


Fig 2: Relationship between API gravity, fluorescence emission and oil maturity.  
(Adapted from Feely et al., 2016)

### Identification of Hydrocarbon Type from Spectral Signature

Aliphatic hydrocarbon have been characterized by their symmetric and antisymmetric stretching vibration bands of  $\text{CH}_2$  molecules respectively at  $2856 \text{ cm}^{-1}$  and  $2930 \text{ cm}^{-1}$  and  $\text{CH}_3$  molecules respectively at  $2875$  and  $2960 \text{ cm}^{-1}$  (Guilhaumou et al, 1990).

Aromatic components can be identified by the bands of  $\text{CH}$  in the  $3000$  to  $3200 \text{ cm}^{-1}$  region (Fig 3). Carbon dioxide ( $\text{CO}_2$ ) has been characterized by the antisymmetric vibrations around  $2336$  and  $2345 \text{ cm}^{-1}$  depending on the pressure and state of the fluids. When absorbance is strong, the combination of bands at  $3606$  and  $3711 \text{ cm}^{-1}$  is used. The methane ( $\text{CH}_4$ ) component has been characterized by vibration bands at  $1304$ ,  $3013$  and  $3084 \text{ cm}^{-1}$  (Guilhaumou et al, 1990).

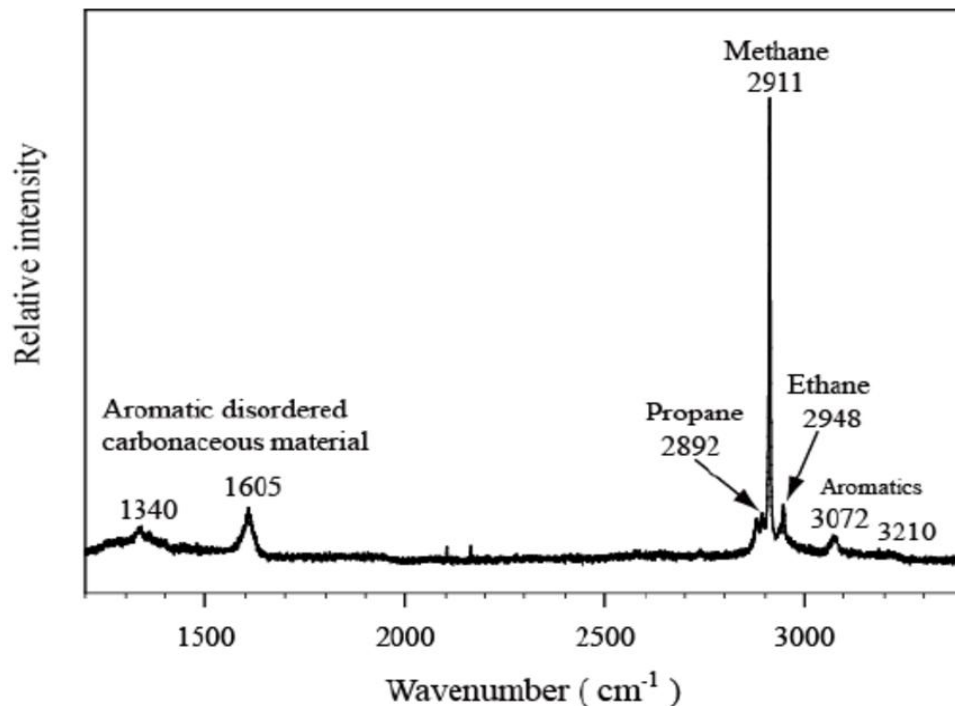


Fig 3. Spectral bands of some hydrocarbon components (From: Billstrom et al., 2012).

### Temperature and Depth of Entrapment

Microthermometric techniques rely on heating two - phase inclusions on the stage until they homogenize (i.e. change to one phase). The temperature at which homogenization takes place can therefore be considered a "minimum T" for fluid entrapment. If the pressure of entrapment (or mineral formation) is known by some independent means (e.g. phase relations or geobarometry), then the temperature of entrapment can be immediately determined by the intersection of the isochore passing through the homogenization T with this pressure. Also if the geothermal gradient of the area is known, the depth of entrapment can be calculated.

### FLUID INCLUSION ASSEMBLAGES

Determining the temporal classification of inclusions may be difficult, resulting in a fluid history that is equivocal. To minimize the emphasis on the primary, secondary and pseudo-secondary classification of inclusions, Goldstein & Reynolds (1994) introduced the concept of the Fluid Inclusion Assemblage (FIA) to describe *a group of fluid inclusions that were all trapped at the same time*. An FIA thus defines the most finely discriminated fluid inclusion trapping event that can be identified based on petrography (Goldstein, 2003). This requirement further implies that the inclusions in the FIA were all trapped at approximately the same temperature and pressure, and all trapped a fluid of approximately the same composition. Therefore, the FIA represents a "fluid event" in the history of the system, and the fluid in the inclusions making up the FIA represents the fluid that was present during that event.



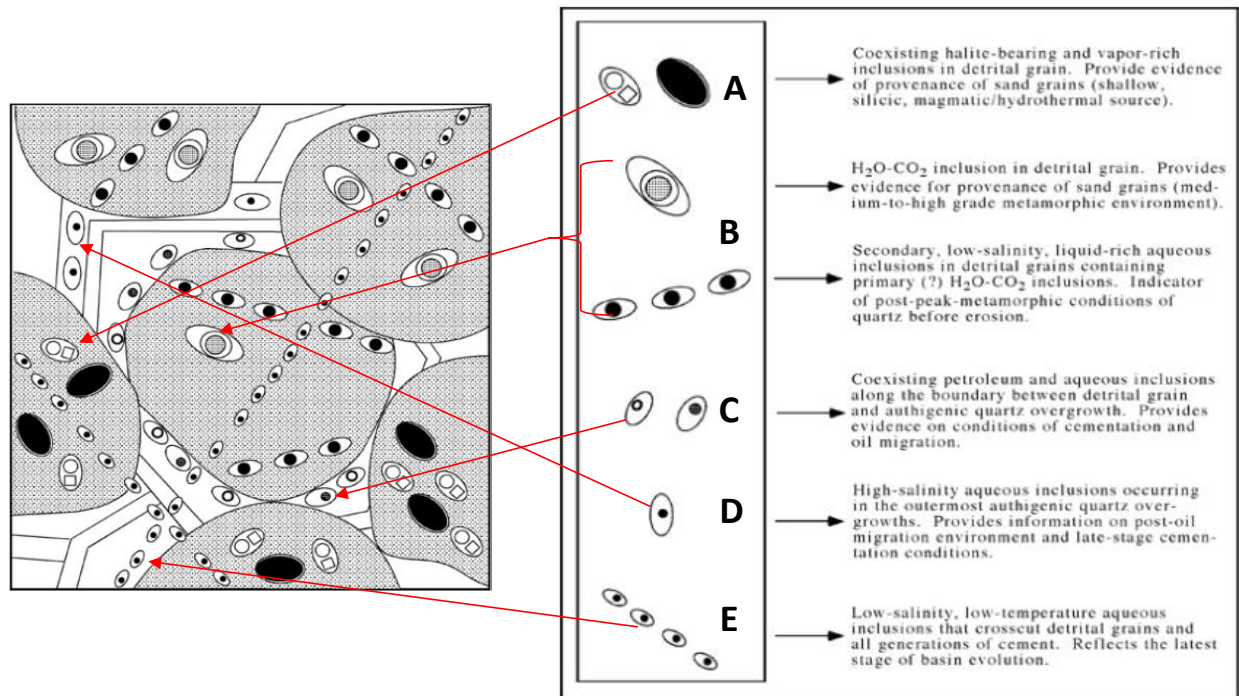


Fig. 4: Schematic representation of the various FIAs that might be observed in a well-cemented sandstone from a hydrocarbon basin.

(from Bodnar, 1994)

Most samples contain numerous fluid inclusion assemblages, only some of which may be relevant to the problem being considered.

Figure 4 is a schematic representation of a well-cemented sandstone from a hydrocarbon reservoir, showing several different FIAs and the type of information each FIA might provide. The geological problem that is being investigated will dictate which of the many FIAs should be studied. For example, if the major focus of the study is to understand the tectonic history of the area, then an important question concerns the source(s) of sediments in the basin and the directions of sediment transport.

To address this question, one would be interested in the geology of the source region(s). The illustration (fig 4) as described by Bodnar (1994) showed inherited inclusions in the detrital quartz grains which suggest at least two sources for the quartz – a medium-to-high grade metamorphic environment (as evidenced by H<sub>2</sub>O-CO<sub>2</sub> inclusions containing both liquid and vapor CO<sub>2</sub>) and a shallow granitic intrusive source (as evidenced by coexisting halite-bearing and vapor-rich fluid inclusions). By determining the relative amounts of the two different types of detrital grains and their variation within a given stratigraphic horizon, it may be possible to determine relative distances to the two different source regions. Variations in the two different detrital FIAs vertically within the sandstone unit may reflect changing tectonic conditions (rates of exhumation) in the two different source regions with time.

He further observed that a petroleum geologist studying the same sample might not be interested in the source of the sediments, but rather with the timing of hydrocarbon migration relative to cementation and porosity loss or gain. In this case, one would not study FIAs containing inherited inclusions in the detrital grains, but instead would focus on FIAs containing petroleum inclusions and occurring in authigenic quartz near the detrital grain/overgrowth interface. Similarly, analysis of the very latest FIA that contains (secondary) aqueous inclusions and crosscuts all generations of cement as well as the detrital grains might help to determine the thermal history following oil migration. Such information is crucial to (1) understanding the post-migration history of the basin, and (2) whether the original liquid hydrocarbons that filled pore spaces in the rock were subsequently buried beyond the oil window, resulting in degradation of the liquid petroleum into methane and other light gaseous hydrocarbons.

## **CONCLUSION**

Petroleum geoscientists must continue to develop technologies which lower risks associated with exploring for petroleum, help prevent the unknown drilling of near misses and aid in the efficient production of established reserves. Significant variables which affect exploration success, such as (1) evidence for migration, (2) product type, quality and volumetrics, (3) timing of migration with respect to porosity evolution, and (4) effectiveness of petroleum seals over geologic time can be addressed, to some extent, by fluid inclusion studies. However, fluid inclusion techniques remain underutilized in the petroleum industry due, in part, to questions about their significance and a limited understanding of fluid phase relationships within petroleum fluid inclusions.

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