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New insights on rock alteration by oil: An *in-situ* investigation at the nano-scale using atomic force microscopy

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Abstract:
From oil-recovery, through environmental remediation of oil spills, to CO_2 storage in depleted reservoirs, the alteration of rock by oil is known to impact flow dynamics in porous reservoirs and hence controls the efficiency of reservoir development and environmental remediation projects. Whereas many studies focus either on the adherence of individual oil components in model systems or on the related macro-scale multiphase flow responses, this study investigates nano-scale mechanisms of oil alteration along the internal rock surface providing insights how these length scales interconnect. The use of atomic force microscopy allows to identify the location of oil along the internal rock surface after alteration by oil and after water flooding. The results show a persistence of water films in one out of three crude oils tested. Oil components were observed to adsorb patchy to the rock surface and fluid-fluid interfaces. After the waterflood, oil remains trapped within the roughness of the grain surface. These findings illustrate that underlying assumption of a homogeneous alteration along a grain surface, used for common wettability alteration models are too simplistic and may need adjustments for specific oil-brine-rock systems.

1. Introduction

In hydrocarbon reservoirs as well as oil spills into the environment, the alteration of rock or soil by the adsorption of oleic compounds is known to impact flow dynamics in the subsurface and to control the efficiency of reservoir development and environmental remediation projects (Amro, 2004; Donaldson and Alam, 2008). This process, often referred to as ageing, alters the wetting state, the preference of one fluid to stay in contact with the surface in the presence of another fluid. In narrow pores of a porous medium, the change in wetting manifests as a change in the pressure gradient needed to move a fluid/fluid interface. Thus, the wetting alteration may trigger changes in pore-scale displacement events: Rücker et al. (2019) and Mascini et al. (2021) reported oil-filling events to happen much slower in mixed-wet systems than the Haines jumps observed in water-wet systems (Haines, 1930; Armstrong et al., 2014). At the core-(Darcy)-scale, ageing manifests in the change in relative permeability - and capillary pressure - sa,turation functions used for the assessment of a reservoir's production capacity or remediation efficiency (Blunt, 2017). This process has the potential to change otherwise favourable conditions for fluid displacement in the reservoir to insufficient or vice versa.

However, how the various underlying mechanisms of age-

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ing constitute the macroscopic response is poorly understood. This currently limits our ability to recreate these processes for the laboratory assessment of cored rock contaminated by drilling fluids and how to model this behaviour in numerical simulations of fluid displacement in the reservoir. The polarity of oil and rock, asphaltene precipitation, disjoining pressure effects (Anderson, 1986; Basu and Sharma, 1996; Buckley et al., 1997; Tang and Morrow, 1997) were the molecular mechanisms found to be contributing to ageing. Furthermore, chemical and structural heterogeneities contribute at larger length scales (Kovscek et al., 1993; Xiao et al., 2024).

In many computational models, these processes are lumped into fitting parameters such as contact angles and shape factors (Valvatne and Blunt, 2004; Xiao et al., 2022). Contact angle variations are thereby supposed to reflect the molecular attributes of the wettability alteration, assuming that the process can be fully described through the adjustment of surface tension between the two fluids and the solid. Shape factors account for structural attributes, with the potential to inhibit oil-rock contact considered essential to the alteration of the surface.

In experimental work, ageing is addressed in various ways: In some studies, the reservoir core with the original fluids obtained from the drilling is used, acknowledging potential contaminations but assuming that this remains the best approximation of the original conditions (Anderson, 1986; Hassenkam et al., 2009). Others clean the entire core and aim to restore the conditions by reintroducing the liquids and exposing the sample again to reservoir temperature and pressure (Anderson, 1986). Some restore the reservoir conditions with static ageing (Lin et al., 2019), where the samples are first saturated with brine and then desaturated with crude oil, e.g. with a centrifuge, and after the sample is placed into a vessel reflecting reservoir temperature and pressure conditions. Again others restore the system with dynamic ageing (Alhammadi et al., 2017), during which the oil is continuously injected through the rock, whilst the temperature and pressure are raised to reflect the reservoir conditions. Proponents of static ageing, emphasise that the system needs to equilibrate to reflect the conditions in the reservoir, whilst proponents of dynamic ageing doubt that the apparent equilibrium within the experiments would match the state of the reservoir. In core floods, the ageing procedure mostly causes a shift of relative permeability-saturation curves to more oil-wet characteristics (Anderson, 1986), with dynamic ageing being assumed to turn the sample more oil-wet than static ageing due to the higher amount of surface active components exposed to the rock surface as the oil is continuously flowing.

Insights into the nature of wettability alteration by oil, therefore, can significantly contribute to the choice of measurement type or computational model and improve the accuracy of the obtained data. In this study, atomic force microscopy (AFM) is used to investigate the process of wetting alteration by oil within rock at a spatial scale of nanometers.

In previous studies, AFM has been used to investigate the adsorption of crudes or crude oil components to minerals, either by altering model mineral surfaces (Toulhoat et al., 1994; Buckley and Lord, 2003; Freer et al., 2003) or by modifying the AFM probe to reflect those specific components (Basu and Sharma, 1996). Hassenkam was the first to do AFM measurements on real rock (Hassenkam et al., 2009, 2012). For their studies, they grained the rock and picked representative grains which exposed a flat surface towards the probe to investigate how modified AFM probes with $-CH_3$ or $-COO-$ groups would interact in the presence of different brines. In a later study, the authors repeated this measurement on a preserved reservoir rock to study the natural adsorbed material (Matthiesen et al., 2014).

More recently, AFM was utilized to investigate the effects of the morphology of the internal rock surface. Instead of focusing solely on flat surfaces, the aim is to capture the natural roughness of the internal surface to assess how these contribute to the fluid-solid interactions (Rücker et al., 2020a; Yesufu-Rufai et al., 2020; Ekanem et al., 2021). In a modelling study the imaged natural roughness was used to model how these would influence nano-scale fluid configuration and what it would mean for static ageing as it is considered in larger-scale computational models (Rücker et al., 2020b). The results showed that for the investigated rock significant variation of surface area coverage of the solid surface by water can be established for a range of capillary pressures where the rock would be considered at connate water saturation. With the advancement in *in-situ* measurement of liquid films with AFM (Rücker et al., 2020a; Savulescu et al., 2021), underlying assumption of the models can be tested. This qualitative study presents a novel methodology to visualize the internal surface of a porous rock prior to and after treatment with crude oil close to connate water saturation and after waterflooding at the nano-scale and interpret those in respect to fluid configuration to determine the underlying mechanisms connecting wettability alteration to fluid displacement observed at the pore-scale.

2. Materials and methods

2.1 Fluids and rock samples

In this study, Ketton carbonate (Hudson and Clements, 2007) and Estaillades carbonate (Le Guen et al., 2007), two rocks frequently used for *in-situ* investigation of oil-recovery with a homogeneous chemical composition ($>97\%$ calcite), but different structural complexity are used. Three different crude oils have been used in this study. However, only one (crude A) is discussed in detail as it illustrates the full variety of results. Crude A has a viscosity η of 4.8731 cp, density ρ of 0.8339 kg/m^3 at 20 °C and a composition of 58.45% saturates (sat), 36.92% aromatics (aro), 4.36% resins (res) and 0.28% asphaltenes (asp) as well as the total acid number (TAN) of 0.07 mgKOH/g and a total basic number (TBN) of 83.9 mg/kg. The properties of crude B and C are listed in the Appendix. The brine composition was 12.68 wt% NaCl; 2.72 wt% $MgCl_2 \cdot 6H_2O$; 5.32 wt% $CaCl_2 \cdot 2H_2O$.

2.2 Sample preparation

The rock samples were first placed under vacuum, then saturated with brine and after desaturated with decalin using a centrifuge. Two Ketton samples were centrifuged at a rotation

Table 1. Full list of experiments.

Sample	Fluids	Centrifugation (kPa)	Wetting alteration (°C, MPa)	Flooding	Section
Ketton	Air	/	/	/	3.1
	Water/decane	Low P_c: 8-15	/	/	3.2
		High P_c: 18-36	/	/	3.2
	Water/crude A-C	Low P_c: 8-15	70, 3.5-5	/	3.3
		High P_c: 18-36	70, 3.5-5	/	3.3
Estaillades	Air	/	/	/	3.1
	Water/decane	Low P_c: 13-26	/	/	3.2
		High P_c: 65-130	/	/	3.2
	Water/crude A-C	Low P_c: 13-26	70, 3.5-5	/	3.3
		High P_c: 65-130	70, 3.5-5	/	3.3
	Water/crude A	Low P_c: 13-26	70, 3.5-5	Yes	3.4
		High P_c: 65-130	70, 3.5-5	Yes	3.4

speed of 1,300 and 2,000 rpm, corresponding to capillary pressures of 8-15 and 18-36 kPa. One sub-sample of each sample was placed in decane for measurements to determine nano-scale fluid configurations prior to the wettability alteration and into crude oil for treatment. Additional sub-samples were submerged into different crudes and treated for 4 weeks at a temperature of 70 °C at a pressure ranging between 3.5-5 MPa. Before the scan, the samples were first dropped shortly into decalin and then into decane to replace the crude with a transparent liquid in which AFM measurements could be performed.

Furthermore, two Estaillades samples were centrifuged at a rotation speed of 1,700 and 3,800 rpm corresponding to a capillary pressure of 13-26 and 65-130 kPa, respectively. For these samples also sub-samples were taken to investigate nano-scale fluid configuration prior to treatment with crude. Additionally, a sub-sample centrifuged at a speed of 1700 rpm and treated with crude A (at 80 °C and 3 MPa) used in micro-CT flooding experiments (Garfi et al., 2022) was investigated for nano-scale fluid films with AFM after the waterflood experiments. This experiment was only performed with crude A. The full list of experiments is shown in Table 1.

2.3 AFM measurement and data processing

A Nanowizard 4 AFM (JPK Instruments, now Brucker) was used to visualize the structure of the rock surface and liquid films down to nanometer resolution. The measurements were conducted in approachable adjacent pores not affected by drilling in air or in liquid. The samples were scanned with a silicon tip (PPP-NCHAuD from NANOSENSORSTM) in Quantitative ImagingTM-mode. In Quantitative ImagingTM - mode the tip is raster scanning the surface by approaching and disengaging from the surface at each location, whilst the deflection of cantilever is monitored with a laser. For each point a force distance curve can be reconstructed. Moreover height maps were obtained from the deflection once the tip reaches the surface manifesting in a sharp rise in pushing force in the force-distance curve. The slope maps are derived from the rise in the force-distance curve once the surface contact is detected and hence indicative of the stiffness of the sample. Adhesion maps were derived from the maximum pull force required to detach the tip from the surface resembling the lowest dip in force distance curve. In case of the presence of multiple fluids, the detected adhesion force may relate to capillary action (Kaltenbach et al., 2018; Peppou-Chapman and Neto, 2018; Savulescu et al., 2021; Wensink et al., 2024). The images were levelled, filtered using a low pass and median filter and cleaned from line-artefacts using the JPKSPM data processing software (JPK instruments). Force distance curves representative of specific attributes were extracted and processed in Excel (Microsoft) to adjust for the sensitivity and spring constant calibrated using the Sader method (Sader et al., 1999), contact point, baseline offset and tilt for the approach and retract.

The simple bead-pack-like structure of Ketton rock is better suited for AFM studies as it eases the identification of suitable locations for AFM scanning. Due to the higher complexity of Estaillades the approach of the internal surface of a pore fails frequently. However, in respect to flow dynamics occurring during waterflood, Estaillades is considered more representative for reservoir conditions.

3. Results and discussion

To assess the impact of ageing on the fluid distribution along the rock surface, AFM measurements were obtained for dry samples of Ketton and Estallades (discussed in Section 3.1), for Ketton and Estallaides close connate water saturation

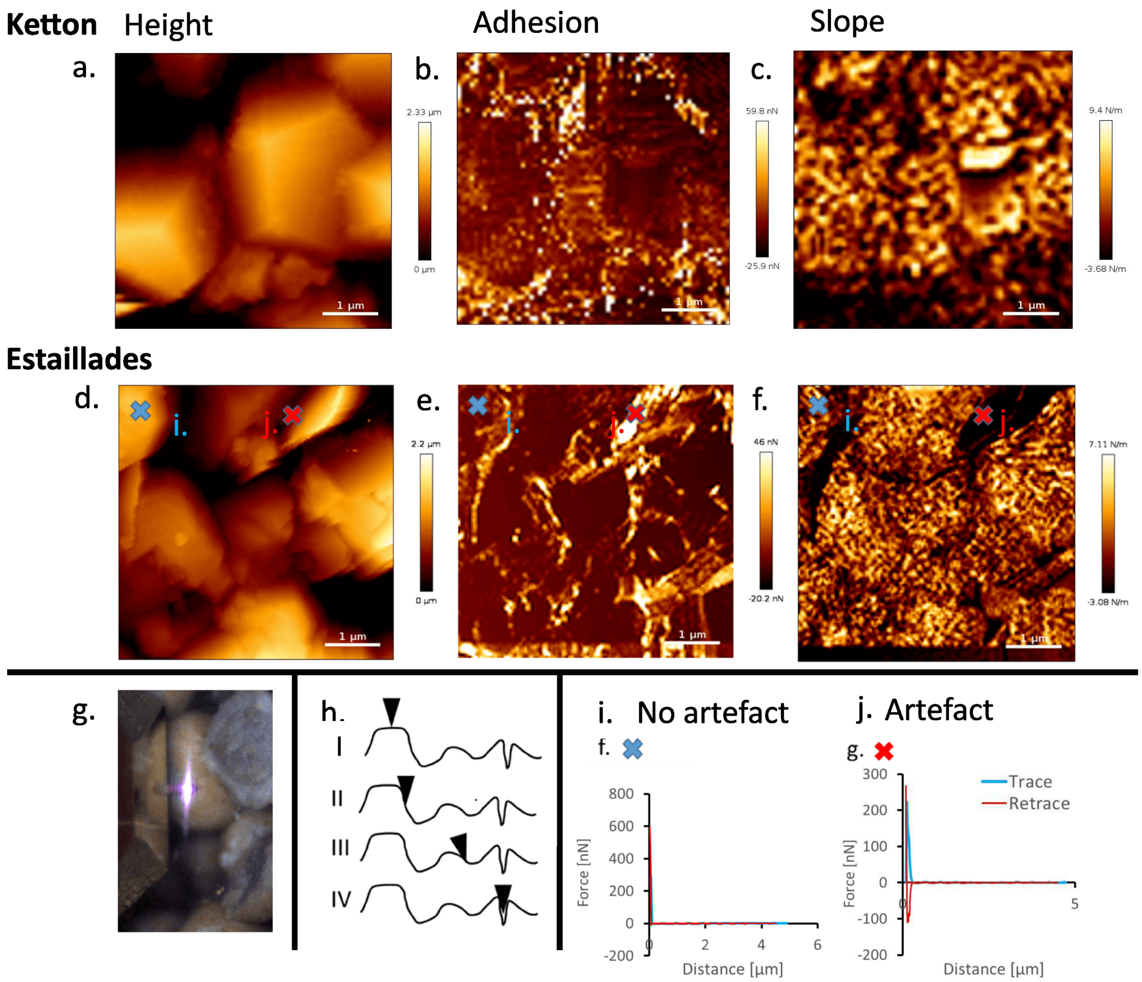

Fig. 1. (a)-(c) Surface of Ketton carbonate and (d)-(f) Estaillades carbonate measured with AFM. (a) and (d) reflect the topography, (b) and (d) the adhesion and (e) and (f) the Slope analysis of the respective surface. (g) displays the positioning of the AFM probe on the surface of a grain. The roughness of the surface can cause the AFM tip to expose a larger area to the surface, slip or get stuck (h), affect the recorded force-distance curves with blue representing the approach and red the retract (i) and (j) and create image artefacts which need to be considered in the interpretation.

prior to the exposure to crude (discussed in Section 3.2), for Ketton rock close to connate water saturation after exposure to crude (discussed in Section 3.3) and for Estaillades rock at residual oil saturation (discussed in Section 3.4).

3.1 Natural roughness of rocks - a challenge for AFM interpretation

The AFM measurements obtained from the natural internal surface of the two carbonates, Ketton and Estaillades investigated in air in absence of liquids are shown in Figs. 1(a)-1(f) respectively. An example of a scanning location, with the probe monitored by the laser (violet dot) focusing on a grain surface of the rock is shown in Fig. 1(g). The height images (Figs. 1(a) and 1(d)) represent the structure, which is dominated by crystal facies and cleavage. In each sample, only a few individual crystals are visible. Hence the images cannot be considered representative. The adhesion images (Figs. 1(j) and 1(e)) reflect the attraction of the slightly positively charged tip experiences when approaching the surface at a particular location and the slope (Figs. 1(c) and 1(f)) the resistance of the surface when it is pushed against it by the piezo. Adhesion and slope can be indicative of the mineralogy, e.g., if different minerals have varying surface charges or hardness (Yesufu-Rufai et al., 2020). The two carbonates used in this study show a rather homogeneous composition and hence should exhibit only minor variation in these parameters. However, distinct regions of higher and lower adhesion or slope are observed. This is mainly due to imaging artefacts: The tip is approaching each position with fixed x/y piezos whilst the z piezo keeps moving. If the tip lands on a horizontal surface as schematically drawn in Fig. 1(h)(I), one obtains a force-distance curve reflecting the very forces described before (Fig. 1(h)(I)). However, on a tilted surface, the tip might get in contact with a larger surface area (Fig. 1(h)(II)), slip (Fig. 1(h)(III)), or get stuck (Fig. 1(h)(IV)), increasing the tip-rock contact area and accordingly the measured adhesion or appearing softer than it is, which manifests in a lower slope as shown by the force-distance curve in Fig. 1(j).

These effects indicate uncertainties in these measurements

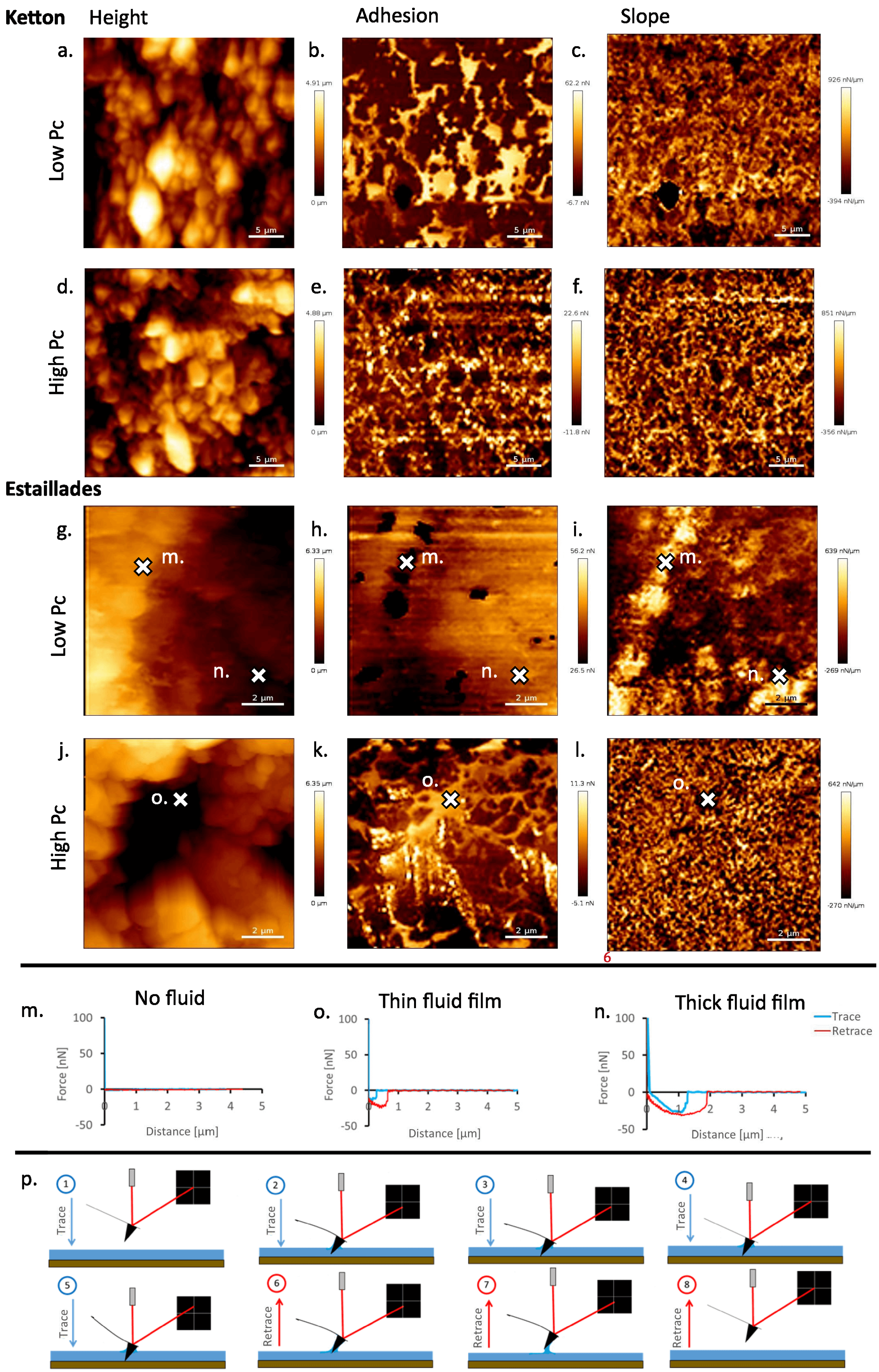

Fig. 2. (a)-(f) Topographic, adhesion and Slope analysis image of water films after centrifugation for high and low capillary pressures for Ketton and (g)-(l) Estaillades, respectively. (m), (o) and (n) The force-distance curves illustrate how the tip interacts with the fluid-fluid interface and affects the adhesion response due to capillary effects during the tip approach (blue) and retraction (red) for locations exhibiting different adhesion. (p) illustrates the movement of the tip through the water-film.

and need to be taken into consideration when interpreting fluid configurations detected in the other measurements. Generally, the more steep the surface in relation to the movement direction of the tip and the narrower the asperities, the more likely it is affected by an error. Each measurement was taken at a different location, as at this scale, finding the same spot after the sample has been moved for treatment is impossible with the techniques available. Accordingly, the data presented in this study is for qualitative interpretation and cannot be used quantitively.

3.2 Nano-scale fluid coverage close to connate water saturation

The measurements in Fig. 2 show the samples, Ketton (Figs. 2(a)-2(f)) and Estaillades (Figs. 2(g)-2(l)) close to connate water saturation prior to exposure to the crude.

The presence of the water film can be seen in the adhesion image (Savulescu et al., 2021; Wensink et al., 2024). This is as capillary action pulls down the water-wetting tip and is recorded as an increase in adhesion. The force-distance curves shown in Fig. 2 show the recorded adhesion response varying for cases where no (Fig. 2(m)), a thick (Fig. 2(n)), or a thin film is present (Fig. 2(o)) and Fig. 2(p) a schematic of the AFM probe at different stages of the approach and retract in the presence of the water film. Overall, the measurements of low capillary pressure samples (Ketton: Figs. 2(a)-2(c) and Estaillades: Figs. 2(g)-2(i)) show higher adhesion responses, with up to 62 and 56 nN, respectively, than the high capillary pressure samples (Ketton: Figs. 2(d)-2(f) and Estaillades: Figs. 2(j)-2(l)) with an adhesion force up to 22,6 and 11,3 nN, which hints to deeper water layers for low capillary pressure samples. Also, water coverage, which is reflected by the area of higher adhesion (yellow) in the images Figs. 2(b), 2(e), 2(h) and 2(k), appears higher for low capillary pressure samples than for high capillary pressure samples. The water coverage at the measured location in the high capillary pressure Ketton sample appears so low that the measured adhesion response in the displayed image is of insufficient quality to prove its existence (Fig. 2(h)). Overall, the adhesion observations are similar to the coverages modelled in (Rücker et al., 2020b). In the respective paper, it is hypothesized that these films inhibit alteration of the surfaces underneath, which is discussed in the following section.

3.3 Nano-scale observations of the rock alteration by oil

The measurements for the low capillary pressure Ketton samples and high capillary pressure samples after ageing in crude A and replacement of the crude with transparent model oil are shown in Figs. 3(a)-3(c) and Figs. 3(d)-3(f) respectively. The low capillary pressure sample again displays with 47.5 nN a higher adhesion than the high capillary sample with 31.2 nN. However, surface coverage is more difficult to derive for this sample as the force-distance curves appear different in the aged samples as evident from the examples shown in Figs. 3(e)-3(h).

In contrast to the measurements obtained before ageing, the tip appears repulsive to the fluid-fluid interface. This is assumed to relate to surface active components from the crude not only adhering to the crude-solid interface but also arrange along the fluid-fluid interface forming a layer, which tends to resist the AFM-tip to push through. In Fig. 3(g), the force-distance curve indicates that during the approach (blue) the tip is not able to penetrate until very close to the surface. However, the adhesion it experiences when retrieving (red) hints at the presence of a water film. A potential explanation could be that during the approach, the tip pushing against the layer along the fluid-fluid interface also pushes the water underneath aside. However, once in contact with the tip, capillary forces start acting, causing the adhesion response observed during retraction. In Fig. 3(f), the tip first reacts repulsive as in Fig. 3(g), though, significantly less. The tip pushes through the fluid-fluid interface and capillary forces pull it down before it reaches the rock surface and the retract curve shows a strong adhesion, too. Such observation may happen where the layer of surface active components is thin or close to non-existent. Noticeable is the distribution of high adhesion, in particular, in the high capillary pressure Ketton sample aged with crude A. As in the unaged, samples the water resides mainly in the valleys of the surface structure. Image artefacts, e.g. due to waves created by the tip penetrating the fluid-fluid interface in the aged low capillary pressure sample, could cause the pattern to be disturbed in the corresponding image.

Examples of force-distance curves without a response in adhesion during retraction.These locations appear without the presence of water films are shown in Figs. 3(i) and 3(j). However, also these can be distinguished into force-distance curves with (Fig. 3(i)) and without (Fig. 3(j)) repulsion responses during the approach. Given the similarity of Fig. 3(i) to Fig. 2(m), these locations are assumed to display oil-rock contacts without any layer of crude oil components. Whilst Fig. 3(j) may be a crude oil layer residing directly on the rock surface. For samples aged with crude B and C, no observations of any Figs. 3(g) and 3(h) - type of force-distance curves were made, which indicates that in those, the water film is not preserved. However, also in those samples, adsorbed crude oil components were evident from the Fig. 3(j)-type force-distance curves.

From these experiments 4 types of possible fluid arrangements illustrated in Fig. 3(i) can be concluded: Blank rock surface, water film with a small amount of surface active components, water film with a high amount of surface active components and crude oil adsorption on the rock itself An important finding is that the crude oil adsorption during ageing is inhomogeneous and depends on the type of crude used.

3.4 The impact of oleic alteration on flow dynamics at the nano-scale

A remaining question is how these ageing patterns observed influence the flow dynamics. AFM measurement after the core-flooding experiment performed by Garfi et al. (2022) for a low capillary pressure Estaillades sample and an additional flooding experiment on a high P_c sample aged with crude A with the respective height, adhesion and Slope anal-

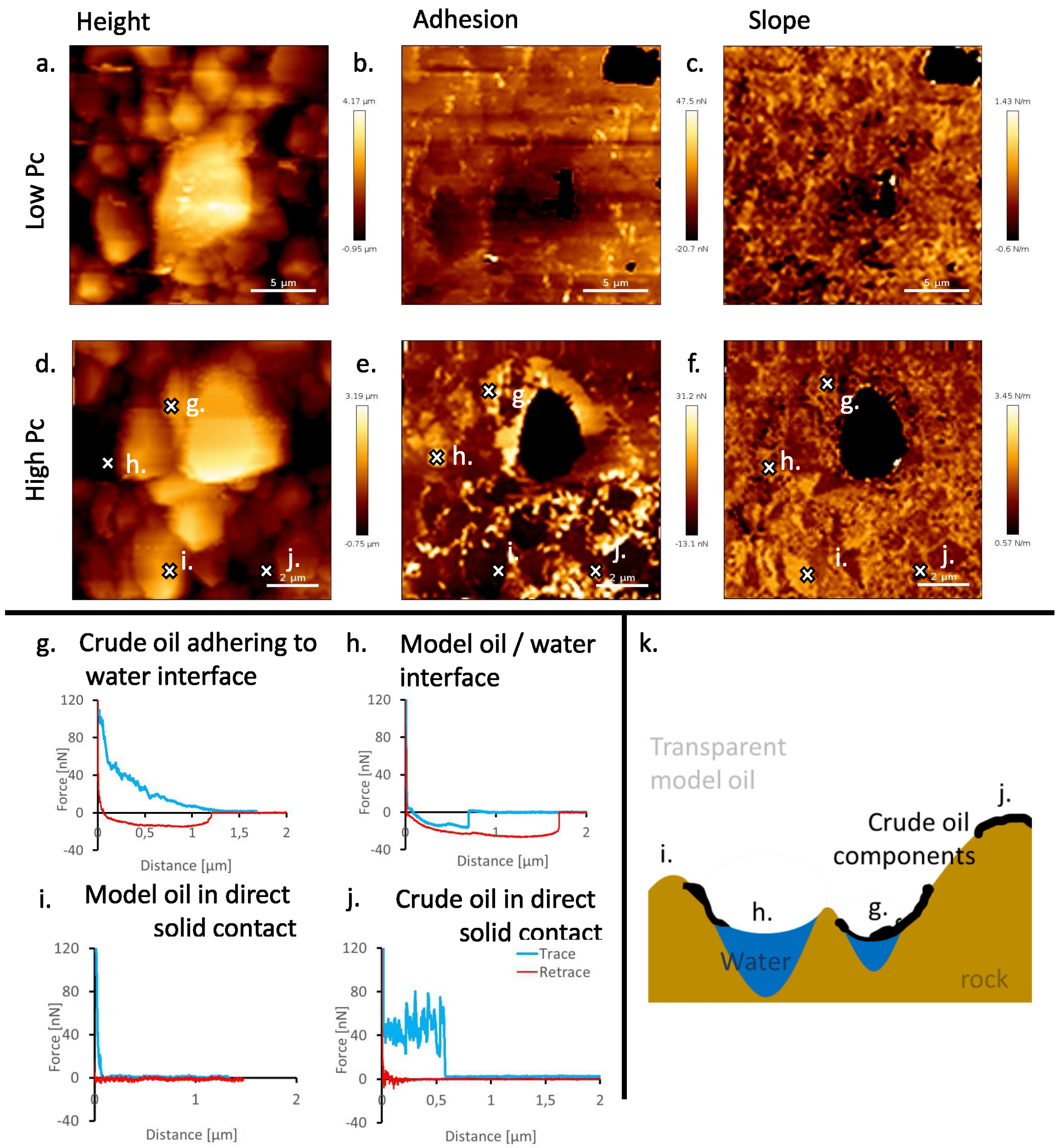

Fig. 3. Topographic, adhesion and Slope analysis image of Ketton rock aged with crude A after centrifugation for (a)-(c) low and (d)-(f) high capillary pressures. (g)-(j) The force-distance curves illustrate different types observed, which were interpretted as ageing states as illustrated in (k).

ysis images are shown in Figs. 4(a)-4(f). In both adhesion images, distinct areas of low, moderate, high and very high adhesion can be observed. The pattern is related to the topography of the sample. However, the increase in adhesion does not directly correlate to the depth of a valley as observed in the unaged and aged samples prior to flooding.

The force-distance curves show different characteristic for the low (Fig. 4(h)), moderate (Fig. 4(g)), high (Fig. 4(e)) and very high (Fig. 4(f)) regions. Again, the examples with low adhesion (Fig. 4(h)) are interpreted as locations without any crude oil-component and direct water-solid contact, whereas in all other cases, the tip appears to first repulse from the surface, indicating the presence of crude. In Figs. 4(e) and 4(f), the tip pushes through the fluid-fluid interface into the oil phase; however, in Fig. 4(f) another push-through is observed which significantly exceeds the attraction observed in Fig. 4(e). This is assumed to be the crossing of another fluid-fluid interface. This would indicate a water layer remaining underneath the oil layer. The force-distance curve Fig. 4(g) shows similarities to Fig. 3(e), which is interpreted as the tip indenting the fluid-fluid interface and only pushing through close proximity to the solid surface resulting in a moderate adhesion response when retracting.

The nano-scale observations on flow configurations before and after waterflooding provide new insights important for the interpretation of core-scale behaviour. It shows that the wettability pattern does not solely depend on mineralogical distribution but also on crude oil composition and on topographical

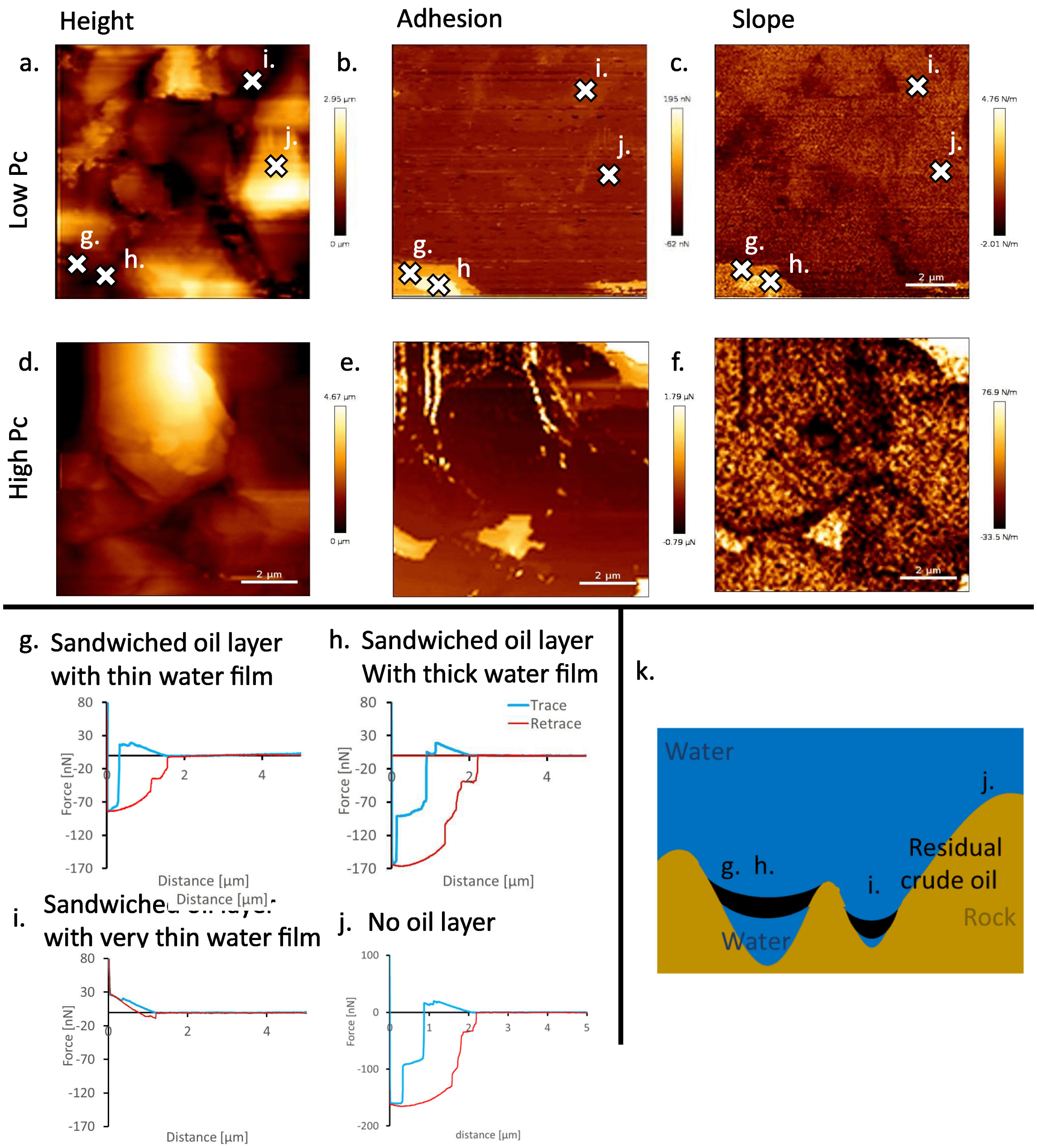

Fig. 4. Topographic, adhesion and Slope analysis image of Estaillades rock aged with crude A after centrifugation for (a)-(c) low and (d)-(f) high capillary pressures and waterflooding. (g)-(j) The force-distance curves illustrate different types of force-distance curves observed. (k) represents the different configurations derived from the respective images and force-distance curves. It appears that oil is remaining predominantly in valleys, entrapping a small amount of water underneath, with no sign of oil components adhering to the tips of the solid rock.

features down to the nano-scale. This demonstrates that many pore- and macro-scale models are based on too simplistic mental pictures, where wettability alteration can be either linked to mineral maps (Idowu et al., 2015), attributed through shape factors assuming alteration only where crude is in direct contact (Valvatne and Blunt, 2004) or a macroscopically determined thermodynamic contact angle dismissing surface generation below resolution (Blunt et al., 2021). Although, the variability of results shows that there may be cases where respective simplified models could be of use. On the other hand, the results do shed light on previously observed ambiguities in experimental data from pore- and core-scale with unexpected wetting responses and flow mechanisms (Alyafei and Blunt, 2016; Rücker et al., 2019; Mascini, 2022).

4. Conclusions

This study presents novel AFM approaches to investigate the alteration of rock by oil at the nanometer scale along its naturally rough internal surface, in which both molecular interactions and flow dynamics play a role.

The results showed that water films can prevail during the wetting alteration process. However, only one out of three crudes provided evidence for such water films. The surface active components of the oil were found to inhomogeneously attach to the fluid-fluid and fluid-solid interfaces in the respective samples. The measurements after the water flood further revealed water entrapped by an oil layer as well as regions of different adhesion following a pattern similar to the water distribution observed prior to the wetting alteration. Previous studies at the larger pore scale demonstrated that the flow behaviour very much depends on the exact oil, brine, rock composition, temperature, pressure and flow history (Anderson, 1986, 1987; Alyafei and Blunt, 2016). The variability of observations may relate to the alteration mechanisms and resulting fluid configurations observed at the nanometer scale presented in this study.

Further studies of this kind may help to understand which pore- and core-scale responses relate to the nano-scale effects described and what structural and chemical attributes facilitate these phenomena Computational work could help explore how such small scale effects translate to larger scale fluid displacement. Such results would help in developing more sophisticated pore-scale modelling tools to predict reservoir development or environmental remediation projects.

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Supplementary file

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Conflict of interest

The authors declare no competing interest.

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