

Magn. Reson. Discuss., referee comment RC2
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Comment on mr-2022-7

Anonymous Referee #2

Referee comment on "Magnetic expression in kerogen reveals impact on fluid transport" by Benjamin Nicot et al., Magn. Reson. Discuss., <https://doi.org/10.5194/mr-2022-7-RC2>, 2022

This work reports on a multimodal approach to the morphology and fluid magnetic resonance properties of a particular type of shale: the authors ask the question about the origin of slow fluid transport in shales, and present a mechanism they call "magnetic locking" as a possible explanation. With this term, to the best of my understanding, they suggest a kind of interaction of adsorbed alkanes ("oil") with surface radicals, in particular vanadyl in kerogen, that physically hinders molecular motion and reduces diffusion below a value that is expected from geometric reasoning alone. The claims are supported by a wide range of experimental data from different techniques including SEM, EPR, HYSORE, NMR relaxation, as well as literature models for the underlying relaxation processes. Experiments are carried out and compared for native shale, dried shale, and extracted kerogen with and without dodecane as a model oil.

Let us begin with the positive aspects: I appreciate very much the combination of different techniques, especially those that are not available to the average researcher in a particular combination; this paper uses an approach that combines methods that, to the best of my knowledge, have not been discussed in conjunction before. The SEM images over different scales provide a direct visualization of the pore space, but also the richness of morphologies of this material. They serve as a starting point for a determination of pore size distributions and fractal dimensions of this distribution, respectively. Whereas EPR spectroscopy gives an overview of the existing paramagnetic centers and their concentration, advanced pulsed EPR experiments such as HYSORE and PELDOR are employed for a discussion of distance distributions between radicals and nuclei, or radicals and radicals, respectively. This is being carried out for the rock samples as well as for the extracted kerogen. Then, NMRD relaxation data are acquired and compared for different temperatures; they are fitted to Korb's surface diffusion model that assumes dominating relaxation by interaction with unpaired electrons in the vicinity of the surface. These models are applied and characteristic timescales as well as dimensions are obtained.

There are a number of interesting findings that I do not recall from other sources; I particularly like the verification of typical small-scale pore properties by SEM imaging

down to dimensions of a few nm, as well as the convincing HYSORE results that demonstrate the proximity of dodecane molecules with the kerogen surface, and also the proof of an apparent homogeneous (on a larger scale) distribution of both types of radicals within the sample. The detection of antiferromagnetic order arising from carbon radicals and VO₂⁺ ions sounds pretty spectacular as well, though I may be ignorant of the probability. The data presented are of very high quality and provide substantial information, although I must confess that I am not an expert in pulsed EPR and cannot interpret the presented data with the required depth.

Now let's come to the less pleasant aspects. In general, I do have a problem in understanding how all those individual experimental results fit together and support the working hypothesis of a so-called "magnetic locking" of the adsorbed molecules. In fact, I am not convinced that such "magnetic locking" exists or is even necessary, in any case the evidence could be better explained; I am not even certain that the mentioned unexpectedly low mobility of oil even exists. It is certainly known that shales, in particular their kerogen component, has a very low permeability, much of it is because of the large tortuosity, the latter being linked to the small pore size and, often but not always, a low porosity. Of course, small pore size is not a reason for finding a large tortuosity, although both parameters are frequently linked. Having said that, there is also evidence in the literature that interactions between surface and molecules (to keep it general) do exist and they reduce the mobility below the tortuosity limit. This is part of an ongoing discussion and topic of studies: what is the effective tortuosity of different fluids in a given porous medium? It seems to be certain that, as the specific surface becomes larger, such interactions - one might also call them "locking effects" - become relevant. While one may usually think in hydrogen bonds or Coulomb interactions, or mere molecular stacking in a narrow geometry, I was not aware of the concept of "magnetic locking" before. (Neither was Web Of Science). The question is simply: what is meant by magnetic locking? Is it responsible for the observed low mobility of molecules, and is this proven by this work? I think the answer to the latter question is "no", let me explain what I don't understand and open the discussion:

In my opinion, the paper provides an extended list of individual facts, many of them indeed being stated as facts but not proven sufficiently; the authors do not go the extra mile to convince the reader that these observations have the discussed consequences, neither by explanation nor by corresponding references. Explanation of experiments and their results is often superficial; the list of references is, unfortunately, incomplete. This in particular as a number of quite different methods and topics are being covered, for which hardly any readership can call themselves experts in all of them. From the point of view of the reader, therefore, the manuscript leaves the impression of a range of high-quality results with rather different techniques, but conclusions that are not explained and proven with the necessary depth. This manuscript should probably be significantly extended in order to fully exploit the value of its individual results.

Here's a list of comments, in order of appearance, in order to explain my point:

- As mentioned, “magnetic locking” appears to be a buzzword but it is not substantiated; it should be avoided if it cannot be explained precisely
- I wonder whether the abbreviation “EMR” needs to be used, it is not common; I would prefer “EPR” but this could be a matter of taste
- The beginning of the introduction may highlight the importance of kerogen for understanding evolution, but it does not seem to constitute the main focus of this work
- The presentation on ll. 40ff suggests that the study of water/oil distribution in shales, and understanding of their relaxation properties, has been finalized once and for all – I doubt this is the case. The presented model, like any model, is a suggestion with the result of fitting parameters that may or may not describe the system realistically; alternative models exist, and there is a wide range of shales that may have quite different geometry and composition. The paragraph ends with the quest for describing “transport”, yet transport occurs on a wide range of scales in space and time. I would suggest that the authors present findings on the local scale of a molecular dimension; a macroscopic diffusion coefficient, a transport coefficient or a permeability are not determined and, in my opinion, cannot be inferred from the presented data.
- In the same paragraph (and in the following), it is mentioned again that the low mobility of molecules, and/or the low permeability, in shales is unexpected and unexplained; (i) I tend to say that it is not unexpected and (ii) there are only two references cited in this context, unfortunately both of them not readily available to the reader (Le Bihan not properly cited; Sondergeld a special journal) while there are tons of paper discussing the question of permeability in shale, for obvious commercial reasons, quite a lot of them also aiming at a molecular description – I find this problematic because the authors start out with a hypothesis that does not seem to be obvious to the reader
- 2.1. samples: what are the “native fluids”? this is anything but obvious, and rather important. Are these mixtures of water and oil; which aromaticity ratio; has a SARA analysis been made of the oil? These details would be required preferably in this section, or at least in the Supplementary Information
- In the same context, please explain the “HCl/HF” demineralization process. If I threw a shale sample into acid, what would I get? What is the recipe? Why are kerogens totally unaffected, or are they – especially their structure needs to be maintained to appreciate the similarity argument from the HYSORE experiments. A non-expert would not know this. In general, “sample preparation” is insufficiently described.
- 87ff: does this image analysis study a planar surface with depth zero, or does the image represent an average through a depth of xx nm? Could this affect the interpretation?
- Same paragraph: as I understand it, the automated algorithm measures circumference and pore area – this would be information for determining S/V ratio or a shape factor, although the shape information is dismissed; first computing an equivalent disk diameter and then a fractal dimension from the distribution of these diameters just appears a bit too complicated – how good is the disk representation? (apparently not very good for the clay structure in Figure 2)
- 2.4: at the end, it should be explained that a separation between brine and oil is only possible after applying particular models, they are not separable per se
- 182: what is the significance of the fractal dimension of the PSD? Is this a continuous function within boundaries, and if it is, what are the lower and upper limit? I can imagine that a fractal dimension of pore sizes will be reflected in diffusion properties, and possibly also in relaxation properties if the length scale is appropriate – yet the authors do not make use of this information at all in their work
- 193f: no it doesn't. there may well be organic radicals also in the rock - but it is unlikely; however, there could be an underlying quartz defect line at a similar g value which often overlaps with the organic radical line – has this been tested?
- 209ff: I can follow the general argument, but since I am not familiar with HYSORE: what does “low mobility” actually mean, can it be quantified? Can it be translated into a

residence time within a given distance, or a characteristic rotation or translation time?
The description appears too qualitative

- 228: how can the rather sharp features for the pure kerogen be explained? Why should the Mn ions actually have a rather well-defined distance of 2 nm, why are they not more randomly distributed?
- 235: what is meant by "reinforcing"? Is the effect not merely a change in distances, which leads to an increase of coupling strength due to the distance dependence? I am not sure if I understand how swelling leads to a reduction in these distances – maybe a sketch would help?
- 252: I suggest to remove the remark about the relation between line shape and age; or supplement it by an accessible reference, if indeed there is such a clear correlation (the given reference is a conference contribution)
- 254: I assume that the apparent multiplet (red line) in figure 6b is supposed to be the vanadyl line; have the authors confirmed this by fitting to the expected lineshape, or is this based on the (realistic) assumption that the suspect can only be VO₂⁺? Is it possible to estimate an amount of VO₂⁺ from this spectrum? (see also Figure S10, which may be discussed in more detail)
- 256ff: what would be the requirement for an antiferromagnetic ordering? Does this indicate a certain (maximum) distance? How frequent is this occurrence, in other worlds – is such an ordering, stemming from two different types of radicals, regularly observed in comparable systems? I am not familiar with this phenomenon, and I feel that it deserves much more explanation because it would represent a major finding of this study. As in several other cases in this paper, unfortunately, this effect is merely mentioned en passant, though the reader may not be able to assess its importance
- 282: what is learnt from the ²⁹Si signature in the native shale sample? Can this be interpreted by average distances of radicals to the solid matrix?
- 319: I do not understand what the authors want to conclude at this point – it seems that the dodecane molecule assumes a particular position with respect to the solid phase; this may or may not be between the mentioned units, thereby suppressing the coupling; even if the molecules "dock" at a particular position, or a preferential position, why can this be considered as "magnetic locking"? (Note: there is some limited body of literature about the respective location of carbon radicals and VO₂⁺, this has been studied with respect to crude oil but possibly also for solids – would be worth going into this and provide citations).
- Figure 8: at this point we see the different dispersions of water and oil in shale; before, it was mentioned as "native fluids" (see comment above), it may be clarified in the experimental session what fluids, and in which composition, are present in the shale; also one might explain why all experiments up to this point do not detect the presence of water. After all, the distribution of water and oil with respect to the surface would be an important parameter
- 354ff: it appears the for the two liquids, fitting to the corresponding equations (in the Supplementary Information) delivers the numbers given in the text. However, I have the impression that at least some of them were determined independently; one reason certainly is that the parameters appear as products in eq. 5 and 6. Text following eq. 5 clarifies that the specific surface area for clay is perhaps taken from a reference (or is it?). Following eq. 6 the specific area and the radius R are given values, while in I. 368f they are suggested as results – this is unacceptable and need to be clarified. Also, the diffusion coefficient is found under (iv) as a particular value but there is no mentioning how it is derived, neither in the main text or in the SI.
- As mentioned earlier, even if we believe that this D is the correct macroscopic value, since it is derived from microscopic processes on a nm-scale, I do not necessarily agree that this is a particularly low value, given the possibly high tortuosity of kerogen
- It should indeed be clarified that these two models deliver correlation times, and the fact that the function either fits or not; the value of the models then is in the interpretation of the fitted correlation times
- At some stage, the authors should at least mention that PFG NMR allows the

is this correct? What is the consequence?

- In general: eq. 1 is a representation of a two-component situation with exchange; on the other hand, this approach is seldom used for liquid relaxation in porous solids – why is this the case? Are most people doing it wrong? Which approximations can be made to allow the “simple” approach (with Brownstein/Tarr averaging)? I assume that the two alternative approaches eq. 5 and 6 serve to compute the “liquid” contribution according to eq. 3 which also appears in eq. 2. If the experimentally observed results are fitted with the full equation 2, then one would need to know the “solid” contribution of R_1 , or rather: its frequency dependence. However, I don’t think this has been done, so the $R_{1\text{solid}}$ term may be neglected – but if the authors cite eq. 2, they need to explain all relevant contribution, including $R_{1\text{solid}}$ – is this really the value that is mentioned as the low-frequency plateau in line 126? Then, what exactly are the protons in the solid phase, especially in the mineral phase?

- Figure S5 is difficult to read. Usually, T_1/T_2 is a diagonal line parallel to the main diagonal. There is such a line but it is not labelled. On the other hand, there are three averages $\langle T_1/T_2 \rangle$ (how have these averages been computed? For which field strength?). I do not understand which part of the 2d spectrum these three averages relate to; I do not understand how the experimental data are similar to the theoretical prediction (dashed and full lines); colors should be the same for each field strength.