

The Use of Dielectric and NMR Measurements to Determine the Pore-Scale Location of Organic Contaminants

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I

Introduction/Objectives

A critical issue in the transport and effective remediation of groundwater contaminants is the pore-scale location and mobility of the contaminant: Is it adsorbed to the solid surface or carried in the fluid phase? Can geophysical methods be used to obtain this information? Specifically, in this research, we ask:

Can we use NMR and dielectric measurements to detect or monitor the sorption of organic contaminants...
...in the lab?
...in situ?

II

Sample Description

Water-wet: water spontaneously coats the surface.

- a) natural sand (Wedron, surface area $\sim 1 \text{ m}^2/\text{g}$, density 2.6 g/cm^3)
- b) pure quartz sand (Aesar, surface area $\sim 1 \text{ m}^2/\text{g}$, density 2.6 g/cm^3)
- c) silica gel (Fisher, surface area $\sim 200 \text{ m}^2/\text{g}$, density 2.1 g/cm^3)

Samples b,c were soaked in 10% HCl and rinsed several times with distilled, deionized water to remove impurities.

Hydrophobic: water is repelled from the surface by an organosilane coating. Prepared from water-wet pure quartz sand and silica gel by reaction with 5% octadecyltrichlorosilane in toluene at 110°C for 48 hours, then rinsed with toluene and dried at ambient temperature with a flow of dry a

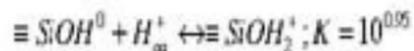
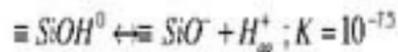
III

Characterization of Solid-Fluid Interface by Acid-Base Titration

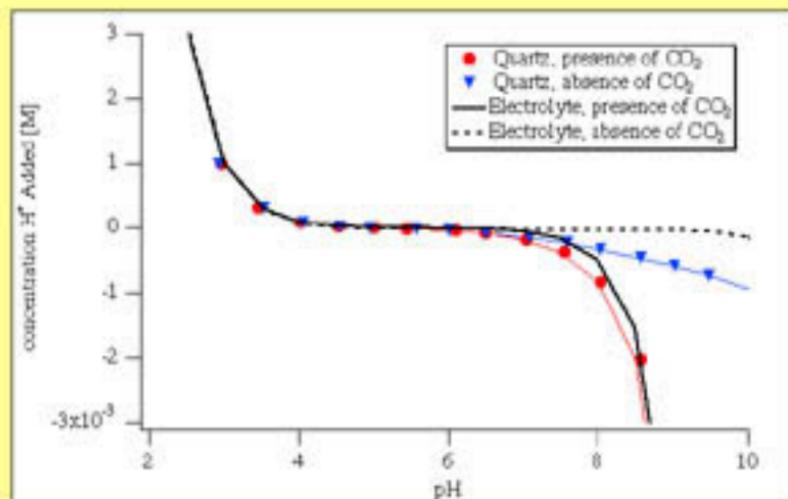
The NMR and dielectric response of a solid-fluid mixture depends not only on the composition and volume of the solid and the fluid phases, but on the chemistry of the solid-fluid interface. Important parameters include:

- 1) the type of chemical species present at the solid-fluid interface,
- 2) the absolute concentration of these species at the interface,
- 3) the extent to which these chemical species react with the fluid, and
- 4) the magnitude and sign of electric charge at the solid-fluid interface.

Titration data for **pure quartz sand** in the presence and absence of CO_2 are noticeably different from the background electrolyte above pH 7. Buffering is due to: (\equiv indicates surface species)



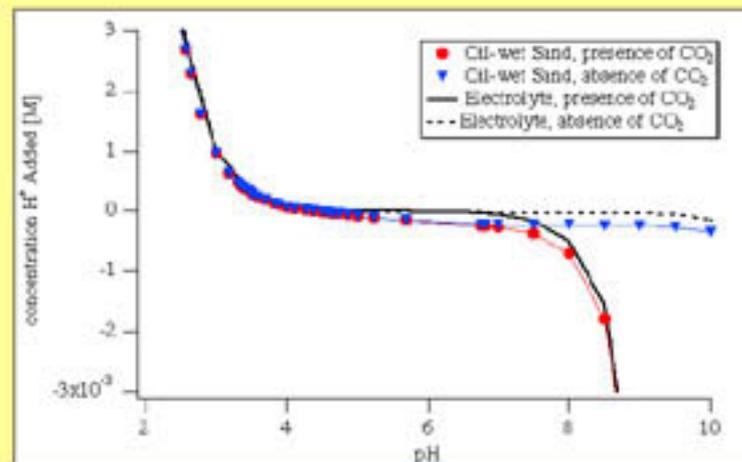
Pure quartz sand displays $\sim 2.1 \times 10^{-6}$ equivalents of charge/ m^2 surface site concentration.



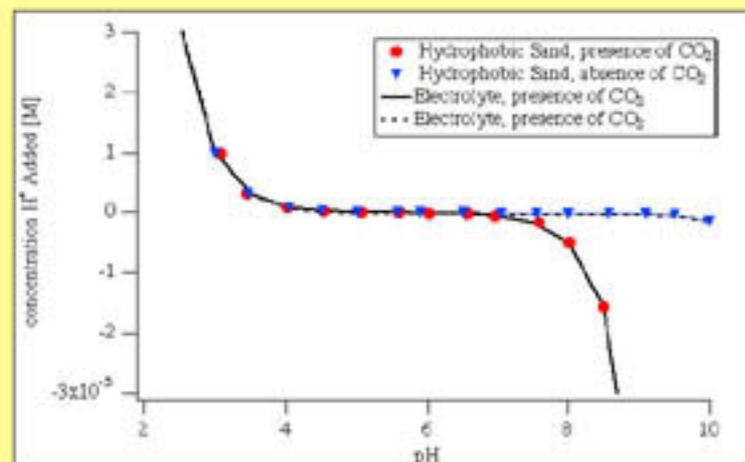
Oil-wet sand displays behaviour markedly different from all other systems examined in this study. The data are modelled well by carboxylic and amine groups on the surface of the oil.



Oil-wet sand has a surface site concentration of 4.45×10^{-7} equiv/m². (R = organic molecule)



Hydrophobic sand displays acid-base behaviour indistinguishable from that of the background electrolyte. This suggests that there are **no interactions** between protons in solution and the surface of the hydrophobic sand.



The titration data permit us to characterize the electric charge at the solid-fluid interface, and its relation to fluid pH.

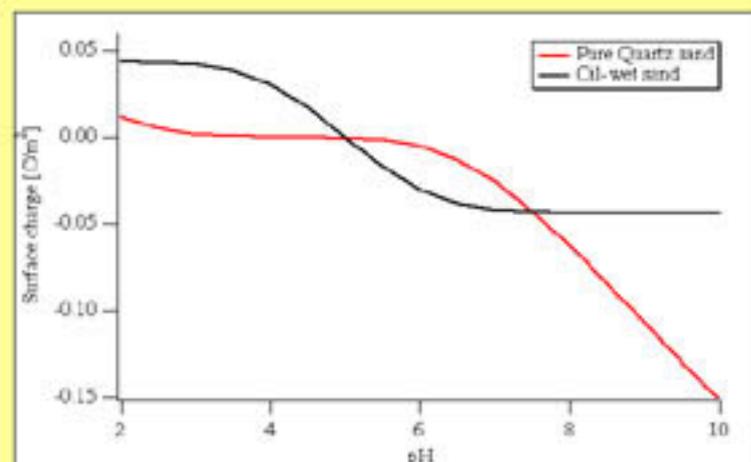
•pure quartz sand

pH < 3: positive charge
pH > 3: negative charge

•oil-wet sand

pH < 5: positive charge
pH > 5: negative charge

•hydrophobic sand surfaces do not accumulate an electric charge, regardless of solution pH.



IV

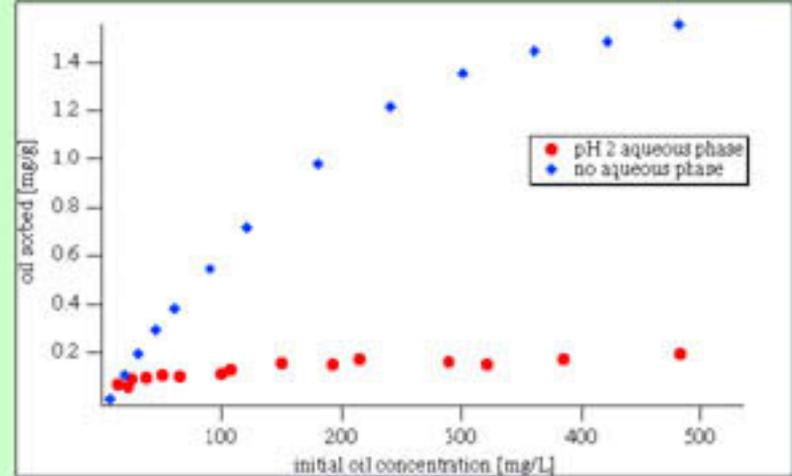
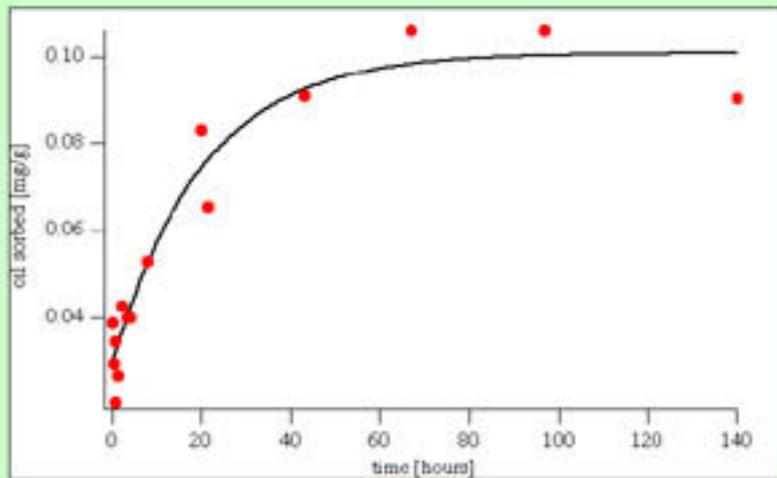
Sorption of Crude Oil by Water-wet Quartz

In a system containing water-wet pure quartz sand, an aqueous phase (0.01M NaCl) and an organic phase (a known amount of crude oil dissolved in toluene-heptane), sorption of crude oil is controlled by:

- 1) the presence of an aqueous phase,
- 2) the equilibrium time,
- 3) the amount of oil initially present in the organic phase, relative to the weight of the solid present, and
- 4) the pH of the aqueous phase.

We can now model the sorption process, allowing us to better understand in situ processes and to prepare controlled lab samples.

Sorption of crude oil by water-wet quartz in the presence and absence of an aqueous phase. The oil has low solubility in water, so oil sorption is greatly reduced when water coats the quartz surface.

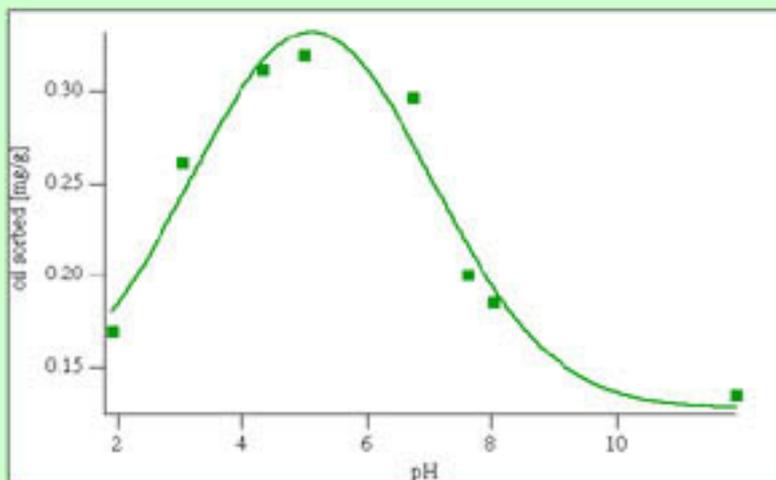
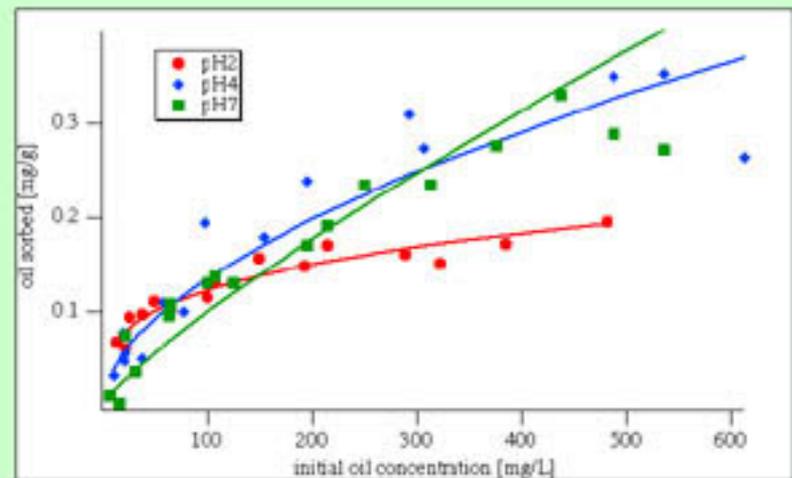


Sorption of crude oil by water-wet quartz as a function of equilibrium time. These systems require ~90 hours to reach steady state.

Sorption of crude oil by water-wet quartz as a function of initial concentration of oil in the non-aqueous phase. The experimental data are described well by Freundlich isotherms:

$$D = K C^n$$

- D: amount of oil sorbed at steady state (mg/g)
- K: distribution coefficient
- C: initial concentration of oil in the organic phase (mg/L)
- n: slope factor



Sorption of crude oil by water-wet quartz as a function of solution pH. The trend observed results from electrostatic interactions between the oil and the quartz surface.

- pH < 3 - both oil and quartz surface are positively charged
- oil sorption is inhibited
- pH 3-5 - enhanced sorption due to opposite or neutral charges
- pH > 5 - both oil and quartz surface are negatively charged
- oil sorption is inhibited

V

¹H NMR Relaxation

One of the central issues in our research is to understand how and why NMR measurements are affected by the chemistry of the solid-fluid interface. The measured NMR parameter for a porous, fluid-saturated sand sample is the T₁ proton relaxation time, which can be related to the material properties of the sample by the equation:

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \rho \left(\frac{S}{V} \right) \quad (1)$$

T_{1b}: relaxation time for the bulk pore fluid

ρ: surface relaxivity

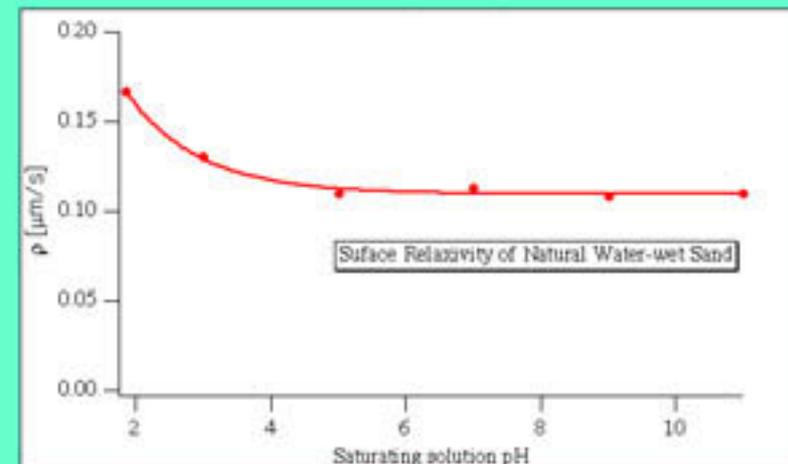
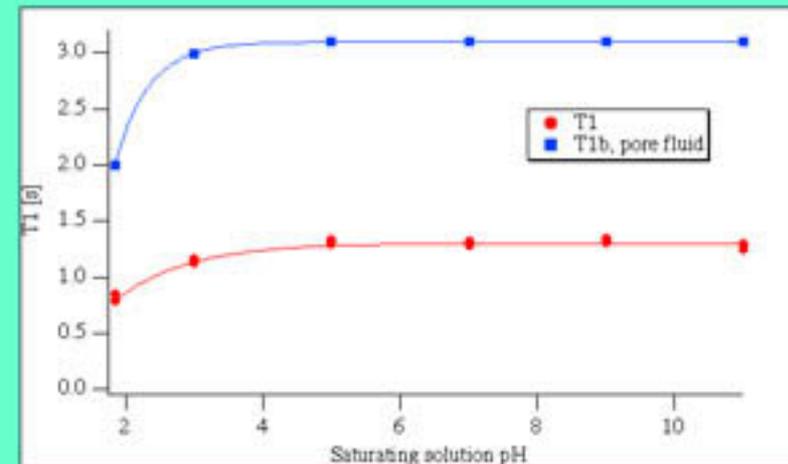
S/V: surface area to volume ratio of the pore space

ρ is the key parameter linking the NMR response to the presence of surface sorbed contaminants.

NMR of Natural Water-wet Sand

Spin-lattice relaxation times for natural water-wet sand (T₁) and extracted pore fluid (T_{1b}) as a function of pH show:

- T₁ << T_{1b} at all pH values.
- T_{1b} constant above pH 3 (3.0 s), but decreases below pH 3.
- ρ increases below pH~5.

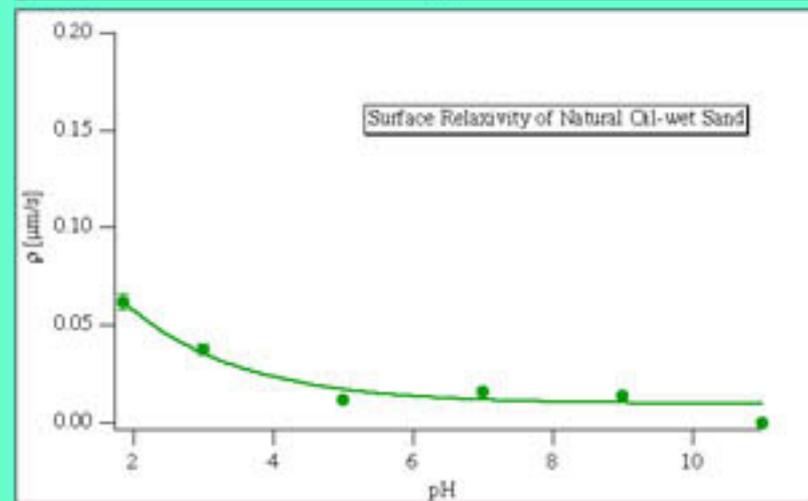
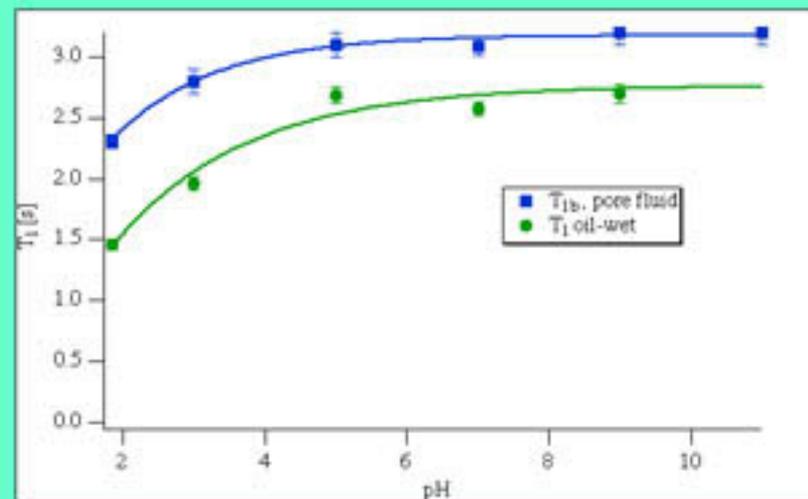


NMR of Natural Oil-wet Sand

Spin-lattice relaxation times for natural oil-wet sand (T_1) and extracted pore fluid (T_{1b}) as a function of pH show similar response to water-wet sand but:

- oil-wet $T_1 >$ water-wet T_1

The presence of sorbed oil reduces ρ .



There is an NMR response to the sorption of oil, but the following questions must be addressed:

What causes the increase in relaxivity at low pH values?

- 1) dependence on surface charge?
- 2) dependence on concentration of paramagnetic sites at the sand-fluid interface?

Do paramagnetic species affect the NMR response differently if they are:

- 1) adsorbed to the solid surface,
- 2) precipitated on the surface of the sand grains
- 3) present as separate mineral grains?
- 4) dissolved in solution

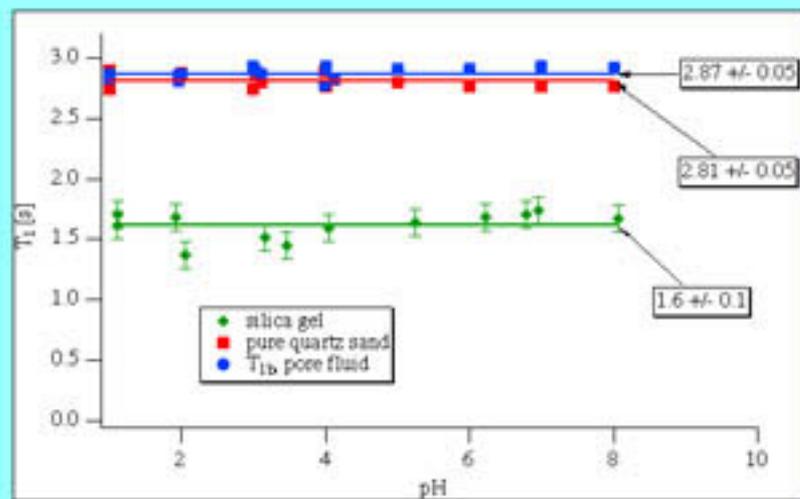
VI

NMR of Model Systems: Building "Real" Materials

If surface relaxivity is different for each chemically distinct solid-fluid interface, then ρ in equation 1 is an average relaxivity. Equation 1 should be modified to include multiple surface relaxation mechanisms:

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \sum_i \rho_i \left(\frac{S}{V} \right)_i \quad (2)$$

It should be possible to measure the surface relaxivity of well characterized pure systems and model the relaxation behaviour of natural materials.



Pure Quartz Sand and Silica Gel

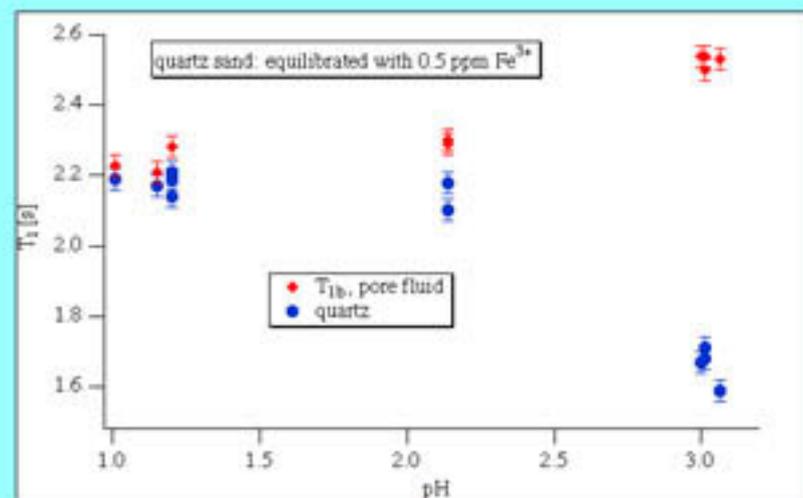
- constant relaxation times over the entire pH range studied.
 - relaxivity is independent of surface charge in the absence of paramagnetic species
- ρ is very low (Si $\sim 4 \times 10^{-4}$, quartz $\sim 1 \times 10^{-3} \mu\text{m/s}$) in the absence of paramagnetic species.
- T_1 for quartz sand $\sim T_{1b}$ bulk pore fluid
- T_1 for silica gel is lower due to high S/V

Fe³⁺ Sorbed to Solid Surface

Does adsorption of paramagnetic ions explain the increase in surface relaxivity in natural sands at low pH?

quartz sand: equilibrated with 0.5 ppm (mg/L) Fe³⁺

- $T_1 \approx T_{1b}$ at pH 1
 - chemical analysis: no sorbed paramagnetic ions on positively charged surface
- $T_1 < T_{1b}$ at pH 3
 - chemical analysis: 20% of the iron(III) is sorbed
 - paramagnetic ions sorbed on a surface are more effective relaxation sites than when dissolved in the pore fluid



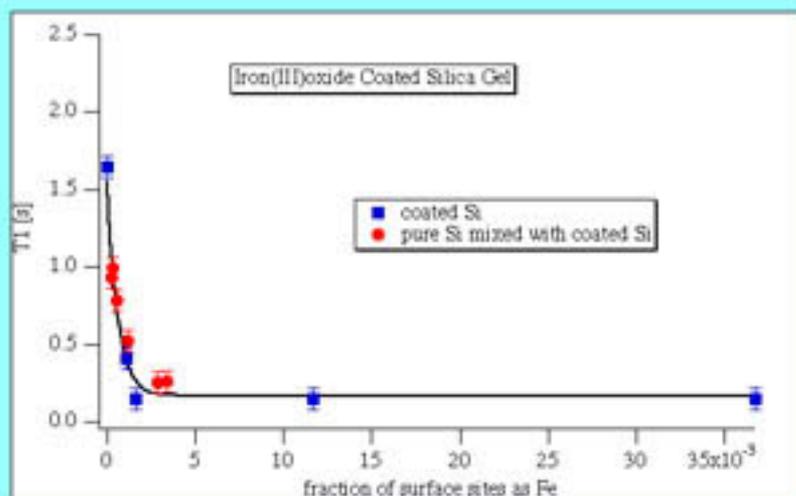
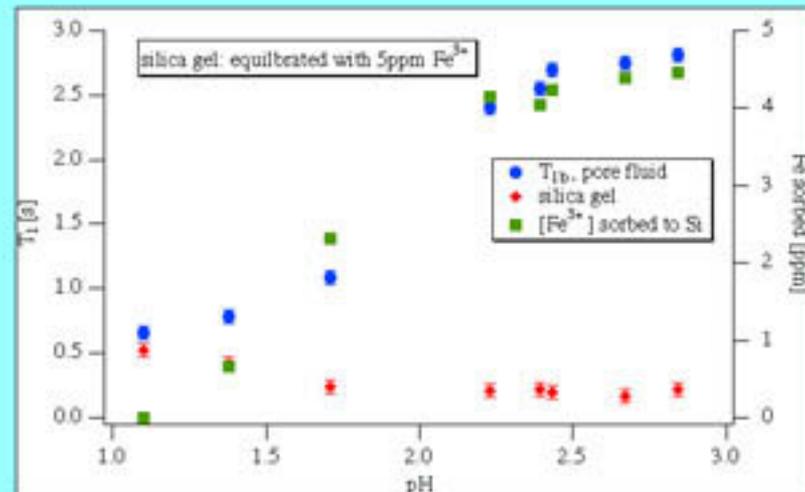
silica gel: equilibrated with 5.0 ppm (mg/L) Fe^{3+}

- T_1 decreases with Fe^{3+} sorbed
- average relaxivity (from eq. 1) increases with Fe^{3+} sorbed
- but using site specific relaxation calculations (eq. 2):

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \left(\frac{S}{V}\right) (f_{\text{Si}} \rho_{\text{Si}} + f_{\text{Fe}} \rho_{\text{Fe}})$$

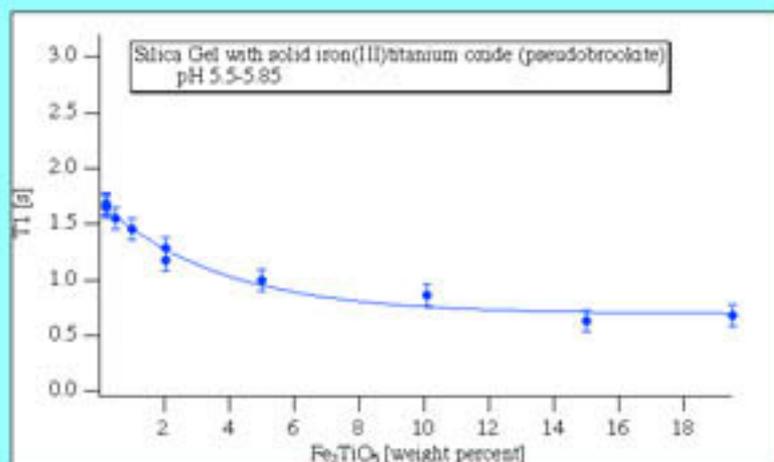
where f is the fraction of surface as Fe^{3+} or silica
we find that relaxivity of surface Fe is constant ($31 \pm 5 \mu\text{m/s}$)

Thus, we find that surface relaxation depends on the fraction of surface area covered by paramagnetic species, but adsorption of dissolved paramagnetic species alone does not account for the NMR response of natural sands.



Iron(III)oxide coated silica gel

- observe exponential dependence of T_1 on the fraction of silica gel surface area covered with Fe(III)oxide
- as little as 0.1% of the surface as Fe^{3+} cuts T_1 in half
 - surface Fe^{3+} ρ calculated using equation 2 is $\sim 2 \mu\text{m/s}$



Separate Paramagnetic Mineral Grains

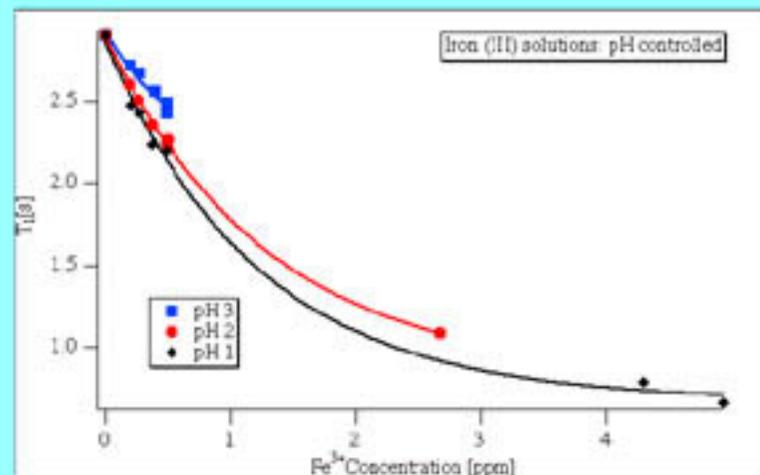
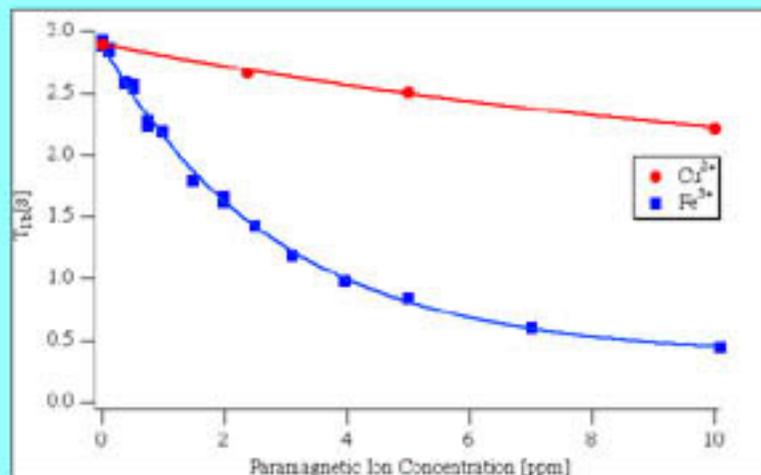
Mixtures of silica gel and pseudobrookite (Fe_2TiO_5) as a function of pH show:

- exponential dependence of T_1 on the fraction of Fe(III) mineral grains
 - suggests form of equation 2 may be appropriate
- ρ (for Fe(III)) calculated using equation 2 is $\sim 40 \mu\text{m/s}$

Dependence of T_{1b} on Fluid Chemistry

Pore fluid in equilibrium with geological materials at acidic pH values contains paramagnetic ions such as Fe^{3+} , Mn^{2+} and Cu^{2+} .

- T_{1b} of bulk water decreases exponentially with increasing concentration of paramagnetic species (e.g., Fe^{3+} , Cu^{2+}).
- T_{1b} varies with chemical species as a consequence of the number of unpaired electrons in each complex.
- T_{1b} at any specific ion concentration changes with pH as a result of chemical speciation.



VII

Dielectric Measurements

The dielectric constant of a material is a frequency-dependent parameter which provides a measure of the polarizability or separation of charge within that material in the presence of an applied field. In a system comprised of silica gel saturated with an aqueous brine, the electrical response is controlled by:

- 1) the properties and proportions of the individual phases present,
- 2) the geometry of the phases with respect to each other, and
- 3) the interaction between the phases.

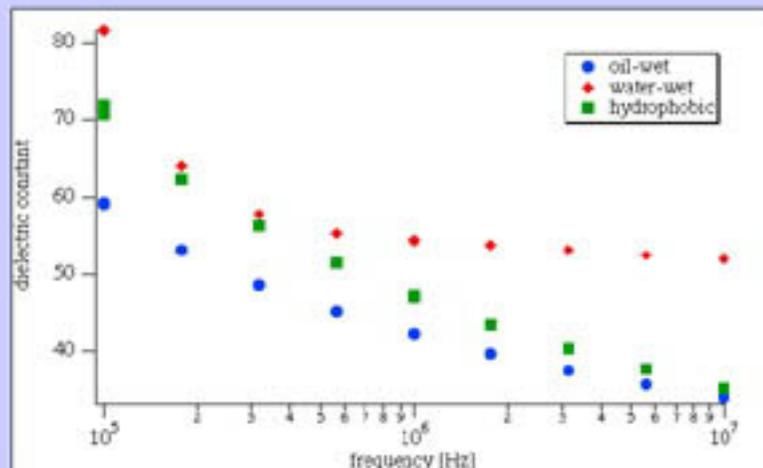
By examining the differences in the frequency response of water-wet, oil-wet and hydrophobic silica gels, an attempt can be made to identify the signatures of the various interfaces.

Comparison of Oil-wet & Water-wet

Water-wet and oil-wet samples of silica gel were prepared to parallel the NMR experiments.

- dielectric constant of an oil-wet system is consistently higher than dielectric constant of a water-wet system
- dielectric constant of a mixture of 50% oil-wet surface and 50% water-wet surface falls between the pure endmembers

We conclude that the presence of sorbed oil decreases the dielectric constant in the frequency range 10^5 to 10^7 Hz.



Hydrophobic compared to Oil-wet & Water-wet

- dielectric constant of hydrophobic silica gel falls between water-wet and oil-wet
- the dielectric response flattens out at higher frequencies as the effect of the aqueous phase diminishes

What causes the differences in the dielectric response of the three types of wettability?

- surface conductivity at the solid-brine interface?
- different chemical sites at the solid-fluid interface?

