Feasibility of a 785 nm diode laser in Raman spectroscopy for characterizing hydrocarbon-bearing fluid inclusions in Mumbai Offshore Basin, India

J. L. Jayanthi[1], V. Nandakumar[1]* & S. S. Anoop[2]

[1] National Facility for Geofluids Research and Raman Analysis, ESSO-National Centre for Earth Science Studies, Government of India, Thiruvananthapuram 695 011, Kerala, India
[2] Department of Mining & Geology, Government of Kerala, Thiruvananthapuram 695 004, Kerala, India
* Correspondence: v.nandakumar66@gmail.com

Abstract: Detection of the chemical constituents of hydrocarbons in the hydrocarbon-bearing fluid inclusions in diagenetic mineral cements, secondary fractures and overgrowths could be a useful indicator of the nature of oil in a basin. Microscope-based Raman spectroscopy is a non-destructive, optical vibrational spectroscopic technique that can precisely isolate and analyse hydrocarbon fluid inclusions (HCFIs). The main challenge with Raman spectral studies on natural HCFIs is the common presence of fluorescence emission from minerals and aromatic compounds in HCFIs leading to the masking of Raman signals. The present study is a demonstration of how best the Raman signals from natural hydrocarbon-bearing fluid inclusions could be detected using an excitation wavelength of 785 nm with suitable optical parameters and with special wafer preparation techniques to negate the background fluorescence. Using the laser Raman technique we were able to detect peaks corresponding to cyclohexane (786 and 3245 cm^{-1}), benzene and bromobenzene (606, 1010, 1310, 1486 and 1580 cm^{-1}), carbon monoxide (2143 cm^{-1}), nitrogen (2331 cm^{-1}), ethylene (1296 cm^{-1}), sulphur oxide (524 cm^{-1}), carbonyl sulphide (2055 cm^{-1}), hydrogen sulphide in liquid form (2580 cm^{-1}) along with the presence of a broad peak of liquid water at 3100–3500 cm^{-1}, peaks of calcium carbonate (710, 854 cm^{-1}) and calcium sulphate (1135 cm^{-1}). The study samples were specially prepared with fluorescence-quenching dyes added with a resin-hardener mixture to eliminate background fluorescence. Nine fluid-inclusion assemblages in minerals like quartz, feldspar and calcite from the RV-1 well of the Ratnagiri Block, Mumbai Offshore Basin, India were investigated.

Fluid inclusion studies can provide geological information of fundamental importance to the petroleum exploration and production industry. Organic matter present in sediments is transformed into organic liquids and gases when such sediments undergo diagenesis. The composition of petroleum fluids is complex and its species-wise characterization is fundamental in the geological interpretation of the source and maturity of oils (Goldstein 2001; Munz 2001). The organic fluids present in rock include hydrocarbons ranging from methane to high molecular weight hydrocarbons and these fluids can undergo complex chemical changes depending on the conditions present during their migration and pooling. Hydrocarbon fluid inclusions (HCFIs) can provide information on the composition, as well as the conditions under which the fluids were emplaced (Roedder 1984). Hydrocarbon inclusions are therefore of interest because their compositions are sensitive to the complex interplay between source, transport and deposition, while the variation in composition between present-day crude oils and inclusions can provide information on the genesis of the fluids (Orange *et al.* 1996). The rapid expansion of research on the petroleum inclusions is due to the simple fact that petroleum inclusions are 'hidden petroleum shows' (Lisk *et al.* 2002). Analysis of petroleum inclusions and the application to exploration and reservoir appraisal have experienced rapid development during the last decade. Primary and secondary petroleum inclusions in fractures within cements may give evidence for the presence of petroleum during migration and subsequent cement formation (Karlsen *et al.* 1993, 2004; Munz *et al.* 1998; Munz 2001; Karlsen & Skeie 2006). Petroleum migration can be inferred from compositional differences between inclusions in successive growth

zones of fracture cement samples (Bodnar 1990) or from the presence of different populations of inclusions in different generations of cements (Burruss 2003b).

HCFI analysis can be performed either by crushing bulk rock samples and extracting the trapped fluid for analysis or by the analysis of single fluid inclusions (Kihle 1995; George *et al.* 2001; Anderson *et al.* 1998; Parnell *et al.* 2001). The oil composition data obtained from bulk fluid inclusion analysis (by crushing) suffers from a variety of problems, including sample destruction, mixing of fluids from multiple fluid inclusion populations and contamination from materials within the rock sample itself. The mixing of fluids is especially disadvantageous because the most volumetrically abundant type of inclusion will bias the results, and the constituents of aqueous fluid inclusions could contaminate the extracted fluids. Analysis of fluids entrapped in a single HCFI is potentially much better since the system is a hermetically sealed one, but there are few quantitative techniques. The known techniques require the extraction of the liquid from individual inclusions by drilling (mechanically, laser assisted or ion etched) and subsequent analysis by gas chromatography (GC) and/or mass spectroscopy (MS) (George *et al.* 2001; Parnell *et al.* 2001; Blamey & Ryder 2007). Unfortunately, this results in sample destruction and it is time-consuming, presumably needing big fluid inclusions too. The non-destructive quantitative analysis of HCFIs is therefore a desirable goal for understanding the fluids involved in petroleum migration and is best achieved via optical methods (Guilhaumou *et al.* 1990; Piranon & Pradier 1992). Fluorescence-based methods are widely used for studying HCFIs and the most common identification method is by observing their fluorescence under UV excitation. The use of

visually determined fluorescence colour is widely used as a qualitative guide for assessing the density and, potentially, also the maturity of oil trapped in fluid inclusions. However, the use of fluorescence colour is intrinsically prone to error and does not yield quantitative results, and the method is subjective.

The limitations with the fluorescence technique in studying petroleum inclusions are well explained by Burruss (2003*a*); Blanchet *et al.* (2003) also gave a detailed analysis of fluid inclusions from the North Sea using microspectrofluorometric techniques and they observed that the fluorescence colour of inclusion oils is variable even within a single fluid inclusion assemblage. This necessitates the need for non-destructive optical techniques for accurately characterizing the HCFIs. Compositional studies of individual inclusions have also been conducted using vibrational spectroscopic techniques. Infrared spectroscopic techniques have been used for analysing hydrocarbon inclusions (Barres *et al.* 1987; O'Grady *et al.* 1989; Guilhaumou *et al.* 1990; Piranon & Barres 1990), yet such measurements are limited by diffraction effects to inclusions larger than 15 µm in diameter, and a number of hydrocarbon vibrations are weak or inactive in the infrared (Dollish *et al.* 1974; Wopenka *et al.* 1990).

Raman spectroscopy, being one method of getting detailed compositional data, has been widely applied successfully to aqueous and dry gas inclusions. This is because the fluids are not intrinsically fluorescent, unlike most oils, condensates and some wet gases. Burruss (2003*a*, *b*) detailed the importance of petroleum inclusion studies in petroleum exploration and development, and suggested that there are opportunities to apply Raman spectroscopy to petroleum inclusions if suitable methods to eliminate fluorescence interference can be employed (Kihle *et al.* 2012). Major attention has to be given to eliminate the fluorescence influence while studying Raman peaks in petroleum inclusions. Selection of optimum excitation wavelength is another challenge, while many previous studies noticed the problem of fluorescence from the fluids contained in the inclusions (hydrocarbons) or by the surrounding host mineral with shorter excitation wavelengths around 260 nm used for Raman analysis of HCFIs. Increasing the wavelength of the excitation source – red or near-infrared lasers – is the way to overcome fluorescence, since longer wavelengths excite less fluorescence from fluorophores that have visible wavelength excitation bands (Ahmadjian & Brown 1976; Orange *et al.* 1996; McCreery 2000; Burke 2001; Bourdet *et al.* 2011; Frezzotti *et al.* 2012).

Oil constituents may differ depending on the source rocks, maturity, organic matter trapped and the pressure–temperature conditions of entrapping. In petroleum geology, fluid inclusions have proven to be useful indicators of migration pathways of hydrocarbons, they can delineate the evolution of the chemistry of hydrocarbons, and they remain important for understanding the thermal history of basins and related fluid migration events in the evolution of reservoir systems. HCFIs generally contain complex mixtures of organic compounds that depend on their sources. Accurate analysis of the chemical composition of the entrapped hydrocarbons in HCFIs yields vital information about the history, evolution and migration of petroleum fluids, and is thus crucial data for the petroleum exploration industry (Goldstein 2001; Munz 2001; Frezzotti *et al.* 2012).

The present work is an attempt to characterize petroleum fluid inclusions from Mumbai offshore, India, using a laser exciting at a wavelength of 785 nm, pioneering work in this field in India. The present study highlights the utility of Raman spectroscopy as a powerful tool for characterizing hydrocarbons and for identifying the major functional groups in HCFI samples. The choice of excitation wavelength, laser power and the fluorescence-quenching techniques employed during wafer preparation yielded the best conducive conditions for obtaining adequate Raman signals from the HCFIs studied.

Materials and methods

Sample details

Sidewall cuttings and core samples from the RV-1 well in the Ratnagiri Block of Mumbai Offshore Basin, India were collected from the core library of Regional Geological Laboratory (RGL), Oil and Natural Gas Corporation (ONGC), Government of India, Panvel, Mumbai. The samples were washed, dried and sieved, and were securely stored for specialized wafer preparation in the Lapidary Facility at the National Centre for Earth Science Studies (NCESS). Sieved samples were impregnated with a suitable epoxy resin mixture, doped with a fluorescent-quenching dye and then made into doubly polished wafers for fluid inclusion studies. Such specially prepared wafers were used for petrographical, microthermometric and Raman studies. In RV-1, HCFIs were observed in quartz, calcite, feldspar grains and cements in the sedimentary rock cuttings, especially from the sandstone–siltstone lithologies towards the lower portion of the well depth ranging from 3270 to 3690 m. Using the lithostratigraphic nomenclature of the Mumbai Offshore Basin, the hydrocarbon inclusions are mainly observed in the Panna Formation (Paleocene–early Eocene age), which is both a producing as well as a reservoir horizon. Minor quantities of HCFIs are also found at the 1345–1360 m depth, which falls within the Mukta Formation (Early Oligocene) comprising limestone–shale lithologies. Petrographical studies confirmed the presence of CO_2-rich inclusions and aqueous inclusions, as well as hydrocarbon inclusions. Hydrocarbon inclusions showing fluorescence observed under 365 nm (mercury arc lamp) UV excitation during petrographical studies were selected for Raman studies (Figs 1 and 2). Raman spectral analyses were carried out in nine HCFI assemblages from the RV-1 well (and a minimum of 15 individual inclusions from each assemblage) in order to detail any hydrocarbon species present. Lithostratigraphic details of the study samples are given in Table 1.

Instrumentation and study procedure

Once the HCFIs were identified, Raman studies were carried out at the National Facility for Geofluids Research and Raman Analysis of the NCESS, Government of India, Thiruvananthapuram, using an inVia Raman Microscope (Renishaw, UK, Model No. M-9836–3991-01-A) attached to an inVia Reflex Raman Spectrometer offering automated alignment through Renishaw WiRE 3.4 software. The instrument uses a diode laser exciting at a wavelength of 785 nm (300 mW, CW, Model. No. HPNIR 92E371, Class 3B laser product, Renishaw plc, UK). Instrument calibration performed by measuring Raman spectra of the internal and external silicon sample shows a sharp peak at a full-width half-maximum (FWHM) of 520 ± 0.5 cm^{-1}. The Raman probe that we used in this study has built-in neutral density filters that can reduce the beam intensity by several orders of magnitude, so that the laser beam can be seen in a video image of the inclusion and positioned precisely in the area intended for analysis. The spectral range of the equipment is from 50 to 4000 cm^{-1} shift from the laser line, accomplished with an edge filter. The Raman scattered light is dispersed with a grating of 1200 lines/mm. The detection is done by a Peltier cooled charge coupled device (CCD) detector with 576×384 pixels, with a spectral resolution of 1 cm^{-1}. The Renishaw inVia Raman system used for this study is fully automated and self-validating with auto-aligning and optimization of the input laser power. The operation of the equipment is fully software-controlled using WiRE 3.4 software.

The HCFIs are viewed through the Renishaw inVia Raman Microscope, and focused using a ×100 magnification objective lens at a working distance of 0.33 mm and 0.85 numerical aperture (NA). The HCFI study was performed using a laser power around 1.5 mW with an exposure time of 20 s for three accumulations for each
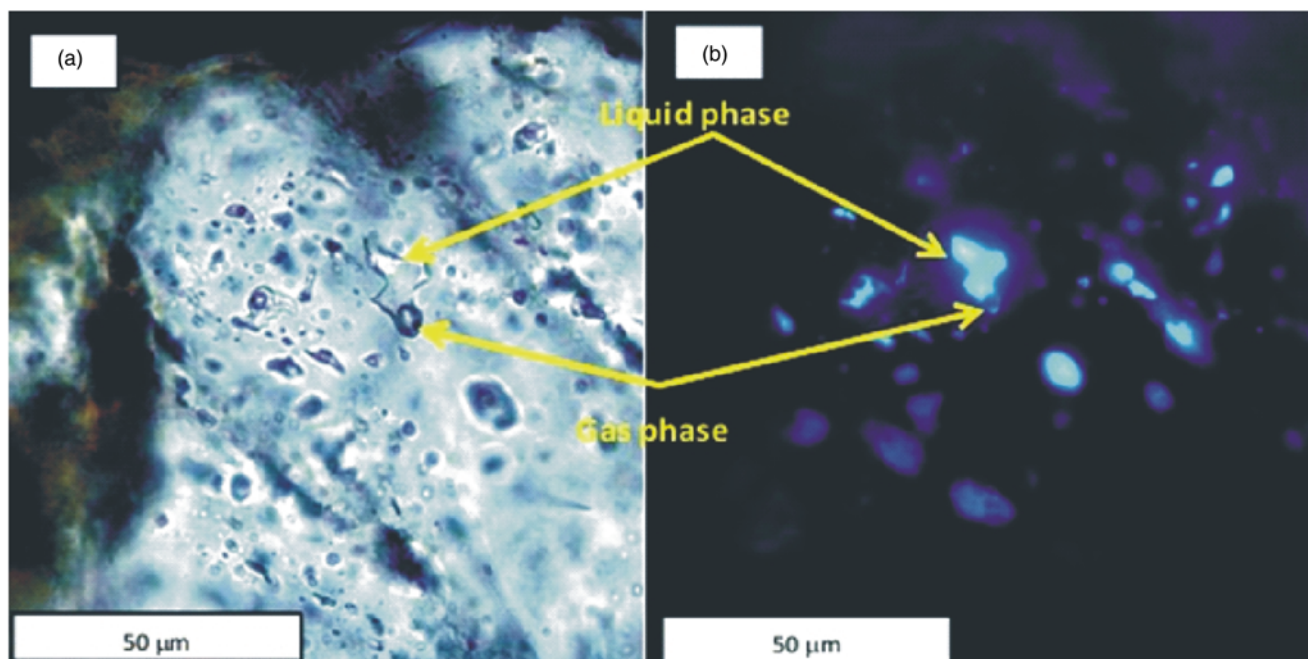
Fig. 1. Bright field and fluorescence images of HCFIs at 3495–3500 m depths from the Panna Formation, Mumbai Offshore Basin, India.

sample. Raman shifts were recorded, and the spectra are baseline corrected and smoothed using the Renishaw WiRE software supplied with the spectrometer system.

Results and discussion

The presence of petroleum inclusions in diagenetic cements or in healed fractures demonstrates that oil was present at the time of cement formation or during fracture healing. This observation can provide a lead on the time of oil generation and migration in the context of the diagenetic and tectonic history of the rock. Most of the petroleum inclusions occur as secondary inclusions within detrital grains (e.g. quartz, calcite and feldspars). The accurate determination of the chemical composition of the hydrocarbon fluids can provide (together with microthermometric studies)

information about the temperature, timing of fluid migration and entrapment. By analysing inclusions on a grain-by-grain basis, it may also be possible to differentiate inclusions from different source rocks. Such information is of significant importance to the petroleum exploration industry, particularly concerning the study of petroleum reservoirs, where it may be necessary to chart small changes in fluid composition (Karlsen et al. 1993; Ryder et al. 2004).

Raman spectroscopy provides useful constraints on the structure and maturity of both HCFIs and crude oils (Orange et al. 1996; McCreery 2000; Burruss 2003b; Bakker 2004; Dearing et al. 2011). Rosasco et al. (1975) published the first results of Raman analyses of natural fluid inclusions. Bény et al. (1982) and Touray et al. (1985) published more comprehensive studies on fluid systems and on the method in general. Raman spectra of natural HCFIs are less
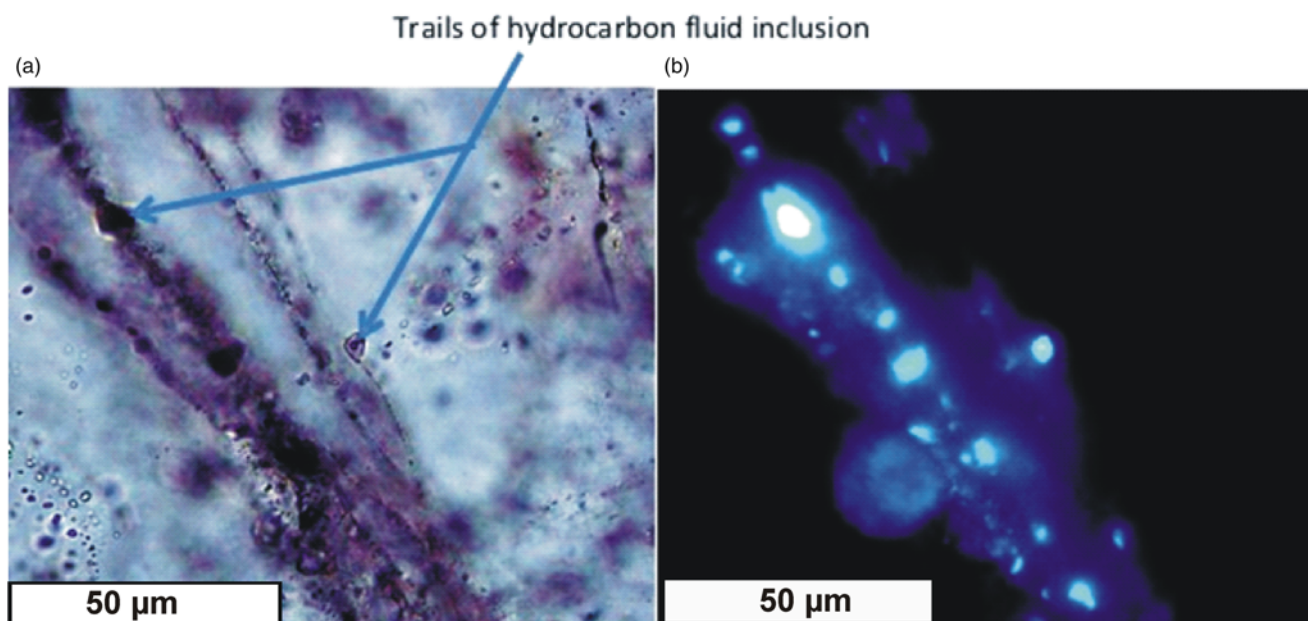

Fig. 2. Fluorescence of the HCFI trail from the Panna Formation, Mumbai offshore, India. (**a**) Bright filed image of HCFIs and (**b**) fluorescence image.

Table 1. *Details of the hydrocarbon fluid inclusions (HCFIs) studied from the RV-1 well along with lithostratigraphic nomenclature, Mumbai Offshore Basin, India*

Sample no.	Horizon (m)	Formation/age	Lithology	HCFIs description
1	3055–3060	Panna Formation/ Paleocene–early Eocene	Sandstone and siltstone	Bi-phase secondary inclusions concentrated along the annealed fractures within quartz grains. Size varies from 2 to 11 µm, and shapes are rectangular, fusiform and elongated. Degree of fill 10–20%
2	3065–3070	Panna Formation/ Paleocene–early Eocene	Sandstone	Bi-phase inclusions concentrated along secondary fractures in quartz grains. Size varies from 2 to 5 µm, and shapes are rounded, eye-shaped, elongated and stretched. Degree of fill 1–5%
3	3270–3275	Panna Formation/ Paleocene–early Eocene	Sandstone	Bi-phase inclusions concentrated along the secondary annealed fractures in quartz grains. Size varies from 5 to 9 µm, and shapes are elongated, irregular and rounded. Degree of fill 5–10%
4	3445–3450	Panna Formation/ Paleocene–early Eocene	Sandstone and shale	Bi-phase secondary inclusions concentrated along the secondary annealed fractures in quartz grains. Size varies from 3 to 12 µm, and shapes are irregular, oval and elongated. Degree of fill 1–5%
5	3455–3460	Panna Formation/ Paleocene–early Eocene	Sandstone and silty shale	Monophase secondary inclusions seen along the secondary trails. Size varies from 2 to 6 µm, and shape is rectangular, fusiform and elongated.
6	3685–3690	Panna Formation/ Paleocene–early Eocene	Shaley siltstone	Bi-phase secondary inclusions in cements. Size varies from 3 to 8 µm, and shapes are rectangular and elongated. Degree of fill 10–20%
7	3495–3500	Panna Formation/ Paleocene–early Eocene	Sandy siltstone and shale	Bi-phase secondary inclusions concentrated along the secondary fractures in quartz and feldspar grains. Size varies from 5 to 17 µm, and shapes are irregular and elongated. Degree of fill 10–20%
8	1345–1350	Mukta Formation/early Oligocene	Limestone and shale	Bi-phase secondary inclusions in cements. Size varies from 5 to 12 µm, and shapes are rectangular, irregular and elongated. Degree of fill 5–10%
9	1355–1360	Mukta Formation/early Oligocene	Limestone	Bi-phase secondary inclusions concentrated along the annealed fractures in sporadic feldspar grains, as well as in cements. Size varies from 2 to 5 µm, and shape is irregular and elongated. Degree of fill 2–5%
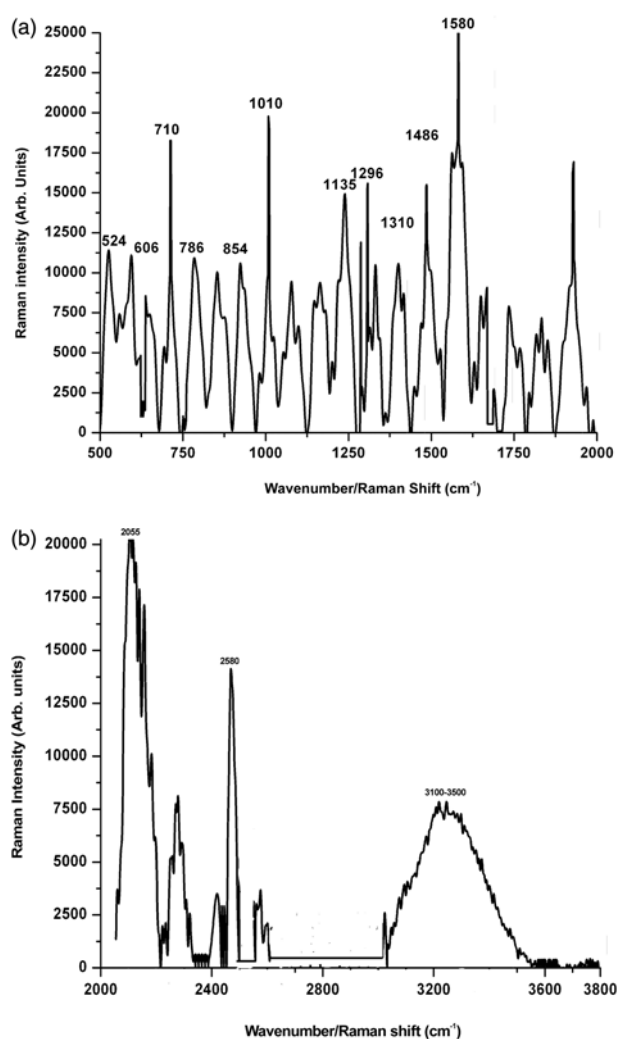
Fig. 3. (**a**) & (**b**) Raman spectrum of natural HCFIs in the study area.

common (Touray *et al.* 1985; Frezzotti *et al.* 2012; Lopponow *et al.* 2012). The reasons for the lack of feasibility of such measurements are: (1) the presence of laser-induced fluorescence from both natural hydrocarbons and many host minerals can mask the Raman scattering signal (Guilhaumou 1982; Guilhaumou *et al.* 1988; Wopenka *et al.* 1990); (2) laser-induced photo degradation may alter the chemical composition of the inclusion (Guilhaumou 1982; Touray *et al.* 1985); and (3) the low laser power required in studies of these inclusions would make the Raman scattering intensity correspondingly low (Berlman 1965; Touray *et al.* 1985). But Guilhaumou (1982), Guilhaumou *et al.* (1988) and Piranon & Pradier (1992) have shown that Raman studies on HCFIs are possible, in spite of the obvious problems and difficulties, by increasing the wavelength of excitation light to red or near infrared (630–1060 nm) and to mitigate background fluorescence. Orange *et al.* (1996) detailed that both photo degradation and fluorescence are critically dependent upon the absorption spectrum of the inclusion or host minerals, therefore avoiding the absorption bands of a hydrocarbon is crucial when choosing a Raman excitation line.

Raman spectroscopy is a non-destructive vibrational spectroscopic technique, which better characterizes liquid and gaseous compounds, solid phases, and solute species in fluid inclusions. Detection of hydrocarbon components in fluids or solids is useful for investigating the nature of fluids that interacted with the various geological formations, as well as the quality of oil in a petroliferous basin. Raman spectroscopy has the advantage of having a small spatial resolution (in our study, it is better than 1 µm while using a ×100 objective), a resolution not possible with conventional petrography, microthermometry or other spectroscopic methods (e.g. infrared spectroscopy). Thus, it is possible to carry out studies on an inclusion-by-inclusion basis in a sample, thereby characterizing multiple phases of fluid interaction.

The main components of petroleum are hydrocarbons, nitrogen–sulphur–oxygen-bearing (NSO) compounds and inorganic gases, such as N_2, CO_2 and H_2S. In the present study, Raman peaks of benzene are observed at 606 cm^{-1} (ring deformation), 1310 cm^{-1} (ring-stretching vibration), 1486 cm^{-1} (ring stretching + deformation)

Table 2. *Raman peaks and the major hydrocarbon species identified by Raman analysis for the natural hydrocarbon inclusions from Mumbai Offshore Basin, India*

Raman peaks/shifts (cm^{-1}) observed	Species/compound identified
606, 1010, 1310, 1486	Benzene
1580	Bromobenzene
786, 3245	Cyclohexane
710, 854	Calcium carbonate ($CaCO_3$)
2143	Carbon monoxide (CO)
2331	Nitrogen (N_2)
1135	Calcium sulphate ($CaSO_4$)
524	Sulphur dioxide (SO_2)
1296	Ethylene
2055	Carbonyl sulphide (COS)
2580	Hydrogen sulphide (H_2S)
3100–3500	H_2O (liquid)

and a bromobenzene peak observed at 1580 cm^{-1} (ring stretching). These vibrations, because of their highly symmetrical character, are quite intense and show the presence of benzene and its derivatives in the inclusions we have studied. The 990–1010 cm^{-1} region is of particular interest since this spectral region is the diagnostic of the presence of aromatic rings. These vibrations are quite intense and we observed peaks at 1010 cm^{-1} corresponding to the breathing vibration of the benzene ring.

Peaks corresponding to cyclohexane are observed at 786 cm^{-1} (CH_2 rock vibration) and at 3245 cm^{-1}. A peak at 2055 cm^{-1} is observed which corresponds to carbonyl sulphide (COS), and another peak observed at 2331 cm^{-1} shows the presence of nitrogen in the inclusions. A peak at 524 cm^{-1} represents the presence of sulphur dioxide and a peak at 2580 cm^{-1} shows the presence of H_2S in liquid form. The presence of carbon monoxide is seen with a peak at 2143 cm^{-1}. Calcium carbonate (calcite) peaks are seen at 710 and 854 cm^{-1}, and a calcium sulphate ($CaSO_4$) peak is observed at 1135 cm^{-1}. A broad peak of water in liquid form is also observed in the region 3100–3500 cm^{-1}. Observed peaks shown in Figure 3a and b have been consolidated and are shown in Table 2.

Orange *et al.* (1996) have carried out a successful Raman feasibility study on natural hydrocarbon inclusions by combining an appropriate selection of the laser excitation line (the 633 nm light of a He–Ne laser) with a minimization of the excitation volume, low laser power and long integration times. This technique, however, remains qualitative because of complications associated with the quantification of the Raman cross-sections. Chen *et al.* (2015) reported the characterization of synthetic polycyclic aromatic hydrocarbons using Raman and surface-enhanced Raman spectroscopy with a 785 nm diode laser at a power of 60 mW and a spectral acquisition time of 10 s. Only a limited number of studies are reported in the analysis of HCFIs using the Raman technique, especially in natural fluid inclusions (Orange *et al.* 1996; Nai *et al.* 2007; Bourdet *et al.* 2011; Verma *et al.* 2012). In a study by Bourdet *et al.* (2011), using an excitation wavelength of 244 nm for Raman analysis, it was observed that the laser excitation at 244 nm caused some photochemical alterations in the inclusions and reported that Raman bands of hydrocarbon molecules in oil inclusions using 244 nm laser are masked by carbon bands related to molecules containing aromatic rings. This is, again, focused on the need for an optimum excitation wavelength for Raman spectral studies. Burke (2001) and Frezzotti *et al.* (2012) provided reviews on Raman spectroscopy in fluid inclusion analysis, and mentioned that the influence of fluorescence might be avoided while considering hydrocarbon inclusions.

The relatively high absorption of many HCFIs in the ultraviolet region produces fluorescence and, because of the high flux of photons associated with laser Raman measurements, even a small amount of sample absorption may cause fluorescence that interfere with the Raman spectrum. Also, even a trace quantity of hydrocarbons, which fluoresce under the incident laser excitation, can generate a background larger than that of the Raman scattering from the sample. All these aspects are considered when we selected the excitation laser for our Raman studies on HCFIs. The primary absorption of simple alkanes and cycloalkanes fall below 200 nm, and, for most hydrocarbons with a number of carbons >10, absorption extends to a wavelength greater than 550 nm (Burdet *et al.* 1955; Berlman 1965; Dias 1987). Therefore, hydrocarbons with significantly more complex molecules might require infrared excitation to avoid samples fluorescence.

In the present study, we used a fluorescence quencher (waxoline blue) with a resin-hardner mix to eradicate the background fluorescence while preparing the wafers and selecting an excitation wavelength of 785 nm, which is above the absorption wavelength of aromatic hydrocarbon, which again eliminates the fluorescence from the hydrocarbons and, thus, also photo-degradation. Advanced Raman spectrometers, such as the Renishaw inVia Raman spectrometer that we used in our studies, avoid the fluorescence effect with the use of notch holographic filters and collect the Raman signal directly from the fluids within the sample. Orange *et al.* (1996) reported that they were not able to see the presence of benzene and its derivatives in the natural fluid inclusions they studied, whereas they observed the same in oil samples. The methodology we followed in wafer preparation and the selection of the excitation wavelength at 785 nm helped us to obtain desirable results.

Raman spectroscopy provides a wealth of information about the composition of microscopic mineral and fluid inclusions. Very fast acquisition times and the lesser amount of laser energy into the HCFIs prevent any kind of alteration in the composition of the fluid inclusions, and the use of notch filters in the latest Raman spectrometers allows the detection of even very weak signals with high sensitivity. Highly polished standard thin sections and doubly polished wafers are used for this purpose. The near-infrared (NIR) region has special importance for ultra-sensitive Raman spectroscopy at the single molecule level in which background fluorescence is reduced and photo-induced degradation from the sample is diminished (Orange *et al.* 1996). High-intensity NIR diode lasers are easily available, making this region attractive for compact, low-cost Raman instrumentation. Further, the development of low-noise, high quantum efficiency multichannel detectors (CCD arrays), combined with high throughput single-stage spectrographs used in combination with holographic laser rejection filters, have led to high-sensitivity Raman spectrometers (Kneipp *et al.* 1999; Dubessy *et al.* 2012). Recently, sophisticated data analysis techniques based on multivariate analysis have made it possible to exploit the full information content of Raman spectra (Tarcea & Popp 2012).

The composition of oils in HCFIs determined using high-resolution Raman spectroscopy can very well be compared with the composition of the bulk oil obtained from the same basin using GC-MS. We, therefore have analysed fresh oil samples from the same basin using GC-MS (Single Quadrupole GC/MS 5977A GC/MSD with 7890B GC and 7693A Automatic Liquid Sampler) with a column HP-5ms (30 m length × 250 μm internal diameter × 0.25 μm film thickness) and working with Agilent Mass Hunter software, which identified the presence of benzene, cyclohexane, ethylene, and reported the presence of sulphur in the form of sulphurous acid, and bromine in the form of bromotetradecane and nitrogen-based compounds. The chemical constituents in natural HCFIs from the same basin identified using laser Raman spectrometric methods with a 785 nm laser excitation agrees well with the GC-MS results of oil in the same basin, which again supports the utility of the laser Raman technique with 785 nm laser for the chemical constituents identification in natural HCFIs.

Conclusions

HCFIs contain entrapped petroleum fluids that have migrated through the rocks in the geological past and are of special interest to the petroleum industry. The characterization of HCFIs using a non-contact, non-destructive, optical Raman spectrometry presents considerable challenges. Fluorescence (background and from the aromatic compounds in HCFIs) and the presence of overlapping bands from the host mineral are the possible competing effects during Raman analysis, and can generally mask the Raman signals. To overcome these hurdles, special wafer preparation techniques, along with the use of fluorescence quenchers, were employed to obtain Raman signals from natural HCFIs. Further, proper selection of excitation wavelength, and appropriate choice of laser power and optics, yielded the best possible Raman signals in HCFIs from the Mumbai Offshore Basin, India. A laser wavelength of 785 nm used for the present study identified Raman peaks corresponding to cyclohexane, benzene, ethylene, carbonyl sulphide, sulphur dioxide, nitrogen and carbon monoxide in HCFIs, along with the presence of calcium carbonate and water. The present study elucidates the potential of Raman spectroscopic methods using a 785 nm laser excitation for detecting the chemical constituents of HCFIs.

Acknowledgements and Funding

References

Ahmadjian, M. & Brown, C.W. 1976. Petroleum identification by laser Raman spectroscopy. *Analytical Chemistry*, **48**, 1257–1259.

Anderson, B., Munz, I.A., Johansen, H. & Johansen, I. 1998. Compositional and Isotope data on hydrocarbon fluid inclusions- atoll for better understanding of light hydrocarbon migration and trapping. Abstract presented at the *215th American Chemical Society National Meeting*, March 29–April 2, 1998, Dallas, Texas.

Bakker, R.J. 2004. Raman spectra of fluid and crystal mixtures in the systems H_2O, H_2O–NaCl and H_2O–$MgCl_2$ at low temperatures: applications to fluid-inclusion research. *The Canadian Mineralogist*, **42**, 1283–1314.

Barres, O., Burneau, A., Dubessy, J. & Pagel, M. 1987. Application of micro FT-IR spectroscopy to individual hydrocarbon fluid inclusion analysis. *Applied Spectroscopy*, **41**, 1000–1108.

Bény, C., Guilhaumou, N. & Touray, J.C. 1982. Native-sulphur-bearing fluid inclusions in the CO_2–H_2S–H_2O–S system – Microthermometry and Raman microprobe (MOLE) analysis – Thermochemical interpretations. *Chemical Geology*, **37**, 113–127.

Berlman, B. 1965. *Handbook of Fluorescence Spectra of Aromatic Molecules*. Academic Press, New York.

Blamey, N.J.F. & Ryder, A.G. 2007. Hydrocarbon fluid inclusion fluorescence: a review. *In:* Geddes, C.D. (ed.) *Reviews in Fluorescence*. Springer, New York, 299–334.

Blanchet, A., Pagel, M., Walgenwitz, F. & Lopez, A. 2003. Microspecfluorometric and microthermometric evidence for variability in hydrocarbon fluid inclusions in quartz overgrowths: implications for inclusion trapping in the Alwyn North field, North Sea. *Organic Geochemistry*, **34**, 1477–1490.

Bodnar, R.J. 1990. Petroleum migration in the Miocene Monterey Formation, California, USA: constraints from fluid inclusion studies. *Mineralogist Magazine*, **54**, 295–304.

Bourdet, J., Burruss, R.C., Bodnar, R.J. & Eadington, P.J. 2011. Assessment of UV-Raman for analysis of petroleum inclusions. *In*: *European Current Research on Fluid Inclusions (ECROFI–XXI)*, Montanuniversität Leoben, Austria, 9–11 August 2011, Abstract Volume, 50–51.

Burdet, R.A., Taylor L.W. & Jones, L.C., Jr. 1955. Determination of aromatic hydrocarbons in lubricating oil fractions by far UV absorption spectroscopy. *In: Molecular Spectroscopy*. Institute of Petroleum, London, 30–41.

Burke, E.A.J. 2001. Raman microspectrometry of fluid inclusions. *Lithos*, **55**, 139–158.

Burruss, R.C. 2003*a*. Petroleum fluid inclusions, an introduction. *In:* Samson, I., Anderson, A. & Marshall, D. (eds) *Fluid inclusions: Analysis and Interpretation*. Mineralogical Association of Canada, Short Course Series, **32**, 159–174.

Burruss, R.C. 2003*b*. Raman spectroscopy of fluid inclusions. *In:* Samson, I., Anderson, A. & Marshall, D. (eds) *Fluid Inclusions: Analysis and Interpretation*. Mineralogical Association of Canada, Short Course Series, **32**, 279–289.

Chen, J., Yao-Wen, H. & Zhaob, Y. 2015. Characterization of polycyclic aromatic hydrocarbons using Raman and surface enhanced Raman spectroscopy. *Journal of Raman Spectroscopy*, **46**, 64–69.

Dearing, T.I., Thompson, W.J., Rechsteiner, C.E. & Marquardt, B.J. 2011. Characterization of crude oil products using data fusion of process Raman, infrared, and nuclear magnetic resonance (NMR) spectra. *Applied Spectroscopy*, **65**, 181–186.

Dias, R.J. 1987. *Handbook of Polycyclic Hydrocarbons: Part A. Benzenoid Hydrocarbons*. Elsevier, Amsterdam.

Dollish, F.R., Fateley, W.G. & Bentely, F.F. 1974. *Characteristics of Raman Frequencies of Organic Compounds*. Wiley, New York.

Dubessy, J., Caumon, M.C., Rull, F. & Sharma, S. 2012. Chapter 3. Instrumentation in Raman spectroscopy: elementary theory and practice. *In*: Dubessy, J., Caumon, M.-C. & Rull, F. (eds) *Raman Spectroscopy Applied to Earth Sciences and Cultural Heritage*. EMU Notes in Mineralogy, **12**, 83–172.

Frezzotti, M.L., Tecce, F. & Casagli, A. 2012. Raman spectroscopy for fluid inclusion analysis. *Journal of Geochemical Exploration*, **112**, 1–20.

George, S.C., Ruble, T.E., Dutkiewicz, A. & Eadington, P.J. 2001. Assessing the maturity of oil trapped in fluid inclusions using molecular geochemistry data and visually determined fluorescence colours. *Applied Geochemistry*, **16**, 451–473.

Goldstein, R.H. 2001. Fluid inclusions in sedimentary and diagenetic systems. *Lithos*, **55**, 159–193.

Guilhaumou, N. 1982. Accurate analysis of fluid inclusions by the laser molecular microprobe (MOLE) and by microthermometry. *Travaux Laboratoire de Geologie, Ecole Normale Superieure, Paris*, **14**, 68 [in French].

Guilhaumou, N., Jouaffred, D., Velde, B. & Beny, C. 1988. Raman microprobe analysis on gaseous inclusions from diagenetically altered Terres Noures (S-E, France). *Bulletin de Mineralogie*, **111**, 577–585.

Guilhaumou, N., Szydlowskii, N. & Pradier B. 1990. Characterization of hydrocarbon fluid inclusions by infrared and fluorescence micro spectrometry. *Mineralogical Magazine*, **54**, 311–324.

Karlsen, D.A. & Skeie, J.E. 2006. Petroleum migration, faults and overpressure, part I: Calibrating basin modeling using petroleum in traps – a review. *Journal of Petroleum Geology*, **29**, 227–256.

Karlsen, D.A., Nedkvitne, T., Larter, S.R. & Bjørlykke, K. 1993. Hydrocarbon composition of authigenic inclusions, Application to elucidation of petroleum reservoir filling history. *Geochemica et Cosmochimica Acta*, **57**, 3641–3659.

Karlsen, D.A., Skeie, J.E. *et al.* 2004. Petroleum migration, faults and overpressure. Part II. Case history: The Haltenbanken Petroleum Province, offshore Norway. *In:* Cubitt, J.M., England, W.A. & Larter, S. (eds) *Understanding Petroleum Reservoirs: towards an Integrated Reservoir Engineering and Geochemical Approach*. Geological Society, London, Special Publications, **237**, 305–372, https://doi.org/10.1144/GSL.SP.2004.237.01.18

Kihle, J. 1995. Adaptation of fluorescence excitation-emission micro-spectroscopy for characterization of complex organic mixtures: Application in petroleum geochemistry. *Organic Geochemistry*, **23**, 1029–1042.

Kihle, J., Hurum, J.H. & Liebe, L. 2012. Preliminary results on liquid petroleum occurring as fluid inclusions in intracellular mineral precipitates in the vertebrae of *Pliosaurus funkei*. *Norwegian Journal of geology*, **92**, 341–352.

Kneipp, K., Kneipp, H., Itzkan, I., Dasari, R.R. & Feld, M.S. 1999. Ultrasensitive chemical analysis by Raman spectroscopy. *Chemical Reviews*, **99**, 2957–2975.

Lisk, M., O'Brien, G.W. & Eadington, P.J. 2002. Quantitative evaluation of the oil-leg potential in the Oliver gas field, Timer Sea, Australia. *American Association of Petroleum Geology Bulletin*, **86**, 1531–1542.

Lopponow, G.R., Shoute, L., Schmidt, K.J., Savage, A., Hall, R.H. & Bulmer, J.T. 2012. UV Raman spectroscopy of hydrocarbons. *Philosophical Transactions of the Royal Society of London*, **A362**, 2461–2476.

McCreery, R.L. 2000. *Raman Spectroscopy for Chemical Analysis*. Wiley-Interscience, New York.

Munz, I.A. 2001. Petroleum inclusions in sedimentary basins: systematics, analytical methods and applications. *Lithos*, **55**, 195–212.

Munz, I.A., Iden, K., Johansen, H. & Vagle, K. 1998. The fluid regime during fracturing of the Embla field, Central Trough, North Sea. *Marine and Petroleum Geology*, **15**, 751–768.

Nai, Z., ZuoJi, T., YingYang, L., HuiTong, W., FuQing, A. & JianHua, M. 2007. Raman characteristics of hydrocarbon and hydrocarbon inclusions. *Science in China Series D: Earth Sciences*, **50**, 1171–1178.

O'Grady, M.R., Bodnar, R.J., Hellgeth, J.W., Conroy, C.M., Taylor, L.T. & Knight, C.L. 1989. Fourier transform infrared microprobe (FTIRM) analysis of individual petroleum inclusions in geologic samples. *In:* Russel, P.E. (ed.) *Microbeam Analysis*. San Francisco Press, San Francisco, CA, 579–582.

Orange, D., Knitile, E., Farber, D. & Williams, Q. 1996. Raman spectroscopy of crude oils and hydrocarbon fluid inclusions: A feasibility study. *In*: Dyar, M.D., McCammon, C. & Scaefer, M.W. (eds) *Mineral Spectroscopy: A Tribute to Roger G. Burns*. Geochemical Society, Special Publications, **5**, 65–81.

Parnell, J., Middleton, D., Honghan, C. & Hall, D. 2001. The use of integrated fluid inclusion studies in constraining oil charge history and reservoir compartmentation: examples from the Jeanne d'Arc Basin, offshore Newfoundland. *Marine and Petroleum Geology*, **18**, 535–549.

Piranon, J. & Barres, O. 1990. Semi-qunatitative FT-IR microanalysis limits; evidence from synthetic hydrocarbon fluid ncluions in sylvite. *Geochimica et Cosmochimica Acta*, **54**, 509–518.

Piranon, J. & Pradier, B. 1992. Ultraviolet-fluorescence alteration of hydrocarbon fluid inclusions. *Organic Geochemistry*, **18**, 501–509.

Roedder, E. 1984. Fluid inclusions. *Reviews in Mineralogy and Geochemistry*, **12**, 1–644.

Rosasco, G.J., Roedder, E. & Simmons, J.H. 1975. Laser-excited Raman spectroscopy for nondestructive partial analysis of individual phases in fluid inclusions in minerals. *Science*, **190**, 557–560.

Ryder, A.G., Przyjalgowski, M.A., Feely, M., Szczupak, B. & Glynn, T.J. 2004. Time-resolved fluorescence micro spectroscopy for characterizing crude oils in bulk and hydrocarbon- bearing fluid inclusions. *Applied Spectroscopy*, **58**, 1106–1115.

Tarcea, N. & Popp, J. 2012. Chapter 5. Raman data analysis. *In*: Dubessy, J., Caumon, M.-C. & Rull, F. (eds) *Raman Spectroscopy Applied to Earth Sciences and Cultural Heritage*. EMU Notes in Mineralogy, **12**, 193–226.

Touray, J.C., Beny-Bassez, C., Dubessy, J. & Guilhaumou, N. 1985. Microcharacterization of fluid inclusions in minerals by Raman microprobe. *Scanning Electron Microscopy*, **I**, 103–118.

Verma, D., Jadav, G.N., Biswal, T.K., Jena, S.K. & Sharma, N. 2012. Characterisation of hydrocarbon-bearing fluid inclusion in sandstones of Jaisalmer Basin, Rajasthan: A Preliminary approach. *Journal of the Geological Society of India*, **80**, 505–514.

Wopenka, B., Pateris J.D. &Freeman, J.J. 1990. Analyis of individual fluid incluions by Fourier transform infrared and Raman microspectrometry. *Geochimica et Cosmochimica Acta*, **54**, 519–533.