Progress Report
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GEOCHEMICAL CONTROLS ON NUCLEAR MAGNETIC RESONANCE MEASUREMENTS

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Introduction and Research Objectives

Proton nuclear magnetic resonance (NMR) is a measurement technique, developed in the 1940's, that investigates the molecular-scale environment of hydrogen nuclei. In the earth sciences proton NMR is most commonly used to measure the response of water in porous geological materials, as a way of obtaining information about the water content and microgeometry of the pore space. Despite many years of the use and study of NMR for borehole logging in the petroleum industry there still remain key questions about the fundamental mechanisms governing NMR relaxation measurements.

The current theoretical basis used to interpret an NMR relaxation time measurement on water in a porous geologic material defines two parameters: ρ and S/V. The surface relaxivity ρ is thought to be determined primarily by the paramagnetic content of the solid surface of the pore space; in geological materials, iron-bearing minerals are the most commonly found source of paramagnetic ions. The surface-area-to-volume ratio of the pore space S/V is taken to be representative of the microgeometry of the pore space. The focus of our proposed research is to explore the unrecognized links between the geochemical properties of geological materials and these two parameters.

Our research objectives are to determine, through an extensive set of laboratory experiments, the effect of the specific mineralogic form of the iron and the effect of the distribution of the iron on NMR relaxation mechanisms. As part of this study we will address the relationship between redox conditions and ρ. We will also design one experiment to study the way in which biological activity, through its effect on the form and distribution of iron, influences NMR relaxation times. An exciting outcome of our research would be the discovery that we can use NMR measurements to detect and monitor geochemical and related biological processes.

Progress to Date

In the first nine months of this project, we have refined the experimental procedures to be used in the acquisition of the laboratory NMR data; have ordered, and conducted preliminary measurements on, the sand samples to be used in the experimental work; and have revised and completed the theoretical model to be used in this project. Our progress in the first year was delayed by a personnel change in the project. Traci Bryar, who was to be the Research Associate on the project, left Stanford for personal reasons. Rather than hiring a new Research Associate, a graduate student in the Geophysics Dept., Kristina Keating (undergraduate degree in Engineering Physics), joined the project. In addition, Manika Prasad, a Research Associate with the Stanford

Rock Physics and Borehole Geophysics Project, joined at 20% time to assist with the laboratory work.

As this is the first laboratory study to be conducted at Stanford with our new Maran Ultra NMR core analyzer (purchased with funds from the National Science Foundation, with matching funds from Stanford), all personnel on the project have spent considerable time becoming familiar with the operation of the system; the technical support provided by the manufacturer has been excellent and included 2 days of on-site training. We have tested the effect of varying the data acquisition parameters on the quality of the data and have decided on the procedure that will be used for all measurements. Both T_1 and T_2 measurements will be made at atmospheric pressure and ambient temperature (30 ^oC). The standard Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence will be used to obtain the T_2 data; 32000 linearly-spaced data points will be collected for each experiment with spacing set by the echo time (t_E). T_2 data will be collected with five different echo times, and with four different levels of an imposed magnetic gradient. T_1 data will be collected using a modified inversion recovery pulse sequence, in which the free induction decay of a (180^o - t – 90^o) pulse is subtracted from that of a 90^o pulse. For each sample, 100 randomly sequenced, exponentially-spaced delay times (0.5 ms $< t <$ 12 s) will be used; the wait time between scans will be set at 15 s. Both intensity and standard deviation of the intensity will be recorded for each t.

In the proposal, we suggested that we would use a very pure form of quartz sand, Alfa Aesar, here referred to as AA sand, as the starting material for the laboratory studies. Measurements have been made of the NMR T_2 relaxation time of bulk deionized water and the AA sand saturated with deionized water. The presence of the AA sand changes the T_2 relaxation time of the water from 3 to 2 seconds, taken as evidence that the sand contains negligible amounts of paramagnetic material. We have therefore confirmed that we will use this as the standard sand for our studies and have ordered the sand needed for all of the experiments.

The other research that has been completed over the past nine months involves the theoretical modeling of the effect of the surface paramagnetic sites on the NMR response. As part of an earlier project, supported by funding from the DOE EMSP program, we had developed a theoretical model that treats the interaction between paramagnetic sites and the water molecules in the pore space. We had assumed that we could use this model as the basis for interpreting the data acquired in the current project. However, when we began to consider the materials to be used in the current project, we became concerned about the possible interactions between paramagnetic sites due to the high concentration of iron. This issue has now been addressed and the paper describing the theoretical model will soon be submitted to the journal Geophysics.

Work Proposed Over the Next Year

At this stage, we have made only minor changes to our proposed work plan. Referring to the proposal, there are three main parts of the research project:

The Effect of Iron-Bearing Minerals on Surface Relaxivity

The Effect of Chemical and Biological Processes on Surface Relaxivity

A Study of the Parameter S/V in Heterogeneous Systems

Over the next year, our focus will be on completing the first phase of the experimental work where the form and distribution of the iron in the sands in varied. This will complete part 1, and will provide the laboratory data required for the theoretical study in part 3.