Assessing the Wetting State of Minerals in Complex Sandstone Rock In-Situ by Atomic Force Microscopy (AFM)

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Abstract

Low salinity waterflooding is a low-cost method of enhancing oil recovery although, no consistent concept has been established explaining why some oil-fields show an increase in oil production when the salinity of the injected brine is reduced, while others do not. Various studies were conducted investigating the underlying mechanisms of the ‘low salinity effect’ using different crude oil, brine and rock compositions. Core floods of sandstone rock and analyses of molecular interactions using model systems indicate that clay content may play a dominant role. However, the spatial configuration of the sheet-like clay particles, which may vary from rock to rock, complicate comparisons of these model scenarios with reality.

In the present study, we report the development of a pre-screening method using Atomic Force Microscopy (AFM) to assess rock-fluid interactions, which has previously only been used either on artificial model systems or minerals from crushed rock, by exploring the capability to operate in-situ in complex rock without crushing. The orientation of clay particles within a pore of an outcrop sandstone, Bandera Brown, was investigated with AFM and these particles were further assessed for changes in adhesion in brines of differing salinity. The results show a decrease in adhesions between CH3-functionalised AFM tips and the rock surface in low salinity brine, predominantly at the clay edges. This demonstrates that the edges of the clay particles, which may pin the oil phase after wettability alteration and therewith prevent oil from getting produced, lose this capacity when exposed to low salinity brine.

Keywords: Low salinity effect; Waterflooding; Atomic Force Microscopy; Adhesion; Clay content; Wettability
1. Introduction

In oil recovery, most relevant processes of producing crude oil from subsurface formations involve the flow of two immiscible fluid phases such as water and oil, inside porous sedimentary rock. The respective wetting properties of the rock have a significant influence on the recovery efficiency with a major impact on technical and economic aspects. While most sedimentary rocks are initially hydrophilic, contact with crude oil and subsequent adsorption of crude oil components on mineral surfaces over geological time scales often alters mineral surfaces to oil-wetting [1–4].

Even though in conventional integrated subsurface workflows wettability does not represent a direct input parameter, wettability has a major impact on the relative permeability-saturation functions which represent direct input to reservoir modelling. While oil-wetting rock leads to a lower residual oil saturation i.e. a higher ultimate recovery, the immiscible displacement processes during e.g. a waterflooding process are less efficient. Therefore, a more water-wet reservoir is in many cases more favourable compared to an oil-wet reservoir [5–7].

For specific recovery processes where the objective is to alter wettability of reservoir rock to improve production, determining wettability at least as a screening parameter could be very beneficial [8]. For instance, in low salinity waterflooding, conditioning of the ionic composition of the injected brine can lead, in certain cases, to an incremental recovery compared to conventional waterflooding with a brine composition similar to the reservoir brine [9–11]. While the underlying mechanism is still very much subject to debate, wettability alteration is one of the considered root causes [8,12]. Decisions on economic aspects will be ultimately based on respective changes in relative permeability and capillary pressure-saturation functions, whereas information on the wettability alteration aspects of minerals by low salinity brine would serve as beneficial pre-screening criteria for selecting candidate fields potentially suitable for low salinity waterflooding [13,14].

The wetting conditions of reservoir rock depend on various factors, where the interaction of minerals, crude oil, and brine composition play a key role. Many studies have contributed to an improved understanding of the interaction between brine and crude oil composition with minerals [2,3,15]. In clastic reservoir rocks, clay minerals are considered most responsive to ionic composition changes. Therefore, many previous studies on the low salinity effect in sandstone rock and wettability research, in general, have focused on clay minerals [11,16–21]. Multiple theories have been developed on the mechanism of low salinity effect of clay particles including pH change effects, salting-in and electronic double layer expansion [22–25]. These
theories have been developed with a focus on the negative surface charge which on clay particles appears along the flat crystal surface. The edges of clay, however, are positive due to cations which hold the negatively charged SiO$_4$ tetrahedra and/or AlO$_4$ octahedra – sheets of the clay mineral together [26,27]. Secor and Radke [28] showed for montmorillonite, that these edges may change polarity when switching from high salinity to low salinity brine.

Cense et al. [29] and later Mahani et. al. [30] therefore proposed a new experimental set-up allowing residence of the clay on a substrate in all possible orientations in contrast to previous studies, where the clay particles were deposited flat on the carrier substrate. In these experiments, oil droplets were attached to the surface and then exposed to different brine compositions, while the configuration of the droplet and the release were monitored. Cense et al. [29] found that the de-flocculating of clays, where the SiO$_4$ tetrahedra and/or AlO$_4$ octahedra – sheets break off along the layer of cations penetrated by water through the clay edges, leads to a large release of oil [31,32]. This supported previous studies, proposing fines migration as a cause for the low salinity effect in sandstone [9,11]. However, an increase in oil production was also seen in brines where the clay particles remained intact. Mahani et al. [30] confirmed this finding, later complementing the results with kinetic concept describing the oil-release processes in low salinity brine for this model. Yet, the configuration of the clay minerals in this model is artificial and may not reflect the configuration of the mineral in natural rock. An alternative would be to measure the rock fluid interactions in-situ within real rock.

Schmatz et al. [33] used cryo-BIB-SEM to investigate fluid configurations resulting from the wetting state of the rock at the nanometer scale. However, the sample preparation for this method is complicated, as the rock sample filled with fluid must be first frozen and cut with an ion-beam and then scanned with SEM. Furthermore, this method only gives 2D cross-sections. The procedure needs to be repeated multiple times, in order to get 3D information.

Another technique is Atomic Force Microscopy (AFM), where an atomically sharp tip raster scans a surface of the rock resulting in 2D and 3D topographical maps. Depending on the imaging mode, AFM is also able to provide information about the stiffness of the scanned material and adhesion of the sample towards the tip, which can be modified with -CH$_3$ or -COOH groups. The adhesion of these oil components to the rock surface gives an indication of the wetting state as it can be related to the contact angle by the Young-Dupré equation [34,35]. The advantage of using the AFM to directly assess the adhesion force over contact angle measurements is that generally, contact angle measurements are taken on a much larger length scale; droplets are typically larger than individual minerals, and often larger than clay
aggregates, and thus would only give average properties, which are also subject to contact angle hysteresis [36]. AFM analyses the response of surface chemistry which is given through the intrinsic contact angle.

Several AFM studies have assessed surface charges of individual clay minerals [37–45] and several focused on the impact of brine salinity using model systems [46–49]. To characterise more realistic systems, Dickinson et al. [50] introduced tip functionalisation with crude oil and Hassenkam et al. [51] performed AFM measurements on grains broken off from reservoir rock and deposited on a carrier substrate. However, in these studies they predominantly focused on flat surfaces, which were assumed to reflect the natural state not affected by the sample preparation procedure [52,53]. Based on this, the low salinity effect has typically been assessed by testing two extremes of salinity, a high and a low salinity condition [54–56].

In this work, we investigated the interactions between crude oil components and the rock surface using an intact rock sample not perturbed by drilling or crushing by moving the AFM tip into a pore of the sample. Topographic imaging and stiffness maps were used to identify minerals. To measure adhesion forces between the sample surface and specific oil components, AFM tips coated with –CH$_3$ functional groups were utilised, mimicking contact with a non-polar fraction of oil. A –CH$_3$ functionalised tip is a good representation of the alkane fraction of crude oil. This functionality was chosen to directly correlate changes in adhesion between the sample and the “model oil droplet” to changes in wettability [53] via the molecular interactions between the functional groups and the sample surface. At this sub-pore scale of measurement, it is improbable to realistically implement an actual oil droplet. Experimental results obtained here serve to approximate reality. Thus, emphasis is not placed on absolute values, but on how much the adhesion changes in high and low salinity brines.

Force-distance curve mapping with CH$_3$-terminated tips on natural rock surfaces immersed in brine reveals significant differences in adhesion forces and salinity response between faces and edges of clay minerals within the sample. This emphasizes the importance of conducting such measurements in-situ on natural rock and the need to develop respective techniques to operate under these conditions.
2. Material and Methods

2.1 Materials

2.1.1 Rock Sample
A sandstone, Bandera Brown, obtained from Kocurek Industries (Texas, USA) was used, primarily for its clay content, as clay is consequential to oil-brine-rock interactions [57–60]. It originates from an outcropping in Pennsylvania (USA) and is of Upper Carboniferous age (305 Ma). The rock is classified as sub-litharenite. It consists of Quartz, Clays (predominantly Illite, Vermiculite, and Kaolinite), Feldspar and low amounts of Carbonates.

Table 1: Mineralogy of Bandera Brown [61]

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>87</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>4</td>
</tr>
<tr>
<td>Clays</td>
<td>7</td>
</tr>
<tr>
<td>Ankerite</td>
<td>1</td>
</tr>
<tr>
<td>Calcite</td>
<td>trace</td>
</tr>
<tr>
<td>Gypsum</td>
<td>trace</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Clay Minerals</th>
<th>Mass fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Illite</td>
<td>38</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>36</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>21</td>
</tr>
<tr>
<td>Illite-Smectite</td>
<td>3</td>
</tr>
<tr>
<td>Chlorite</td>
<td>2</td>
</tr>
</tbody>
</table>

Its mineralogy, as illustrated in Table 1, is representative of most sandstone reservoirs and is thus a good model system. Bandera Brown is additionally analogous of reservoir rocks with its similar surface and adhesion properties, as well as comparable adsorption levels of chemical species in contrast to other rocks such as Bentheimer, Berea, etc. [61].
Figure 1: Scanning Electron Microscopy (SEM) analysis of Bandera Brown showing full mineral distribution.

Bandera Brown has a porosity of 21-23% and permeability in the range 30-45 mD. All samples used were obtained from 12mm diameter cores drilled and segmented into 3mm thick slices suitable for AFM measurements. The surfaces were untreated prior to experiments. A Scanning Electron Microscopy (SEM) image illustrating typical mineral distribution is shown in Figure 1; “typical” as observations have shown the distribution to be quite heterogeneous with a variation in cementation.

2.1.2 Aqueous Solutions

To mimic reservoir conditions of seawater, solutions of high salinity brine prepared in de-ionised water were used containing 0.18 g/l NaHCO₃, 1.43 g/l CaCl₂.2H₂O, 10.26 g/l MgCl₂.6H₂O, 8.31 g/l Na₂SO₄.10H₂O, 0.71 g/l KCl and 22.74 g/l NaCl, with a total salinity of 33,000 ppm. All chemicals were A.C.S. reagent grade of ≥97% purity obtained from Sigma Aldrich (United Kingdom). For brine of lower salinity, the solution was diluted with de-ionised water to 1500 ppm. The pH values of the solutions were not adjusted and measured at 8±1. All topography and force measurements were performed at ambient conditions in brine.

2.1.3 AFM Probes

Force analysis of a reference sample of freshly cleaved mica and topography imaging of the Bandera Brown surface were performed with Silicon Nitride cantilevers obtained from Apex Probes Ltd (United Kingdom), with a nominal spring constant of 0.12 N/m. These probes were cleaned preceding imaging in a UV/Ozone plasma chamber for 20 minutes.

Adhesion forces at the mineral-water interface were mapped using chemically modified silicon tips (Apex Probes). These probes mimic the non-polar components of crude oil via
functionality of their negatively-charged tips with \(-\text{CH}_3\) end groups [62]. A self-assembled monolayer of \(-\text{CH}_3\) groups adequately surrounds the tip in a manner which closely mimics a liquid droplet attached to the AFM tip. The probes were stored in separate vials to prevent surface contamination and dislodgement of the chemical species. The triangular-shaped cantilevers were gold-coated for good reflectivity of the laser spot, with a tip height of 3.5\(\mu\)m, tip radius <40nm and a nominal force constant of 0.08N/m. Prior to the start of every experiment, the probes were rinsed with ethanol and dried with a stream of nitrogen.

The spring constants of the cantilevers in addition to the deflection sensitivities were calibrated at the commencement of every experiment using the Thermal tune method [63] by measuring the contact of the tips against a clean glass slide.

2.2 Methods

2.2.1 Scanning Electron Microscopy

Low vacuum Scanning Electron Microscopy (SEM) was used to provide complementary high-resolution images of an uncoated Bandera Brown core. Images were captured at 5kV, under 60 Pa on a Thermo Fisher Scientific FEI Quanta FEG 650. The sample was sonicated in distilled water and allowed to dry prior to imaging, to lift any residue from the core cutting out of the pores. Micrographs obtained were subjected to false-colour segmentation with ImageJ to better delineate clay content.

2.2.2 Atomic Force Microscopy

The topography of Bandera Brown and its adhesion to a non-polar functionalised tip were analysed using Atomic Force (AFM Microscopy). AFM was developed in 1986 as a tool for imaging surface topography and measuring forces at an atomic scale [64], a viable means of investigating wettability as surface forces are measured directly rather than abstracted into contact angles. It utilizes an atomically sharp tip at the end of a flexible cantilever which, in essence, acts as a spring of known force constant, to detect forces at a sample surface as it scans across it, measuring intermolecular forces and thus providing information about the topography, stiffness/elasticity and adhesion [65]. This adhesion serves as a measure of the spatial variation of wettability, using changes in surface energies as a reflection of wettability alteration [3,34]. The bending moment of the cantilever towards or away from the sample as a result of these intermolecular forces is discerned by a laser beam reflected off its back onto a position-sensitive photodiode as illustrated in Figure 2a. The angle of the laser beam reflected changes with cantilever deflection and its position on the photodiode is used to calculate the
deflection signal. All measurements were performed using a JPK Instruments Nanowizard 4 nanoscience AFM (Bruker Corporation, Germany).

2D and 3D maps of the surface topography of Bandera Brown were taken in Quantitative Imaging (QI) mode. This mode is based on force spectroscopy as a complete force-distance curve is taken at every pixel. Figure 2b shows a typical force curve measured with a silicon nitride tip contacting the surface of mica in air. The AFM tip is extended towards the sample and indented until a pre-defined force is reached and then completely retracted before proceeding to the next pixel, thus enabling the detection of mechanical sample properties such as stiffness/elasticity. At larger tip-sample separation (position A), there is no deflection of the cantilever due to undetectable tip-sample interactions. As this distance decreases on further approach, various intermolecular forces come into play; and short-range attractive forces will cause a jump to contact (position B). The cantilever is deflected upwards upon repulsive contact with the sample until the pre-set force is reached (position C). On withdrawal of the tip from the surface, adhesive forces hold the tip in place causing downward deflection of the cantilever till a snap-off occurs on further increase in separation and the cantilever returns to its initial position (position A).

![Figure 2](image.png)

**Figure 2:** (a) Schematic diagram of the AFM setup [66]. (b) Typical force-distance curve measured with a silicon nitride tip on mica in air.

The magnitude of the forces measured across the sample surface are dependent on the probe specifications: the tip shape and size which directly impact the contact area.

QI mode is advantageous for topography imaging as any lateral forces or the impact of roughness can directly be attributed to actual surface features rather than measurement settings.
as in conventional tapping modes. This is due to the controlled motion path of the tip being vertical over a defined length when approaching and disengaging from a surface.

The stiffness of the sample, which can be mapped to the surface topography, is obtained from the slope, detected via the deflection of the cantilever in the contact region of the force curve. This deflection is fitted with the Hertz model and sample stiffness determined from its Young’s Modulus [67].

Adhesion forces between the -CH₃ functionalised tips and the Bandera Brown surface were measured in Force Mapping mode of the Nanowizard AFM. Adhesion forces are detected from the magnitude of the intermolecular forces between the functional groups on the tip and the sample surface. Similarly, as in QI mode, a force-distance curve is taken by the AFM at every pixel of measurement. However, Force mapping mode does not record as many pixels and thus local changes in forces are easily identifiable. It provides extremely localized information about tip-sample interactions as each measurement is independent of the next. QI mode is basically speed enhanced force mapping thus its suitability to imaging.

Force maps were generated by delineating the imaged area into a 32x32 grid; a force curve measurement was taken at the centre of each grid square, thus resulting in 1024 force curves, with the lowest trough of each force curve signifying adhesion data. This was extracted and used to create an adhesion map by the software. Force mapping mode is quite suited for comparison when varying experimental conditions, as differences in surface interactions can be compared pixel by pixel. The complete force curves obtained at every pixel of measurement can also be extracted individually for further analysis.

2.3 Procedure

To remove air in the rock pores, the Bandera Brown sample was evacuated and thoroughly degassed within a vacuum chamber using a pump. High salinity brine was slowly introduced into the chamber with any air bubbles within expelled as well until the sample was completely saturated. The sample was removed from the vacuum chamber still immersed in brine, covered and left for at least 48 hours. Subsequently, it was introduced into a brine-filled stainless-steel fluid cell complete with stainless steel clamps to hold it in place and mounted on the AFM stage.

Prior to measurements, the AFM tips were lowered into the cell at a distance away from the sample surface and allowed to equilibrate in the brine for 5 minutes. Complete analysis including topographical images and force maps were carried out at two different clay locations
on the Bandera Brown surface (dubbed C1 and C2). Preliminary mineral identification was performed by scanning the surface for locations indicative of clay particles with the silicon nitride tip. Thereafter, the tip was replaced by functionalised ones and low-resolution imaging of the surrounding area was repeated to identify the initially chosen region, as the feasibility of being positioned at the exact same area once the tip has been changed is questionable due to the nanoscopic scale of measurements. Scanning speeds were adequately reduced to preserve the chemical end groups.

Adhesion maps were first taken in high salinity brine, and next, the fluid was changed in-situ by carefully introducing low salinity brine through a silicone tubing. The low salinity solution was flushed through repeatedly at 10 times the volume of the fluid cell, to ensure complete fluid exchange. The clamps within the fluid cell made certain that the sample did not drift during this process. Equilibration time of 1 hour was allowed for and low-resolution topography images were taken once again to confirm that indeed no drift had occurred. Adhesion maps were repeated at the same location, thus taking data of the chosen area under high and low salinity conditions. All experiments were performed at ambient temperature of 20 ± 2°C.

2.4 AFM Data Analysis

All AFM data were analysed using JPK Instruments Nanowizard Data Processing Software Version 6.1.65.

The topography images were subjected to basic flattening to correct for any offset due to large height changes.

Each force-distance curve composing the adhesion force maps underwent identical processing. Firstly, the baseline was automatically subtracted to remove any offset in vertical deflection at the region of the curve where there was no interaction between the tip and the surface. Subsequently, the contact point was also detected and set as the zero position. Thereafter, the height signal was corrected for cantilever bending, thus detecting the vertical tip position. These operations ensured that the quantitative value of adhesion measured was accurate.

Adhesion force histograms were obtained by extracting ASCII data from force maps and plotting in MATLAB (R2019a).
3. Results and Discussion

3.1 In-situ Mineral Identification of Natural Clay Orientation

An initial study of the surface topography of Bandera Brown performed with Scanning Electron Microscopy revealed the heterogeneous nature of the sample with special consideration given to the pore surfaces for characteristics representative of clay particles. Mineral data shows that clay is present within the pores and on mineral surfaces as a coating.

Figure 3a is an SEM micrograph showing an aggregate of blocky particles tinted yellow with false-colour segmentation, possessing an identifiable pseudo-hexagonal morphology indicative of Kaolinite [68–70] with their edge surfaces exposed within the pore. Figure 3b discloses thin crystals perpendicular to the surface suggestive of vermiculite mineral sheets [68]. Surrounding areas look to be covered by a non-uniform bed of smectite clay. These scans were used as a guidance for mineral identification with Atomic force microscopy.

Figure 3: False-colour SEM micrographs of Bandera Brown showing (a) well-defined Kaolinite booklets (b) Vermiculite crystals normal to the surface.

Figure 4a shows a $5 \times 5$ µm AFM 3D topographical height image of the pore surface. Similar stacked pseudo-hexagonal booklets of Kaolinite are also visible as indicated by the yellow arrow. The upper left side of the image pin-pointed by the red arrow shows a neighbouring mineral with a euhedral prismatic crystal structure, tell-tale identifying characteristics of Quartz [71]. The stiffness/slope plots produced by the AFM provide an additional measure of mineral identification based on sample hardness. Harder surface features will have a higher slope due to minimal indentation and thus steeper deflection of the AFM tip. However, softer features will have a lower slope as the AFM tip sinks further into them [72]. AFM stiffness
data overlaid on the height image as shown in Figure 4b identifies this prismatic structure to be made of a harder or stiffer mineral (lighter colour-red arrow) than the stacked aggregate (darker colour-yellow arrow). This would agree with preliminary identification as Quartz has a hardness of 7 on the Mohs scale, compared to Kaolinite hardness of 2-2.5 [73].

Adhesion data obtained using a hydrophilic silicon nitride probe was also overlaid on the height map as in Figure 4c showing higher adhesion (lighter colour) along the basal planes of the clays (green arrow) than at the edge surfaces (blue arrow). Further scans of the sample surface also revealed clusters of large crystals with sheet-like morphology.

Figure 4: 3D topographical image of Bandera Brown surface showing (a) height. Stacked platelets (yellow arrow) indicative of Kaolinite (b) stiffness. Corresponding clay region (yellow arrow) shows a softer mineral of higher elasticity (darker colour) than surrounding areas (lighter colour). (c) adhesion. Basal planes (green arrow) experience higher adhesion (lighter colour) to the hydrophilic silicon nitride tip than edge surfaces (blue arrow) (d) AFM image
of vermiculite sheets with edges oriented towards the pore. The white line denotes cross-section in (e) showing step-like formation.

In Figure 4d, the region to the right of the yellow line shows the sheet edges of a vermiculite mineral aggregate. The white line denotes the location from which the cross-sectional analysis in Figure 4e was plotted, which shows that the step edges of the sheets extend ≤ 80 nm above each other.

Imaging the edge surfaces of clays with the AFM, however, does not reveal minor changes in height thus smaller steps are not detected. The sheets are oriented with basal planes stacked one atop the other and edge surfaces exposed within the pore.

Figure 5: Mineral stiffness analysis performed at two different locations (a, b) with sheet-like formations. Stiffness distributions of areas within the white squares are shown in corresponding histograms below.

The elasticity of this aggregate is shown in Figure 5a and compared to yet another sheet-like area as illustrated in Figure 5b as a further means of validation. Unlike Figure 5a which principally depicts the clay aggregate with the stiffness peaking at 55.7 nN/µm, Figure 5b was chosen for comparison as it shows alternate minerals in the surrounding area (lighter region) in addition to the clay deposit, with peak stiffness measured at 103 nN/µm. Regardless, mineral
stiffness measured across the two areas identified as clays and outlined in the white squares show a similar distribution, both peaking at ~27nN/µm. Similar stiffness distribution indicates analogous mineral at both locations.

The topography images obtained affirm the configuration of clay particles within the Bandera Brown sample. Evaluating changes in wettability due to of low salinity waterflooding ex-situ of the original rock samples as carried out in previous studies disregard the effects that the natural orientations of these clay particles potentially have on the low salinity effect in terms of their anisotropic properties as a result of differing surface chemistry at the edges and basal planes. Thus, efforts were made to replicate measurements on surface orientations representative of the reservoirs.

3.2 Interaction of –CH₃ functionalised tip with the edge surfaces and basal planes of clays

The force curves measured as the –CH₃ functionalised tip approached the clay edge surfaces under conditions of high and low salinity were analysed to evaluate the chemical interaction forces between them as illustrated in Figure 6a. Force mapping mode allows for the extraction of individual force-distance curves at specific pixels within the grid, thus enabling force-curves from identical pixels in high and low salinity brine to be obtained and scrutinized. The delineation of the sample area into individual squares within the 32x32 grid aids comparison of the same position as a force-distance curve is taken at the centre of each square. A specific location on the edge surface of a kaolinite crystal was examined at high salinity, and the corresponding force curve extracted from the same pixel at low salinity.

An attractive force is dominant in high salinity brine with the tip jumping into contact with the sample at a separation distance of ~10nm. However, this attraction between the tip and sample lessened with decreasing salinity, and a slight repulsive force was observed, typified by the upward deflection of the curve.
Figure 6: Approach force curves at high and low salinities between -CH₃ tips and (a) edge surfaces (b) basal planes.

As measurements were performed with a tip functionalised with a non-polar oil component, the resultant interactions serve as a measure of surface wettability in terms of its hydrophilicity or hydrophobicity. Results obtained are indicative of decreasing hydrophobicity at the edge surfaces as salinity was reduced, with the initial electrostatic attraction with the hydrophobic tip becoming repulsive.

Figure 6b illustrates the force curves produced as the -CH₃ functionalised tip approached the basal planes of the clays in high and low salinity brines. Contrary to results obtained at the edge surfaces, the prevailing forces between the tip and the plane surface were repulsive at both salinities. Similarly, however, the magnitude of the repulsive forces was observed to increase with decreasing salinity, with the separation at which the repulsion between the tip and sample began increasing accordingly. The cantilever was deflected upwards due to electrostatic repulsive forces at a separation of 40nm in high salinity brine with the maximum repulsive force recorded at the point of tip contact with the sample. This distance was observed to increase at low salinity to 65nm.

Results obtained at the basal planes, albeit also indicative of decreasing hydrophobicity as salinity was reduced, do not show a significant change in interaction with the non-polar tip as at the edge surfaces, in terms of reversal of electrostatic forces. Findings are in agreement with studies that have shown a change in polarity at the edge surfaces of clays as ionic strength decreased, with electrostatic interactions becoming repulsive [28].

Although variations in separation distances and the magnitude of attractive or repulsive forces as a result of the sample roughness were observed, the force curves chosen for display represent the general trend for force-distance interactions obtained at the edges and at the basal planes.
3.3 Adhesion force mapping of Kaolinite minerals

The topography of the Bandera Brown sample was scanned, and clay minerals identified were subjected to adhesion force mapping under conditions of high and low salinity. The 3D representation of the first clay site chosen for further analysis, dubbed location C1, a 5 µm x 5 µm region, is illustrated in Figure 7a and shows a step-like structure indicative of stacked kaolinite booklets [68,74,75]. Cross-sectional analysis along the white line is plotted in Figure 7b showing steps 200nm high with grains oriented horizontally to the surface.

Adhesion force mapping of the hydrophobicity of the Bandera Brown surface taken using a –CH₃ functionalised tip first in high salinity brine and subsequently in low salinity brine are shown in Figure 7c & d with the range of low-medium-high adhesion represented by the colour code maroon-green-pink respectively. An initial overview of the map generated in high salinity brine shows that areas with higher adhesion seem to correspond to locations with significant changes in height. Adhesion was observed to vary with sample heterogeneity, and reduced non-uniformly when salinity was decreased, as shown in the adhesion distribution in Figure 7e. A wider adhesion distribution is observed in high salinity brine, narrowing considerably as salinity decreased. The roughness of the mineral surface will thus affect adhesion distribution to an extent, as increasing roughness correlates with increasing distribution [76]. This diminished distribution measured in low salinity brine is due to the low salinity effect as the roughness of the sample surface would only influence the absolute value of adhesion measured, and not how much it changes. The benchmark for the adhesion forces obtained in low salinity brine is the previous measurements in high salinity brine. This is because both measurements have been performed using the same tip and at the same location on the sample.
Figure 7: (a) 3D topographical height image of Location C1 with the white line denoting (b) cross-sectional view showing edges of clays oriented outwards towards the pore. Adhesion force maps for Location C1 in (c) high salinity brine (d) low salinity brine. White and black squares denote sample areas at clay edge surfaces and basal planes, respectively, considered for further analysis. (e) Histogram showing distribution of adhesion forces in high and low salinity brines.

The average adhesion measured between the tip and sample was ~60% lower in low salinity brine (168 pN) than in high salinity brine (427 pN).

Similar results were obtained between –CH₃ functionalised tips and sandstone grains [13], Quartz [56], Mica [55] and K-Feldspar surfaces [54].

The edges of the clays showed a stronger adhesion than the basal planes with the hydrophobic -CH₃ functionalised tip in high salinity brine and appear to have been affected significantly in low salinity brine, thus demonstrating that the edge surfaces were more hydrophobic. Results are in congruence with approach curves displayed in Figure 6 which show more affinity with the hydrophobic tip at the edge surfaces than at the basal planes. These findings are consistent with topography results earlier described in Figure 4c as the reverse is the case when measured with a hydrophilic tip, showing higher adhesion at the basal planes of clays than at the edge surfaces.
In order to evaluate the extent to which the orientation of the clay particles influenced the low salinity effect, sample areas at the edges and at the basal planes depicted by the white and black squares respectively in Figure 7c&d, under both conditions of salinity were selected for further analysis. Individual force-distance curves at specific sites within these grids were obtained using force mapping mode at high salinity and from identical pixels in low salinity brine, with the lowest troughs of the retract curves representative of adhesion data evaluated further. At the edge surfaces, adhesion ranged from 1.09 nN - 1.81 nN in high salinity brine, reducing to 0.02 nN - 0.22 nN in low salinity brine. However, at the basal planes, a lower spectrum of adhesion values was recorded in general, ranging from 0.08 nN - 0.52 nN in high salinity brine and decreasing to 0.01 nN - 0.21 nN in low salinity brine.

Figure 8: Average distribution of adhesion over different sites at the edge surfaces and basal planes of clays within location C1 in high and low salinity brine.

Plotting the average of the adhesion values from these sites in Figure 8, inclusive of range bars calculated from how much the maximum and minimum values exceeded the mean, it is evident that the drop in adhesion at the edges of the clays when salinity is reduced is much more significant due to non-overlapping range bars than at the basal planes. This indicates that there is a more considerable low salinity response at the edges of Kaolinite than at the flat surfaces.

3.4 Adhesion force mapping of Vermiculite minerals

Subsequently, adhesion was mapped at an alternate clay location, dubbed C2 as represented in the topographical image in Figure 9a zoomed in to 1 × 1 µm. The location is indicative of a
vermiculite-type aggregate [68] and cross-sectional analysis along the white line as illustrated in Figure 9b shows sheets oriented normal to the surface. Adhesion distributions from the maps in Figure 9c&d were extracted and plotted in Figure 9e.

Figure 9: (a) 3D topographical height image of Location C2 with the white line denoting (b) Cross-sectional view showing upward-facing irregular clay edges in a stacked formation oriented upwards towards the pore. Adhesion force maps for Location C2 in (c) high salinity brine (d) low salinity brine. White and black squares denote sample areas at clay edge surfaces and basal planes, respectively, considered for further analysis. (e) Histogram showing distribution of adhesion forces in high and low salinity brines.

Unlike the previous location, elevated values of adhesion do not only correspond to areas of increased height, thus revealing that adhesion variation is more of a function of surface composition. Adhesion of the functional groups on the AFM tips to the sample surface is influenced by surface energies, which is largely impacted by surface composition. Thus, differences in intermolecular interactions associated with surface energies will present as a variation in adhesion. The magnitude of adhesion measured over the surface is similar to the previous location considered (C1), as well as the reduction in average tip-sample adhesion measured, decreasing by ~52% as salinity was reduced. Adhesion distribution over this
location is broader and also appears to have decreased non-uniformly. The peak value of adhesion detected in high salinity brine was 704 pN and 322 pN in low salinity brine.

![Graph showing average distribution of adhesion over different sites at the edge surfaces and basal planes of clays within location C2 in high and low salinity brine.]

Likewise, sample areas along the edge surfaces and basal planes were extracted for closer examination. Areas outlined in the white squares at the edge surfaces and black squares at the basal planes were analysed and average adhesion values measured are illustrated in the bar charts in Fig 10. Similar to results obtained at location C1, a higher range of adhesion was measured at the edge surfaces than at the basal planes. At the edges, adhesion ranged from 1.97 nN - 2.93 nN in high salinity brine decreasing to 0.17 nN - 0.51 nN in low salinity brine; while at the basal planes, adhesion ranged from 0.56 nN - 0.86 nN in high salinity brine to 0.08 nN - 0.82 nN in low salinity brine.

Thus, in terms of adhesion response to low salinity flooding, the edge surfaces of vermiculite show similar behaviour to kaolinite, displaying a more conspicuous effect than at the basal planes.

The extraction of contact angles from adhesion data is feasible via the Young-Dupré equation:

$$W_A = \sigma_{ow} (1 - \cos \theta)$$  \[35\]

Where $W_A$ represents work of adhesion per unit surface area, $\sigma_{ow}$ is the oil-water interfacial tension and $\theta$ represents the intrinsic contact angle, which is an apparent contact angle on an ideal, totally smooth, chemically homogenous surface. However, this estimation has been
excluded from this work. This is because on a non-ideal surface such as the pore of a rock, the measured contact angle depends on more parameters including roughness and chemical heterogeneity of the surface, surface defects, etc., and these factors lead to apparent contact angles that deviate from the intrinsic contact angle predicted by the Young-Dupré equation [77]. Indeed, Hassenkam et al. [13] have also shown that this could be potentially problematic as adhesion values are not adequately represented due to contact angle limitations [13]. Therefore, an estimation of the contact angle, while useful in visualising the low salinity effect, is likely to be factually inaccurate. Thus, wettability alteration in this study has been more accurately reflected through changes to adhesion between a hydrophobic tip and the sample surface, rather than through a calculated contact angle.

3.5 Role of charge reversal at clay edge surfaces in the low salinity effect

Analysis of orientations at both clay aggregate locations reveals that the values of adhesion measured in high salinity brine at the basal planes are closer in magnitude to the values of adhesion measured in low salinity brine at the edge surfaces. To put this into perspective, adhesion measured at the basal planes before the effects of low salinity waterflooding is more comparable to adhesion measured at the edge surfaces after the effects of low salinity waterflooding. Thus, the low salinity effect at the edges appears to be more significant.

The mechanism for this phenomenon could very well be due to a change in polarity caused by the low salinity brine as suggested by Secor and Radke [28] where numerical simulation revealed a spillover of negative charges from clay basal planes onto previously positively-charged edges as the ionic strength of the surrounding electrolyte was decreased, thereby causing a negative electrostatic charge at the edge surfaces. This observation was also confirmed by Chang and Sposito [78], and more recently by Tournassat et al.[79]. This effectively alters the surface energy at the clay edges, thus impacting oil adhesion.

Results obtained within this study suggest that the overall low salinity effect observed in clay-bearing sandstones is enhanced by this charge anisotropy at clay edges. Clays play a dominant role in alteration of wettability at the surface and the study of tip-sample adhesion at clay basal planes and edges is particularly important because of its pervasiveness in sandstones. Clay basal planes have a prevailing negative charge, while edges display pH-dependent charging behaviour as a result of hydroxyl functional groups. Thus, it stands to reason that the adhesion of oil components would differ at the edges and at the basal planes.
Because the edges and planes exhibit differing charge behaviour, an understanding of their varying contributions is required in order to interpret effects observed at the macroscale. The AFM enables, for the first time, clear interpretation of surface charge contribution of both clay faces and edges to the low salinity effect. Measurements show that the decrease in oil adhesion forces in brine of lower ionic strength, more so for the edges, contributes to the effect at the macroscale, with respect to low salinity recovery.

Drawing a parallel with between our observed phenomenon and results obtained from numerical simulation [28,78,79], at low ionic strength, the spillover of negative charges from the basal planes to dominate the positive charges at the edge surface will consequently lead to a greater reduction in adhesion measured at the edges with the −CH$_3$ tip when compared with the basal planes, as the surface energies have been altered. The elevated values of adhesion measured at the edges of both clay aggregates examined within the sandstone sample, thus, cannot solely be written off as a function of the heterogeneity of surface features. Also, they do not correlate with increased tip-sample exposure in which instance the value of adhesion measured is expected to be high due to contact with the sides of the tip. If that were the case, the low salinity effect observed would not be as palpable. The significance here is that there is a large impact of clay orientation on the low salinity effect, both in terms of quality and quantity.

This work represents an important step change towards establishing AFM as a pre-screening tool for deploying low salinity waterflooding in an industrial workflow. As previously established, [80], in current workflows, there is a critical step missing towards this deployment. While there is general consensus that clays play an important role, and also the anisotropy in clay surface chemistry is known in general, so far it has not been possible to measure it in-situ, i.e. the real response of clay basal planes and edges to crude oil. This paper demonstrates, for the first time, that this is possible, and establishes that the edges are of particular relevance. This closes an important step towards the development of a screening tool, which is an absolute necessity for deployment in practice.
4. Conclusions

In this work, a novel workflow has been developed where the wetting properties of rock can be assessed on the level of individual minerals by Atomic Force Microscopy (AFM) under in-situ conditions which includes not only the natural fluids and minerals but also the minerals in their native orientation within the pore space. AFM is operated at in-situ conditions using functionalized tips, and by combining topography and stiffness imaging, which help to identify specific minerals and their orientation, with force-distance curve mapping, a coherent picture of adhesion forces and their sensitivity to the ionic composition of the brine was obtained. While there are several previous studies that use AFM on natural minerals exposed to brines of different ionic compositions, in all relevant studies, these minerals had been extracted from rock and immobilized on a flat substrate such that only the basal planes were accessible. The novelty in this study is a workflow that is completely in-situ which required overcoming several complications such as the identification of the minerals and their orientation, and respective workflows were developed. The outcome of the study underlines the importance of examining minerals in their natural orientation, particularly with respect to clay minerals. One of the key observations is that the respective response of clay minerals to salinity changes in terms of adhesion forces does indeed depend significantly on their orientation. At high salinity conditions, the edges show approximately five times a stronger adhesion force than the basal planes. Upon reduction of salinity, the adhesion in the basal planes changes only insignificantly, i.e. only within the experimental uncertainty; while there is an about factor six reduction in adhesion forces at the edges, a response that is due to the spillover of negative charges from the basal planes to dominate the positive charges at the edge surface in brine of lower ionic strength.

The effect is reproducible, and – although in different absolute magnitude – very similar relative trends are observed for Kaolinite and Vermiculite. It explains not only why there is a general decrease in adhesion force but also why the de-wetting of crude oil from clay-bearing surfaces occurs in a step-by-step process where the contact line detaches from specific pinning points [30].

This underlines the importance of studying the response of rock to salinity changes with respect to the adhesion of crude oil under fully in-situ conditions, which also includes the minerals in their natural orientation within the pore space towards the crude oil. With this development step, the observations using AFM have become largely consistent with observations in the
wider body of literature such as contact angle studies and core flooding experiments. However, AFM experiments are significantly easier to conduct and have now the potential to become a pre-screening tool for assessing the low salinity response on the basis of small rock sample volumes as can be obtained for instance from cuttings. It is, nevertheless, necessary to go through the complication of developing respective methods and workflows which has been achieved in this work.

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