



## Nuclear magnetic resonance relaxation measurements as a means of monitoring iron mineralization processes

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[1] In this laboratory study, we assessed the measurement of nuclear magnetic resonance (NMR) relaxation times as a means of monitoring iron mineralization processes. We conducted experiments in which columns containing ferrihydrite-coated quartz sand reacted with aqueous Fe(II) solutions to form goethite, lepidocrocite and magnetite. An observed increase in the volume of water relaxing with long relaxation times in the NMR relaxation time distribution corresponds to the formation of goethite and lepidocrocite; a decrease in the average (mean log) relaxation time, and a broadening of the relaxation time distribution, corresponds to the formation of magnetite. These results indicate that NMR relaxation times are sensitive to changes in iron mineralogy and illustrate the potential use of NMR for monitoring iron mineralization processes. **Citation:** Keating, K., R. Knight, and K. J. Tufano (2008), Nuclear magnetic resonance relaxation measurements as a means of monitoring iron mineralization processes, *Geophys. Res. Lett.*, 35, L19405, doi:10.1029/2008GL035225.

### 1. Introduction

[2] Proton nuclear magnetic resonance (NMR) is used in many fields of study (e.g. medicine, chemistry, Earth sciences) to detect the presence of hydrogen nuclei (<sup>1</sup>H) and determine their physiochemical environment. In the Earth sciences proton NMR  $T_2$  spin-spin relaxation time measurements have been made for over 40 years in the petroleum industry, using instruments lowered in wells to detect both hydrocarbons and water, and to determine the properties of oil and gas reservoirs that affect the quantity and movement of fluids [e.g., *Brown and Gamson, 1960; Kleinberg et al., 1992*]. Over the past 15 years, a proton NMR device has been developed that can be deployed from Earth's surface to obtain information about the properties of groundwater aquifers [*Legchenko et al., 2004*]. Here we present the first study to demonstrate that proton NMR can be used to monitor temporal changes in iron mineralization processes in geologic materials. The ability to monitor such processes with non-invasive NMR measurements would be very useful in laboratory and field studies of geochemical reactions.

[3] Iron (hydr)oxides are ubiquitous in the environment and, due to their high reactivity, can strongly influence the mobility and bioavailability of organic and inorganic con-

taminants [*Cornell and Schwertmann, 2003*]. Remediation techniques used to clean up contaminated sites, such as biostimulation and bioaugmentation, often exploit the high reactivity of iron (hydr)oxides to control and sequester contaminants [*Lovley, 2001; Cornell and Schwertmann, 2003*]. Monitoring the geochemical reactions associated with such remediation techniques is an effective way to monitor the progress of remediation. Current monitoring methods rely on direct sampling, an approach that can be costly, incurs the risk of further spreading the contaminant, and provides only localized information. Of interest in our research is identifying geophysical techniques that could be used non-invasively, over large subsurface regions, to monitor the geochemical reactions associated with contaminant remediation. We designed this laboratory study to assess the use of proton NMR to monitor an important geochemical reaction likely to be associated with any remediation strategy that involves changes in iron mineralogy.

### 2. Background

[4] The measured NMR parameter was the proton NMR  $T_2$  spin-spin relaxation time of water in the pore space of a water-saturated sample of sand. During an NMR experiment, water contained in a single pore will display an exponential decay in nuclear magnetization,  $M$ , as a function of time,  $t$ ,

$$M(t) = M_0 e^{-t/T_2} \quad (1)$$

where  $T_2$  is the spin-spin relaxation time and  $M_0$  is the initial magnetization and is proportional to the volume of water in the pore. Three mechanisms, each described by a relaxation time constant, contribute to the relaxation of the water: bulk relaxation of the water, which depends on the concentration of dissolved paramagnetic species (e.g.  $\text{Fe}^{3+}$ ); surface relaxation that arises due to the interaction between the water and paramagnetic sites at the surface of the pore; and diffusion relaxation due to magnetic susceptibility differences between the water and the sand. In a water-saturated porous material, where water is contained in many pores with different physiochemical environments, the relaxation behavior of the water is described by a multiexponential decay,

$$M(t) = \sum_i M_{0i} e^{-t/T_{2i}} \quad (2)$$

where the initial magnetization for each relaxation time,  $M_{0i}$ , is proportional to the volume of water with the relaxation time  $T_{2i}$ . The values of the initial magnetization,  $M_{0i}$ , are plotted versus the relaxation times,  $T_{2i}$ , yielding a

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distribution of relaxation times. The total initial magnetization  $M(0)$  is equal to  $\sum_i M_{0i}$  and is proportional to the volume of water in the measured sample. The arithmetic mean of the log relaxation times in the observed distribution,  $T_{2ML}$ , is used to represent the average relaxation time.

[5] Previous laboratory studies have shown conclusively that the concentration of iron in the solid phase of a water-saturated material has a significant impact on  $T_{2ML}$ ; an increase in the amount of iron increases the number of paramagnetic sites and thus decreases the surface relaxation time [Foley *et al.*, 1996; Bryar *et al.*, 2000]. In a previous study by Keating and Knight [2007] it was found that it was not simply the concentration of iron, but also the mineralogical form of the iron, that determined the NMR response. The NMR relaxation times of water-saturated quartz sands varied significantly when the mineralogy of the iron (hydr)oxide coating on the sand was changed.  $T_{2ML}$  was  $0.0069 \pm 0.0009$  s for magnetite-coated sand,  $0.063 \pm 0.004$  s for ferrihydrite-coated sand,  $0.35 \pm 0.005$  s for goethite-coated sand, and  $0.227 \pm 0.01$  s for lepidocrocite-coated sand. In addition to the low relaxation time of the magnetite-coated sand, this sample also displayed a  $T_2$ -distribution that was distinctly broader than those obtained for ferrihydrite-, goethite-, and lepidocrocite-coated sand. As discussed in detail by Keating and Knight [2007, 2008] the observed differences in the NMR response were due to the effects of mineralogy on the magnitude of both the surface and diffusion relaxation times. These observations of such large differences in  $T_{2ML}$  values and in the relaxation time distributions led to the following hypothesis: we can monitor a geochemical reaction that involves these iron minerals by using NMR measurements.

[6] The reaction selected for this study is the reaction of aqueous Fe(II) with ferrihydrite ( $\text{Fe}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ ), a poorly crystalline iron(III) (hydr)oxide that is an important precursor for other iron (hydr)oxide minerals [Cornell and Schwertmann, 2003]. We used laboratory conditions under which aqueous Fe(II) is known to react with ferrihydrite: a pH of 7.5 and an anaerobic environment [Hansel *et al.*, 2003]. Under such conditions, the reaction of Fe(II) with ferrihydrite results in the formation of goethite, lepidocrocite, and magnetite [Hansel *et al.*, 2003]. While factors such as pH and redox potential will determine the rate and extent of this reaction and the mineralogy of the solid phases produced, the supply rate and concentration of Fe(II) have been shown to be the most important controls on the ferrihydrite transformation [Lovley *et al.*, 1989; Hansel *et al.*, 2003].

### 3. Experimental Methods and Materials

[7] To create the starting material for the experiments, ferrihydrite was synthesized and combined with quartz sand producing a ferrihydrite-coated sand with a solid phase concentration of 1% iron (by weight). (The average concentration of iron found in natural soils is 1 to 3% [Cornell and Schwertmann, 2003].) The ferrihydrite was synthesized by the method of Brooks *et al.* [1996] which results in the formation of 2-line ferrihydrite; this method involves titration of a ferric chloride solution with NaOH to a pH of 7.5. A series of experiments were then conducted involving NMR measurements and/or chemical analysis on

vertical columns (0.7 cm diameter, 10 cm long) packed with the ferrihydrite-coated quartz sand, which was saturated, and reacted with, an Fe(II) solution. Influent solutions were pumped from bottom to top through the columns at a rate of 0.35 mL/min. For all experiments, deoxygenated water was pumped through the sample column for the first 2 h to ensure anaerobic conditions within the sand. After 2 h the influent solution was changed to a Fe(II) solution containing ferrous chloride buffered to pH 7.5 with PIPES (1,4-piperazinediethanesulfonic acid, 10 mM); solutions were prepared, stored in, and pumped from a sealed glove bag held under anaerobic conditions by continuously purging with  $\text{N}_2$ . The effluent solution was collected at the top of the column for disposal.

[8] To obtain NMR measurements, a vertical column of the ferrihydrite-coated quartz sand was positioned in the NMR analyzer so that relaxation time measurements were spatial averages over the entire column. Once the Fe(II) solution began entering the bottom of the column, NMR relaxation time measurements were initiated and made approximately every 30 minutes.

[9] NMR relaxation data were collected with a 2.2 MHz Maran Ultra NMR Core Analyzer (Resonance Instruments) using a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [Carr and Purcell, 1954; Meiboom and Gill, 1958]. The CPMG pulse sequence consists of applying a  $90^\circ$  pulse followed by a series of  $180^\circ$  pulses separated by the echo time,  $t_E$ . A single data point was obtained at each echo in the CPMG pulse sequence; 32000 echoes were used. The acquisition bandwidth was 1 MHz. Data were collected at an echo time of  $t_E = 300 \mu\text{s}$ , resulting in a pulse sequence duration of 9.6 s. The data were stacked 100 times to improve the signal to noise ratio. A 10 s delay time between each pulse sequence was used to ensure that the sample had returned to thermal equilibrium prior to the start of the next pulse sequence. All NMR measurements were made at  $30^\circ\text{C}$ . Each measured decay curve was fit using a regularized nonnegative least-squares inversion routine (auxiliary material).

[10] The first set of experiments was performed with an influent solution Fe(II) concentration of 0.2 mM. Deoxygenated water, followed by the Fe(II) solution, was pumped through two columns filled with the ferrihydrite-coated quartz sand positioned outside the NMR analyzer. One column (referred to as Column 1a) was disassembled after 525 min (equivalent to an input of 0.037 mmol Fe(II)) and the other column (Column 1b) was disassembled after 1150 min (equivalent to an input of 0.080 mmol Fe(II)). At the same time NMR relaxation times were measured on a third column (Column 1c) filled with the ferrihydrite-coated quartz sand, as the Fe(II) solution was pumped through the column, for a total of 1620 min; this is equivalent to an input of 0.110 mmol Fe(II). This column was then removed from the NMR analyzer and disassembled. Reacted solids from all three columns were dried anaerobically and kept for further analysis.

[11] The second set of experiments was performed with an influent solution Fe(II) concentration of 2.0 mM. NMR measurements were made on one column (referred to as

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2008GL035225.

**Table 1.** Concentrations of the Iron Minerals Formed in the Bottom Third of the 0.2 and 2.0 Fe(II) Columns<sup>a</sup>

| Material      | Input of Fe(II), mmol   |                         |                         |                         |                         |
|---------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
|               | 0.2 mM Fe(II) Columns   |                         |                         | 2.0 mM Fe(II) Columns   |                         |
|               | Column 1a<br>0.037 mmol | Column 1b<br>0.080 mmol | Column 1c<br>0.110 mmol | Column 2a<br>0.042 mmol | Column 2b<br>0.504 mmol |
| Ferrihydrite  | 82%                     | 64%                     | 54%                     | 39%                     | 18%                     |
| Goethite      | 18%                     | 15%                     | 16%                     | 42%                     | 21%                     |
| Lepidocrocite | 0%                      | 15%                     | 19%                     | 19%                     | 0%                      |
| Magnetite     | 0%                      | 6%                      | 11%                     | 0%                      | 61%                     |

<sup>a</sup>Concentrations are as the percent moles of Fe.

Column 2a), as the Fe(II) solution was pumped through the column for one hour (equivalent to an input of 0.042 mmol Fe(II)) at which time the column was disassembled. NMR relaxation times were measured on a second column (Column 2b) filled with the ferrihydrite-coated quartz sand; Fe(II) solution was pumped through the column for a total of 12 hours (equivalent to an input of 0.504 mmol Fe(II)) at which time the column was disassembled; the last NMR measurement was made at 10.4 hours (equivalent to an input of 0.436 mmol Fe(II)). NMR measurements were repeated on a third column (Column 2c) of sand for a total of 12 hours. The solid materials from columns 2a and 2b were dried in an anaerobic environment and kept for further analysis.

[12] For chemical analysis on the dried materials, we used the materials from bottom thirds of the columns (auxiliary material). Linear combination fitting of Extended X-Ray Adsorption Fine Structure (EXAFS) spectra of Fe was used to determine the percentage (by mole of iron) of iron-bearing minerals. The results were confirmed by X-ray diffraction (XRD).

#### 4. Discussion of Results

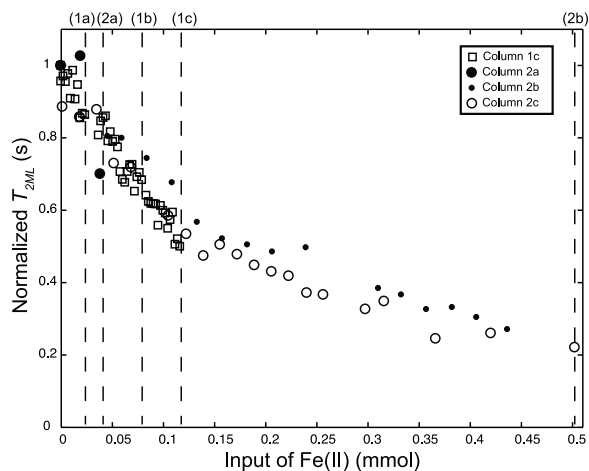
[13] Linear combination fits of EXAFS spectra indicate that, in both the 0.2 mM and 2.0 mM Fe(II) columns, ferrihydrite reacts with Fe(II) to form goethite, lepidocrocite and magnetite (Table 1 and Figure S1). These results were confirmed by X-ray diffraction. In both sets of experiments, mineral transformations began prior to the start of NMR measurements. From the proportion of each mineral formed in the various columns the following observations can be made: (1) Goethite and lepidocrocite formed before magnetite. (2) In the 2.0 mM Fe(II) columns the concentration of lepidocrocite and goethite formed was greater than that formed in the 0.2 mM Fe(II) columns. (3) In the 2.0 mM Fe(II) columns magnetite was formed at the expense of goethite and lepidocrocite.

[14] Let us now consider the NMR data and determine whether these changes in iron mineralogy are reflected in the  $T_{2ML}$  values and/or in the form of the relaxation time distributions. We can use the NMR measurements on the same iron minerals reported by *Keating and Knight* [2007] for comparison. While there will likely be some differences between the  $T_{2ML}$  values by *Keating and Knight* [2007] and the values measured in this study (primarily due to differences in the porosity and surface area of the samples) we are confident, after numerous experiments with these minerals, that the relative magnitudes of the  $T_{2ML}$  values and the forms of the relaxation time distributions will be the same. We therefore would expect to see an increase in  $T_{2ML}$  as

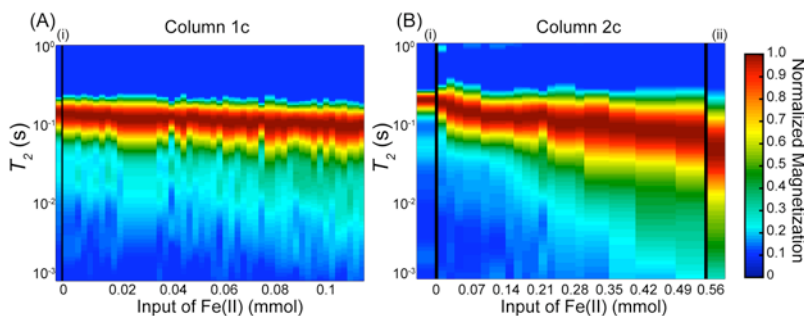
goethite and lepidocrocite are formed, then a dramatic decrease in  $T_{2ML}$  and a broadening of the relaxation time distributions with the formation of magnetite

[15] The observed strong dependence of  $T_{2ML}$  for each column on the input of Fe(II) is the main result of this study. This is shown in the plot in Figure 1, where the calculated  $T_{2ML}$  value for each column has been normalized by the initial  $T_{2ML}$  value for the column. Also shown in Figure 1 are the points (in terms of input of Fe(II)) at which the five columns were disassembled and analyzed to determine the iron mineralogy. The  $T_{2ML}$  values for the 0.2 mM Fe(II) and the 2.0 mM Fe(II) columns all show the same general trend: there is a significant decrease in  $T_{2ML}$  as the input of Fe(II) increases (i.e. as the reaction progresses) with  $T_{2ML}$  of Column 2c decreasing by  $\sim 80\%$  with the highest input of Fe(II) (0.504 mmol). This large decrease in  $T_{2ML}$  is compatible with an increase in the concentration of magnetite in the samples. In three columns the reduction in  $T_{2ML}$  is accompanied by a decrease in  $M(0)$  suggesting that some of the water was relaxing so quickly that it did not contribute to the first measurement at 60  $\mu$ s in the decay curve.

[16] The changes in form of the full  $T_2$ -distributions, each normalized by the maximum value of  $M_{0i}$  in the distribution, provide additional evidence of the link between the NMR data and the geochemical reactions. The distributions for two columns are shown in Figure 2: the distributions



**Figure 1.** Mean log relaxation time, normalized by the initial mean log relaxation time, versus the input of Fe(II). Data are shown for the 0.2 mM Fe(II) column, Column 1c, and the three 2.0 mM Fe(II) columns: Columns 2a, 2b, and 2c. The points at which columns were disassembled (in terms of input of Fe(II)) and the column numbers are indicated on the figure.



**Figure 2.** The relaxation time distributions, normalized by the maximum value of  $M_{0i}$  in each distribution. Data are shown for (a) the 0.2 mM Fe(II) column, Column 1c, and (b) the 2.0 mM Fe(II) column, Column 2c. The section marked (i) contains the initial distribution obtained from measurements on the ferrihydrite-coated sand saturated with deoxygenated water. Section (ii) of Figure 2b shows the normalized  $T_2$ -distribution for water-saturated magnetite-coated sand as measured by *Keating and Knight* [2007].

from Column 1c (the 0.2 mM Fe(II) column) are in Figure 2a and the distributions from Column 2c (a 2.0 mM Fe(II) column) are in Figure 2b. Shown in region (i) in each figure is the normalized  $T_2$ -distribution for the ferrihydrite-coated sand saturated with deoxygenated water at the start of the experiment; the distribution is repeated to enhance the display. The normalized  $T_2$ -distributions for Columns 1c and 2c exhibit a trend towards broader peaks centered at shorter relaxation times as the experiment progresses. The final normalized  $T_2$ -distribution for Column 2c, which corresponded to the maximum input of Fe(II) in the experiments, is very similar to the normalized  $T_2$ -distribution for magnetite-coated sand from *Keating and Knight* [2007], shown in region (ii) of Figure 2b. We conclude that the observed changes in the  $T_2$ -distributions, i.e. a large overall decrease in the average relaxation time and the trend to broader distributions, provide further evidence that the NMR data are responding to the increase in the concentration of magnetite within the columns.

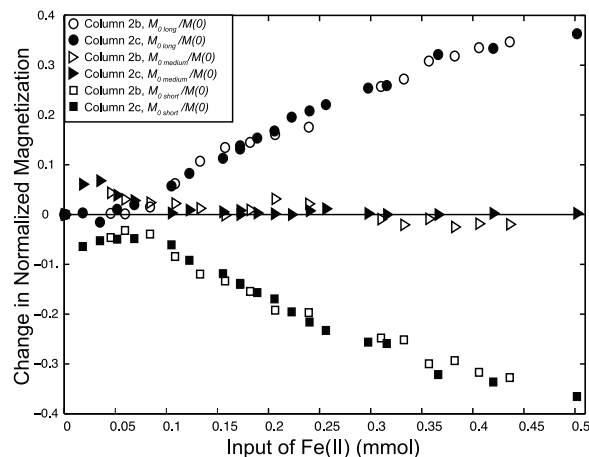
[17] The chemical analysis clearly indicates the presence of goethite and lepidocrocite (Table 1). Can evidence of these two minerals be found in the NMR data? Based on the earlier study of *Keating and Knight* [2007], we would expect to see an increase in  $T_{2ML}$  as goethite and lepidocrocite replace ferrihydrite. While we do not find an increase in  $T_{2ML}$  for any of the columns, we do see a change in the data that we interpret to be an indication of the presence of these two minerals. We see an increase in the volume of water relaxing with long relaxation times in the measurements made on Columns 2b and 2c at low Fe(II) input (<0.1 mmol); chemical analysis of the materials from Column 2a shows the maximum observed concentration of goethite and lepidocrocite at an Fe(II) input of 0.042 mmol.

[18] To better examine this feature in the data, we binned the relaxation times, from each distribution for Columns 2b and 2c, into long ( $T_2 > 0.25$  s), medium ( $0.25$  s  $> T_2 > 0.01$  s), and short ( $T_2 < 0.01$  s) relaxation times, thereby summing the corresponding  $M_{0i}$  values to obtain three values,  $M_{0\text{ long}}$ ,  $M_{0\text{ medium}}$ ,  $M_{0\text{ short}}$ . For each measurement, the fractions of water relaxing at “long”, “medium” and “short” times are given by  $M_{0\text{ long}}/M(0)$ ,  $M_{0\text{ medium}}/M(0)$ ,  $M_{0\text{ short}}/M(0)$ , respectively. We calculated the change in these three values as the experiment progressed. These results are plotted in Figure 3 as a function of the input of Fe(II). Clearly seen in the plot is a steady increase, as the

experiment progresses, in  $M_{0\text{ short}}/M(0)$  and a corresponding decrease in  $M_{0\text{ medium}}/M(0)$ . These changes are directly related to the key observations of our study – the large overall decrease in  $T_{2ML}$ , and the broadening of the relaxation time distribution (both of which are attributed to the formation of magnetite). The feature of interest appears at low Fe(II) input (<0.1 mmol), where there is a peak in  $M_{0\text{ long}}/M(0)$ . The relaxation times reported for goethite- and lepidocrocite-coated sands by *Keating and Knight* [2007] are greater than those reported for either ferrihydrite or magnetite. This peak is therefore consistent with the chemical analysis which shows the formation of goethite and/or lepidocrocite followed by the formation of magnetite, at the expense of goethite and/or lepidocrocite. A similar feature was not seen in the relaxation time distributions for the 0.2 mM Fe(II) columns which have ~40% lower concentrations of goethite/lepidocrocite. Our interpretation is that the concentration of goethite/lepidocrocite formed in those columns was not sufficient to cause a detectable increase in  $M_{0\text{ long}}/M(0)$ .

## 5. Conclusions

[19] NMR relaxation times were found to respond to changes in iron mineralogy during the studied geochemical reaction. The dominant feature was the large overall



**Figure 3.** The change in  $M_{0\text{ long}}/M(0)$ ,  $M_{0\text{ medium}}/M(0)$ ,  $M_{0\text{ short}}/M(0)$  versus the input of Fe(II) for Columns 2b and 2c.

decrease in  $T_{2ML}$  due to the formation of magnetite. More subtle, but present in two columns, was a change in the relaxation time distribution that can be attributed to the presence of goethite and lepidocrocite. This study has demonstrated the potential use of NMR for monitoring iron mineralization processes in the laboratory. While this study also introduces the possibility of using a surface-based NMR system to monitor these same processes in the subsurface, further research is needed to better understand instrument response in the presence of iron-rich soils.

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