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Webber, JBW, Corbett, P, Semple, KT et al. (7 more authors) (2013) An NMR study of porous rock and biochar containing organic material. *Microporous and Mesoporous Materials*, 178. 94 - 98. ISSN 1387-1811

<https://doi.org/10.1016/j.micromeso.2013.04.004>

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An NMR study of porous rock and biochar containing organic material.

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Abstract

With traditional sandstone oil reservoirs coming to the end of their useful lives, there is interest in extracting oil and gas from shale and carbonate rocks. Recovered samples often contain hydrocarbon material, sometimes in a fairly mobile form, sometimes in a tarry form. There is also an interest in studying forms of porous carbon, such as biochar, both for their soil-remedial properties, and for carbon sequestration. Biochars, depending on heat-treatment temperature and duration, also frequently contain resid-

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ual hydrocarbon matter. There are two techniques that will be discussed : Proton NMR Relaxation (NMRR) and NMR Cryoporometry (NMRC) [10.1016/j.physrep.2008.02.001] This study applies proton NMR relaxation to characterise the quantity and mobility of hydrocarbon matter in dried shale and carbonate rock and biochar pores. Curve-fitting is applied to the Free Induction Decays (FIDs) and Carr-Purcell-Meiboom-Gill (CPMG) echo trains to quantify the measurements. This study also applies NMR cryoporometry, to measure structure: pore-size distribution and pore volumes of the rock, and of the stable carbon skeleton. It has the significant advantage of being usable even when there are liquids and volatile components already in the pores. In porous rocks, combining mobility and structural information will provide a measure of the difficulty of removing the tar/oil from the rock. In biochar, combining the mobility of the labile components with the structural information for the stable biochar skeleton will inform calculations of lifetime of the labile components within the biochar. The NMRC data will also inform estimates of the lifetime of the biochar carbon skeleton.

Keywords: NMR cryoporometry, shale, biochar, carbon sequestration, oil recovery

1. Introduction

The application of NMR to studying porous rocks and biochar appears to have wider possibilities than seem to yet be commonly applied. In shales, NMR so far mainly seems to have been used to study rock that has been filled with water or organic liquids, so as to estimate pore dimensions using NMR Relaxometry [1].

The aim of this paper is to describe a protocol for studying porous materials that already, to some degree, contain organic matter. There are two main techniques, and their application, that are to be discussed : Proton NMR Relaxation (NMRR), in particular of dried samples, and a fairly recent technique NMR Cryoporometry (NMRC) [2, 3].

NMRR gives the information on organic fraction and the dynamics/mobility of this component; NMRC gives information on the nano-to micro-structure and pore-size distribution of the open porosity, directly relevant to the multi-phase flow in porous rocks, and to the diffusion controlled sequestration lifetime in the biochar case. Combining these two techniques gives additional information.

In the case of porous rock, this protocol is particularly relevant to helping determine the quantity and mobility of any included organic fractions, and the likely difficulty of extraction of this organic fraction through the tortuous network of pores. In the case of biochar, this protocol is relevant to determining the quantity and mobility of the labile component, relevant to both soil amendment and to carbon sequestration lifetime, and of the lifetime of the stable fraction, also relevant to carbon sequestration lifetime. The Kyoto Protocol specifies a 100 year carbon residence life-time as being necessary to claim carbon-credits.

Example data is shown for three rock types : a sandstone, a carbonate, and a shale. Data is discussed for the shale as received and after heating. An example sequence of biochar is also discussed, fired to 7 heat-treatment temperatures.

1.1. Apparatus and measurement protocols

The NMR spectrometer used was based on a Lab-Tools Mk1 (1970s) solid-state NMR spectrometer with digital-switching transmitter, upgraded with USB interfaced field programmable gate array (FPGA) peripheral instrumentation, giving computer control of most functions including transmitter and receiver fine-tuning. The magnet used was a low-field (0.5 T) Mullard permanent magnet with a 34mm pole-gap, with a low homogeneity, often deliberately degraded to $\sim 20\mu\text{T}$ over the 12mm long 2.4mm dia. sample, in order to have a clear echo at 1ms. Sample inhomogeneities in rock samples are often higher still. The transmitter generates ~ 2 to 3 mT of R.F. in the sample, giving a 2 to 3 μs $\pi/2$ proton pulse (3mm / 5mm probe). With active quench and active damping, this gives a fully-recovered time from the centre of the $\pi/2$ pulse of 6 to 8 μs (3mm / 5mm probe).

A $90^\circ\text{-}\tau\text{-}90^\circ$ pulse sequence was used for the relaxation measurements, with $\tau = 500\mu\text{s}$. The very small residual ring-down and short-lived mechanical ringing of the probe and coil was measured (equivalent to $\sim 100\text{nl}$ water, time-constant $\sim 30\mu\text{s}$) and has been subtracted from the results presented here. A question remains whether residual surface OH etc. on a dried porous sample gives a measurable signal that could be confused with a hydrocarbon signal. A sample of 100 Å pore diameter sol-gel silica was dried overnight at 110°C , and a tiny FID was measurable; rescaling this to equivalent surface area, for comparison with the signal from a typical shale, showed this to be negligible.

A $90^\circ\text{-}\tau\text{-}180^\circ\text{-}\tau\text{-echo}$ sequence was used for the NMR cryoporometry (NMRC) measurements, with echo at time $2\tau = 1\text{ms}$, with the cryoporometric ampli-

tude taken from an analytic maximum of a polynomial fit to the upper part of the echo.

Instrumental control, including temperature measurement and control, was provided by a 14 task multi-tasking set of routines, written in the array processing language Apl (AplX, MicroApl [4])

1.2. NMR Relaxation (NMRR)

NMRR has the capability to determine the quantities and dynamics of contained hydrocarbon organic matter (i.e. the mobility, ranging from a light liquid through a viscous oil to a tar).

This study uses proton NMRR to characterise the quantity and mobility of this hydrocarbon organic matter in the dried pores, applying curve-fitting techniques to the Free Induction Decays (FIDs) and the Carr-Purcell-Meiboom-Gill (CPMG) echo trains that were used to quantify the longer relaxation components. A longer relaxation time suggests there is more motional averaging (line-narrowing), and hence the presence of a more mobile component. More robust dynamical information can be achieved by making NMRR measurements as a function of temperature, so as to measure the activation energies of the molecular motions. This second stage of measurement has as yet not been carried out routinely on these shale and biochar samples.

In the case of shale and carbonate rocks NMRR can probe the dynamics/mobility of the hydrocarbon component within the porous rock skeleton. It may help give information on the expected ease with which this organic component can be recovered, based on this measured mobility. i.e. a light, volatile, oil should be easier to extract than a stiff tar stuck on the pore

surfaces.

Similarly, with biochar, NMRR probing the dynamics of the mobile (labile) hydrocarbon component may help give information on the expected life-time of this labile component within the biochar, based on this measured mobility. i.e. a volatile oil is likely to evaporate out of the porous structure more quickly than a tar-like material.

1.3. NMR Cryoporometry (NMRC)

Nano-structuring a liquid changes the Gibbs-Free Enthalpy : the effect of surface tension on the curved interface is directly equivalent to a volumetric energy, and this then changes the Gibbs-Free-Enthalpy. This in turn lowers the melting point, such that a compound can melt at 10s of degrees below the normal bulk melting point.

The technique is closely related to that of gas adsorption but uses the GibbsThomson equation rather than the Kelvin equation. They are both particular cases of the Gibbs Equations [5, 6]; the Kelvin equation is the constant temperature case, and the GibbsThomson equation is the constant pressure case. NMRC uses the Gibbs-Thomson effect to measure free-pore volume distributions, and can currently measure over a length scale from 1nm to around 10 μm .

For these measurements water was used as the probe liquid, and a recent Gibbs-Thomson coefficient calibration was employed [7] : $k_{GT} = 580 \text{ K}\cdot\text{\AA}$; $\epsilon = 0$, where, for a pore of diameter x , with a surface layer of thickness ϵ , the melting point depression = $\Delta T_m = k_{GT}/(x - 2\epsilon)$

2. NMR studies of porous rock (Shale, Carbonate), containing organic material.

NMRC measurements have been performed on porous rocks for a number of national and international companies and universities, and, in response, more than one leading geologist has stated that "*NMRC may be one of the most appropriate techniques for studying small-pore rock systems such as porous shales*". Many of these samples have already been exceedingly well characterised by a range of other techniques [8, 9, 10], and the NMR techniques presented here have been shown to add valuable information to these data-sets. NMRC has the significant advantage of being usable even when there are liquids and volatile components already in the pores, which can cause problems for other techniques such as gas adsorption, where the presence of the organic materials can lead to greatly extended pre-measurement out-gassing times. More detailed papers comparing results from different techniques are in preparation.

2.1. NMR Relaxation (NMRR) studies of the organic material in dry porous rock.

A number of different carbonate and shale rocks from different sources (and different continents) were studied by NMRR; FIDs were measured and, where appropriate, Carr-Purcell-Meiboom-Gill (CPMG) sequences used to measure longer T_2 components. They were first measured as received. Some samples were heated in the NMR probe, making measurements every 10C from room temperature to 150C. Other samples were just dried overnight at 120C, and then re-measured. One particularly interesting case is shown

in figure 2. The upper curve (as received) shows two fitted components, both a shorter exponential component, characteristic of a very stiff material, and also a longer, two-component exponential, characteristic of a more mobile/plastic, reptating, component.

The action of the overnight "drying" (lower curve) appears to have been to just halve the amplitude of the more mobile component, and to approximately halve the dominant T_2 . The shorter component has had its amplitude slightly reduced, and again the T_2 slightly reduced. These changes are interpreted as having been due to the "driving-off" of more volatile organics from the hydrocarbon matrix. This behaviour was very different to the complete removal of mobile liquid components (leaving signals with even shorter T_2 s than in this case), seen in some other samples, the change then considered to be due to the removal of water. Thus the NMR measurements have identified a clear case where, in spite of the stiff tar-like nature of the included organic fraction, it is possible to extract lighter organic fractions from within this tar-like component in the pores.

For comparison, the two thin lines are suitably scaled FIDs for two common road tars. These tars were studied in more detail, using FIDs and CPMG measurements, out to 3ms, extracting the fit parameters for the tars, to compare with organic fractions in the shale: Figure 3 shows fitted NMR Free-Induction Decays and CPMG data for Tar1. The straight line is a stretched exponential fit to the measured data in region $x = 1.5$ to $2.2 \mu s^{0.112}$, characteristic of a mobile, reptating component. However extrapolation to zero time gives an unphysical amplitude. The curve through $y=2$ is then an equivalent exponential distribution fit in same range, which gives a realistic

amplitude at zero time. Subtracting this from the data gives the lower circles, which are well fitted by a Gaussian. The total data is thus found to be well fitted by the sum of a short Gaussian (rigid) component and a slower relaxing component, characteristic of a mobile, reptating constituent.

Thus this suggests that the main organic component in this particular shale is of tar-like consistency, but that significant quantities of more mobile organic components are incorporated into this tar-like matrix, that then become mobile at slightly elevated temperatures. This additional oil recovery may well make gas recovery from these particular shales more financially viable.

Also important for this financial viability is knowing how much organic material is in the pores, These additional measurements on tar samples gave an "instrumental sensitivity" coefficient; i.e. Volts of signal per gram of tar-like organic matter. This was then used to obtain calibrated hydrocarbon quantity measurements for both the stiff and mobile organic components in the various shale and carbonate samples that were studied.

2.2. NMR Cryoporometry (NMRC) studies of porous rock free volume distributions.

NMRC has been applied to measure the remaining free volume in sandstone, carbonate and shale pores, as well as the pore-size distributions and pore surface areas. Figure 4 shows example NMRC pore-size distributions, with duplicated measurements, for a Barnett shale, a carbonate, and a sandstone, showing the significantly different range of pore-sizes into which they typically fall; the upper limit of the sandstone data is limited by the current resolution of the NMRC technique.

The smaller the pore, and the more tortuous the path connected to the pore, the more difficult will be the task of extracting this hydrocarbon. This NMRC data will, it is hoped, in the future be used to inform multi-scale diffusional and flow models, so as, in the case of oil-bearing porous rocks, to apply the mobility data measured using NMRR to estimating the difficulty of extracting the oil/tar from the pores.

3. NMR studies of porous carbon (Biochar), containing organic material.

”Sustainable biochar is a powerfully simple tool to fight global warming. This 2,000 year-old practice converts agricultural waste into a soil enhancer that can hold carbon, boost food security, and discourage deforestation. Sustainable biochar is one of the few technologies that is relatively inexpensive, widely applicable, and quickly scalable.” [11]. A range of measurements have been made on biochar to help determine the long-term stability of the carbon [12, 13, 14]. However it is the physical properties that tend to dominate the rate at which the labile hydrocarbons in the pores, and the stable carbon skeleton, evaporate / diffuse / ”burn” and return to the environment as CO₂. This can then be expressed as the 1/2-life of the amount of carbon in a particular biochar sample. This paper offers a method of applying NMR to study these physical properties, in particular the mobility / dynamics of the labile hydrocarbons, and the porous structure of the stable carbon skeleton through which the gases must diffuse. To fully interpret the results presented here will require a more extensive project involving multi-scalar modeling.

Contacts established world-wide, including through the International Biochar

Initiative, have lead to the receipt of numerous biochar samples for analysis. A particularly informative set of samples have been a set of seven Mesquite chars, with different heat-treatment temperatures (HTT), from Prof. Masiello of Rice University.

3.1. NMR Relaxation (NMRR) studies of the labile organic material in dried Biochar.

Proton NMR is selected to study the labile fraction in the biochar, rather than carbon NMR - partly because proton NMR offers a far higher sensitivity than Carbon NMR, enabling the measurement to be completed more quickly and cheaply, partly because it can be done on simpler and less costly NMR instruments (both of which are important if this technique is to become a routine analysis technique to be applied to all biochar sources), but mainly because we particularly wish to probe the quantity and dynamics of the mobile hydrocarbon fraction, and not be swamped by a larger signal from the stable carbon skeleton. Figure 5 shows the measured FIDs (thick lines), and their fits (thin lines), for the above seven Mesquite chars. As with the shale samples, the biochar FIDs show a predominantly two component decay. However the short components are best fitted with a Gaussian (normal) distribution, indicating a solid-like nature. The longer components are again well fitted with a stretched exponential, which in figure 5 have been converted to distributions of (two) exponentials.

The samples show decreasing amplitude, in order, as increasing amounts of the labile component are driven off with higher HTT. The NMR transverse relaxation time Gaussian T_2s surprisingly show a slight but steady increase, suggesting that this organic is transformed from a more solid/rigid form to a

slightly more mobile form. However the longer exponential components show a decrease in T_2s , suggesting that the more mobile plasticising components are being preferentially driven off by the higher HTTs.

For comparison, FIDs were also obtained for pine resin, in the form of freshly collected resin and a piece of old amber. Figure 6 shows NMR Free-Induction Decays for Amber (upper circles) and fresh Pine Resin (lower circles), compared with two biochar with heat treatment temperatures (HTT) : 300°C and 700°C (thick lines). Again these showed the typical short-Gaussian and longer stretched exponential (transformed into a distribution of exponentials), with the pine resin having longer relaxation times and a higher fraction of mobile component than the labile components in the biochar. Amber on the other hand was very rigid (the FID showing ringing from dipolar splitting), with only a tiny mobile component. As before, this data was used to provide a hydrocarbon quantity calibration, to enable measurements of the labile component rigid and mobile quantities.

3.2. NMR Cryoporometry studies of Biochar free volume distributions.

NMRC measurements were used to determine the location of the labile hydrocarbon component as a function of pore-size. Figure 5 shows these components being increasingly driven off with higher HTT. Correlating this information is with the increasing free pore volumes shown in figure 7, we may deduce the location of the labile component as a function of pore size, shown in figure 8. Thus we now know the mass of the labile material that is being removed by the increased heat-treatment, and the corresponding volume that is being freed-up. It is then possible to calculate the density of these components - progressive specific densities in the range 0.22 to 0.14

are found as HTT is increased. However the expected densities for pine resin and amber are just under unity. This leads to the conclusion that the hydrophobic labile components are having a pore blocking effect, and that increasing HTT is also exposing these blocked pores as the labile material is driven off. In the case of biochar, NMRC will, it is hoped, also be used to inform diffusional models to estimate the expected half-life of the conversion of both the labile component and the stable biochar carbon skeleton back to atmospheric CO₂.

4. Conclusions

This paper has discussed combining NMR relaxation (NMRR) and NMR Cryoporometry (NMRC), to study both porous rock and porous carbon/biochar. Data has been presented showing the measurement of the quantity of organic matter in shale and carbonate rock pores, the mobility of this material, and the size of the pores in which this material is located, relevant to extracting these hydrocarbons. Similar information has also been presented for the quantity and mobility of the labile material in Biochar, relevant to the carbon sequestration lifetime, and to claiming Carbon Credits, as specified in the Kyoto Protocol. Pore occluding information for the labile material has also been discussed, relevant to the soil enhancement properties of the Biochar.

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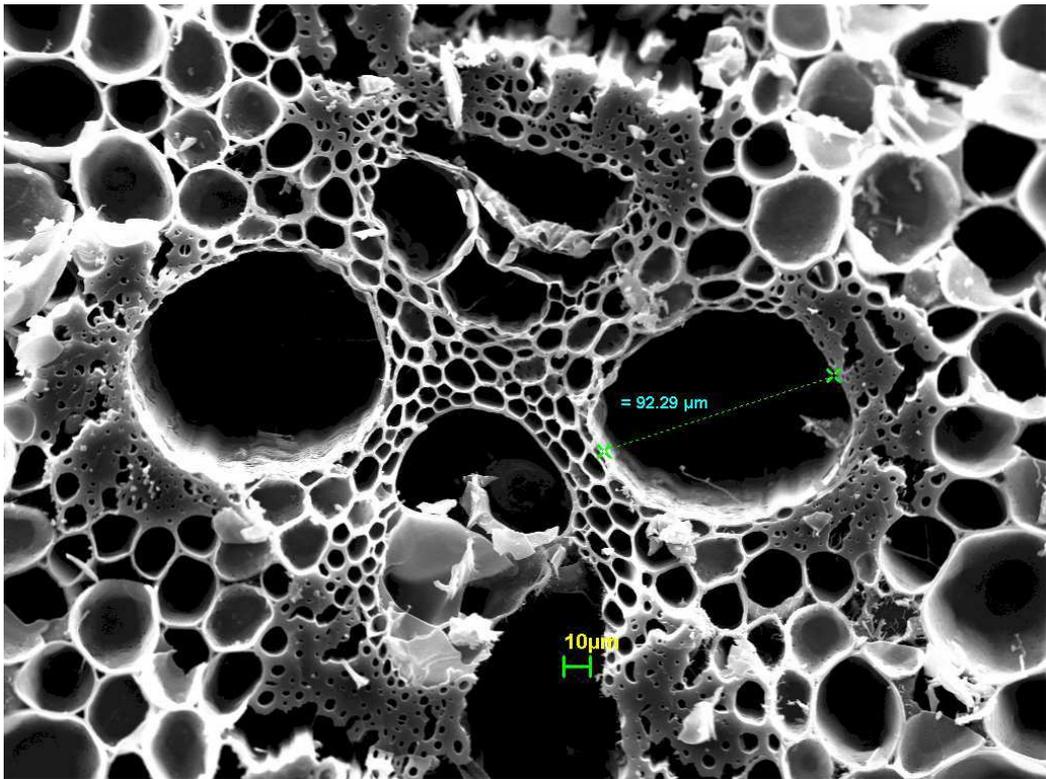


Figure 1: Microscopic structure of a Bamboo Biochar. (W.S. Teel).

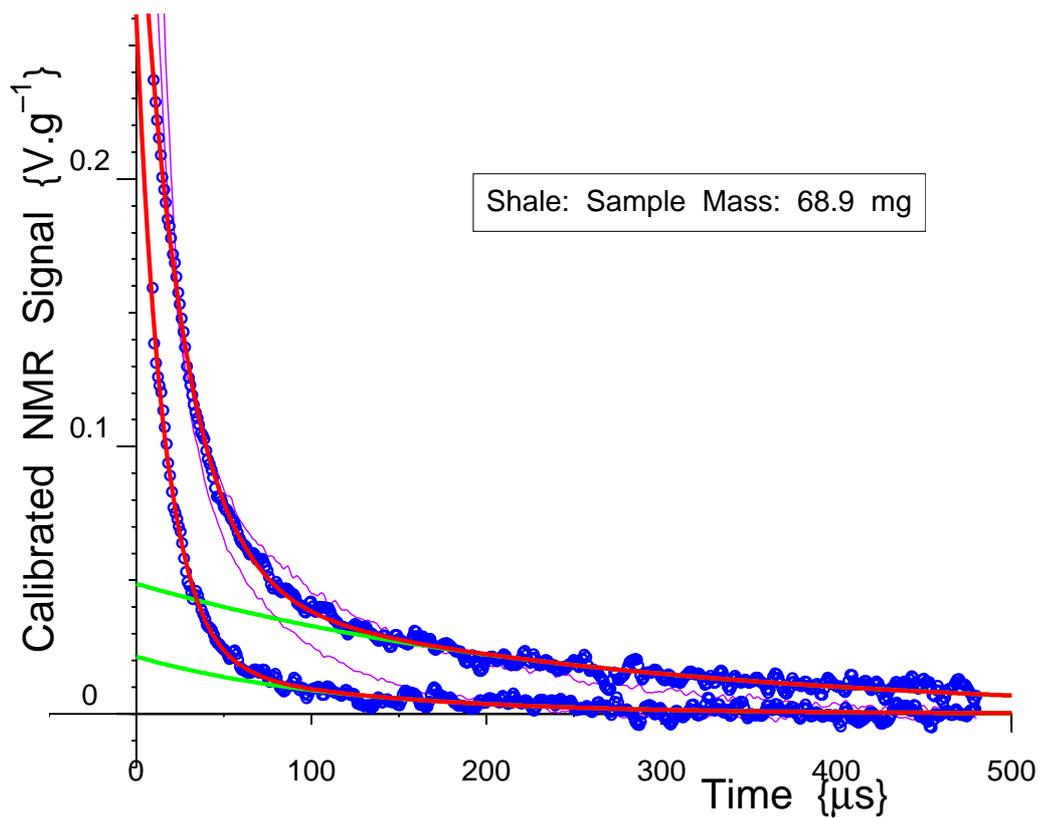


Figure 2: Two measurements of hydrocarbon quantity and dynamics/mobility in the pores of a sample of porous rock : NMR Relaxation (NMRR) Free-Induction Decays (FIDs) for organic matter in a shale, both as received (top) and after "drying" (lower). The difference is actually believed to be due to the driving off of volatile organic fractions. Also plotted (thin lines) are suitably scaled FIDs for two common road tars, for comparison.

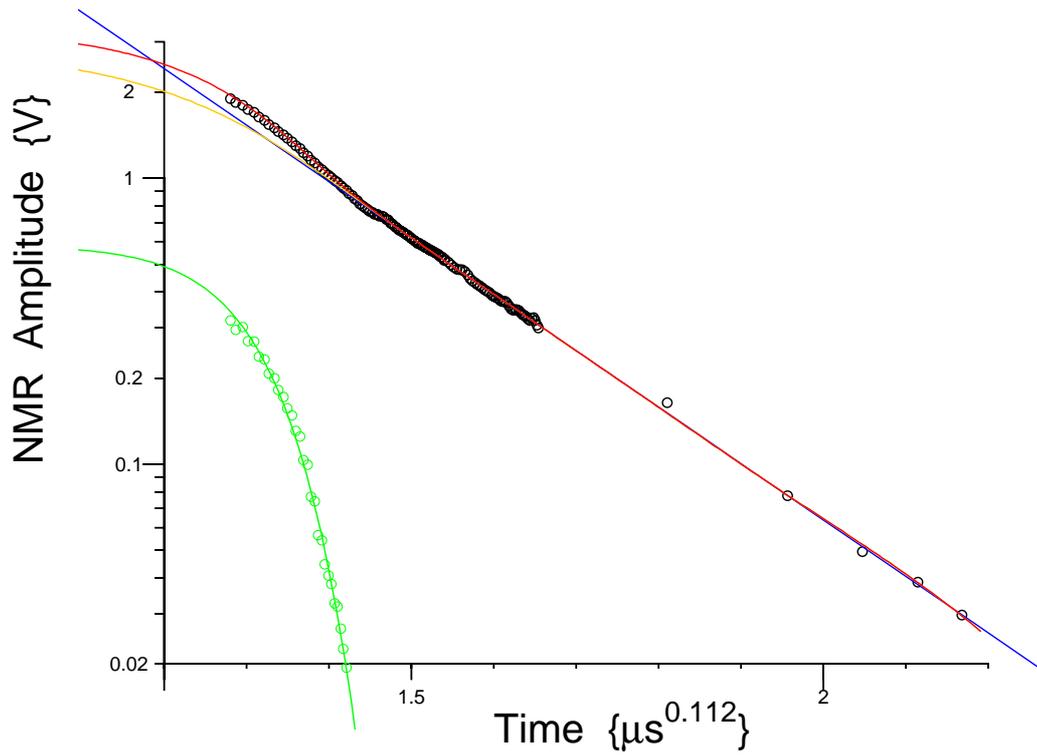


Figure 3: Extraction of fit parameters for tars, to compare with organic fractions in shale: Fitted NMR Free-Induction Decays and CPMG data for a common road Tar. Straight line : stretched-exponential fit to measured data in region $x = 1.5$ to $2.2 \mu s^{0.112}$. Curve through $y=2$: equivalent exponential distribution fit in same range. Lower circles : residual difference, with a Gaussian fit.

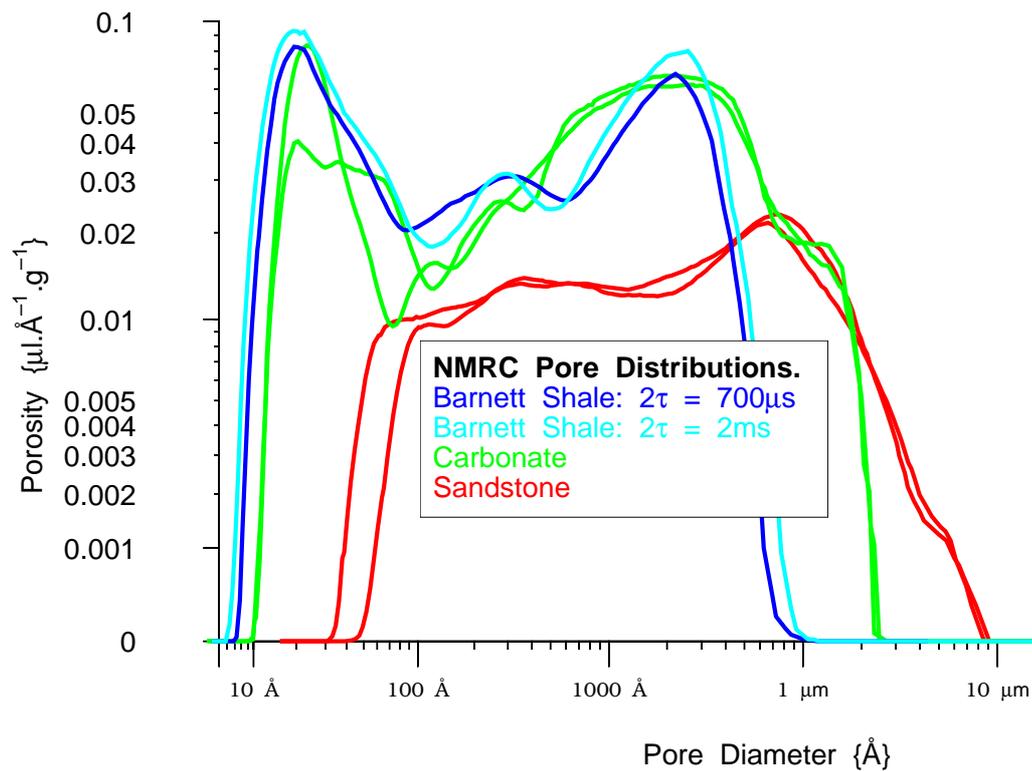


Figure 4: Measurements of open pore volume distributions in three different types of porous rock : NMR Cryoporometry (NMRC) pore-size distributions for a Barnett Shale, a Carbonate and a Sandstone, with duplicated measurements to show repeatability.

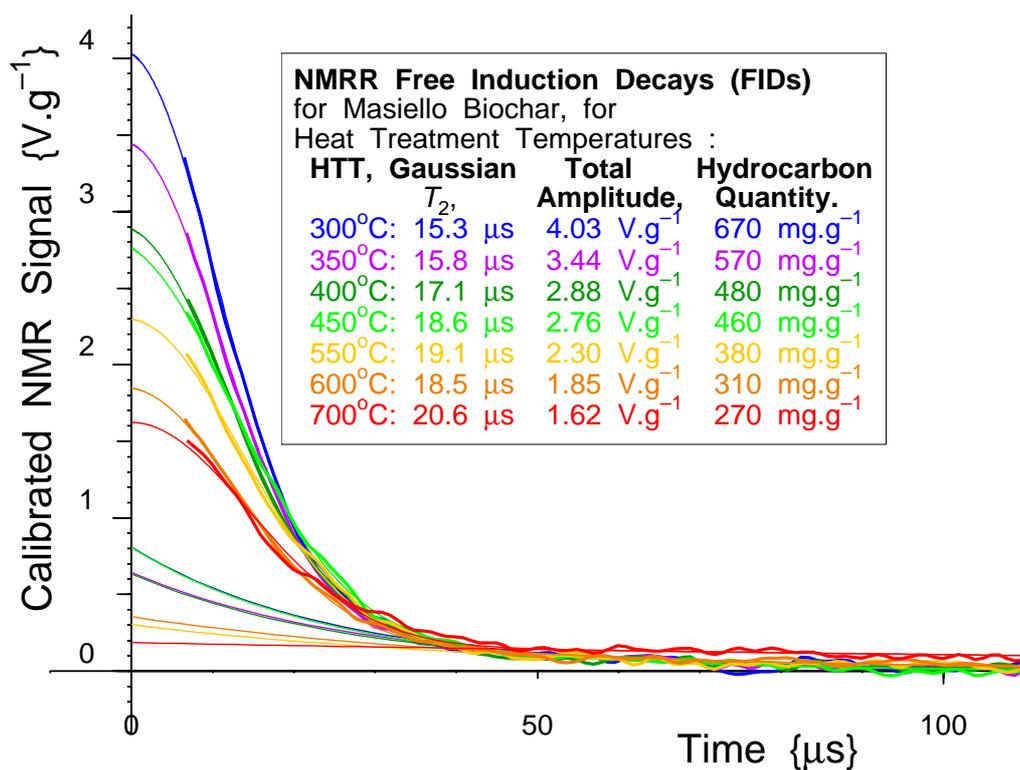


Figure 5: Measurements of hydrocarbon quantity and dynamics/mobility in the pores of biochar prepared at different HTTs : NMR Free-Induction Decays for seven biochars, with heat treatment temperatures (HTT) : 300°C, 350°C, 400°C, 450°C, 550°C, 600°C, 700°C. The samples show decreasing amplitude, in order, as increasing amounts of the labile component are driven off with higher HTT.

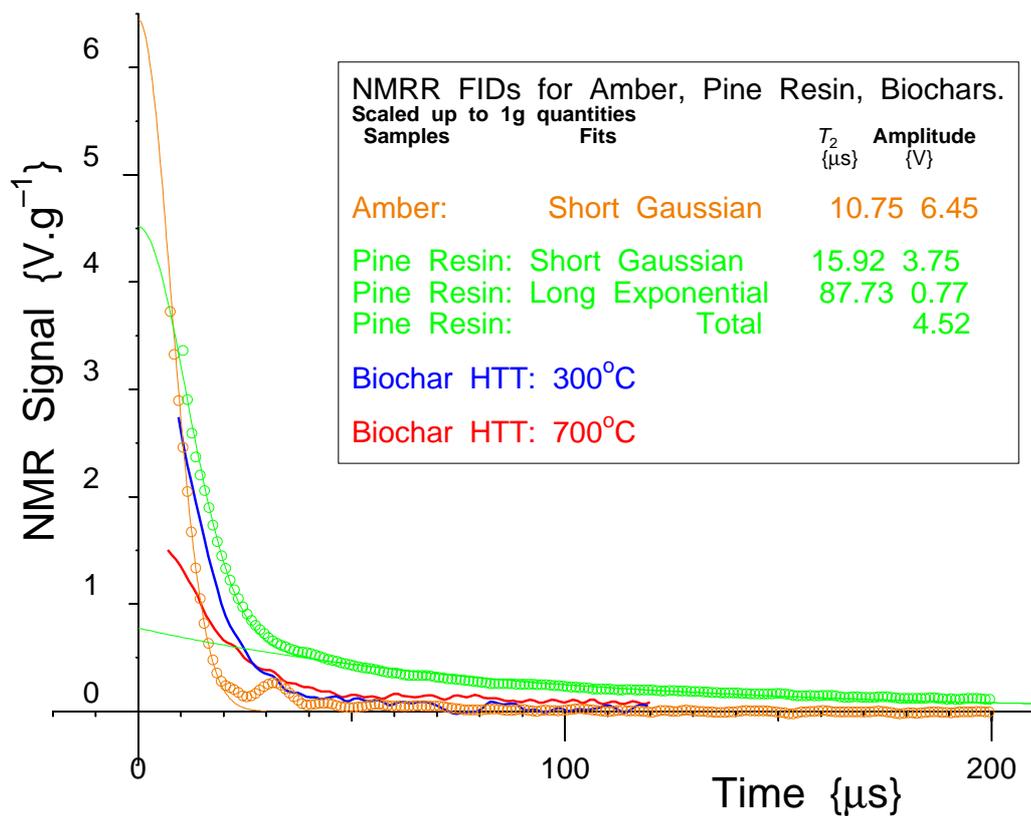


Figure 6: NMR Free-Induction Decays for Amber (upper circles) and fresh Pine Resin (lower circles), compared with two biochar with heat treatment temperatures (HTT) : 300°C and 700°C (thick lines).

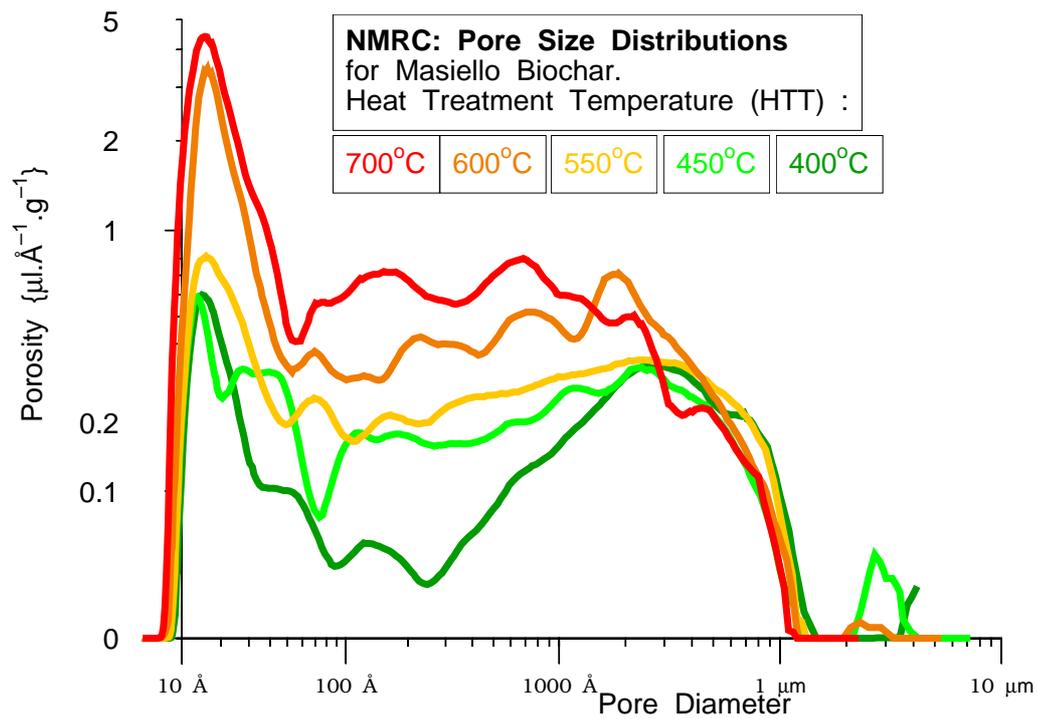


Figure 7: Measurements of open pore volume distributions for biochar prepared at five different HTTs : NMR cryoporometric measurements on five biochars, with heat treatment temperatures (HTT) : 400°C, 450°C, 550°C, 600°C, 700°C. The samples show increasing pore volumes, in order, as increasing amounts of the labile component are driven off with higher HTT.

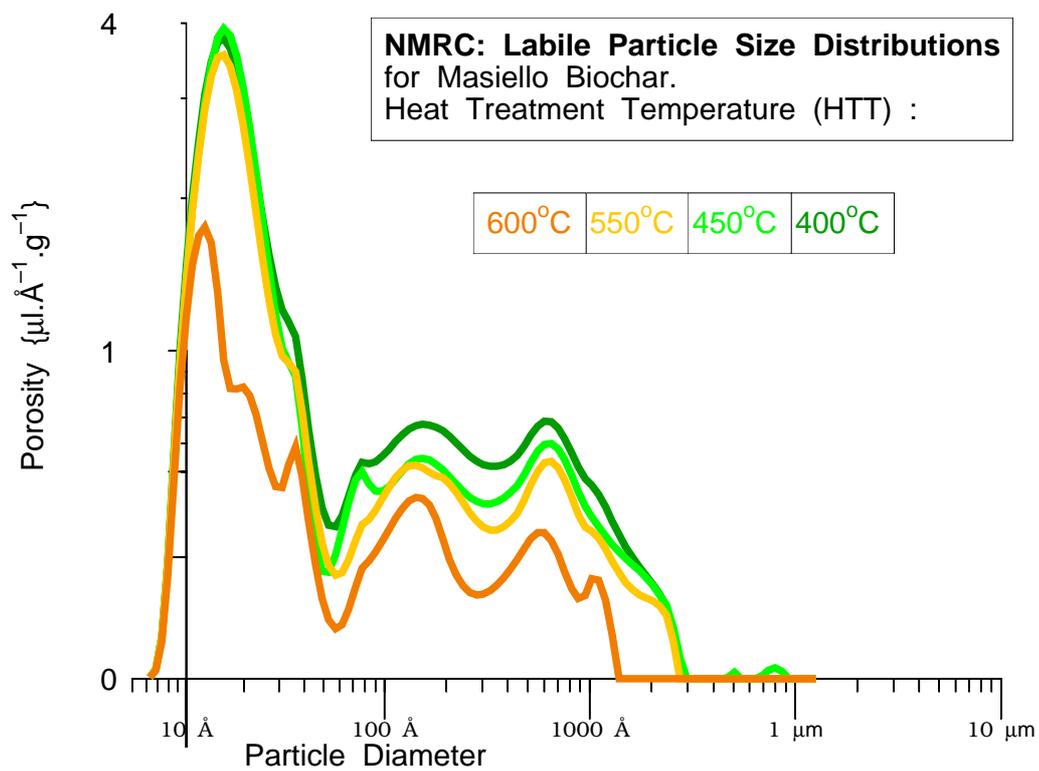


Figure 8: Particle volumes and sizes for organic fractions in biochar at a series of HTTs : NMR cryoporometric differences for four biochars, with heat treatment temperatures (HTT) : 400°C, 450°C, 550°C, 600°C; compared with the NMRC measurement for HTT 700°C. These graphs show, in order, the location and particle size distribution of the labile fraction changing, as increasing amounts of the labile component are driven off with higher HTT.