Preliminary data on oil and aqueous fluid inclusions of the fracture-fill in the Corones and Armàncies Fms, Eocene, SE Pyrenees

Datos preliminares de las inclusiones fluidas (petróleo y acuosas) en las fracturas cementadas de las Fms. Corones y Armàncies, Eoceno, Pirineo oriental.

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RESUMEN

Las calizas del Eoceno del Pirineo sur-oriental están afectadas por fracturas con direcciones N-NE, buzamientos subverticales (55-72º), espesores centimétricos y longitudes de varios metros. En ocasiones también se observan cavidades vacuolares. Tanto las fracturas como las cavidades vacuolares están rellenas por cementos carbonáticos que no ocluyen totalmente la porosidad. Además, la presencia de indicios de petróleo es muy abundante en las fracturas que afectan a la parte alta de la Fm Armàncies (Cuisiense, Eoceno) y son menos abundantes, pero están también presentes, en la Fm Corones (Cuisiense inferior). El objetivo principal de este trabajo es caracterizar los tipos de inclusiones fluidas (IF) en los cementos carbonáticos que rellenan fracturas como primera aproximación a la historia de migración del petróleo. El estudio detallado de petrografía, fluorescencia y microtermometría ha revelado que en la Fm Corones aparecen tres tipos de inclusiones con dos fases (líquido y vapor): i) IF de petróleo con fluorescencia amarilla; ii) IF de petróleo con fluorescencia amarilla y color marrón en luz transmitida; ambos tipos de IF aparecen como trazas de pequeña longitud que afectan sólo a uno o dos cristales de calcita, lo cual sugiere un origen secundario; iii) IF acuosas de tamaños muy pequeño (5-10 µm) que aparecen en los bordes de los cristales indicando un origen primario. En la Fm Armàncies aparecen cuatro tipos de inclusiones con dos fases (líquido y vapor): i) IF de petróleo con fluorescencia amarilla; ii) IF de petróleo con fluorescencia amarilla y color marrón en luz transmitida; iii) IF petróleo con fluorescencia azul y azul intenso, que son las más abundantes; todas las IF de petróleo aparecen como trazas de gran continuidad, paralelas a los márgenes de las fracturas, lo cual sugiere un origen primario; iv) IF acuosas que son muy escasas y aparecen como trazas.

En resumen, los datos preliminares del estudio de inclusiones fluidas sugieren que el petróleo en la Fm Armàncies migró a través de fracturas de forma coetánea con la precipitación de los cementos carbonáticos. Por el contrario, el petróleo fue atrapado en el cemento carbonático de las fracturas de la Fm Corones, pero no durante su precipitación, sino posteriormente.

Key words: *cemented fractures, oil fluid inclusions, fluorescence, Eocene, South-Eastern Pyrenees*

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Introduction

Fluid inclusions are minute volumes of fluids trapped in minerals. They may represent a closed system with respect to composition and volume, and can be considered as a record of fluids migrating in sedimentary basins. Therefore, fluid inclusion data can provide relevant information about trapping conditions, timing and spatial distribution of fluids and help to determine fluid flow paths. When petroleum inclusions are present, the migration history, maturity and different sources involved can be unraveled (Goldstein, 2001; Munz 2001).

The Pyrenees constitute a narrow, asymmetrical, double wedge mountain range that includes a relatively wide southern foreland basin. The south-eastern sector is formed by a stack of south-vergent units that include both sedimentary cover and basement. The study area is located in the Cadí thrust sheet (Fig. 1). The Cadí thrust sheet consists of very thick Lower-Middle Eocene series and Palaeocene rocks (Martínez *et al*., 1997; Vergés *et al*., 1998). Eocene limestones are affected by fractures characterized by N-NE trending, dipping steeply from 55º to 72º, slightly subvertical, with a cm thickness and a length of several meters. Occasionally, vugs can be observed as well. Fractures and vugs are partially filled by carbonate cements (Permanyer, 2004; Caja *et al*., 2005). Oil shows are very abundant in the fractures affecting the Armàncies Fm (Cuisian, Eocene) and they are scarce in the Corones Fm (lower Cuisian).

The main aim of this work is to understand oil migration through Armàncies and Corones Fm in the

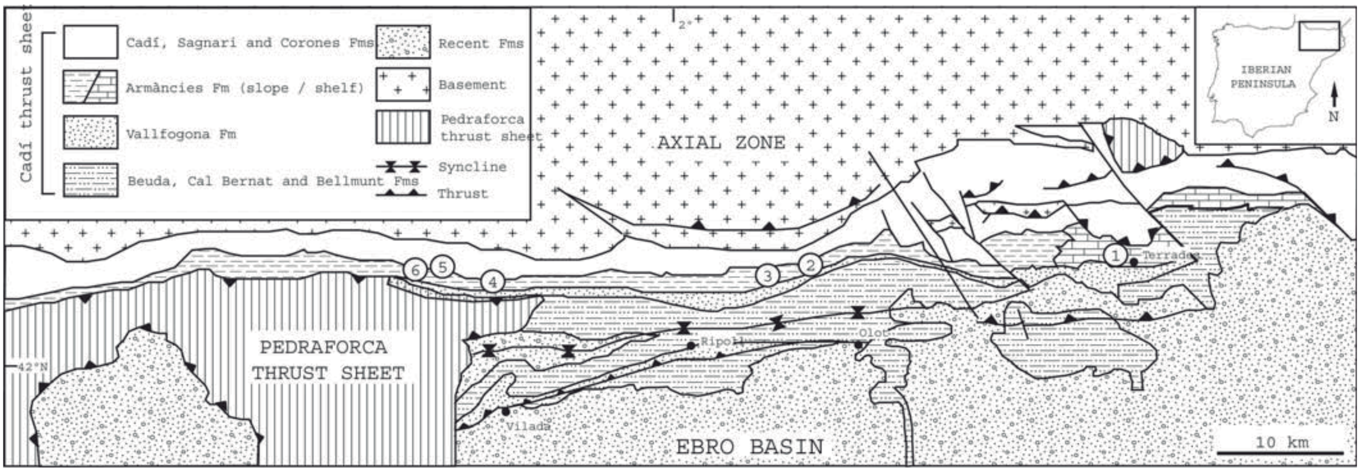

Fig. 1.- Schematic geologic map of the study area in the southeastern Pyrenees (modified after Giménez-Montsant et al., 1999) showing the sampled locations. 1: Terrades quarries (Armàncies Fm shelf facies), 2: Sant Pau de Segúries quarry (Armàncies Fm), 3: Perella Mine (Corones and Armàncies Fm), 4: Riutort Mine (Corones and Armàncies Fm), 5: El Paller section (Armàncies Fm), 6: Bagà section (Armàncies Fm).

Fig. 1.- Mapa geológico esquemático del área de estudio en el Pirineo Suroriental (modificado de Giménez-Montsant* et al.*, 1999) donde se han señalado los afloramientos muestreados. 1: Canteras de Terrades (Fm Armàncies en facies de plataforma), 2: Cantera de Sant Pau de Segúries (Fm Armàncies), 3: Mina Perella (Fms Corones y Armàncies), 4: Mina de Riutort (Fms Corones y Armàncies), 5: Serie de El Paller (Fm Armàncies), 6: Serie de Bagà (Fm Armàncies).

Pyrenees by petrographic, fluorescence and microthermometric characterisation of fluid inclusions (FI hereafter) in fracture-filling carbonate cements (Fig. 1).

Sampling and methodology

A total of 84 limestone samples were collected in the Corones and Armàncies Fms based on the presence of fractures filled with calcite cements, as well as the occurrence of oil shows (Fig. 2 A). Sampling locations are shown in figure 1. Up to 72 thin sections were examined by conventional light microscopy and cathodoluminescence petrography. Cathodoluminescence was very useful for distinguishing the different generations of calcite cements. Fluorescence observations of fluid inclusions were done using the same set of wafers as for microthermometry. A monochromatic excitation wavelength of 365 nm was used. Fluid inclusion microthermometry was carried out on 15 samples on a Fluid Inc. (Denver, USA) heating-cooling stage. The stage was calibrated by various international standards. The samples were not heated during preparation of the wafer. Homogenisation of the oil inclusions was measured before the homogenisation of the aqueous inclusions. Leakage during analyses was observed in several petroleum inclusions. The present data set only includes inclusions that did not show leakage upon repetitive analyses. The salinity of aqueous inclusions has not been analysed.

Fluid inclusion petrography

In the Armàncies Fm four types of two-phase (vapour and liquid) FI occur: i) colourless oil FI showing yellowish fluorescence; ii) oil FI showing yellowish fluorescence, brown colour under transmitted light and small vapour bubbles; iii) colourless oil FI showing blue and deep blue fluorescence, which are very abundant; all oil FI occurs as long trails, parallel to the fracture margins (Fig. 2 B, C); and iv) aqueous FI are very scarce and occur as trails. In a previous work, oil inclusions were reported only in Fe- and Mg-poor calcite cement characterised by clean and large blocky equidimensional crystals (Caja *et al*., 2005). However, the present study shows that oil inclusions occur in Fe- and Mg-rich calcite cement characterised by twinned and cloudy fence-like crystals as well.

In the Corones Fm three types of two-phase (vapour and liquid) FI occur: i) colourless oil FI showing yellowish fluorescence and small vapour bubbles; ii) oil FI showing yellowish fluorescence, brown colour under transmitted light, and large vapour bubbles; both oil FI types occur as short trails in only one or two calcite crystals (Fig. 2 D); and iii) aqueous FI, which are very small in size (5 to 10 µm) and occasionally very abundant in the borders of the crystals.

Oil inclusions in both Formations have comparable sizes, ranging from 5 to 20 µm. However, oil FI with yellowish fluorescence, brown colour, large vapour bubbles have the biggest sizes, up to 32 µm.

Fluid inclusion microthermometry

In the Armàncies Fm all types of FIs homogenise to the liquid phase. Oil FIs show wide ranges in homogenisation temperatures, but several mode values can be observed (Fig. 3 A). Oil FI showing blue and deep blue fluorescence have two marked homogenisation temperature modes, 55-60 ºC and 125-130 ºC (n=118). Oil FI showing yellowish fluorescence show mode homogenisation temperatures of 135-140 ºC (n=35) and oil FI showing yellowish fluorescence and brown colour under transmitted light have a homogenisation mode of 100-110 ºC (n=7). Aqueous FI homogenise between 80 and 130 ºC (n=7), without a clearly defined mode.

In the Corones Fm all types of FI show homogenisation to the liquid phase. Oil FI homogenise at relative low and high temperatures (Fig. 3 B); mode between 55-60 ºC (n=32) for oil FI showing yellowish fluorescence and 90-95 ºC (n=15) for oil FI showing yellowish fluorescence and brown colour under transmitted light. Occasionally, oil FI with yellowish fluorescence, brown colour, showing the biggest sizes (up to 32 µm) and the largest vapour bubbles do not homogenise below

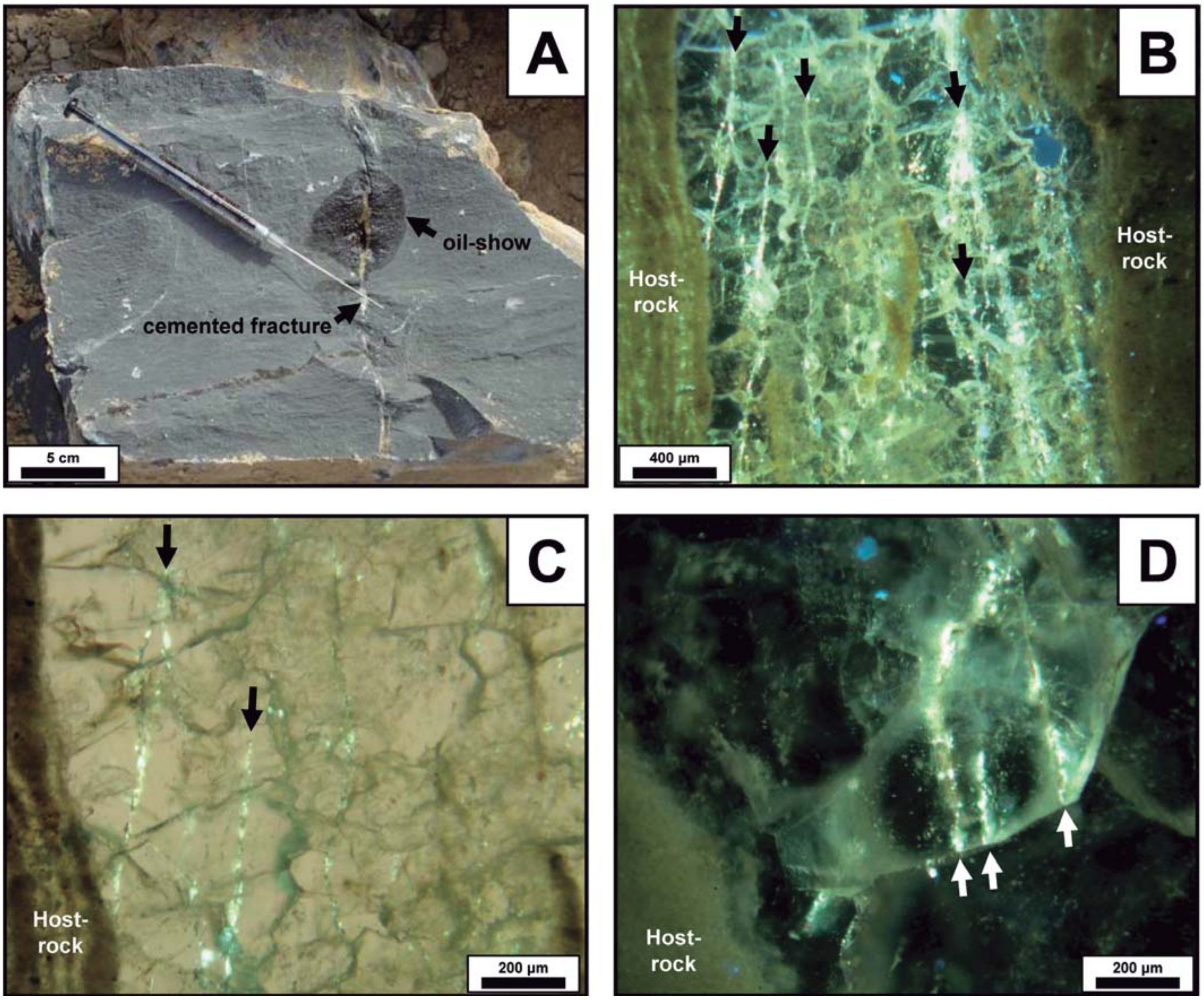

Fig. 2.- (A) Oil show associated to a fracture filled by carbonates in the Armàncies Fm (shelf facies, Terrades area); (B) Oil FI with yellow and blue fluorescence occurring in the Armàncies Fm fractures; note the high abundance of oil FI (combined transmitted and UV 365 nm light); (C) Detail of the previous microphotograph showing trails of yellow fluorescent oil FI occurring in several calcite crystals (crossed nicols and UV 365 nm light); (D) Trails of yellow fluorescent oil FI in the calcite-cemented fractures of the Corones Fm (crossed nicols and UV 365 nm light). Note the short length of trails, which occur only in one calcite crystal.

Fig. 2.- (A) Fractura cementada en la Fm. Armàncies (en facies de plataforma, Terrades) donde se aprecia el petróleo expulsado de forma natural; (B) Inclusiones fluidas de petróleo con fluorescencia amarilla y azul en las fracturas de la Fm Armàncies. Obsérvese la gran abundancia de inclusiones fluidas de petróleo (luz transmitida combinada con luz UV; 365 nm); (C) Detalle de la fotografía anterior donde se observa como las trazas de IF de petróleo (con fluorescencia amarilla) están presentes en varios cristales del cemento de calcita de las fracturas de la Fm Armàncies (nícoles cruzados y luz UV; 365 nm); (D) Trazas de inclusiones fluidas de petróleo (fluorescencia amarilla) en el cemento de calcita de las fracturas de la Fm Corones (nícoles cruzados y luz UV; 365 nm). Obsérvese como las trazas sólo afectan a un cristal de calcita.

165 ºC, which is the maximum temperature that wafer reached when the other populations of inclusion were measured. Aqueous FI homogenise to liquid, which takes place at the mode range between 110-115 ºC (n=14).

Discussion

One of the most significant aspects of the studied cemented fractures is the high abundance of petroleum FIs (Fig. 2 B) in the Armàncies formation, whereas the abundance in Corones fractures is more variable. The petrographic study of fluid inclusions revealed the relationship between diagenetic growth of the host mineral and trapping of the inclusions. The observed short trails of oil FI are clearly cross-cutting one or two calcite crystals in the Corones Fm, which suggest a secondary origin. In contrast, the high abundance of oil fluid inclusions in Armàncies Fm and their occurrence as long trails, parallel to the strike of the fracture suggest a primary origin (Van den Kerkhof and Hein, 2001). Timing of oil migration was therefore coeval with the fracture cementation in the Armàncies Fm. In the Corones Fm migration must have occurred at a later time than the calcite cementation of fractures.

Fluorescence was very effective for distinguishing oil and aqueous FI, and different populations of oil inclusions. Petroleum emits light in the visible range, whereas aqueous fluids are non-fluorescent. The fluorescence emission represents a very important fingerprint

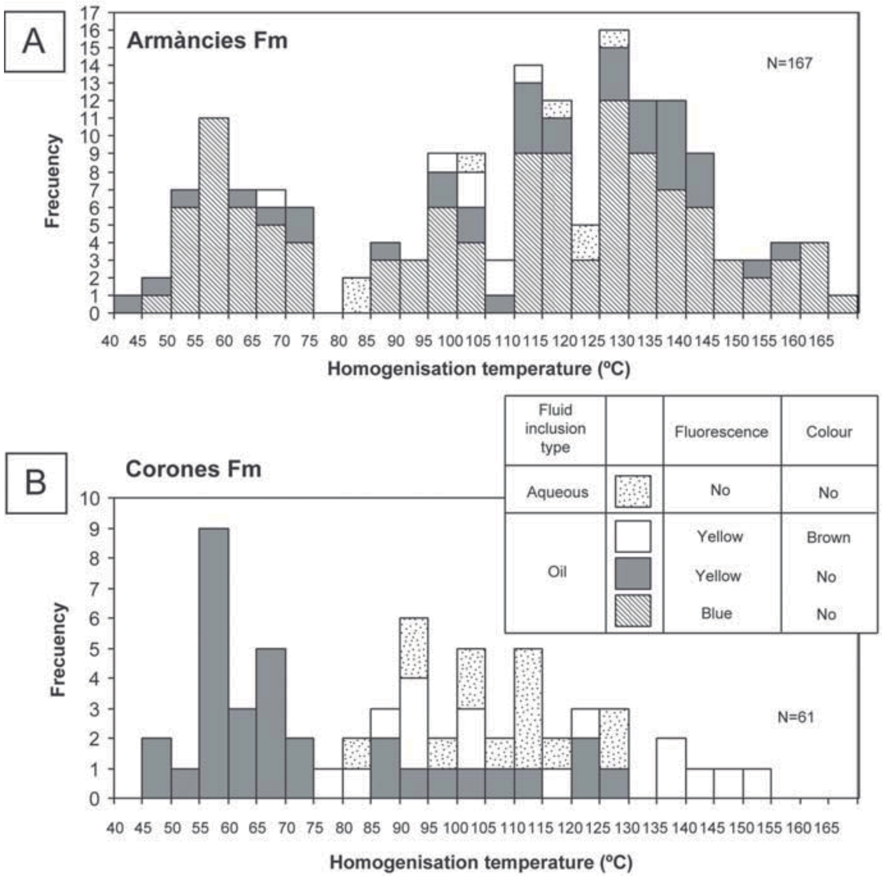

Fig. 3.- Microthermometry of oil and aqueous inclusions in the Armàncies Fm (A) and the Corones Fm (B).

Fig. 3.- Histograma de temperaturas de homogeneización para las inclusiones fluidas de petróleo y acuosas en la Fm Armàncies (A) y en la Fm Corones (B).

on composition. The heavy oils show fluorescence emission at higher wavelengths than lighter oils based on the correlation between fluorescence and bulk fluid properties (i.e., API gravity; Stasiuk and Snowdown, 1997; Munz, 2001). Thus, the yellow fluorescence of oil fluid inclusions indicates a heavy oil composition and the blue fluorescence lighter oil, possibly a gas-condensate type. So, Corones Fm fracture-fillings trapped only heavy oil, whereas the Armàncies Fm fracture-fillings recorded the presence of both heavy and light oil.

Microthermometry revealed that most of the petroleum inclusions homogenise at lower or similar temperature than the aqueous inclusions (Fig. 3 B) as many other authors have reported in the literature. In sedimentary systems, the trapping temperature is often close to the homogenisation temperatures of aqueous inclusions. The lower homogenisation temperatures of coeval oils commonly reflect that the oils are undersaturated with respect to gas content.

The large range in homogenisation temperatures of oil inclusions is clearly caused both by variations in composition and in pressure and temperature conditions of trapping. These variations may be time-related, reflecting differences between different generations of inclusions. However, there are several processes, which can result in almost contemporaneous variations: i) pressure fluctuations may occur during fracturing; and ii) processes like biodegradation may rapidly result in a large range of compositions within small areas. In order to quantify the pressure and temperature conditions of trapping, the composition of the oils must be known. Future work will include fluorescence spectrometry of oil seeps and fluid inclusions, compositional analyses of seeps and PVT modelling.

Conclusions

Fluid inclusion preliminary data revealed that oil migrated through fractures coevally with the precipitation of carbonate cements in the Armàncies Fm. In contrast, oil was trapped at a later time than the calcite cementation of fractures in the Corones Fm. Oil composition based on fluorescence colours suggests that fluid inclusions in Corones Fm fracture-fillings are heavy oils. Armàncies Fm fracture-fillings recorded the presence of both heavy and light oils. Future work involving fluorescence spectroscopy and pressure-volume-temperature modelling will help to unravel if variations in fluorescence and homogenisation temperatures are related to differences in composition or trapping conditions.

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