Advances in Hydrocarbon Fluid-inclusion Microanalysis and Pressure-volumetemperature Modeling: Diagenetic History, Pressure-temperature, and Fluid-flow Reconstruction— A Case Study in the North Potwar Basin, Pakistan

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ABSTRACT

S everal advances have been made for the reconstruction of fluid circulations and diagenetic history in subthrusted petroleum reservoirs because of the combination of the in-situ microanalysis of hydrocarbon fluid inclusions by Synchrotron Fourier transform infrared spectroscopy and PVTX modeling coupled to diagenetic history and tectonic setting. Integrated study has been made in the Eocene Chorgali formation (North Potwar Basin, Pakistan), where the shallow-marine carbonates formed important fractured reservoirs. Hydrocarbon fluid inclusions recognized in authigenic quartz and calcite from

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hydroveins show atypical association of CO₂-rich light oil depleted in H₂O in sulfatesquartz-calcite along simultaneous dissolution recrystallization processes at micrometer scale. Synchrotron Fourier transform infrared spectroscopy analyses, microthermometry, and pressure-volume-temperature modeling led to the beginning of quartz and calcite recrystallization at no more than 75–85°C and 150–180 bar in conditions of sulfate-calcite transformation. Temperatures of 150°C measured in aqueous fluid inclusions from calcite hydroveins are in favor of a thermosulfatoreduction mechanism. Early diagenetic sulfates are reduced by organic acids, and CO₂ comes from organic matter decomposition and/or previous decarbonation. A second phase of quartz growth is evidenced by the homogeneous entrapment in fluid inclusions of more mature oil in 60% CH₄ and a large amount of water at temperatures reaching 150–170°C. This late production of CH₄ agrees with δ^{13} C depletion (–20 and –36‰) measured in veins and the crystallization of saddle dolomite.

Thrustpack[®] modeling shows that the onset of hydrofracturing and quartz precipitation at 1.5 km (1 mi) depth and 15–10.8 Ma (middle Siwalik) began when temperatures of $65 \pm 10^{\circ}$ C were reached at the end of sedimentation in the basin. It lasted until 4–6 km (2.5–4 mi) depth at temperatures as much as 170°C and reached the development of the thrust sheet at 5 Ma. Thus, circulations of hydrocarbon-rich fluids may be considered in thermal equilibrium with host rocks in both cases. The oil could then be derived from source rocks in the deep Mesozoic formation for the first input. The second input originated from the deep part of the basin itself and mixed with tectonic and meteoric water along the circulation pathways. The fluids are mainly driven by tectonics. They are expelled from the hinterland farther to the north and move updip toward the south in the Chorgali conduits, below the Kuldana seals. The potential source rock for organic matter is known as type II and type III kerogens in coal and black shales from the Paleocene.

INTRODUCTION

As migration of oil in reservoirs involves a multiphase mixture of oil, gas, and water (e.g., Rudkiewicz et al., 1994), fluid inclusions entrapped in diagenetic minerals commonly contain hydrocarbons. Hydrocarbons are allowed to migrate in a mixed phase of oil and water, and the oil-bearing fluid inclusions formed during diagenetic events are in the immiscible region and can be made up of pure oil or a mixture of oil and water in any proportion (Rudkiewicz et al., 1994). Since their first description by Murray (1957) in fluorite mineral, several studies involving the composition and densities of these particular fluid inclusions have been made for understanding the pressure-temperature (P-T) conditions of fluid circulations in sedimentary basins and ore deposits (reviewed in Roedder, 1984; McLimans, 1987; Karlsen et al., 1993; Goldstein and Reynolds, 1994; Goldstein, 2001). A combination of trapping temperature, molecular composition, and isochoric pressure-volume-temperature (PVT) modeling of oil-bearing fluid inclusions lead directly to define the P-T conditions of the fluid circulations that occurred during structural events. The microanalyses of several phases associated with hydrocarbons found in these fluid inclusions as dissolved components or daughter minerals aim to define the conditions of diagenesis along these fluid circulations. In subthrusted reservoirs, data from fluid-inclusions lead directly to the reconstruction of the diagenetic history of sediments during syntectonic deformation (Larroque et al., 1996; Guilhaumou et al., 2000; Benchilla et al., 2003).

The trapping temperature is currently measured by microthermometry (Roedder, 1984), and the molecular composition has been tentatively obtained by various destructive techniques involving decrepitation (Barker and Underwood, 1992), crushing, and leachates analyses (George et al., 1998). From exceptionally large fluid inclusions (Guilhaumou et al., 2000), the composition and biomarkers were obtained by individual extraction under the microscope and gas chromatography-mass spectrometry (GCMS) analysis, but the analysis of the C1-C5 fraction is missing. Jones and Macleod (2000) proposed a sophisticated, time-consuming methodology to extract and clean up the sample before crushing for leachate analyses. The main limitations include a possible contamination during the extraction and the mixing of several generations of oil. Additionally, oil-water fluid inclusions are commonly encountered in heterogeneous

trapping; the use of hydrocarbon isochores may be inappropriate in such fluid inclusions, because it precludes the linking of the individual homogenization temperture with the real composition for PVT modeling.

In the last 10 yr, advances in molecular infrared microspectrometry (Guilhaumou et al., 1990; Rankin et al., 1990; Pironon et al., 2001) enabled us to perform quantitative, nondestructive molecular analyses in a single fluid inclusion under the microscope. The size of the fluid inclusions analyzed is currently restricted to the wavelength of the incident beam $(20 \,\mu m)$. The interfacing of a Synchrotron source to a microscope aims to overcome this limit and to perform analyses and mapping of the components at a few-micrometer scale. Using internal calibration, semiquantitative analyses can be done, and the composition of individual fluid inclusions can be linked directly to its density. At the same time, progress in isochoric modeling using modified equations of state (Aplin et al., 1999; Guilhaumou et al., 2000; Thiery et al., 2000; Benchilla et al., 2003) led us to calculate thermodynamic properties, i.e., the phase envelopes and isochoric P-T path from analytical data of petroleum-bearing fluid inclusions.

In this work, in-situ microanalyses, microthermometric data, and isochoric modeling of petroleum fluid inclusions from cemented fractures of the Eocene Chorgali reservoir (Potwar Basin, Pakistan) have been performed and integrated with kinematic and thermal two-dimensional basin modeling. Then, the diagenetic history could be related to the burial and thermal evolution of the reservoir. Finally, an interpretation on the way these parameters controlled the quality of the reservoir could be deduced (Benchilla, 2003).

GEOLOGIC SETTING

The Potwar Plateau and Salt Range are located in the southwestern foothills of the Himalayas in northern Pakistan. The region extends more than 120 km (75 mi) from the main boundary thrust in the north to the Jhelum River in the south. The Jhelum River limit constitutes an ill-defined border of the Potwar Plateau to the east, whereas its boundary is rather sharply defined by the Mianwali reentrant to the west (Figure 1A).

Summary of Sedimentology and Diagenesis of the Chorgali Formation

Shallow-marine carbonate strata of the Eocene Chorgali formation form an important hydrocarbon-producing horizon in the northern part of the Potwar Basin (northern Pakistan, Figure 1B). Based on limited core samples from the Dakhni gas-condensate field and on data gathered from an outcrop analog located at Chorgali Pass north of this producing field, the sedimentary, early diagenetic, and fracture-related characteristics of this dualporosity reservoir were studied and compared with fold and thrust belt evolution of Benchilla (2003).

The paragenetic sequences were defined from petrography and microtectonic data. Details may also be found in Benchilla (2003). The Eocene succession represents a shallowing-upward sequence, starting with open-marine, bioclastic, medium-bedded limestones, which grade into fabric-destructive, massive sucrosic, and subsequently, fine-crystalline dolomites. The presence of anhydrite nodules and chicken-wire-shaped calcite pseudomorphs after anhydrite, as well as the existence of dolomitized algal mats, points toward restricted sedimentary conditions. The near-surface sedimentation conditions are also reflected by the presence of flat channel conglomerate and breccia beds in the upper part of the dolomites. The breccias display features typical for early diagenetic evaporite collapse breccias. These dolomites, which are 15 m (50 ft) thick, are overlain by a 32-m (105-ft)-thick shale and marl succession, in which few lacustrine limestone beds are intercalated. Subsequently, a few meters of pedogenetically overprinted marine limestones develop below the regionally recognized Kuldana sealing shales, above which Fateh Jang conglomerates occur. This is followed by shales and fine-grained sandstones of the Miocene Murree Formation that unconformably overlies the Eocene strata. The δ^{18} O and δ^{13} C values of the dolomite host rock test for marine dolomites that were recrystallized by meteoric water infiltration. The marine limestones were also affected by this recrystallization and possibly by additional interaction with hot fluids.

Fracturing

Late diagenesis is mainly characterized by hydrofracturing, whereby at least seven distinct fracturing (Figure 2) episodes were recognized. They are well developed in the limestones just below the Kuldana shales.

An attempt was made to characterize individual vein generation as recognized from petrography and by its stable isotopic signature, as described in Figure 1C. In general, there is a major overlap in stable isotopic composition, both in δ^{13} C and $\delta^{18}O_{PDB}$ between the vein generations V1 and V5. A clear covariant behavior between both parameters is present. Authigenic quartz developed in these hydroveins during mesogenesis as diagenetic crystals with carbonates, but they could not be dated precisely. They are surprisingly rich in primary and pseudosecondary (Roedder, 1984) hydrocarbon-bearing fluid inclusions.

Veins-filling calcite developed prior to quartz in the fractures in which anhydrite and gypsum needles and barite minerals are commonly observed. In some calcite crystals, two generations of small-sized $(1-5 \ \mu m)$, primary biphasic oil fluid inclusions are distinguished by



FIGURE 1. (A) Geological setting of the Potwar Plateau and Salt Range (modified after Roure et al., 1999). MBT = Main Brain thrust; NPDZ = near Potwar deformation zone.

ultraviolet (UV) fluorescence, attesting to the fact that they were formed during the migration of two successive oil-bearing solutions. Locally, open fractures are cemented by authigenic quartz rich in hydrocarbon fluid inclusions. Some partly dissolved and recrystallized crystals of carbonates and sulfates are accompanying the quartz crystallization. Several generations of hydrocarbon-bearing fluid inclusions were observed in both diagenetic quartz and calcite. Isolated crystals made up of recrystallized carbonates are common in quartz. They show elongated primary oil inclusions filling cavities, having a fluorescence emission in the light blue region. Some dissolution features are observed, suggesting intensive dissolution-recrystallization processes during the hydrocarbon entrapments; however, there is no indication of fractures or cleavages, supporting the hypothesis of a secondary oil recharge of the primary cavities.

FLUID-INCLUSIONS DATA

Analytical Process

Unmounted, doubly polished sections were prepared for the study of fluid inclusions by optical observations in transmission and polarized light. Fluorescence emission was collected during transmission using a UV source (365 nm). Microthermometric runs were carried out on aqueous and hydrocarbon fluid inclusions to measure the temperatures of the phase transitions (homogenization temperature, $T_{\rm h}$; temperature of first melting or eutectic temperature, $T_{\rm fm}$; and last melting temperature, $T_{\rm mi}$) using a Linkam THMSG 600 heating-cooling stage coupled to a video system controlled by a computer. Fourier transform infrared molecular microanalyses in point spectroscopy and mapping modes were then acquired using a Synchrotron radiation as excitation source in the midinfrared range on selected samples in the 1000-4000-cm⁻¹ frequency domain. We used a $3 \times 3 \mu m^2$ aperture ($32 \times$ Schwarzschild objectives) and a confocal arrangement. The experimental station consists of an FTIR Thermo-Nicolet Magna 860 spectrometer (spectral range = $650-4000 \text{ cm}^{-1}$) coupled to an optical microscope (Nicplan), beamline Mirage, Laboratoire pour l'Utilisation du Rayonnement Électromagnétique (LURE), Orsay, France. The high brightness of the Synchrotron source allows an aperture setting of $3 \times 3 \,\mu m$ while achieving high signal-to-noise spectra. These aperture dimensions set the probed area close to those obtained by Raman microspectrometry $(1 \times 1 \mu m)$. A Linkam microthermometric stage was adapted to the microscope by Thierry Marin (LURE), allowing us to perform analyses from room temperature to 400°C. Error

FIGURE 1. (cont.) (B) The Chorgali Pass area: Emplacement of the three units recognized and interpreted cross section of the stratigraphic outcroppings.

is presented at ±1°C. Heating runs in these experiments were performed from 25°C to homogenization temperatures (T_h) using a heating rate of 1°C/min. The liquid/vapor volume ratios of hydrocarbon fluid inclusions have been measured at room temperature through a microscope using a Biorad Radiance confocal laser unit and an Olympus X100 dry objective using the method described in Aplin et al. (1999).

Description of Oil-bearing Fluid Inclusions in Authigenic Quartz and Calcite

In the authigenic quartz formed in veins (Figure 3A), two generations of hydrocarbon fluid inclusions are identified. First are exceptionally large-sized primary fluid inclusions (Figure 3B), ranging from 10 µm to 1.2 mm. They systematically contain a liquid and vapor organic phase and one or several brown bodies. The liquid oil displays a light yellow color and gives a fluorescence emission in the light blue region of UV light,

whereas the brown parts do not give any visible fluorescence (Figure 3C, D). Such brown bodies were also encountered in oil-bearing fluid inclusions hosted in fluorite from other areas studied in Pakistan (Guilhaumou et al., 2000; Benchilla et al., 2003). They were commonly observed in fluid inclusions hosted in quartz and fluorite occurring in veins from the Mississippi Valley-type (MVT) deposits and found as ore mineralizations (Richardson and Pinckney, 1984; Roedder, 1984) closely associated to petroleum migration episodes. These bodies are organic phases and are

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considered to be asphaltenes formed inside fluid inclusions by the precipitation of the heavy-oil fraction by the dissolved CO₂ and/or a decrease in temperature and pressure (Guilhaumou et al., 1990). They should be distinguished from bitumens formed by bacterial sulfate reduction (BSR) and/or thermosulfatoreduction (TSR) (never observed in diagenetic mineral assemblages). In these samples, additional pleochroic minerals are commonly seen in the oil, either inside the fluid inclusions or close to the oil-quartz interface (Figure 3B). They could be daughter minerals and/or mechanically







FIGURE 1. (cont.) (C) Fracture succession of the Chorgali Formation in the Chorgali Pass section from eogenesis (Eo) to telogenesis (Telo) (modified from Benchilla, 2003). The calcite in V7 fractures and development of Fe oxides are not dated.

entrapped phases (Roedder, 1984). Numerous, very small, unidentified solid particles ranging from 1 to 5 μ m are systematically scattered in the oil phase of some primary cavities (S in Figure 3B). This was never observed before in such oil fluid inclusions and relates probably to a very specific composition of the migrating fluid during the growth of a single crystal.

Another generation of fluid inclusions called pseudosecondary fluid inclusions occurs as polygonal features subparallel to the walls of authigenic crystals (Figure 3E, F). Their entrapment was directly controlled by a lateral overgrowth of quartz crystals. They are smaller than primary fluid inclusions, range from 1 to $10 \,\mu m$ in size, and constitute regular arrangements. Their fluorescence emission under UV light is in the yellow to orange region. The homogenization temperatures of primary hydrocarbon-bearing fluid inclusions in quartz range between 40 and 75°C, with a maximum at 55-60°C. Homogenization temperatures (T_h) of the generation of pseudosecondary fluid inclusions range from 70 to 125°C, with a peak at 70–75°C. This later distribution is similar to the first one, suggesting a continuous increase in temperature during the quartz growth. However, a correction caused by the difference in compositional parameters should be applied before comparison.

Some small-sized authigenic calcite crystals that crystallized inside the authigenic quartz also contain biphasic hydrocarbon fluid inclusions (Figure 4), as revealed by their fluorescence emission in the light blue region. Their small size (less than 5 μ m) does not permit the measurement of their homogenization temperatures.

OIL COMPOSITION: SYNCHROTRON FOURIER TRANSFORM INFRARED SPECTROSCOPY MICROANALYSIS

Molecular analyses and mapping were performed by Synchrotron infrared microspectroscopy on the two generations of hydrocarbon fluid inclusions, which are described below in quartz and in primary fluid inclusions in calcite crystals.

Primary Oil Fluid Inclusions in Authigenic in Quartz and Calcite

The absorbance spectra from primary fluid inclusions in quartz (Figure 5A) show the characteristics of the early petroleum generation. These fluid inclusions are mainly composed of linear alkanes that are detected in the whole cavity by their absorption at 2800-3000 cm⁻¹ (Colthup et al., 1990). They have a high CO₂ content, now occurring as (1) a phase dissolved in the alkane fraction (absorption at 2336 cm^{-1} ; Barres et al., 1987; Guilhaumou et al., 1990, 1998; Berreby, 1983) and as (2) gaseous CO_2 under pressure in the vapor phase (additional typical absorption at 2340 cm^{-1}). The molecular mapping indicates that most of the CO₂ and CH₄ (main absorption at 3010 cm^{-1}) are now concentrated in the vapor phase. This is consistent with the thermodynamic properties of such organic-fluid systems in current pressure-temperature reservoir conditions. Aromatics and water are not detected. Semiquantitative analyses using an internal CH₄ calibration and following the procedure of Pironon et al. (2001) have been performed on several primary fluid inclusions in five different quartz crystals. They lead us to define a typical composition of aliphatic light oil in C_{10} – C_{12} enriched in CO_2 , with an average content of 30% CH₄ and free from water. The microanalyses of all fluid inclusions show that this oil

FIGURE 2. Microscopic observations on thin sections showing the main types of veins and cements along the fracturing episode in the Chorgali Pass: (A) Tectonic stylolites layer-parallel shortening (LPS) crosscutting the veins V2. (B) Calcite cementation in "crack and seal" in V3 calcite veins. (C) Several generations of veins are distinguished by their cathodo-luminescence emission. (D) The pyrites (Py) are crosscut by V6 and V7 veins. (E) Calcite veins associated to barite crystals. (F) Fibrous anhydrite as cement in dolomites (polarized light). (G) Other examples of fractures filled with anhydrites; some oil droplets may be seen in the intergranular spaces. (H) Bioclastic carbonate wackestone with tectonic stylolites LPS, in transmitted light showing the opening of a secondary porosity (black arrow).





was entrapped homogeneously at the beginning of the crystal growth (Table 1).

Very small crystals with sizes between 1 and 6 µm are scattered in oil (Figure 5B); they show an additional absorption at 2520 cm⁻¹, which is unambiguously attributed to the CO_3^{2-} bonds and identifies these solid phase as carbonates (Farmer, 1974; Salisbury et al., 1991). Comparison with some spectra recorded from calcite hosted in quartz shows that they are probably small seeds of calcite minerals (Figure 5B). These solids have been observed dissolving at least partly during heating runs. Experiments were performed by heating this type of fluid inclusions using a microthermometic stage from room temperature to homogenization temperature under the Synchrotron IR beam. Some spectra recorded on the same point show the slow decrease of the CO_3^{2-} absorption until its complete disappearance at homogenization temperature (Figure 5B) and its subse(Mandal and Mandal, 2002). Crystal B shows an absorption near 2520 cm⁻¹, typical of carbonate microcrystals (Legodi et al., 2001). Some polarizing minerals 5–20 μ m in size are also identified as carbonates; they occur at the interface between quartz and oil in those fluid inclusions. This assemblage could represent the typical replacement of hydrated calcium sulfates [as gypsum or anhydrite(?)] by calcium carbonate as calcite, the reaction being fossilized because of the formation of primary oil fluid inclusions in authigenic quartz.

Primary oil fluid inclusions in coeval calcites entrapped in quartz (Figure 6) have been tentatively analyzed by Synchrotron Fourier transform infrared spectroscopy (SFTIR). To avoid the effect of the overlapping of alkane absorption to the absorption of carbonates in the 2800–3000-cm⁻¹ range, a spectra of the calcite matrix having the same intensity (calibrated on the 2520-cm⁻¹ absorption) has been subtracted (Figure 6,

FIGURE 3. Different types of hydrocarbon fluid inclusions in authigenic quartz. (A) Typical authigenic quartz; (B) primary oil fluid inclusions in small solid phases (S); (C, D) primary oil fluid inclusions in transmitted and UV light; (E, F) pseudosecondary fluid inclusions in external crystal growth in transmitted and UV light.

quent reappearance during decreasing temperature. This identifies these carbonates as calcite daughter minerals.

The FTIR microanalysis of a large-sized hydrocarbon fluid inclusion (Figure 5C) reveals an exceptional assemblage of minerals entrapped in oil as a key point for diagenesis reconstruction. A round-shaped, highly pleochroic sulfate crystal A (polarized light) similar to some observed inside quartz occurs close to a small crystal B in the center of the fluid inclusions. Crystal A has a high absorption in the OH area, having a main band near 3620 cm^{-1} . This suggests that this mineral is a partly dissolved crystal of hydrated sulfate that could be the hemihydrate calcium sulfate

FIGURE 4. Primary hydrocarbon fluid inclusions in calcites recrystallized inside authigenic quartz in transmitted and UV light.

spectrum 4). This led to an oil composition comparable to the composition of the oil fluid inclusions in quartz (Table 1) with no water being detected. These results hereafter would confirm the crystallization of diagenetic quartz and calcite at the same time in the same organic fluid environment enriched in CO_2 .

Pseudosecondary Oil Fluid Inclusions in Quartz

The SFTIR analyses of the oil fluid inclusions of the second generation (Figure 7) indicate a water-oil mixture depleted in CO_2 (not detected). Molecular mapping shows that the trapping is homogeneous from one inclusion to another along

crystal-growth zones. In particular, the oil phase always appears associated with a noticeable water phase. High detection level of FTIR suggests that the water is not the dominant phase but is just wetting the walls of the cavities. Therefore, such low quantity allows water to be dissolved in oil at least partly during migration. Quantitative estimates led to a more mature hydrocarbon in $C_{15}-C_{17}$, with a high content of CH_4 reaching 60% (Table 1). These compositions would indicate a more mature and/or partly degraded oil that is consistent with the difference in color (shifted in the red region) observed in the fluorescence emission under UV light (Korashani, 1986; Guilhaumou et al., 1990).

Aqueous Inclusions in Veins

Very few primary aqueous fluid inclusions were found on one quartz crystal only; they are generally not observed associated to oil fluid inclusions in quartz. Their $T_{\rm h}$ values display temperatures between 60 and 90°C (six measurements). The $T_{\rm h}$ values of primary fluid inclusions in calcite V3 (detailed in Benchilla,



2003) range from 120 to 150°C; the salinities range between 0.4 and 16.1 equiv. wt.% NaCl. The T_h values of late aqueous inclusions range from 40 to 140°C, with two distinct modes near 70 and 120°C, respectively. Salinities range between 0 and 30 equiv. wt.% NaCl, with a mean value at about 2 equiv. wt.% NaCl. The broad range in T_{mi} in all types of inclusions is best explained by the presence of fluid of different salinities (at least two fluids) that mixed (Parry et al., 1991). Such an observation, together with the occurrence of higher temperatures, has already been described by Muchez and Slobodnik (1996) and interpreted as the result of a complex history of mixing, stretching and/or leakage, and refilling of the cavities. However, the homogeneity in content of the oil fluid inclusion populations and the correlated higher temperatures-higher maturity of the hydrocarbon fluid inclusions (i.e., higher CH₄ content) suggest here an increase in temperature. The succession of several pulses of fluid migration is also attested by the differences in composition observed for the latter oil-bearing fluid inclusions mixed with water and without significant CO₂ at the periphery of quartz crystals. They are in agreement with the large



FIGURE 5. Synchrotron Fourier transform infrared spectroscopic microanalyses and mapping of primary hydrocarbon fluid inclusions. (A) Detection of CO_2 and alkanes into liquid oil phase and mapping of the CH_2 – CH_3 in primary fluid inclusions in quartz. Water is not detected. On the right side, comparison with a typical spectrum of the quartz matrix shows OH in the defects (3380 cm⁻¹). (B) Fourier transform infrared spectra of the solid microphases S included in the flat primary oil fluid inclusions during the heating experiment. The CO_3^{2-} absorption at 2520 cm⁻¹ recorded at room temperature is disappearing slowly until the homogenization temperature of 60°C is reached (T_h). The band reappears at the same point during cooling. (C) Microphothographies of primary oil fluid inclusions (transmitted and polarized light) in quartz and punctual FTIR analyses of a typical association of mechanically entrapped minerals. The bands are characteristics of a sulfate-hydrated mineral, hemihydrate(?) (solid, 1), and calcite (solid, 2) in the 2000–4000-cm⁻¹ spectral range. Spectrum 2 in the 2800–3000-cm⁻¹ range is composed of both alkane and carbonate absorptions. Absorption of oil nearby in spectrum 3 is shown for comparison in the same spectral range. The 3381-cm⁻¹ absorption belongs to OH in the quartz matrix. Abs = absorbance.

FIGURE 5. (cont.).

В

spectrum in isotopic δ^{18} O and Sr data reported by Benchilla (2003).

DISCUSSION

Two hydrocarbon-rich fluid circulations are identified during veining and diagenetic recrystallization. Both result from a homogeneous trapping of a single fluid system.

The first fluid was entrapped in large cavities in authigenic quartz and calcite cements. It is composed of a light oil enriched in CO₂. Water is surprisingly not detected, but OH is detected in the defects of the quartz matrix. This was soon observed in other samples from different occurrences (Guilhaumou et al., 1996). The injection of the CO₂ in previous oil may account for the asphaltene bodies that are systematically found inside these fluid inclusions only (never found in the host minerals) and are common in oil fluid inclusions from MVT deposits (reviewed in Roedder, 1984; Goldstein, 2001). The composition in mole percent derived from in-situ SFTIR microanalyses is nearly 30% CH₄, 60% alkanes, and 1% CO_2 , with an average chain length of C_{10} - C_{12} , which is close to that of normal oil (Montel, 1993). Almost the





same oil rich in CO_2 and without water detected is found in fluid inclusions hosted in recrystallized calcite, the overestimate of CH_4 being in the error margin in this case.

Some solid calcite minerals are identified inside primary fluid inclusions as mechanically entrapped and/or daughter minerals. Fourier transform infrared spectroscopy during heating runs until homogenization temperature unambiguously shows that some of these calcite "seeds," which are scattered inside the oil phase, are at least partly disappearing in the liquid phase at homogenization temperature. Some carbonates are also observed to be closely associated with hydrated sulfates, partly dissolved and probably

Reference	Primary Fluid Inclusions					Pseudosecondary				
	A1 (6)	A2 (8)	Q12 (6)	Q6 (5)	Q5P (5)	IF3 Ca(5)	Q18 (6)	IF4 S1	IF5 S2	IF6 S3
SH ₂ O	0	0	0	0	0	0	0	++	++	++
S1 CH ₃ /CH ₂	0.65	0.57	0.69	0.70	0.70	0.81	0.58	0.61	0.61	0.63
S2 CH ₂ /CH ₃	1.54	1.74	1.45	1.43	1.43	1.24	1.72	1.65	1.64	1.57
S CH ₄ /S alkanes	0.11	0.07	0.09	0.08	0.09	0.14	0.09	0.29	0.31	0.32
Chain length equiv.	C10	C10	C10-C12	C12	C12	C10	C12	C17-C19		
CH ₄ (mol%)	37.33	30.36	33.00	30.00	31.00	41.00	34.00	62.61	64.13	63.29
CO ₂ (mol%)	0.09	1.29	0.00	3.10	5.00	0.50	2.22	0	0	0

TABLE 1. Composition of hydrocarbon fluid inclusions by SFTIR for primary fluid inclusions and pseudosecondary alignments in authigenic quartz.

preserved in intermediate state by the formation of oil fluid inclusions by heterogeneous trapping during the dissolution-crystallization process. These results are of prime importance, because they identify at micrometer scale the replacement of sulfates by carbonates, which implies a mechanism of sulfatoreduction like BSR and/ or TSR, whereby sulfates are reduced by hydrocarbons with a concomitant oxidation of the organic matter. The hypothesis of TSR is supported in this case by several arguments. Temperatures are slightly lower than 100°C,



generally considered for the beginning of TSR conditions, but higher than 80°C, which is stated as the upper limit for bacteria in BSR. The TSR has no sharply defined minimum temperature (Worden et al., 1995; and Bildstein et al., 2001, considered that it may be effective at low temperature, e.g., 80°C). In this occurrence, TSR may have occurred in the range of 85-140°C, the upper limit being near the entrapment of the second generation of oil fluid inclusions in quartz (e.g., 140-160°C). The reactants are branched and n-alkanes, which are the main components of the fluid inclusions, instead of organic acid involved in BSR.

FIGURE 6. FTIR microanalysis and calculation of CH_2/CH_3 ratio from hydrocarbon fluid inclusions in recrystallized carbonates. The spectra of the matrix at the same intensity (2) are subtracted from the whole spectra (1) to obtain oil spectra in (3). In (4), the spectrum of the carbonate matrix nearby (uncalibrated) is shown. FI = fluid inclusions; Hcc = hydrocarbons. **FIGURE 7.** FTIR microanalysis of the pseudosecondary oil fluid inclusions in quartz. Alkanes and a large amount of water are systematically detected. The alkanes mapping show their regular repartition in the quartz matrix.

In this sample, water content is very low (undetected by FTIR), indicating that water release during the reaction is negligible (Machel, 2001). In TSR mechanisms, the main organic reactant is considered to be CH₄ (Bildstein et al., 2001). However, we know very little about the chemistry of such possible reactions with low water activity, because most of the TSR studied are located in the gas-water transition zone of petroleum reser-



voirs (gas cap), where hydrocarbons and large amount of water are present. An explanation could be that rapid fluid circulations induced in fractures along tectonic evolution, as observed in thrust belts, probably change the condition of the chemical reactions. As exploration is now developing in these zones, models considering these parameters will be very helpful.

The second fluid influx consists of a mixed wateroil solution enriched in methane and depleted in CO_{2} , with a composition of 60% CH₄ and an average chain length of C₁₅, thus indicating a more mature hydrocarbon source. This fluid is entrapped along parallel crystal growth in the outer parts of quartz crystals. It probably migrated when carbonates were stabilized and during a temperature increase of the circulating fluid, as attested by the high CH₄ content, the increase in chain length, and higher homogenization temperatures. The homogeneity of the content for the fluid-inclusion population evidenced from SFTIR mapping in these late hydrocarbon fluid inclusions does not support the hypothesis of a secondary in-situ modification process of fluid inclusions, such as stretching or refilling of old cavities through overheating and/or fracturing (Roedder, 1981; Goldstein and Reynolds, 1994).

PVTX Properties of the Hydrocarbon Fluid Inclusions

The liquid-vapor curve and isochoric P-T path of the oil content in primary hydrocarbon fluid inclusions have been calculated using a software developed at the Institut Français du Pétrole (Ungerer and Batut, 1997) and validated on Pakistani samples from Baluchistan by Guilhaumou et al. (2000) and Benchilla et al. (2003). The software uses a modified Peng Robinson equation of state to do PVT iterative runs to calculate the liquidvapor curves and the fluid inclusion isochores from the oil composition analyzed by GCMS and the PVT properties of the oil fluid inclusions. These are later defined using the liquid/gas volume ratio and the two fitting parameters α and β controlling the natural hydrocarbon distribution in the database of Montel (1993). More details on the optimization procedure may be found in Benchilla et al. (2003). The first version has been adapted to consider only the semiquantitative composition derived from SFTIR microspectrometry as analytical data (instead of GCMS analyses). The C1 fraction measured by FTIR (Pironon et al., 2001) is used as an additional parameter to the liquid vapor volume ratio at room temperature measured by confocal microscopy (Guilhaumou et al., 2000). The two sets of data were checked and found to be in good agreement. Other models were developed by Aplin et al. (1999), and a similar approach has been developed recently by Thiery et al. (2000). In this new version of the model, we tried to be closer to the experimental data currently obtained by in-situ nondestructive analyses. We introduced the alkane equivalent, i.e., CH₂/CH₃ ratio, the experimental percentage of CO₂ and CH₄, and a fixed aromatic percentage of 25% corresponding to the alkane equivalent greater than C_5 (database, Montel, 1993). The phase envelopes and isochores have been calculated for seven primary hydrocarbon fluid inclusions hosted in

TABLE 2. Experimental data used for isochoric modeling of the primary hydrocarbon fluid
inclusions and resulting distribution parameters. The percent of gas is measured by UV confocal
microscopy. Homogenization temperatures $T_{\rm h}$ are also indicated. In inclusion A, the gas volume
is overestimated because of the large amount of solid phases inside the fluid inclusions (FI).
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Inclusion	Volume of Gas (µm ³)	Volume of FI (µm ³)	Volume of Oil + Bitumen	% Gas	T_h (°C)	CH4 (%)	CO ₂ (%)	R* CH ₂ /CH ₃ n-Alkanes (equ.)
E	64	1977	1913	3.35	60	29.7	1.13	1.45 C9-10
C (2)	101	2632	2531	3.99	65	31.8	1.2	1.43 C9-10
G	15	869	854	1.76	58	26	0.4	1.56 C10
D	38	2595	2557	1.49	56	27	0.4	1.62 C10
В	17	1478	1461	1.16	60	30	1.1	1.49 C9-10
A**	35	544	510	6.86	68	36	0.5	1.81 C12
C	47	3703	3656	1.29	55	26	0.8	1.49 C9-10

*R = area of CH₂ absorption/area of CH₃ absorption from spectra registered in fluid inclusions. This is expressed after internal calibration (Guilhaumou et al., 1998) as an equivalent of the hydrocarbon chain length because it could be compared with the database made by gas chromatography-mass spectrometry for oil types and compositions by petroleum chemists.

**Sure estimated gas volume.

different quartz crystals analyzed by SFTIR, with the data reported in Table 2. The volume ratios were measured by confocal microscopy with an accuracy of 0.1%. The α and β distribution parameters obtained from the data above in Chorgali led to a P-T path showing a slightly different phase envelope (cricondenbar) for inclusion A but a similar isochoric evolution for all fluid inclusions in quartz (Figure 8). However, the liquid/vapor ratio and CH₄ amount in case A may be overestimated because of the high asphaltene content.

Conditions of Fluid Circulations in Hydrofractures

Thrustpack[®] modeling led us to consider that the temperatures of $80 \pm 10^{\circ}$ C corresponding to trapping temperatures of primary hydrocarbon fluid inclusions were reached during the lower Siwalik (Benchilla, 2003). The burial would indicate corresponding pressures of 150-180 bar. Therefore, the entrapment of this fluid and quartz and calcite precipitation would have occurred at the onset of fluid migration and initial conditions close to 75-85°C and 150-180 bar (first hydrocarbon fluid inclusions entrapment), along with the replacement of sulfate by calcite. The hypothesis of sulfate reduction and calcite precipitation is supported by the presence of solid calcium sulfates closely associated to calcite inside hydrocarbon fluid inclusions. The association of sulfates and organic matter in sediments is thermodynamically unstable, and the branched and n-alkanes are considered as the main reactants for TSR mechanism in all diagenetic environments (Pierre and Rouchy, 1988; Machel, 2001). Along a second input, the fluids reached minimal temperatures of 125°C $(T_{\rm h} \text{ of the second hydrocarbon fluid inclusions entrap-}$ ment) during the second episode of peak oil generation and migration within water influx and late quartz precipitation. Temperatures as much as 150°C measured in aqueous fluid inclusions and low values of carbon and oxygen isotopes signatures for calcite in the hydroveins reported by Benchilla (2003) are in favor of TSR mechanism (Bildstein et al., 2001; Machel, 2001). The conditions agree for the second fluid input, the mechanism of the first input, and the beginning of sulfate-calcite recrystallization process, with very low amount of water presently being not well understood. The origin of CO₂ in primary oil generation may come from either the decarbonation of early calcite or the decomposition of the organic matter itself. High content of CH₄ and CO₂ depletion for the second generation of hydrocarbon fluid inclusions suggest a



FIGURE 8. Results of the isochoric modeling of primary oil fluid inclusions. Three main groups of fluid inclusions may be defined from their liquid vapor curves calculated from their chemical compositions and volumetric properties (Table 2); the isochores have the same P-T slopes but initiate at different pressures values. The entrapment P-T conditions fall in the range $80 \pm 5^{\circ}$ C and 165 ± 15 bar.

reducing environment. This is in agreement with low values of δ^{18} O for the hydraulic veins (-7.8 to -14.1‰), which represent high temperatures of crystallizations for calcite from meteoric water, i.e., 90–150°C. The low values of δ^{13} C (-7.81 to -14.55‰) in calcite veins reflect the conditions of TSR (Benchilla, 2003).

CONCLUSION

The combination of in-situ micro-FTIR analyses, microthermometry, and PVT modeling of the successive generations of hydrocarbon-rich fluid inclusions entrapped in the hydroveins of the Chorgali formation supports the hypothesis of hydrofracturing and diagenetic veining during the reduction of sulfates and calcite precipitation, along with an increase in temperature. The onset at near 75-85°C and 150-180 bar and final temperatures as much as 150-170°C suggests a TSR mechanism instead of a BSR. However, the two mechanisms may have followed each other along successive inputs of fluids in the hydroveins. The late production of CH₄, the depletion in δ^{13} C (-20 and -36‰) measured in the veins, and the crystallization of saddle dolomite (Benchilla, 2003) favor the TSR mechanism. The reactants may be mostly n-alkanes during the first input of light oil rich in CO₂, having very low water content, and then a mixture of more mature hydrocarbons enriched in CH₄ and acid waters coming from compaction and meteoric infiltration during the second input at temperatures higher than 140°C. The very low content of water (undetected by FTIR) in quartz cements and the presence of hydrated sulfates partially transformed in carbonates in primary oil fluid inclusions suggest that these reactions and quartz precipitations may occur when oil becomes present in the reservoir. Such quartz precipitations in the presence of organic fluid depleted with water were observed in diagenetic quartz formed in the Terres Noires (southeastern France; Guilhaumou et al., 1990, 1996).

The correlation of these data with Thrustpack[®] modeling (Benchilla, 2003) shows that hydrofracturing was initiated at 1.5 km (1 mi) depth and was reached at 15-10.8 Ma. It lasted until 4-6 km (2.5-4 mi) depth was reached at -5.7 Ma during the development of the thrust sheet in Dock Patan formation. The fluids appear in both cases in thermal equilibrium with the carbonaceous sediments around and are driven mainly by tectonics from the hinterland farther to the north to the Chorgali Pass. The origin of the oil in former circulation has to be found outside the Paleogene, in which organic matter was not mature. One hypothesis could be the migration of the oil from the deep Mesozoic sediments, where the source rock is known as being mature at near 15-

10.8 Ma. The later hydrocarbon fluid entrapment in quartz occurred when the sediments were in the oil window in the whole basin.

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