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Advances in Hydrocarbon fluid inclusions microanalysis an modelling: A powerfull constraint for Diagenesis history and fluid flow reconstruction in reservoir appraisal

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Since their description by Murray, (1957) in fluorite, there have been a lot of studies involving the composition and densities of these particular fluid inclusions (FI) for the understanding of petroleum formation and migration. Combination of trapping temperature, molecular composition and isochoric PVT modelling lead directly to the conditions of petroleum formation and migrations in petroleum occurrences.

As trapping temperature is currently measured by microthermometry, the molecular composition has been obtained tentatively by various destructive techniques involving decrepitation, crushing and leachates analyses (George et al., 1998). In exceptional great size fluid inclusions (Guilhaumou et al., 2000), the composition and biomarkers are obtained by individual extraction under the microscope and GCMS analysis, but the analyse of theC1-C5 fraction is missing. Jones and Macleod, (2000), proposed a sophisticated methodology to extract and clean up the sample before crush leach analyses. This method " is many time consuming". The main limitations remain a possible contamination during the extraction and the mixing of several generations of oil. Additionally oil-water fluid inclusions are frequently encountered in heterogeneous trapping that precludes to link the individual homogenisation temperature with the composition for PVT modelling.

In the last few years advances in Molecular infrared microspectrometry enable to perform quantitative non destructive molecular analyses in a single fluid inclusion under a microscope and to link directly their individual composition to their density, allowing PVT modelling of single fluid inclusion.

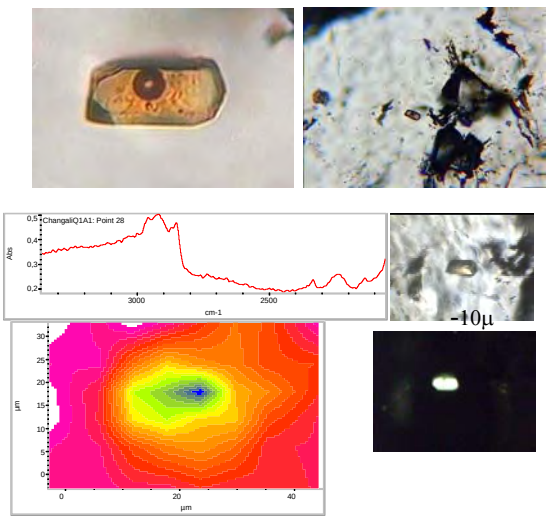

Figure 1
Early generation of petroleum Inclusions > 10 µ. in quartz CH4 37mole %, C02 0,08 mole%, CH3/CH2 : C8 equ., H20 undetected , CH4/Chalk = 0,10 Homogeneous trapping

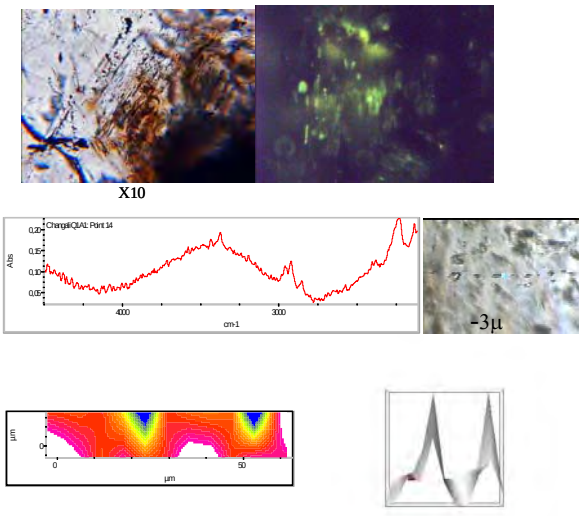

Figure 2:
Secondary generation of petroleum Inclusions < 10 µ. CH4 60mole %, C02 0%, CH3/CH2 : C8 equ., H20 : ++, CH4/Chalk = 0,3. 5 FI Measured. Homogeneous trapping

Petroleum fluid inclusions encountered are often sub micron to ten micron length. Thanks to the brightness of the Synchrotron source (Guilhaumou 1999, 2000) and a confocal arrangment, all the organic components could be quantitavely analysed by infrared microspectroscopy at a micron scale (Figure 1). Molecular mapping aim to control the band attributions and the localisation of CH4, CO2 and water content, even they coud not be seen optically. Homogeneity or heterogeneity of trapping may be cheked in growth zones (Figure 2). Even H2S, known as having low absorption may be detected too in gseous phases. The several generations may be, then easily distinguished and analysed in cements. In carbonates the limitation due to the CO3—stretching may be overcome by matrix soustraction referring to an appropriate internal calibration. (Figure 3). In the sample shown in example in figure 1 to 3, two generations of FI could be easily distinguished in the quartz cement. The hydrocarbons entrapped in FI from carbonates cements have the same composition as those entrapped in quartz cements and some small authigenic carbonates are identified in primary oil FI.

After quantitative calculations, the composition may be directly linked to the homogenisation temperature allowing for each inclusion, PVT modelling and entrapment temperature and pressure determination (Figure 4). We could then be able to reconstruct the diagenetic history and petroleum migration (Benchilla et al., 2002).

Raman spectroscopy aim to quantitatively analyse the light organic components (C02-CH4-C3H8) and non or weak fluorescent hydrocarbon in fluid inclusions The content of CH4 dissolved in water has been quantified and modelised to obtain the pressure and temperature of trapping in gas occurrences. It has been applied particularly in north sea samples (Dubessy et al., 2001).

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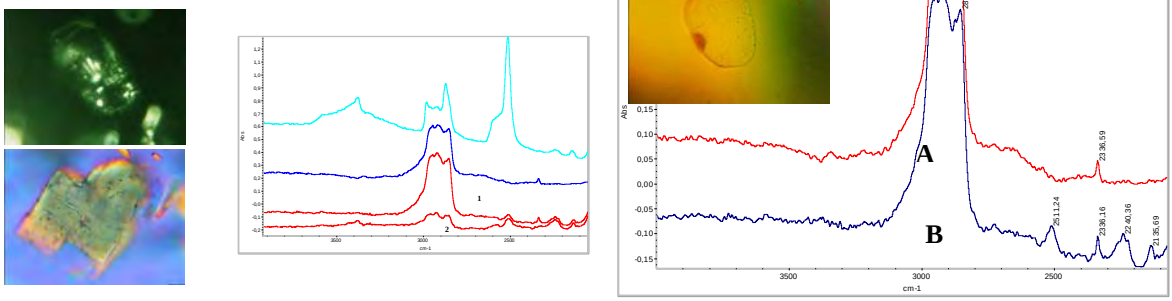


Inclusions in carbonate cement: CH4 : 35 mole % C02 0, 06%, CH3/CH2 : C8 equ. N alkanes.
matrix)
CH4/Chalk = 0,12, H2O undetected

Small carbonate crystals in oil (quartz

spectra B: additional CO3 band at 2511 cm –1

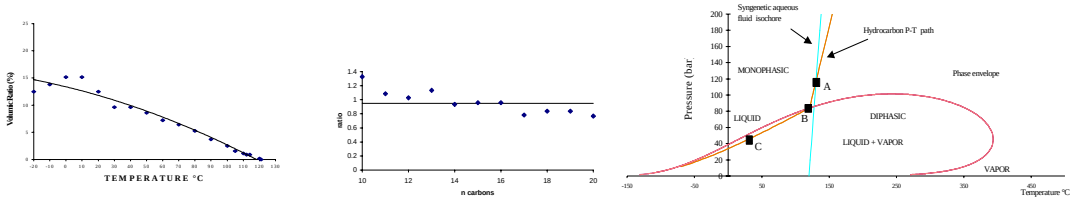
Figure 3

The interpretation in term of Pressure Temperature entrapment need accurate knowledge of the current hydrocarbon evolution in PVT path. With P. Mougin , (1999), we have developed at the IFP a software using a modified Redlich Kong EOS to calculate the liquid vapour curves and corresponding isochores. We used a combination of volumetric data obtained by measurements of the liqui/vapor ratios in petroleum FI from room temperatures to homogenisation temperature (Th), and the calculation of α and β parameters corresponding to the analysed composition and using a data base of Montel, (1993) for the reconstruction of the properties of oil found in reservoirs (Figure 4, A, B,C).

The results show first, that among the components involved, CH4 and the alkane chain length are the main sensitive parameters, as CO2, SO2 and H2O (dissolved) are of minor effect on P-T path determination**.** The water content in mixed oil- water FI should be relevant for Th interpretation (Pironon et al., 2000), but because of low solubility of water in oil at current temperatures, it may have a minor effect on the homogenisation temperature measured. Other models using EOS has been developed by

Comment:

CALSEP (Applin et al., 1999) , and Thierry et al., (2000), who used confocal UV laser spectroscopy for the measurementent of liquid/vapor ratio.



A **B** **C**

Figure 4: Determination of the P-T Entrapment path by PVT modelling of known composition petroleum FI. A : liquid vapor ratio, B : α parameter, C: Isochores crosscut.

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Some sensibility test have been done in Tunisia and Pakistan (Guilhaumou et al., 2000, Benchilla et al., 2002). The composition measured by SFTIR in liquid phases are in agreement with those obtained by GCMS and simulated by PVTX modeling. Microthermometric data thus indicate that the initial stage of fluorite cementation at Hammam Zriba occurred under fluid pressures of 115 ± 2 bars and at a temperature close to 130°C. At Koh-i-Maran, the F3 geodic fluorite mineralisation developed under hydrostatic pressures of 200 ± 5 bars, and at quite similar temperatures of 125-130°C. These data are integrated with the kinematic and thermal 2D basin modelling .The results suggest a Cenozoic age for the fluorite mineralisation and a dual fluid migration model for both ore deposits (Benchilla et al ., 2002).

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