THE ROCK MAGNETIC FINGERPRINT OF CHEMICAL REMAGNETIZATION IN MIDCONTINENTAL PALEOZOIC CARBONATES

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Abstract. Results of a paleomagnetic and rock magnetic survey of Paleozoic carbonates from 39 sites in the midcontinental U.S. show that many of these sites carry a stable remanence of apparent Permian age. Many of these remagnetized sites also have relatively high anhysteretic susceptibilities, and higher saturation remanence than most of the sites where the late Paleozoic remanence is absent. However the correlation between late Paleozoic remanence and high anhysteretic susceptibility or high saturation remanence is imperfect. The most diagnostic rock magnetic parameter for recognizing remagnetized sites is a ratio of anhysteretic remanence/saturation remanence exceeding 10%. We have found high ratios in almost all remagnetized sites, but in very few sites where the Late Paleozoic remanence is absent. The high ratios reflect the presence of a significant fraction of extremely fine-grained magnetite (a few tens of nanometers), spanning the superparamagnetic-single domain threshhold.

Introduction

Abundant evidence has accumulated in recent years indicating that the Paleozoic carbonate strata of cratonic North America were extensively remagnetized during the late Paleozoic Kiaman reverse polarity superchron [e.g., McCabe and Elmore, 1989; Van der Voo, 1989]. At least three principal lines of evidence favor a chemical mechanism for the remagnetization, involving growth of new magnetite. First, petrographic studies have shown that Ti-free magnetites with apparent diagenetic or authigenic morphologies (e.g., spheroidal or botryoidal) occur in most remagnetized carbonates [e.g., McCabe et al., 1983; Suk et al., 1990 a, b; Lu et al., 1990]. Second, many remagnetized strata occur in areas for which there is little or no evidence of any significant burial or heating; this by default favors a chemical mechanism. Finally, recent detailed rock magnetic studies or several well-documented examples of remagnetized strata (Trenton limestone [McCabe et al., 1984], Knox dolomite [Bachtadse et al, 1987], and Onondaga limestone [Kent, 1979, 1985]) have shown that these units share a set of quite unusual magnetic properties, apparently due to 1) an absence of uniaxial (shape or stress) anisotropy in the magnetic grains, and 2) the presence of a significant fraction of ultrafine-grained magnetite, near the boundary between single-domain (SD) and superparamagnetic (SP) sizes [Jackson, 1990; Jackson et al, 1992].

In this paper we describe results of a paleomagnetic and rock-magnetic survey of midcontinental Paleozoic carbonates. The principal goal of this paper is to determine whether the unusual rock-magnetic properties previously identified in the Knox, Trenton, and Onondaga samples may be used to distinguish remagnetized sites in other stratigraphic units and geographic areas. A majority of the localities for this study were chosen to coincide with sites where Craddock and van der Pluijm [1989] analyzed mechanical twinning in calcite. A comparison of magnetic anisotropy with calcite twinning strains will be presented in a separate paper [Sun et al, 1992].

Rock-magnetic Signature of Chemical Remagnetization

In previous studies of "type" remagnetized carbonates, samples of Knox dolomite, Trenton limestone, and Onondaga limestone have all been found to exhibit moderately high ratios of saturation remanence to saturation magnetization (M_{rs}/M_s ranging from about 0.20 up to 0.65) [Jackson, 1990]. This indicates dominantly fine-grained magnetic carriers [Day et al., 1977], in contrast to the relatively coarse grains commonly observed in extracts [e.g., McCabe et. al., 1983]. Most of the samples also had very high ratios of remanent coercivity to bulk coercivity (H_{cr}/H_c as great as 15), which is generally characteristic of mixtures of grain sizes or mixtures of magnetic minerals [e.g., Kneller, 1969; Parry, 1982]. The two ratios were found to be related by the law $M_{rs}/M_s = 0.87(H_{cr}/H_c)^{0.6}$; the constant 0.87 represents the M_{rs}/M_s ratio of the finer-grained (or magnetically harder) component in the mixture [see Parry, 1982], and this value agrees closely with the value for randomly-oriented single-domain particles with cubic anisotropy [Joffe and Heuberger, 1974] (i.e., the magnetocrystalline anisotropy of magnetite). Further studies [Jackson et al, 1992] have led to the conclusion that as much as half of the total mass of magnetite in the same samples is in or near the superparamagnetic size range. Evidence for this includes anomalously high ratios of k_f/M_s (where k_f is the ferrimagnetic component of low-field susceptibility k_0), strong frequency-dependence of k_0, ratios of k_a/k_0 (where k_a is anhysteretic susceptibility) exceeding ten, and ARM/SIRM ratios (anhysteretic remanent magnetization / saturation isothermal remanent magnetization) of up to 25%.

Both the absence of strong shape anisotropy and the presence of a significant population of ultrafine particles are clearly compatible with an authigenic origin for the magnetite in these "type" remagnetized units. Some of the same characteristics have also been reported in association with pedogenic magnetite [e.g., Özdemir and Banerjee, 1982; Maher, 1988], which forms by inorganic chemical processes during soil formation. The hysteresis ratios and other inter-

parametric ratios described above thus appear to be potentially useful as fingerprints of chemical remagnetization. In this study we compare these rock magnetic properties with the paleomagnetic behavior of a large set of Paleozoic carbonates.

Methods

Magnetically-oriented hand samples were collected at thirty-nine sites over a large area of the midcontinent. At least three samples were obtained from each site. Several standard cylindrical core specimens were subsequently cut from each sample for paleomagnetic and rock-magnetic analysis, as well as for anisotropy measurements. Low-field susceptibility was measured at two frequencies (477 Hz and 4.77 kHz) using a Bartington AC bridge. Natural remanent magnetizations (NRM's) were measured on a 3-axis 2G Corp. superconducting rock magnetometer, and stepwise demagnetized in a Schonstedt alternating field (AF) demagnetizer. A few samples were thermally demagnetized for purposes of comparison. Results were analyzed using standard methods [Zijderveld, 1967; Kirschvink, 1980]. ARM's were imparted with the same AF demagnetizer and a DC coil which generated a bias field of 80 A/m (1 Oe). Room-temperature hysteresis measurements were made on an automated vibrating sample magnetometer (VSM) and on an alternating-gradient force magnetometer (AGFM).

Results

Paleomagnetic behavior of the samples can be grouped into three categories: 1) dominantly Kiaman; 2) pre-Kiaman; and 3) post-Kiaman or unstable. Samples from sites in the first category all exhibited a stable magnetization oriented toward the south-southeast, with shallow inclination. These sites yielded virtual pole positions very close to the mean Permian pole of Van der Voo [1989]. All of the samples from these sites also contained a steeply downward, northerly component removable by AF or thermal cleaning; we interpret this as a viscous overprint acquired in the recent field. In some cases, the steep component was also present in the highest coercivity fraction: the Kiaman component decayed toward a northerly downward direction rather than to the origin. In these samples it is apparent that weathering has produced magnetically hard antiferromagnetic minerals such as hematite or goethite, carrying a young chemical remanence.

The category 2 sites contained no magnetizations in the direction of the Kiaman field. Some samples carried a remanence close in orientation to the field direction at the time of deposition, as calculated from the apparent polar wander path of Van der Voo [1989]. Many of the samples from these sites only contained recent viscous or weathering overprints, or were unstable. Sites in the third category contained only samples with this latter behavior. Figure 1 summarizes the types of behavior identified at each of the sampling sites.

Low-field susceptibilities were very low in all cases, less than 50×10^{-9} m^3/kg. They were in fact too low for most sites to enable reliable determination of either frequency-dependence or susceptibility anisotropy. High-field susceptibilities calculated from hysteresis measurements are very close to low-field susceptibilities for most
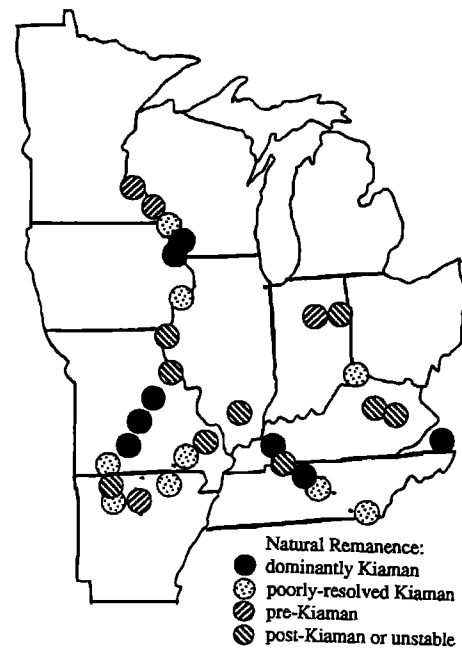

Fig. 1. Summary of paleomagnetic behavior.

sites, indicating that k_0 derives primarily from paramagnetic material. Figure 2 summarizes the susceptibility data.

Anhysteretic remanence exhibits strong between-site variations, but small within-site differences. Figure 3 shows that high-ARM sites are concentrated in a few geographic areas; these tend to coincide with tectonic arches, as noted by Lu et al [1990], and they also coincide with mineralized areas [Bethke and Marshak, 1990]. Comparison of figures 3 and 1 shows that there is a strong but not perfect correlation between high ARM values and dominant Kiaman paleomagnetism.

Hysteresis measurements for many sites produced nearly straight-line loops, reflecting a paramagnetic signal much larger than that from magnetite (or other ferro- or ferrimagnetic minerals). The paramagnetic signal probably arises from iron-bearing clay minerals, or possibly from iron car-
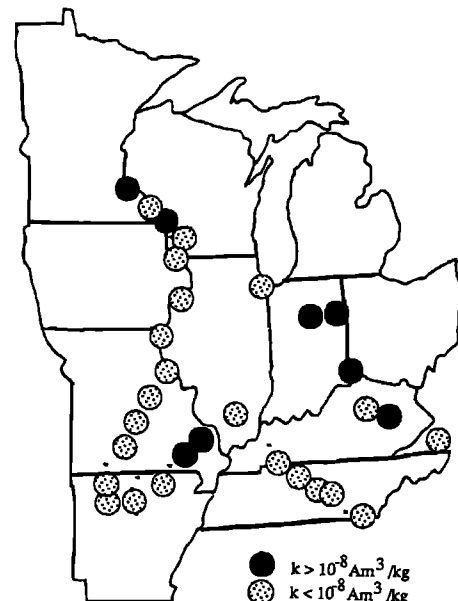

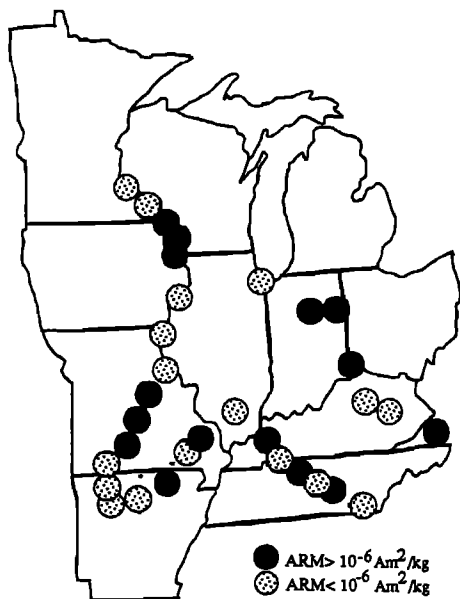Fig. 2. Mean low-field susceptibility values.

Fig. 3. Mean values of anhysteretic remanent magnetization (ARM).

bonates. For sites where a ferrimagnetic signal could be reliably isolated, the loops were strongly constricted or "wasp-waisted", and were very similar to those found previously for the Knox, Trenton, and Onondaga samples. Because of the strong paramagnetic contribution to most samples, saturation remanence was re-measured with the superconducting magnetometer; agreement with the values from the VSM was generally fair (within about 50%), and where there were discrepancies, the superconductor measurement is clearly more reliable. Figure 4 summarizes the SIRM data; the pattern is very similar to that of ARM. Again, there is a strong but not perfect correlation between rock magnetic properties and paleomagnetic behavior.

The very high ratio of paramagnetic to ferrimagnetic signal for applied field measurements (susceptibility,
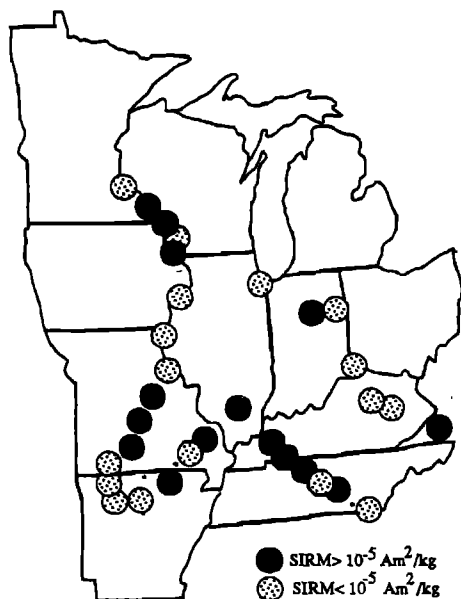
hysteresis) hampers our ability to compare the properties of these samples with the diagnostic features found in the Knox, Trenton and Onondaga samples. The ratio k_f/M_S is quite high for all of the sites in the present study, as it was for the "type" remagnetized units; however, the reliability with which these parameters can be determined for the present samples is limited by the large paramagnetic signal. The most robust parameters in such samples are those related to remanence (measured in zero-field, thus there is no paramagnetic signal). Figure 5 shows the measured values of the ratio ARM/SIRM for each site. The ratios range from about 1% up to nearly 25%. As we have described previously [Jackson et al, 1992], ARM/SIRM ratios greater than 10% are characteristic of the "type" remagnetized carbonates. Comparison of Figures 2 and 5 shows a very strong correlation: sites having ARM/SIRM ratios of 10% or greater nearly all have a dominant Kiaman NRM component, whereas almost none of the sites where the ratio is less than 10% show any indication of the Kiaman remanence.

Discussion and Conclusions

As noted previously, [Saffer and McCabe, 1991; Lu et al, 1990], there is a general correlation between relatively high magnetite concentrations (as indicated by ARM and/or SIRM) and the presence of a Kiaman component of NRM. Saffer and McCabe have further pointed out that the magnitude of the Kiaman component in Onondaga samples is closely related to the ratio ARM/k_0 [see Banerjee et al., 1981], and thus that the late Paleozoic remanence is associated with fine-grained magnetite. Unfortunately, for the midcontinent carbonates k_0 is dominantly paramagnetic (unlike the Onondaga samples), and thus the ratio ARM/k_0 is not a useful indicator of relative grain size. However, the results of our study indicate that the ratio ARM/SIRM is a very robust indicator of the presence of very fine-grained magnetite produced by the chemical remagnetization event during the late Paleozoic.

Similar ARM/SIRM ratios have also been reported for ultrafine (20 nm) biogenic magnetites [Moskowitz et al.,

Fig. 4. Mean values of saturation isothermal remanent magnetization (SIRM).
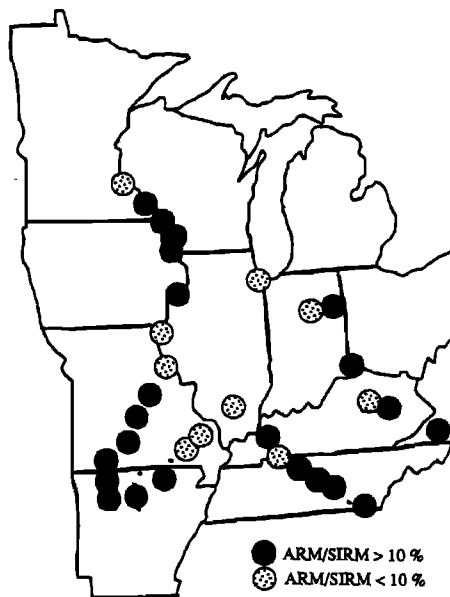

Fig. 5. Ratio of mean ARM to mean SIRM.

1988], but have never found for particles much larger than about 30 nm. The occurrence of such high ratios in these samples can therefore be considered clear evidence that a substantial fraction of the magnetite has sizes near the SP-SD boundary. This inference is supported by the strong frequency-dependence of susceptibility and by the very high normalized susceptibilities (k_f/M_s) in the "type" remagnetized samples from the Knox, Onondaga, and Trenton formations [Jackson et al, 1992]. The presence of a large SP fraction also accounts for the strongly constricted hysteresis loops in the "type" samples and in the samples of this study.

It is now clear that the Kiaman remagnetization event in the midcontinent involved precipitation of authigenic magnetite. Our results indicate that most of the magnetite was precipitated as extremely fine particles, whose presence can be easily and reliably detected by measurements of ARM and SIRM.

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