PETROPHYSICS, VOL. 52, NO. 1 (FEBRUARY 2011); PAGE 00-00; 7 FIGURES; 2 TABLES

Sensitive Carbonate Reservoir Rock Characterization From Magnetic Hysteresis Curves and Correlation with Petrophysical Properties[1]

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ABSTRACT

Recent work has shown how magnetic susceptibility and hysteresis measurements correlate with several petrophysical parameters in clastic reservoir samples. The present paper applies these techniques to carbonate samples. Carbonate rock typing can be achieved from high field magnetic susceptibility, which indicates a sample's diamagnetic plus paramagnetic mineral content. High field measurements are very sensitive and can quantify small differences in paramagnetic clay content that X-ray diffraction (XRD) or scanning electron microscopy (SEM) cannot. Temperature dependent hysteresis measurements can also identify and quantify small concentrations of paramagnetic minerals.

Experimental magnetic hysteresis curves demonstrated subtle differences between samples in a suite of Middle East carbonates. Significantly, the high field magnetic susceptibility values from the hysteresis curves exhibited extremely good correlations with permeability (small variations in paramagnetic clay content seem responsible for this) and porosity. The low field magnetic susceptibility values, however, did not correlate well with these petrophysical parameters merely because some samples contained small concentrations of ferrimagnetic impurities that contributed to the low field signal. The low field part of a hysteresis curve provides a further sensitive means of characterizing carbonate samples, and can be used to quantify these extremely small concentrations of ferrimagnetic material (down to a few parts per million) that XRD cannot.

Magnetic susceptibility values (both low and high field) for some US and North Sea carbonates were generally higher than the Middle East samples, indicating increased ferrimagnetic and paramagnetic (mainly clays) content. This suggested that the reservoir quality of the Middle East carbonates studied was generally better.

Keywords: magnetic hysteresis, permeability, porosity, magnetic susceptibility, high field measurements, temperature dependence, anisotropy

INTRODUCTION

Recent studies (Potter et al., 2004; Ivakhnenko, 2006; Ivakhnenko and Potter, 2004; Ivakhnenko and Potter, 2006; Ivakhnenko and Potter, 2008; Potter, 2007; Potter and Ivakhnenko, 2008) have demonstrated the potential uses of magnetic susceptibility and magnetic hysteresis measurements for reservoir characterization, quantifying mineralogy, and for predicting important petrophysical parameters in clastic reservoirs. These measurements provide a rapid, non-destructive complement to XRD for determining the content of permeability-controlling clays such as illite (Potter et al., 2004; Potter and Ivakhnenko, 2008), and subsequently predicting permeability (Potter, 2007; Potter and Ivakhnenko, 2008), even in cases where the relationship between porosity and permeability is very poor (Potter, 2007). The measurements have also correlated with the cation exchange capacity per unit pore volume (Q_v), the flow zone indicator (FZI) and the downhole gamma ray signal (Potter, 2007).

In clastic reservoirs high field magnetic susceptibility measurements, derived from hysteresis curves, have shown even better correlations with permeability than low field (Potter and Ivakhnenko, 2008), since the high field signal usually reflects only the sum of the diamagnetic (generally the main matrix mineral quartz) plus paramagnetic (generally permeability-controlling clays such as illite) components in the sample. Estimates of paramagnetic permeability-controlling clay content were improved since the effects of any ferro- or ferrimagnetic impurities were minimized at high fields, since they saturated at lower fields. In contrast, low field measurements can be influenced by small amounts of these strongly magnetic

Manuscript received by the Editor May 17, 2010; revised manuscript received December 7, 2010.
[1]Originally presented at the International Symposium of the Society of Core Analysts, Abu Dhabi, United Arab Emirates, October 29–November 2, 2008.
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TABLE 1: Mass magnetic susceptibilities of carbonate minerals and some other typical reservoir minerals. D, P and F refer to diamagnetic, paramagnetic and ferrimagnetic classes respectively. The values for the diamagnetic minerals were theoretically calculated by Ivakhnenko (2006). The values for the other minerals are from Hunt et al. (1995).

	Mineral	Mass Magnetic Susceptibility (10^{-8} m^3 kg^{-1})	Magnetic Class
Carbonate Minerals	Calcite, $CaCO_3$	−0.4839	D
	Dolomite, $CaMg(CO_3)_2$	−0.4804	D
	Magnesite, $MgCO_3$	−0.4762	D
	Witherite, $BaCO_3$	−0.3643	D
	Cerussite, $PbCO_3$	−0.2855	D
	Siderite, $FeCO_3$	122.57	P
	Rhodochrosite, $MnCO_3$	124.63	P
Other Reservoir Minerals	Quartz, SiO_2	−0.6191	D
	Anhydrite, $CaSO_4$	−0.4508	D
	Gypsum, $CaSO_4{\cdot}2H_2O$	−0.5461	D
	Halite, NaCl	−0.6451	D
	Kaolinite, $Al_2[Si_2O_5](OH)_4$	−0.6474	D
	Illite,$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH_2,(H_2O)]$	15	P
	Magnetite, Fe_3O_4	20,000-to-110,000	F

ferro- or ferrimagnetic components if they are present in the sample, and may be responsible for weaker correlations between low field magnetic results and permeability. The presence of these ferro- or ferrimagnetic components can easily be recognized by characteriztic “kinks” or “loops” in the hysteresis curves at low fields.

The present paper extends the work to carbonates, building on a preliminary study (Al-Ghamdi, 2006). Subtle differences between carbonates can rapidly and non-destructively be recognized by the magnetic measurements. Small differences in the content of paramagnetic clays, or differences in the type of carbonate, should be reflected in the slope of the high field hysteresis curve (Potter and Ivakhnenko, 2008). We will demonstrate that high field magnetic susceptibility exhibits strong correlations with permeability and porosity, which is a completely new and unexpected result for carbonates. We will discuss the possible reasons for these correlations. In contrast, there was no strong correlation between the low field results and the petrophysical properties due to the presence of small amounts of ferrimagnetic material, which dominated the low field signal in some of the samples.

MAGNETIC CHARACTERIZATION OF CARBONATES

Magnetic Susceptibility of Typical Carbonate Reservoir Minerals

The main carbonate matrix minerals, calcite and dolomite, are diamagnetic with low negative magnetic susceptibilities (Table 1). In contrast, some carbonates (e.g., siderite and rhodochrosite) are paramagnetic with significantly higher positive magnetic susceptibilities. Table 1 also shows values for other typical reservoir minerals. Note that kaolinite is diamagnetic, whilst illite (an important permeability-controlling clay in many clastic reservoirs) is paramagnetic. Note also that ferrimagnetic minerals such as magnetite have extremely high magnetic susceptibilities, and small amounts of such impurities can on the one hand be useful in distinguishing different carbonates, and on the other hand can sometimes dominate low field measurements obscuring any correlations between the magnetic and petrophysical properties. Fortunately at high fields the influence of these ferrimagnetic minerals is generally negligible (since they usually saturate at lower fields) and the magnetic properties are dominated by the diamagnetic and paramagnetic minerals comprising the bulk composition of the reservoir rocks.

Characterization of some Middle East Carbonates from Magnetic Hysteresis Curves

A suite of Middle East carbonate samples from the Arab-D reservoir were used for this study. The samples were conventional core plugs consisting primarily of calcite and dolomite. A series of magnetic hysteresis curves at room temperature for these samples were determined (Figure 1). The experimental curves were obtained by a Variable Field Translation Balance (VFTB) in the rock magnetic laboratory of the Ludwig-Maximilians University in Munich, Germany using the same methodology as described by Ivakhnenko and Potter (2008). Note that the slope at any point on a curve represents the magnetic susceptibility at that point, and so hysteresis curves allow the magnetic susceptibility to be obtained over a range of low and high applied fields.

All samples exhibited a negative high field slope, demonstrating that the bulk of each sample comprised a diamagnetic matrix mineral or minerals. These samples generally contained a mixture of calcite and dolomite, though in some cases anhydrite (which is also diamagnetic, see Table 1) was present. Some samples exhibited straight line hysteresis behavior indicating that there were no ferrimagnetic impurities present (red curves in Figure 1). In these cases the magnetic susceptibility is the same for all the applied fields.

A number of the curves, however, showed a small kink at low fields, indicating the presence of a small amount of ferrimagnetic impurities (blue curves in Figure 1). The ferrimagnetic material present in these samples is likely to be a mineral such as magnetite, since it saturates in relatively low fields. The small kinks also mean that the ferrimagnetic content is extremely small (much less than 1 percent in most cases). Note that a large kink at low fields would immediately pin-point a sample with a larger ferrimagnetic content that could potentially give anomalous nuclear magnetic resonance (NMR) results.

The high field slopes of most of the samples in Figure 1 are actually slightly higher than expected for pure calcite or dolomite, and so it is expected that very small amounts of paramagnetic clay are also present. Based on the theoretical mixture modeling methodology of Potter and Ivakhnenko (2008) small variations in total illite content (e.g., below 1 percent) could produce the observed variation in the high field slopes of Figure 1 if the bulk matrix mineral was calcite or dolomite. Lambert et al. (2006) have also observed small amounts of such clay in a similar Middle East carbonate formation. SEM analysis on our samples was also consistent with small variations in the content of paramagnetic clay being responsible for the differences in the high field slopes of the hysteresis curves. For instance, SEM analysis for the sample with one of the highest high field slopes (394-62H) indicated the presence of some fine grained paramagnetic amorphous illite (Figure 2(a)) in some parts of the sample. In contrast, the sample with the lowest high field slope (394-41H), which is the most diamagnetic sample and therefore would be expected to contain the least amount of paramagnetic clay, was consistent by exhibiting far less evidence of such clay in the SEM analysis (Figure 2(b)).

The above two samples 394-62H (a typical blue curve sample from Figure 1) and 394-41H (a typical red curve from Figure 1), which have one of the highest and the lowest high

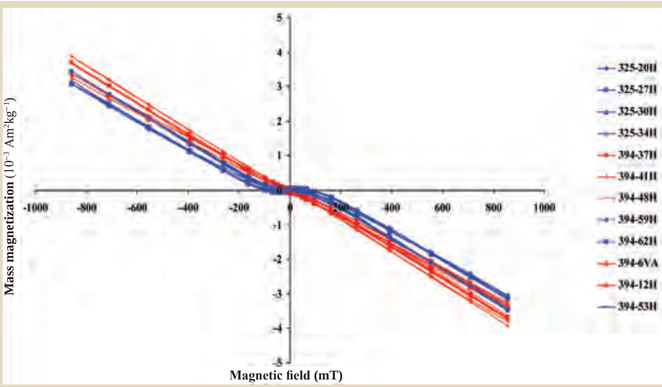

FIG 1. Room temperature magnetic hysteresis curves for a series of Middle East carbonates from the Arab-D reservoir. The red curves indicate samples exhibiting straight line behavior and therefore contain no detectable ferrimagnetic material. The blue curves indicate samples exhibiting a small kink at low fields, indicating the presence of a small amount of ferrimagnetic material.

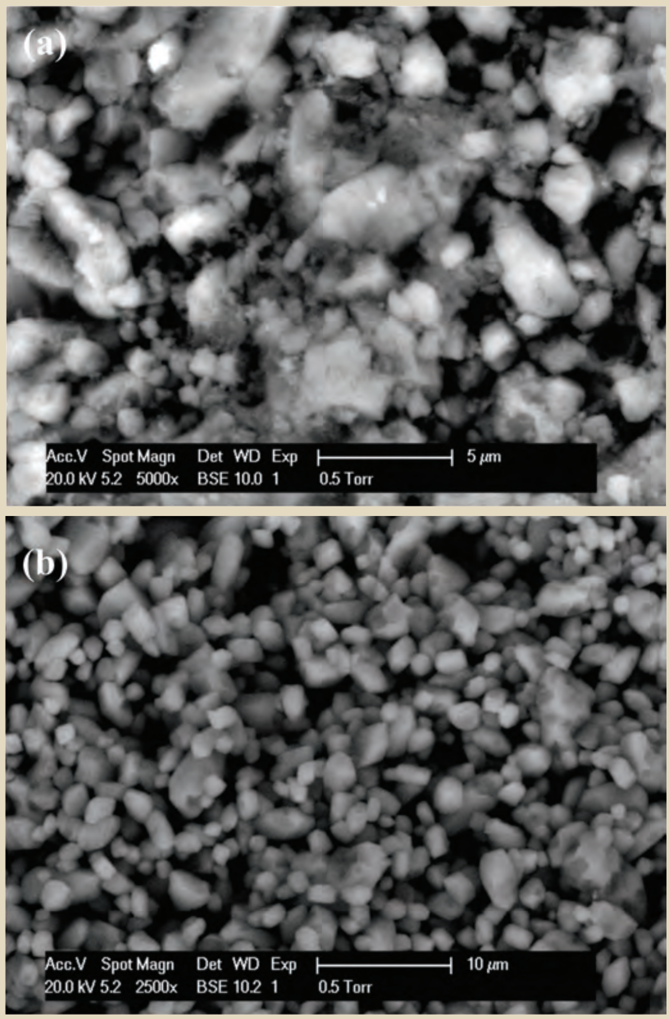

FIG 2. SEM images of (a) sample 394-62H (one of the blue curves in Figure 1 and which exhibits one of the highest high field slopes) showing small amounts of amorphous fine-grained illite (the fine material between the calcite and dolomite grains), and (b) sample 394-41H (one of the red curves in Figure 1 and which exhibits the lowest high field slope) showing virtually no clay in this image.

TABLE 2: A comparison of XRD derived results and magnetic susceptibilities derived from the hysteresis curves of Figure 1 for two samples from Figure 1 (a blue curve sample and a red curve sample). The low field magnetic susceptibility values were calculated from the slopes of the hysteresis curves in the applied field range 0-to-50mT, and the high field values from the straight line slopes above 750mT.

Sample	XRD Analysis	Calculated Mass Magnetic Susceptibility Based Only on the Calcite Plus Dolomite Content From XRD (10^{-8} m^3 kg^{-1})	Measured Mass Magnetic Susceptibility From Hysteresis Measurements (10^{-8} m^3 kg^{-1})	Comments
394-62H (blue curve sample with one of the highest high field slopes in Figure 1)	85 percent calcite. 14 percent dolomite. Trace of illite clay (<1 percent).	−0.48	−0.05 (low field) −0.36 (high field)	Low field magnetic susceptibility identifies some ferrimagnetic material (around 4-21 ppm if magnetite) not seen by XRD. High field magnetic susceptibility suggests a slightly larger paramagnetic clay content (around 0.8 percent if illite) than the red curve sample below.
394-41H (red curve sample with the lowest high field slope in Figure 1)	22 percent calcite. 77 percent dolomite. Possible trace of illite clay (much less than 1 percent).	−0.48	−0.42 (low field) −0.42 (high field)	No ferrimagnetic impurities, since low and high field magnetic susceptibility is similar. Magnetic susceptibility values suggest a very small paramagnetic clay content (around 0.4 percent if illite).

field slopes respectively, were analysed in more detail to compare their magnetic properties with XRD. Table 2 shows the XRD and magnetic susceptibility results at low and high fields. For the blue curve sample 394-62H the low field mass magnetic susceptibility is higher (the kink in the hysteresis curve in Figure 1) than the high field value, indicating the presence of a small amount of ferrimagnetic material. It is worth noting that these magnetic measurements are perhaps unique in being capable of readily identifying extremely small concentrations of ferrimagnetic material. In this case it would be around 4 -to- 21 parts per million if the material was magnetite (depending on which value one uses for the magnetic susceptibility of magnetite in Table 1). XRD is not capable of detecting such small amounts of ferrimagnetic material. The measured high field mass magnetic susceptibility is much closer to the calculated mass magnetic susceptibility derived from the XRD analysis, which assumed a composition of calcite and dolomite, than the low field magnetic susceptibility value. This is because the high field magnetic susceptibility is not influenced by the ferrimagnetic component (which saturates at lower fields). The measured high field value is slightly higher than the calculated value based on the XRD composition (assuming a calcite plus dolomite composition) most likely due to the presence of a small amount of paramagnetic illite clay. The high field magnetic measurements suggest a content of up to 0.8 percent illite in sample 394-62H, if the entire paramagnetic component was illite, which is higher than in the red curve sample 394-41H as discussed below.

For the red curve sample 394-41H Table 2 shows that the mass magnetic susceptibility is identical at low and high applied field strengths indicating that there are no ferrimagnetic impurities. The calculated mass magnetic susceptibility based on the XRD analysis (assuming the sample was composed solely of calcite and dolomite) closely matches the measured mass magnetic susceptibility values. The fact that the measured values are very slightly higher (less negative) is most likely due to the presence of a small amount of paramagnetic clay. The XRD analysis suggested a slight trace of illite clay but was not sensitive enough to quantify the amount accurately. The magnetic results, however, are able to make a quantitative estimate and indicate that there is at most 0.4 percent illite present if the entire paramagnetic component was illite.

CORRELATION WITH PETROPHYSICAL PROPERTIES

Correlation of Permeability with High Field Magnetic Susceptibility

Figures 3(a) and (b) show crossplots of the measured horizontal core plug permeability values and the low and high field mass magnetic susceptibility results derived from the hysteresis curves in Figure 1. The low field values were calculated from the slopes of the hysteresis curves in the applied field range 0-to-50mT, and the high field values from the straight line slopes above 750mT. The low field results did not show a good correlation with the permeability values (Figure 3(a)). This is because the low field results are influenced by small amounts of ferrimagnetic material in some samples (those marked with an “F” in Figure

3(a)). These samples exhibited a kink at low fields in their hysteresis curves (the blue curves in Figure 1).

Significantly, however, the high field results show an extremely good correlation with permeability (Figure 3(b)). The high field behavior reflects the contribution of the diamagnetic and paramagnetic minerals that make up the bulk volume of the rock. Therefore, if these minerals primarily control the petrophysical properties of the rock, then one is more likely to see correlations between the high field magnetic susceptibility and petrophysical properties like permeability. Nevertheless, this is a completely new and somewhat surprising result. In clastics the amount of paramagnetic clay (such as illite) can be a primary control on the permeability. This explains correlations between low field magnetic susceptibility and permeability (Potter, 2007) when there is little or no ferrimagnetic material in the sample, and between high field magnetic susceptibility and permeability (Potter and Ivakhnenko, 2008) even if the low field signal indicates the presence of ferrimagnetic material. Strong correlations between high field magnetic susceptibility and permeability were not necessarily expected in carbonates. The reason could be subtle variations in the paramagnetic clay content. Small increases in paramagnetic clay can significantly decrease the permeability in clastics, and perhaps the same is true of some carbonates. The high field magnetic results are consistent with this interpretation. The SEM and XRD analysis was also consistent in that sample 394-62H contained more illite clay (Figure 2(a) and Table 2) and had a lower permeability (0.06 mD) than sample 394-41H, which contained less clay (Figure 2(b) and Table 2) and had a higher permeability (3.53 mD).

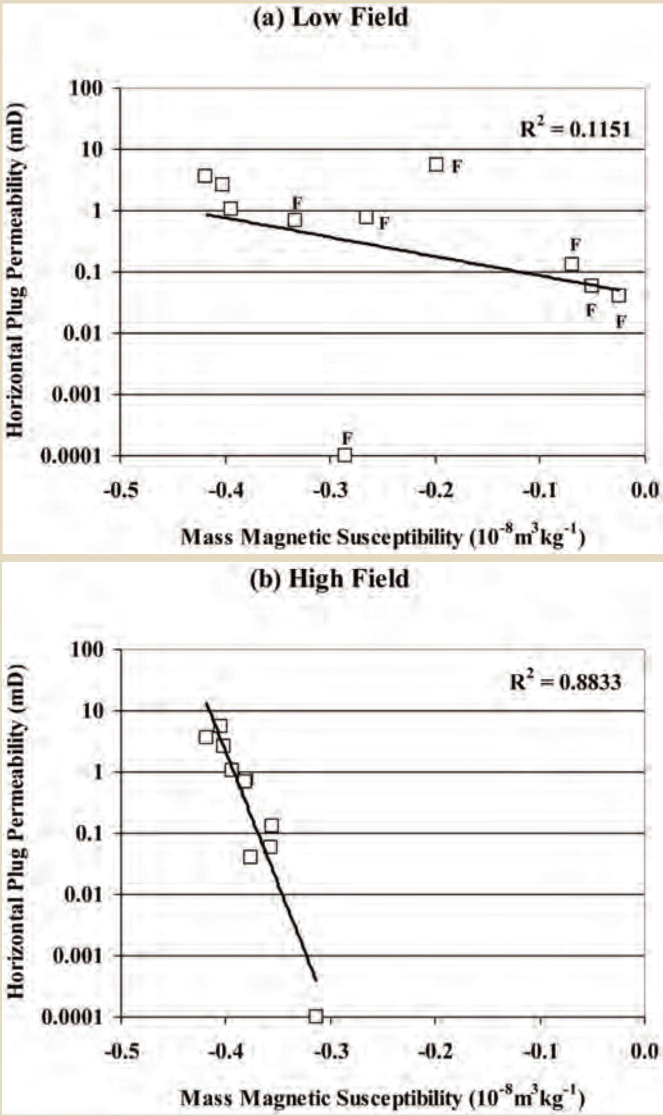

FIG 3. (a) Low field magnetic susceptibility versus plug permeability. The low field results are influenced by small amounts of ferrimagnetic material in some samples (those marked "F"). (b) High field magnetic susceptibility versus plug permeability showing a strong correlation. The ferrimagnetic material saturates at lower fields and does not affect the high field results.

Correlation of Porosity with High Field Magnetic Susceptibility

The core plug porosity (helium) values were also compared with the low and high field magnetic susceptibility results (Figure 4). The low field results did not show a good correlation with the porosity values (Figure 4(a)), due to the influence of the small amounts of ferrimagnetic material in some of the samples (those marked with an "F" in Figure 4(a)). Significantly, the high field results showed an extremely good correlation with porosity (Figure 4(b)). The reason for this good correlation is not altogether clear at present. If the correlation between permeability and high field magnetic susceptibility is due to the variations in the paramagnetic clay content, and there is a reasonable correlation between porosity and permeability (the core plug porosity versus permeability crossplot for these samples gives a regression coefficient $r^2 = 0.71$ using an exponential regression line, or 0.90 using a power regression line), then the correlation of porosity and high field magnetic susceptibility may merely be an indirect consequence of this. In clastic reservoirs, where there is little correlation between permeability and porosity, the permeability correlates with magnetic susceptibility but the porosity does not (Potter, 2007). This is because small amounts of illite clay create microporous illite rims around the quartz grains. Increasing illite content reduces the permeability, increases the magnetic susceptibility signal, but has little effect on the porosity.

Note that two of the twelve plug samples from Figure 1 did not have permeability or porosity data, and thus were not plotted on Figures 2 and 3. This is because they developed fractures. This, however, did not affect our ability to obtain the magnetic information, which is a further advantage of the magnetic techniques.

COMPARISON OF MAGNETIC HYSTERESIS CURVES FOR DIFFERENT CARBONATE RESERVOIRS

Magnetic hysteresis curves for samples from carbonate reservoirs in the USA and the UK are compared with the

Middle East carbonates in Figure 5. The USA and UK carbonates studied generally have slightly more ferrimagnetic material, as shown by slightly larger kinks at low field. In most cases they also have slightly higher slopes at high field than the Middle East carbonates, indicating increased paramagnetic mineral content. The North Sea calcite plus clay dogger sample (P81.3) is very different to all the other samples. The high field slope is positive, indicating a significant amount of paramagnetic minerals (in this case paramagnetic clays) compared to the other samples. This increased clay content appears to have been responsible for the low permeability of this sample (0.01 mD) compared to most of the Middle East samples. Only one of the Middle East samples has a lower permeability, and that is because it contains a significant amount of anhydrite.

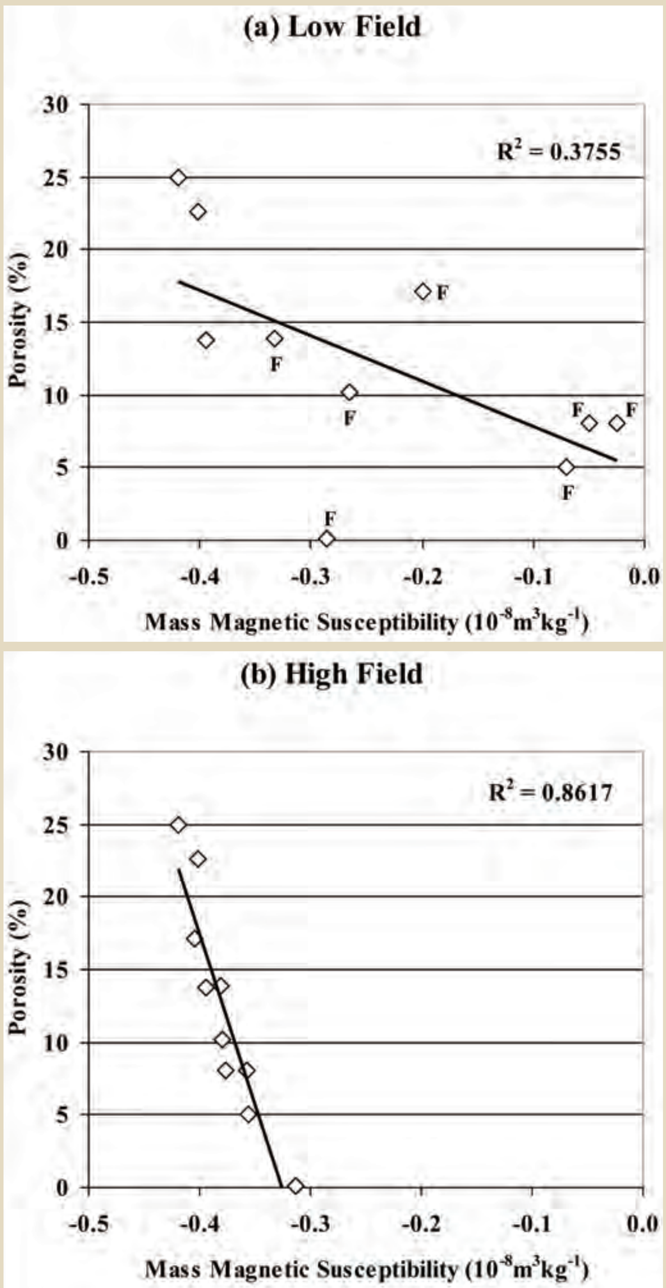

FIG 4. (a) Low field magnetic susceptibility versus plug porosity. The low field magnetic results are influenced by small amounts of ferrimagnetic material in some samples (those marked "F"). (b) High field magnetic susceptibility versus plug porosity showing a strong correlation. The ferrimagnetic material saturates at lower fields and does not affect the high field results.

Effect of Temperature on Magnetic Hysteresis Curves

The magnetic hysteresis curves of samples containing pure diamagnetic carbonate minerals (calcite, dolomite etc) should theoretically exhibit no temperature dependence. Sample 394-41H, which had the lowest high field slope at room temperature in Figure 1 (and thus would be expected to be the most diamagnetic sample), showed virtually no dependence of the magnetic hysteresis curve to temperature from ambient to beyond typical reservoir temperatures (245 ºC). This is further evidence that this sample contains little detectable paramagnetic clay. Samples with a higher initial high field slope than sample 394-41H at room temperature would be expected to contain more paramagnetic material, and thus would be expected to exhibit slightly greater decreases in the slope of the high field part of the hysteresis curve with increasing temperature in accordance with the Curie law for paramagnetic substances. Figure 6 shows the results for one such sample (the Limestone (UK) sample) with a higher high field slope than sample 394-41H at room temperature. Slight decreases in the high field slope with increasing temperature are apparent, indicating a very small content of paramagnetic material.

Samples containing much larger amounts of paramagnetic material, with higher room temperature high field slopes, should show even greater decreases in the high field slope with temperature. Figure 7 shows the results for sample P81.3 (a North Sea calcite plus clay dogger sample). This sample exhibits very significant decreases in the high field slope of the hysteresis curves (decreases in the high field magnetic susceptibility) with increasing temperature, consistent with this sample's higher paramagnetic clay content. The high field slope is positive at room temperature, 89 ºC and 125 ºC, and then goes negative at 245 ºC.

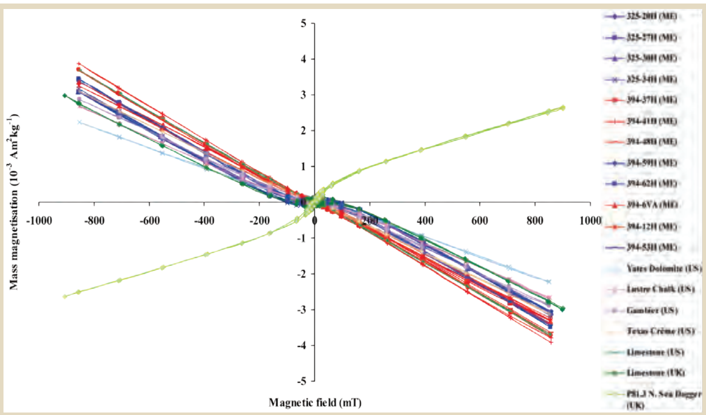

FIG 5. A comparison of room temperature magnetic hysteresis curves from some Middle East (ME), United States (US) and United Kingdom (UK) carbonate samples.

Magnetic Anisotropy

The low field anisotropy of magnetic susceptibility (AMS) of the North Sea calcite plus clay dogger sample (P81.3) is around 5 percent, where percent anisotropy is defined as 100 (max. − min.) / (max. + int. + min.), and is significantly higher than the AMS of most of the Middle East samples (which are generally around 1 percent). The increased anisotropy of sample P81.3 appears to be due mainly to the higher paramagnetic clay content. Previous studies on mudstones have suggested that the degree of anisotropy is directly related to the amount of paramagnetic clay (Charpentier et al., 2003), and this may also be the case for carbonates. However, there may be some influence of the ferrimagnetic material in sample P81.3 on the low field AMS. Further work is planned on high field anisotropy in order to minimize the influence of any ferrimagnetic components present and therefore better quantify the clay anisotropy.

CONCLUSIONS

Subtle mineralogical differences in carbonates can be quantified by their magnetic hysteresis curves. The slope of the hysteresis curve (the magnetic susceptibility) at high fields indicates the combined contribution of the diamagnetic plus paramagnetic minerals in the carbonate. Extremely small variations in the content of the paramagnetic component (between about 0.4 percent and 0.8 percent if that component was entirely illite) in a suite of Middle East carbonates from the Arab-D reservoir Jurassic formation could be quantified from the high field hysteresis curve slope. The higher the high field slope the greater the paramagnetic clay content. XRD and SEM analyses were consistent in indicating higher illite clay content in samples whose high field slope was higher. However, XRD and SEM are less capable of accurately quantifying the small variations in illite content compared to the sensitive magnetic technique.

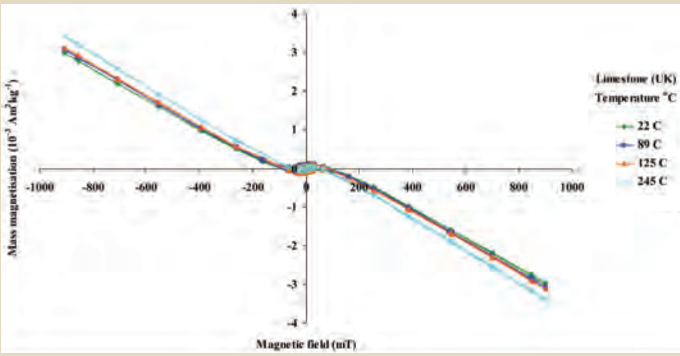

FIG 6. Temperature dependence of the magnetic hysteresis curves of one of the mid range carbonate samples (the Limestone (UK) sample) containing a small amount of paramagnetic material.

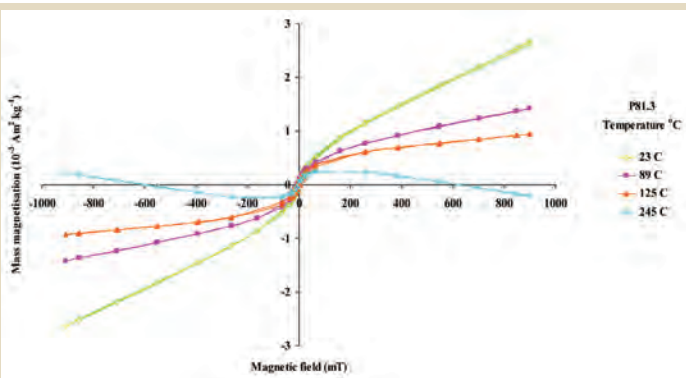

FIG 7. Temperature dependence of the magnetic hysteresis curves of the North Sea calcite plus clay dogger sample (P81.3). The significant decreases in the high field slope with increasing temperature demonstrate that the P81.3 sample contains a larger paramagnetic mineral content than the Limestone (UK) sample shown in Figure 6.

The high field magnetic susceptibility exhibited very strong correlations with both permeability and porosity in the Middle East carbonates. This is the first time, as far as we are aware, that high field magnetic susceptibility has been compared with petrophysical properties in carbonates, and provides a new tool for carbonate characterization. Extremely small variations in paramagnetic clay content appear to be responsible for the strong correlation between permeability and high field magnetic susceptibility.

The temperature dependence of the magnetic hysteresis curves can also provide an indication of the paramagnetic mineral content in a sample, even without other prior information regarding the mineralogy. Experimentally a decrease in high field magnetic susceptibility (i.e., a decrease in the slope of the high field part of the hysteresis curve) was observed for samples containing paramagnetic clay as expected theoretically. The greater the initial paramagnetic mineral content the greater the decrease in the slope of the high field hysteresis curve with increasing temperature. This represents a further means of detecting small amounts of paramagnetic clay in a sample, which might not be detected by XRD. In contrast, pure diamagnetic carbonate matrix minerals (such as pure calcite or dolomite) do not exhibit any temperature dependence of magnetic susceptibility.

The low field hysteresis behavior can indicate the presence of any ferrimagnetic material, via kinks or loops, and can provide a further means of sensitive carbonate characterization. The magnetic measurements can identify extremely small amounts of ferrimagnetic material (down to a few parts per million), which cannot be done by other techniques, such as XRD. The low field magnetic susceptibility did not exhibit good correlations with permeability and porosity. This can be explained entirely by the influence of small amounts of ferrimagnetic impurities in some of the samples, which contribute to the low field signal. This ferrimagnetic material does not influence the high field results, however, since it saturates at lower fields.

Carbonates with a greater paramagnetic clay content also exhibited a higher low field anisotropy of magnetic susceptibility (AMS). Future anisotropy measurements should determine the high field AMS to better characterize the diamagnetic and paramagnetic components in the samples without the influence of any ferrimagnetic material.

NOMENCLATURE

AMS Anisotropy of magnetic susceptibility
FZI Flow zone indicator
NMR Nuclear magnetic resonance
Q_v Cation exchange capacity per unit pore volume
SEM Scanning electron microscopy
VFTB Variable field translation balance
XRD X-ray diffraction

ACKNOWLEDGEMENTS

The Industry Technology Facilitator (ITF) "Low Permeability Reservoir" program, funded by BP, Chevron, Shell, Total, and Scottish Enterprise is gratefully acknowledged. We thank Nicolai Petersen and Valerian Bachtadse for the use of the VFTB at the Ludwig Maximilians University, Munich. We thank Jim Somerville and Sally Hamilton for the Middle East carbonate samples, and Norman Morrow for the US carbonate samples.

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