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## Wettability of Shales as Petroleum Reservoir Seals

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### SUMMARY

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Conventional surface methods, such as contact angle measurements, are combined with petrophysical probes, including nuclear magnetic resonance and broadband dielectric spectroscopy, to understand wetting mechanisms in clays and shales.

Shales or mudrocks can act as seals to petroleum reservoirs because of their low permeability and high capillary entry pressure. Capillary sealing of hydrocarbons requires that the rock is substantially water-wet. If the cap-rock shale were to become oil wet, then the underlying oil column could be lost [see: Boulton et al. 1997, Bennett et al. 2004, Aplin et al. 2005].

Little is known about shale wettability, and to understand it we need to study several parameters of the system, such as mineralogy surface texture, micro-morphology of the porosity, brine composition and oil composition and phase state at the prevailing pressure-volume-temperature conditions [Drummond and Israelachvili, 2004]. The same physico-chemical interactions that control interfacial interactions in the subsurface also exert a combined effect on wettability measurements made in the laboratory. As a result, we had to divide our study into several steps and build up knowledge of the individual phenomena involved [Borysenko, et al., 2006]. We used conventional assays such as contact angle determination, and time lapse experiments involving forced or spontaneous fluid displacements. These were combined with petrophysical studies: nuclear magnetic resonance at low and high field and dielectric spectroscopy. Each method probes one or more fundamental properties or processes (adhesion forces, displacement kinetics, swelling, ionic mobility, nuclear spin dynamics...). By applying several methods together and complementing them with direct microscopic observations, we obtain an understanding of how these competing physico-chemical effects interact in a range of shales.

It is not practical to inject oil into nano-darcy permeability shale, so we prepared from cleaned, dried shale samples powders of the polymineralic aggregates to ensure easy access of the test fluids to internal and external surfaces. The behaviour of the various shale powders listed in Table 1 was compared with standard minerals: kaolin, smectite, clean quartz (two grain sizes, 40 and 150 micron) and quartz with a surface methylation treatment that renders it strongly oil wet.

**Table 1** XRD-derived Mineralogy of Shales Investigated.

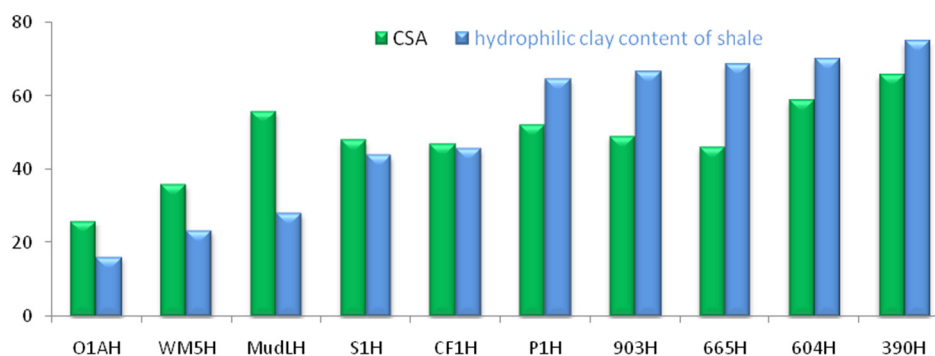
	O1A	WM5	MudL	S1	CF1	P1	L1_903	L1_665	L1_604	L1_390
Quartz	41	29	46	26	27	29	33	22	25	20
Kaolin, Chlorite	42	45	26	30	25	8	3	13	5	2
Smectite	0	10	0	0	27	26	0	0	0	49
Illite, Muscovite, Mica	16	8	20	44	9	24	29	45	35	0
Orthoclase, Dolomite, Albite	1	4	8	0	8	13	31	19	29	24
Others: oxides, carbonates, pyrite	0	4	0	0	4	0	4	1	6	5

Proton Nuclear Magnetic Resonance at low field has been used successfully for reservoir wetting studies, [e.g. Zhang et al. 2000]. We used a Maran Ultra 2 MHz spectrometer to measure  $T_2$  relaxation time distribution for shale grain packs containing oil, water or both. NMR spectroscopy allows us to follow the stages of fluid saturation over time in spontaneous and forced imbibition. In water wet shales such as L1\_390 we observed a growing peak of clay-bound water at  $T_2$  around 1 ms and water entering the inter-particle pore space at  $T_2$  around 10 ms. In shales that are mixed wet (e.g. MudL, CF1) the oil does not exhibit its bulk  $T_2$  so it must be in at least partial contact with surfaces to undergo preferential relaxation. In strongly oil-wet shales such as O1A the clay-bound water peak barely develops, whereas oil  $T_2$  is reduced by surface interaction.

Previous studies, [e.g., Bona and Capaccioli 2002], have suggested that dielectric measurements can be useful for diagnosing reservoir wettability, and we were interested to see the applicability to shales. Indeed, our inferences from low-field NMR were confirmed by dielectric constant measurements made in the frequency range 40 Hz to 100 MHz. We could see that significantly different values of dielectric constant can be observed depending on the sequence of oil or water saturation. While low field NMR is very good when there are reasonable volume fractions of both oil and water, it does not permit discrimination of small amounts (< 10%) of a non-wetting phase, or show small changes in wetting tendency. Dielectric measurements have enormously more intrinsic signal to noise than low field NMR, and reveal very small changes in surface states, since it is at the surfaces that most low

frequency electrical polarization occurs. At MHz frequencies thin oil or water films are especially apparent, while in the GHz frequency range we have found the dielectric constant is mainly determined by the saturation, and to a far lesser degree by fluid geometry (wetting). Finally, we applied high field NMR, using a Bruker 300 MHz spectrometer for both protons and  $^{13}\text{C}$  nuclei [Borysenko et al. 2008 details the methods]. At high field, signal to noise is thousands of times higher than at 2 MHz using the Maran, and while the experiments (Cross-Polarized Magic Angle Spinning- CPMAS and Double-Decoupled Magic Angle Spinning-DDMAS) are more complex to implement, they enable us to zoom in on processes occurring in thin films on surfaces, with just milligrams of the protonated species being detectable. Among many findings from high field NMR, we have discovered that the degree of anisotropy in the chemical shift (CSA) of protonated species in the crude oil within “aged” shale samples correlates with the proportion of hydrophilic minerals in shales (Fig. 1). We have a quantitative indication of the water-wetting tendency from high field NMR.

**Figure 1** Positive correlation between Chemical Shift Anisotropy and Hydrophilic Mineralogy.



Our study to date has not encompassed all of the variables existing in a natural petroleum system, but has focused on the fundamentals related to mineralogy and texture, with fluid compositional variation limited to three oils and three salinities under ambient conditions. While we have not investigated this dimension so far, we note that high field NMR is particularly useful for the study of organic matter in sediments, and an extension of our approach to elevated pressure and temperature “maturation” experiments could prove fruitful.

## References

- Aplin, A.C. and Larter, S.R.. 2005. Fluid Flow, Pore Pressure, Wettability and Leakage in Mudstone Cap Rocks. In: Peter Boulton, John Kaldi, ed. Evaluating Fault and Cap Rock Seals. Tulsa, Oklahoma: American Association of Petroleum Geologists, pp. 1-12.
- Bennett, B., Buckman, J. O., Bowler, B. F. J. & Larter, S. R., 2004 Wettability alteration in petroleum systems: the role of polar non-hydrocarbons, *Petrol. Geosci.* 2004, 10, 271-277.
- Bona, N. A. and Capaccioli, O., S. 2002. Advances in understanding the relationship between rock wettability and high-frequency dielectric response. *J. Pet. Sci. Eng.* 2002, 33, 87-99.
- Borysenko, A., Clennell, M.B., Sedev, R., Ralston, J., Raven, M. & Dewhurst, D.N. 2006. Wettability measurements in model and reservoir shale systems. Society of Core Analysts International Symposium, Trondheim, Norway, 12-16 September. SCA2006-03 pp. 1-12.
- Borysenko, A., Clennell, M.B., Burgar, I., Dewhurst, D. Sedev, R. & Ralston, J. 2008. Application of low field and solid-state NMR spectroscopy to study the liquid/liquid interface in porous space of clay minerals and shales. 9th International Meeting on Magnetic resonance in Porous Media, Boston, Mass. Paper 3F.
- Boulton, P. J., Theologou, P. N., & Foden, J. 1997. Capillary seals within the Eromanga Basin, Australia: Implications for exploration and production, *AAPG Memoir*, 67, 143-167.
- Drummond, C.; Israelachvili, J., Fundamental studies of crude oil-surface water interactions and its relationship to reservoir wettability. *J. Pet. Sci. Eng.* 2004, 45, 61- 81.
- Zhang, G.Q., Huang, C.-C. & Hirasaki, G. J. 2000. Interpretation of wettability in sandstones with NMR analysis. *Petrophysics* 41, 223-233.