

WETTABILITY CHARACTERIZATION AND NON- INVASIVE MONITORING OF THE EFFECT OF CRUDE OIL TREATMENT ON CAP-ROCK SHALE MINERALS

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ABSTRACT

Reliable assessment of top-seal risk requires investigation of cap-rock wettability to hydrocarbons in their natural state as well as study of conditions of wettability alteration. We used a series of petrophysical and physicochemical methods to obtain comprehensive information on the properties of shale minerals as potential seals.

In our study we investigated water-, oil- and mixed- wet shales from wells in Australia, which were compared to simplified model shales (single and mixed minerals) artificially treated in crude oil. The intact natural shale samples, preserved with their original water content, were characterized petrophysically by x-ray CT, dielectric and NMR (CPMG – T₂) methods. Mineralogy, chemical composition, CEC, BET surface area and Hg-injection pore size of dried samples of the natural shales were determined by standard methods. We also made scanning electron microscope observations on polished sections of all the samples.

The effect of oil treatment (simplified aging procedure) was studied using optical and fluorescence microscopy and spectrophotometry as well as low vacuum SEM. Spontaneous imbibition and pigment extraction methods were used to study the influence of crude oil treatment on oil recovery. The wettability alteration - water/air and water/oil contact angle measurement was performed on flat fragments of shale rocks using the sessile drop and Wilhelmy plate methods.

Combining permeability tests and NMR spectroscopy allowed us to assess quantitatively liquid/liquid displacement and solid/liquid interactions. Comparing pure mineral and natural shale responses for which XRD determinations were made we could investigate the influence of mineralogy on liquid/liquid displacement and equilibrium distributions. It is clear that mineralogically and texturally distinct shales show quite different affinities for oil and water, ranging from strongly hydrophilic to strongly hydrophobic. There is some indication from our data to reinforce previous findings that kaolinite has a relatively high affinity for oil, and also we can infer that textural differences (pore size, roughness)

interplay with the effects due to mineral chemistry. Moreover petrophysical properties were consistent with wetting behaviour and swelling tendency of shale minerals. Through correlations of these responses we foresee the potential for application of wettability assays in downhole environments. Identifying petrophysical signatures of the prevailing wetting state, and susceptibility to wettability alteration (e.g. by drilling fluids or production processes) would be very valuable for shales as well as for reservoir lithologies.

INTRODUCTION

Seal wettability is of first order importance in oil exploration for the assessment of top-seal risk. We have therefore commenced a systematic investigation of the wettability of cap-rocks to hydrocarbons in their natural state and after wettability alteration. A mud or shale layer in the subsurface is often assumed to be a perfect seal to oil: the implicit assumption is that fine, clay-rich rocks are inherently water wet (hydrophilic) so that there is a capillary barrier formed. There is no oil leakage at all until there is sufficient driving pressure to overcome the capillary forces. If the surfaces of minerals constituting the seal are naturally hydrophobic, or become so with time, then the supposed barrier may leak, and retardation of oil or contaminant flow through the seal will only be by virtue of its low permeability, not capillary forces.

For our comprehensive study, it is necessary to consider shales as multimineral composites with wetting behaviour determined by their various components. Other parameters that influence wettability are the chemical composition and physicochemical properties of the brine and the crude oils, which vary depending on the nature of the source rocks, maturation history, migration, biodegradation and so on.

TECHNIQUES AND METHODS

The same physico-chemical interactions that control the surface interactions in the subsurface also exert a combined effect on any technique of wettability measurement used in the laboratory. As a result we had to break this study into several single steps and build up knowledge of the individual phenomena, (Clennell et al, 2006; Borysenko et al, 2006). Each test has advantages and disadvantages; generally each method probes one or more fundamental properties and processes (hydrophobicity, adhesion forces, displacement kinetics, swelling etc.). By applying several methods together with direct microscopic observations and spectroscopic analyses we gain an understanding of how these competing effects will interact in real world situations.

We used model systems of pure minerals and multimineral shales in their original state, after aging in crude oil, and in the case of pure quartz, after surface methylation to render the surface hydrophobic. We used a simple ageing protocol to modify the surface properties of these samples: heating at 70 °C for 24 hours with crude oil (Table 1).

Table 1. Crude oil and tested samples of quartz, clays and shale minerals (additional letters in sample abbreviation corresponds to C – crude oil treated and W – hydrated).

Sample	Composition
Crude oil	Barrow Island WA: 35-37 API; 0.84 specific gravity; 1.59 mPa·s viscosity at 20 °C
QN	Quartz (specially cleaned)
QM	Quartz (methylated)
L1_390	Quartz 20 %, Orthoclase 11 %, Illite 49%, Chlorite 2%, Hematite 5%, Dolomite 13%
O1A	Quartz 41 %, Kaolin 42%, Hematite <1 %, Mica 16 %, Siderite <1 %

First the oil/water interface was studied in rather simple systems—flat fragments of quartz and shales. The contact angle was determined using the Sessile Drop method by drawing a tangent to the liquid/liquid interface at the solid surface, as described by Neumann (1979).

The structural changes that occur on quartz and powdered shale surfaces as a result of crude oil treatment were studied using UV fluorescence and natural light microscopy (Liu, 2003). The distribution of petroleum on mineral surfaces was investigated using X-ray elemental analysis in the SEM. In addition, the dilution test where three sequential cycles (20 min each) of samples washing using a polar solvent (dichloromethane, DCM) was used to assess the stability of the oil film, following Liu and Eadington (2005).

A number of different powdered shale samples were studied using pigment extraction techniques published by Fuerstenau (1991) where the particles become distributed between water and oil phases according to the relative affinities of their surfaces to water and oil. During the test 1 g of powdered sample (grain size <10 µm) is placed inside the separating funnel together with 20 ml of water and 20 ml of single component oil (hexadecane). The funnel is thoroughly shaken for 5 minutes and let to settle. As a result the distribution of the particles could be determined—some particles sank in the water, while other particles kept floating in the oil. The competition between oil and water for the surfaces is being examined in this test, and this gives us a quantitative measure of hydrophobicity through the percentage of oil-borne particles.

The liquid distribution on the surfaces of polymineral rocks is known to affect the rate and amount oil recovery and this can be studied using spontaneous imbibition tests. The setup used for our measurements follows Morrow (2001). Mineral powder is packed in a small vial, fully saturated with crude oil and immersed in water within a sealed glass test cell. The oil recovery (in % OOIP) is determined by measuring the volume of oil expelled from the sample as percentage of oil at initial saturation.

Spontaneous imbibition tests probe how surface forces lead to rearrangement of initial fluid distributions towards a new distribution of contacts that express a local free energy minimum. Forced imbibition represents a more general case where there is an external driving force acting on the system. The flow pressure gradient in a co-current flow test allows local energy minima to be overcome in displacement process involving water and

the non-aqueous phase. Several parameters can be obtained from such a test. We are particularly interested in the threshold entry pressure for the non-wetting phase to enter the pack, relative permeability to water and oil, the sweep efficiency (residual saturation) and the spatial distribution of the trapped fluid on the pore scale.

The displacement processes in either spontaneous or forced imbibition may be monitored by NMR (the whole cell is placed within the magnet bore) to provide a time series of transverse relaxation time (T_2) spectra that can be used to deduce the relative amounts of oil and water, and the relative sizes of the pores in which the mobile and trapped phases reside. The effect of oil-film coating and water adsorption within porous space of mineral was studied using proton NMR spectroscopy. Sequential measurements of the proton T_2 spectrum were made and matched against to the pressure over time record, so that the progress of forced injection of fluid, and subsequent redistribution of phases, could be monitored. Using the CPMG pulse sequence with full spin polarization and 64 stacked scans we were able to acquire a T_2 spectrum every 10 minutes during dynamic flow tests.

RESULTS

Contact Angle

The results of contact angle measurement are presented in Fig.1. In a natural state most rock is water wet, i.e. water spontaneously spreads on its surface (Fig. 1a) and the contact angle is $10^\circ - 60^\circ$. However on the surface of a naturally oil-wet reservoir rock – shaly sandstone from a field in the Perth Basin – water does not spread spontaneously (Fig. 1b) but drop with a sharp mineral/water/air contact line (the contact angle above 90°). When the water droplet is placed on the surface, but immersed in mineral oil, because of strong hydrophobicity of both shale and oil, the contact angle of water is very large (Fig 1c). Thus the contact angle for naturally oil-wet rock and artificially crude oil treated shale O1AC is equal to $140^\circ - 160^\circ$. Nevertheless on shale L1_390C that can be referred to as hydrophilic the contact angle remains below 60° even after crude oil treatment, see Fig 1d.

The value of contact angle $140^\circ - 160^\circ$ measured on artificially aged shale samples (Fig. 1c) corresponds well to contact angle measured on the naturally oil-wet rock (140°). This value can be considered as the relevant contact angle for capillary invasion through an initially water-saturated caprock above an oil reservoir, and to use it predictively one would have to make a correction for the anticipated interfacial tension changes with temperature. However, for screening purposes, ambient condition water-air contact angles are useful to distinguish shales that have hydrophilic or hydrophobic tendencies, and for assessing the affect of treatments such as methylation or oil aging on samples.

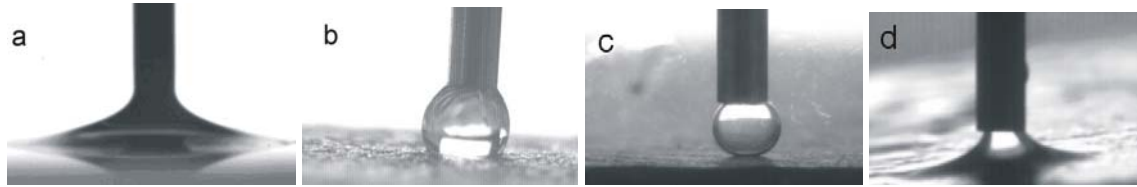


Fig. 1. Sessile drop measurement: the water drop on the surface of water-wet shale L1_390 (a) and reservoir rock from Cliff Head of Perth Basin (b). Oil/water contact angle for artificially crude oil treated shale O1AC (c) and L1_390C (d).

Optical and fluorescent microscopy

Optical and fluorescent microscopy reveals that the quartz samples become coated with an oil film (QC in Fig. 2 top), it also fills the space between grains so that they aggregate. Surfaces of shale granules (L1_390C and O1AC) subjected to the same aging process shows a similar pattern to the powdered quartz - their surface becomes profoundly imbued by oil (Fig. 2 top). SEM X-ray elemental analysis also indicates the presence of oil film on the surface by comparison of carbon and silicon distribution (QC, L1_390C, O1AC in Fig. 2 bottom).

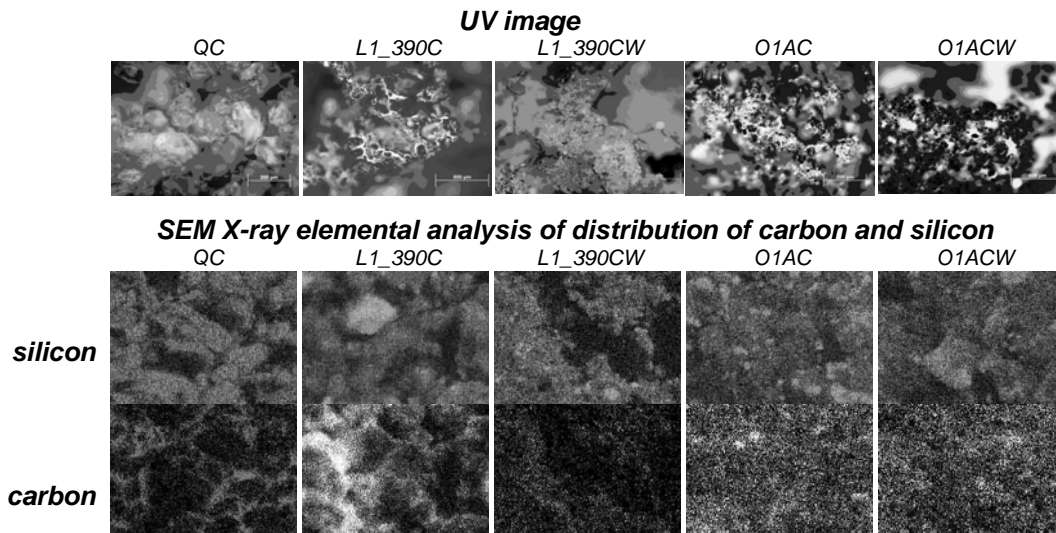


Fig.2. UV fluorescence image and SEM X-ray elemental analysis of samples after crude oil treatment (QC, L1_390C, O1AC) and subsequent hydration (L1_390CW, O1ACW).

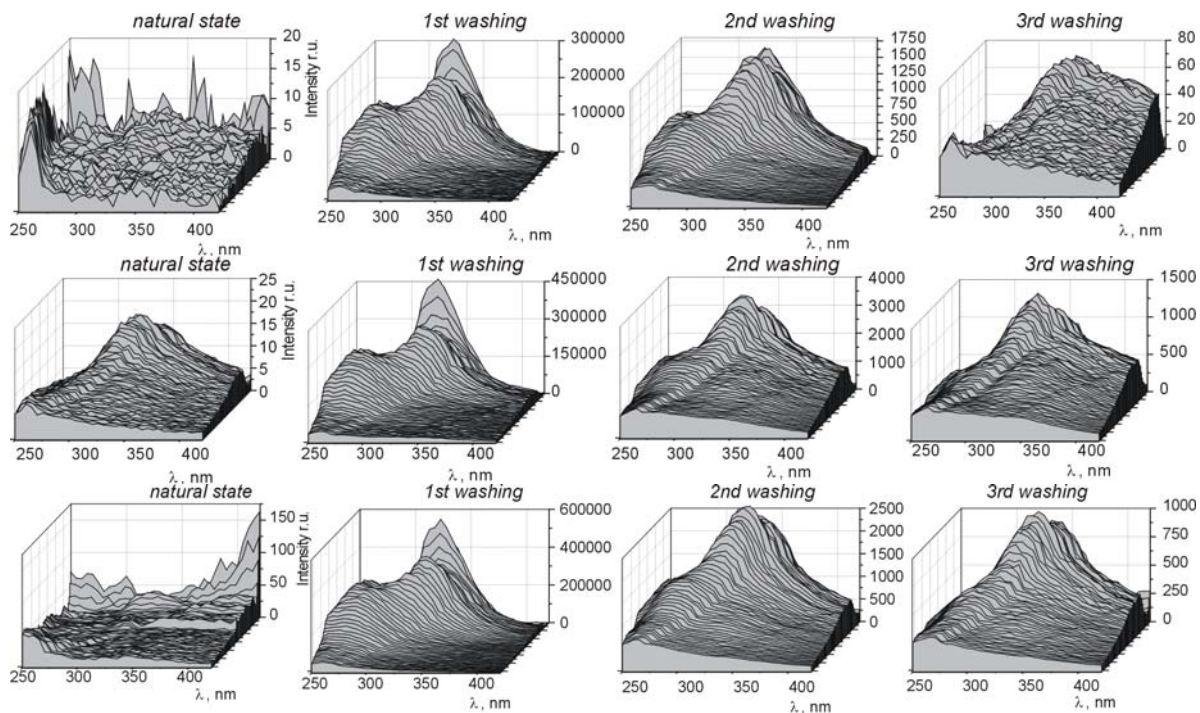


Fig. 3. Fluorescence spectra of DCM solvent recovered from washing over the following samples: top) quartz QC; middle) O1AC shale; bottom) L1_390C shale.

It is possible to see that after hydration the oil film is displaced by water on the surface of hydrophilic shale L1_390CW (Fig. 2). The remaining film was located in pockets and surface heterogeneities (micro-pores and micro-cracks). That was not the case on the surface of hydrophobic shale (O1ACW in Fig. 2) washed with water, where the oil remains practically intact.

Moreover the dilution test using a polar solvent (DCM) shows that the film of crude oil created on the surface is quite stable. A measurable portion of oil remains on the surface and can be detected in the fluorescence of the washed-over solvent even after three cycles of washing of the aged quartz (Fig. 3). The dilution test provides evidence for a persistent oil film on the hydrophobic shale: there is stronger adhesion to the surface than for the hydrophilic shale, where a considerably larger portion of oil is removed even after first washing (Fig. 3).

Pigment extraction

The quantitative results of the pigment extraction test are presented in Fig. 4 for samples in their natural state and oil treated. Before ageing the majority of samples are preferentially water-wet, but after crude oil treatment they acquire oil-wet character (Fig. 4). L1_390 shale and smectite are not permanently altered though, and recover to a water-wet state. Smectite shows oil-wet properties immediately after hydration and yet reverted to a water-wet behavior after several hours of being exposed to water again. On the

contrary, kaolin has a relatively high affinity for oil and this persists when it is exposed to water. Our observations are generally in line with previous findings of Rueslåtten (1994), Bantignies (1997) and Cosultchi (2005).

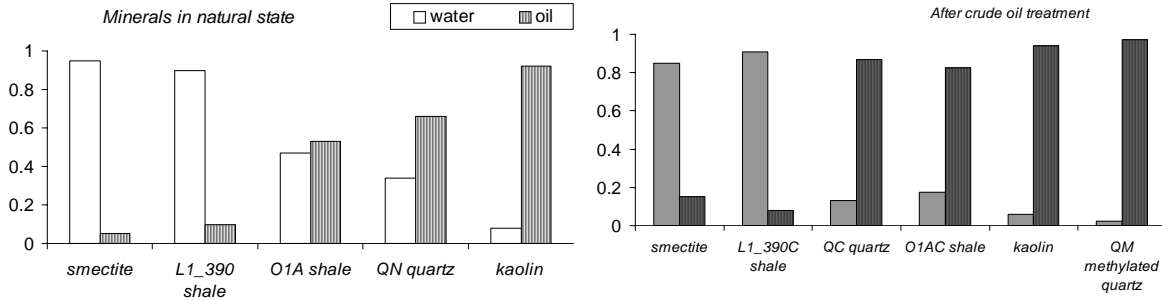


Fig. 4. Distribution of mineral particles between two phases of water and oil before and after ageing in crude oil.

Spontaneous and forced imbibition

The spontaneous imbibition test shows that the highest rate of oil recovery is measured for clean quartz QN followed by the most hydrophilic shale L1_390 (Fig. 5). A lower spontaneous imbibition rate is found for methylated quartz QN and practically no oil displacement by water is observed in the hydrophobic shale sample O1A. In contradiction to general wetting behavior of clays observed in powder flotation, smectite shows slower oil recovery then kaolin (Fig. 5). We can attribute this difference not to inherent wettability but to intensive swelling of smectite powder during hydration that causes a reduction in pore and inter-particle space and thus trapping of both liquids. Also, certain organic molecules can enter the interlayers of smectite and these are not easily displaced: not strictly a surface wettability effect.

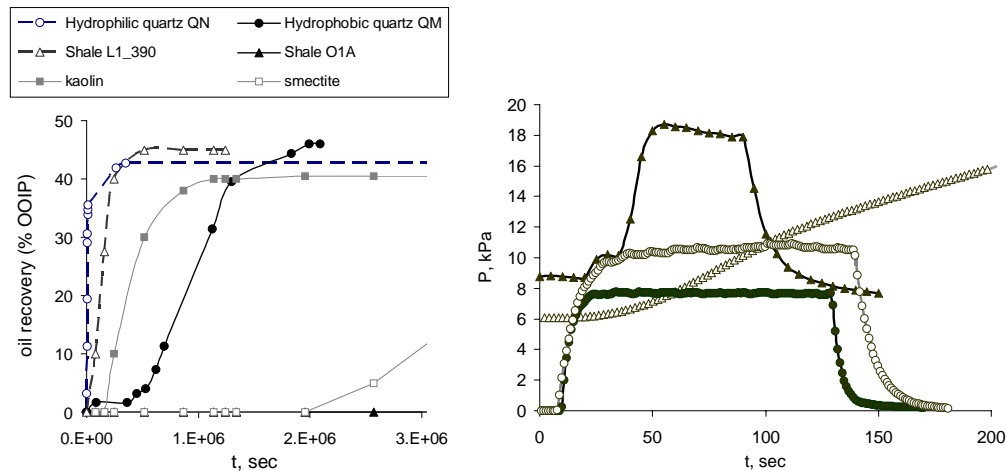


Fig 5. Oil recovery versus time for selected shales and clays (left). Flow pressure measured versus time at 1 ml/min rate (right).

We used forced imbibition (permeability cell tests) to investigate the process of liquid penetration and interface formation in packed particle beds. (Packed beds of approx. 100-250 micron sized shale particles are used because it is clearly impractical to force fluids at a reasonable rate through intact shales; the packed beds present multiple mineral surfaces to the invading and retained fluid and should represent the relative wettability of the mineral assemblage.) The differential pressure generated by constant-rate-of-flow injection of water was recorded in time. This pressure initially increased slowly as the water penetrated the dry pack, and then rose again up to the value corresponding to a steady laminar flow once the bed was saturated with the permeant (Fig. 5).

The degree of hydrophobicity can be quantified from the pressure required to break through the sample's capillary resistance and induce an essentially steady state flow condition. While in quartz QN and QM samples the pressure was rising from 0 value to 8-10 KPa in the sample of powdered shales it was necessary to overcome a threshold differential pressure of 6-8 kPa to initiate flow formation. Nevertheless in contrast to hydrophobic shale O1A where the steady laminar flow was formed at 19 kPa, in hydrophilic shale L1_390 water is absorbed into the clay granules leading to swelling and adsorption, which was so intense that flow vs. pressure function was not linear either. Thus as a result of decrease of the flow pathways between the expanded granules after saturation the ultimate relative permeability was lower in hydrophilic shale L1_390 ($k=2.5$ millidarcy) in comparison to hydrophobic shale O1A ($k=234$ millidarcy). Similarly to shale samples we saw lower relative permeability of $k=98$ millidarcy in hydrophilic quartz QN in comparison to $k=150$ millidarcy in hydrophobic quartz QM. That was probably due to low affinity to water in hydrophobic medium that makes the water mobility higher.

NMR spectroscopy

NMR spectra acquired at time intervals in the tests (Fig. 6) show that hydrophilic (clean) quartz has a main T_2 peak at longer relaxation times 10^4 - 10^6 μs than hydrophobic (methylated) quartz, the latter is broader and located in the range of $T_2 = 10^3$ - 10^5 μs . This result is the opposite of what is expected, since the relaxation rate scales with surface area to volume ratio.

The final series of forced imbibition experiments used packed beds of hydrophilic shale and hydrophobic shale that were tested both as dry powder and after the crude oil aging process. The distribution of T_2 peaks after injection of approximately 5-8 ml of water into each sample (> 50% water saturation) is shown in Fig. 6. The clean samples without any oil have quite distinct T_2 spectra: the clay bound water peak in the packed hydrophilic shale powder is much more distinct than in the hydrophobic shale pack. The latter sample has a series of water peaks at long T_2 , which represent inter-particle pore space, and also some bulk water ($T_2 = 3$ seconds). This implies that water is not filling the pore space, but rather it is avoiding the surfaces and further water injection actually pushes the granules apart.

During water penetration into aged hydrophilic shale the oil T_2 peak grows and water peak shifts to higher values and changes its shape. That reflects displacement of surface oil films by water. We could also follow water penetration into the porous space of hydrophobic shale packs where the change of water peak is related to water penetration and partial oil/water redistribution.

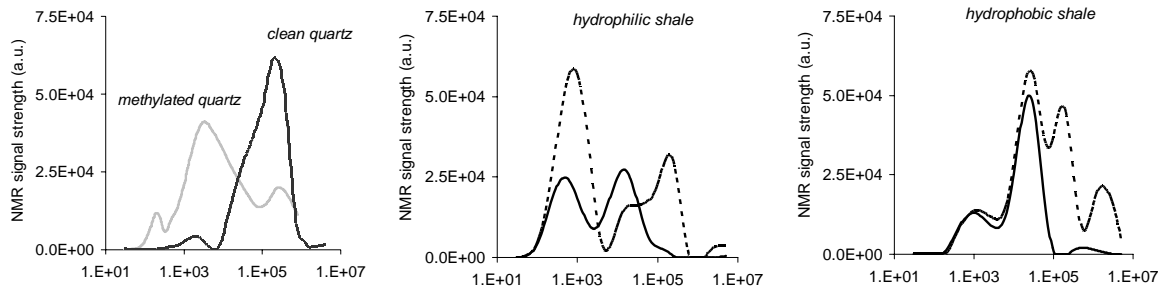


Fig. 6. NMR T_2 spectra of clean and methylated quartz containing imbibed water (left). NMR spectrum of hydrophilic (middle) and hydrophobic (right) shales after oil treatment (solid line) and water injection (dashed line).

DISCUSSION

Our most important finding is that not all shales are the same! There is a significant variation in surface affinity for oil versus water, as determined by particle partition experiments, contact angle measurements on the intact sample and a wide range of porous pack experiments on crushed samples. Initial correlations suggest that hydrophilic shales have higher surface activity (surface charge density and specific area, combining to produce higher CEC), and that illitic and smectitic mudrocks are more hydrophilic whereas kaolinitic mudrocks are potentially hydrophobic, being wet preferentially by oil and retaining that tendency after hydration.

The effect of oil treatment was studied using optical and fluorescence microscopy and spectrophotometry as well as low vacuum SEM. These direct observations confirmed our interpretations of the petrophysical responses concerning which shales are hydrophilic and which have a tendency to adsorb oil and even become oil wet. The findings are consistent with the measurements of wetting and swelling tendencies of the powders and intact shales that we conducted using standard methods.

Some of our NMR results with methylated quartz remain puzzling, especially as they are repeated in different grain sizes and in both spontaneous and forced imbibition tests. We suggest that the shorter T_2 in the methylated quartz is in part caused by a slightly different packing arrangement compared with clean quartz due to modified surface electrostatic interactions (samples are packed dry to the same bulk density). It is also possible that the NMR T_2 signal is affected somewhat by the methylation of the quartz surfaces, leading to enhanced surface relaxivity that also was observed by Al-Mahrooqi (2003) and Zhang (2000). However, the methylation process, unlike some wettability treatments using

commercial compounds, does not involve any reagents that are paramagnetic (e.g. transition metal ligands or catalysts) or that are aggressive to the surface texture, so the results are surprising. In fact it prompted us to start an investigating using high resolution NMR methods (400 MHz carbon and hydrogen solid state and chemical shift spectroscopy) sensitive to the tiny amounts of surface adsorbed compounds to investigate directly chemical treatments and identify the products deposited by ageing procedures (see our companion poster paper).

While our results from wettability assays show a highly consistent pattern, most of our work so far has focused on a detailed understanding of two end-member shales (L1-390; which is hydrophilic and O1A that is hydrophobic), and now we need to understand how representative these two shales are when compared with a wider range of mudrock categories. We are therefore proceeding to apply our various screening methods on a wider variety of preserved and dried shales, to confirm and reinforce the predictive value these have for petroleum systems worldwide.

To understand and ultimately predict rock wettability and its changes over time we need to study several parameters of the system, such as surface texture, micromorphology of the porosity, oil composition and PVT state at the prevailing conditions. Another important parameter is brine composition: both ionic species concentrations and pH influence the surface charges of silicates, and thereby wettability. Brine composition also controls double layer thickness, hydration and swelling behaviour in clays and shales. These primary parameters in turn affect macroscopic properties such as capillary pressure, water/oil adsorption and residual saturation. Our future work will investigate these variables by controlled parametric methods.

CONCLUSIONS

It is clear that mineralogically and texturally distinct shales show quite different affinities for oil and water, ranging from strongly hydrophilic to strongly hydrophobic. Comparing pure mineral and natural shale responses for which XRD determinations were made, we could investigate the influence of mineralogical structure and wettability of individual shale components (clay minerals, quartz, feldspars, carbonates) on liquid/liquid displacement and distribution inside shale porous medium.

Petrophysical properties were consistent with wetting behavior and swelling tendency of shale minerals. Through correlations of these responses we foresee the potential for application in downhole environments, where identifying petrophysical signatures of the prevailing wetting state, and susceptibility to wettability alteration (e.g. by drilling fluids or production processes) would be very valuable.

These results give us confidence that a combination of petrophysical measurements holds promise for rapid laboratory and in-situ investigations of wettability in complex natural systems. Future work will build on the most promising parts of our investigations so far,

with particular emphasis on natural samples and moving to more realistic prevailing conditions.

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