Characteristics of magnetic carriers responsible for Late Paleozoic remagnetization in carbonate strata of the mid-continent, U.S.A.

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ABSTRACT

Magnetic analysis of carbonate strata of the mid-continent region of the United States indicates that the Late Paleozoic remagnetization already recognized in the Appalachians also affects almost the entire mid-continent. Magnetic intensity is regionally variable, with more intense magnetizations occurring on intracratonic arches. Magnetization is carried predominately by magnetite, which often occurs in tiny hollow spheroids composed of well formed octahedral microcrysts. Spheroid chemistry and morphology suggests that the magnetite is authigenic, composed of iron extracted from pre-existing pyrite or clay. The timing of the remagnetization, the character of the magnetite, and the regional variation in magnetic intensity support the idea that the remagnetization is a diagenetic consequence of tectonically-driven brine migration.

1. Introduction

In recent years, pervasive remagnetization has been recognized in the sedimentary strata of the Appalachian/Ouachita fold-thrust belt, Appalachian basin, Arkoma basin, and in scattered localities of the mid-continent region [e.g., 1-7]. Most measurements indicate that the dominant remagnetization occurred during the Kiaman long reversed polarity interval (Late Pennsylvanian/Early Permian), and thus about the time of the Alleghanian/Ouachita orogeny. Because of this temporal and spatial association, many authors have suggested that the remagnetization was triggered by the orogeny [e.g., 3-9]. A favored driving mechanism appears to be uplift of groundwater recharge areas during orogenesis, which creates hydrostatic pressure sufficient to drive basin brines toward the continental interior [9]. These warm brines react with strata as they pass, leading not only to remagnetization, but also to various diagenetic effects (dolomitization, feldspathization, smectite illitization), ore formation, and petroleum migration [3-16].

Though much is already known about the Kiaman remagnetization, there are still several outstanding questions including: (1) how widespread are the effects of the event in mid-continent North America, and (2) what are the characteristics (e.g., mineralogy, morphology, origin etc.) of the magnetic carriers and how did they form? Our initial results [17] demonstrate that evidence for Kiaman remagnetization is widespread in the mid-continent (Fig. 1), though at several sites in Iowa and Minnesota, magnetizations proved to be very weak or unstable and thus the presence or absence of Kiaman remagnetization could not be determined. In addition, we show that there is a spatial association between remagnetization and regional arches; more intense magnetizations were measured in samples on or near the regional arches [17]. The details of our paleomagnetic and rock-magnetic measurements will be dealt with in a separate paper (Kent et al., in prep.). The principal purpose of the present paper is to describe the magnetic carriers. We were able to obtain remarkably clear SEM images of the magnetic grains, as well as EDX and XRD analyses of the grains. Earlier studies have noted and illustrated
Fig. 1. Map of the sample localities. Solid circles = localities where samples have an ARM measurement greater than 4 mA/m; open circles = localities where samples have an ARM measurement smaller than 4 mA/m; squares = localities where the magnetization of the samples was unstable and the Kiaman pole was not identified. ARM measurements are only for a subset of samples.

LA = Lincoln Anticline; LSA = La Salle Anticlinal Belt; ND = Nashville Dome.

2. Methods

We collected about 500 oriented cores in carbonate rocks at 53 sites in the mid-continent region (Illinois, Indiana, Iowa, Ohio, Kentucky, Tennessee, Missouri, Minnesota, Michigan, Wisconsin; Fig. 1, Table 1). Samples were obtained from both limestone and dolomite beds of all ages from Cambrian through Pennsylvanian which are exposed in quarries and road cuts. The natural remanent magnetization of these samples is variable, but in general is very weak. Likewise, magnetic susceptibilities are very low; they are on the order of $10^{-6}$ emu/Oe cc (Kent et al., in prep.). These data likely reflect the low concentration of the magnetic carriers in these rocks. Thus, in order to visually examine the magnetic carriers efficiently, we extracted them from the bulk rock. To do this, the rock was pulverized and placed in a solution 1N acetic acid buffered with sodium acetate to a pH of 5. Each day for about three weeks, the reagent was changed and the mixture of reagent and rock-powder residue was sonified. About 5% by weight of the original rock remained after dissolution. This residue was mixed with distilled water and passed through a Frantz L-1 isodynamic magnetic separator. Magnetic separation yielded an extract that was about 5% by weight of the original residue, or about 0.25% of the total rock.

Examination of the concentrated magnetic extract was carried out using a variety of techniques. A JEOL-840A scanning-electron microscope (SEM) permitted us to observe the grain mor-
TABLE 1

Characteristics of samples used for rock-magnetic measurements

<table>
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<th>Sample no.</th>
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<th>ARM</th>
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</table>

ARM is measured in mA/m. Grain-size: Calcilutite (10–30 μm); Calcisiltite (30–60 μm); Calcarentite (60μm–2.5 mm); Calcirudite (greater than 2.5 mm). Age of geologic units is specified by a letter (C = Cambrian, O = Ordovician, S = Silurian, D = Devonian, M = Mississippian, IP = Pennsylvanian). The letter before the system symbol represents the subdivision in that system (L = Lower; M = Middle; U = Upper). The lower-case letter after the system symbol represents the stages or subgroups. (UIPm = Matton Subgroup and McLeansboro Supergroup of the Upper Pennsylvanian. UIPb = Bond Subgroup and McLeansboro Supergroup of the Upper Pennsylvanian. IPmK = Kansas City Subgroup and Missourian Supergroup of the Middle Pennsylvanian. Mm = Meramecian Supergroup of the Mississippian. Mko = Chesterian Supergroup of the Upper Mississippian. Mv = Valmeyeran Supergroup of the Middle Mississippian. Mko = Kinderhookian–Osagian Subgroup of the Lower Mississippian. Omu = Undivided Middle Ordovician and Upper Ordovician strata.

physics, and the energy-dispersive X-ray analyzer (EDX) attached to the SEM permitted us to determine the identity of elements in individual grains. We used high-resolution X-ray diffraction (XRD) analysis of the concentrated magnetic extract to confirm the mineralogy of grains present, and optical petrography (transmitted and reflected) to examine original rock fabrics. Rock-magnetic and paleomagnetic measurements were carried out at Lamont-Doherty Geological Observatory.

3. Description of magnetic carriers

We examined the characteristics of magnetic carriers in ten samples in detail. SEM examination
of the concentrated magnetic extract indicates that it contains about 1% iron-rich and sulfur-free grains, which are considered to be magnetic carriers. We roughly estimate the concentration of these grains in the original bulk rocks to be no more than $5\% \times 5\% \times 1\% = 25$ ppm by weight. Based on our study, four morphological types of magnetic carriers can be distinguished from one another in the extracts: spheroidal grains, framboidal aggregates, botryoidal aggregates, and flaky-habit aggregates.

3.1. Spheroidal grains

Spheroidal grains (spheroids) are the most common morphological type observed in our samples. These grains are about 5–15 $\mu$m in diameter, and they have a somewhat bumpy surface. A few of the observed spheroids were broken, and reveal a hollow center (Fig. 2a). EDX spectra of the samples show very strong Fe, moderately strong Si, Al, and Ca peaks, and no S peaks, suggesting that the spheroids are composed of iron oxides (magnetite, goethite, or hematite) coated with silicate...
3.2. Framboidal aggregates

A "framboidal aggregate" (framboid) is a spheroidal cluster that consists of many smaller, discrete, equant individual crystals called microcrysts. The framboids found in the concentrated magnetic extracts of our samples range in size between 10 and 20 μm, and are composed of individual microcrysts that range in size between 1 and 3 μm. We found several spectacular examples in which the microcrysts displayed an unmistakable octahedral crystal habit (Fig. 2b). In most examples, the microcrysts were partially hidden by a thin amorphous-looking coating (Fig. 2c). EDX analysis of the grains shows that well exposed octahedral crystals have only dominantly strong Fe peaks (Fig. 2b), whereas the partially coated grains have not only Fe peaks but also Si, Al, and Ca peaks (Fig. 2c). The grain shown in Fig. 2c looks quite spheroidal, but individual microcrysts are slightly visible alluding to the underlying framboidal morphology. We infer that the octahedral crystals are iron oxides, that the framboids are therefore composed of clusters of iron-oxide grains, and that at least some spheroidal grains are actually framboids with an authigenic clay coating.

The well developed octahedral habit and absence of sulfur peaks suggest that the microcrysts are most likely magnetite, and not solid goethite or hematite. However, the framboids observed in thin section and the concentrated magnetic extracts suspended in mineral oil are somewhat red in color, suggesting the possibility of goethite/
hematite alteration on the surface of the framboids. We also note that some grains of pyrite, identified by their appearance in reflected-light petrographic analysis, are partially altered by pseudomorphic replacement to goethite/hematite. There is a possibility that some of the red framboidal grains contain goethite that formed as an oxidation product derived from framboidal pyrite during sample treatment in solvent, but we do not consider this possibility to be likely because such a reaction would probably not completely remove sulfur from the precursor pyrite. We assume that goethite is a low-temperature alteration product reflecting shallow-level reaction of rocks with meteoric water, and that it is not associated with the remagnetization.

3.3. Botryoidal and flaky-habit aggregates

In addition to the framboidal and spheroidal grains described above, an iron-rich and sulfur-free mineral, as identified by EDX spectra, occurs in two other forms. The first is in grape-like clusters of spheroids referred to as botryoidal aggregates (Fig. 2d). Botryoidal aggregates could be a morphological form for magnetite, hematite, or goethite, but the distinction between these minerals cannot be made on the basis of EDX spectra alone. The second form is in clusters of tiny flakes. The flakes were extracted from a reddish scum that formed on the surface of reagent during dissolution of a few samples (e.g., IL0207). The flakes are 1–3 μm across (Fig. 2e). Based on the flaky morphology, the strong iron peak, and the
reddish color, we interpret these grains to be hematite. The hematite is not widespread and may reflect more recent weathering.

3.4. Summary of magnetic mineralogy data

Our work suggests that carbonate strata throughout the mid-continent region contain four morphological classes (spheroidal, framboidal, botryoidal and flaky) of iron-rich and sulfur-free minerals. We estimate that, in general, spheroidal and framboidal grains account for about 25 ppm of the rock. In all cases, the grains or aggregates are very small (< 20 μm), yield a strong iron peak, no titanium peak, and no sulfur peak in EDX spectra. There is an apparent morphological gradation between the spheroidal grains and framboidal aggregates, the difference being the degree to which octahedral microcrysts are obscured by a silicate (probably clay) coating.

Based on the EDX spectra and the octahedral crystal morphology, we consider the spheroidal grains and framboidal aggregates to be magnetite, in agreement with previous authors [e.g., 3,18]. The botryoidal aggregates could be magnetite, hematite, or goethite, and the flaky-habit aggregates are probably hematite.

To confirm the identification of these candidate magnetic minerals, we examined extracts using a very sensitive Rigaku X-ray diffractometer. The XRD pattern for the concentrated magnetic extract from sample IN0703 (fine-grained limestone; Middle Mississippian; sampled at southern Indiana) shows pronounced peaks for magnetite (Fig. 3) and the pattern for the scum obtained from the reagent after dissolving sample IL0207 (coarse-grained limestone; Pennsylvanian; sampled at central Illinois) shows subtle but identifiable peaks for hematite and goethite (Fig. 4). IRM acquisition curves for our samples, described by Kent et al. (in prep.), also point to the occurrence of magnetite in most samples and the co-occurrence of hematite at about one-quarter of the sampling sites. Further confirmation of the identity of the crystals will require X-raying of individual grains, if they can be isolated.

In sum, it appears that magnetite is the dominant magnetic mineral in mid-continent carbonate strata, and that it occurs as spheroidal clusters of octahedral microcrysts which may or may not be coated by clay and may occur individually or in botryoidal aggregates. If the coating is absent, the grain appears as a framboid, whereas if the coat-
Fig. 4. XRD pattern obtained with Rigaku X-ray diffractometer for IL0207 (red scum taken from surface of reagent). Q = quartz; K = K-feldspar; G = goethite; H + G = hematite and goethite. Operation settings: voltage = 45 kV; current = 20 mA; scan speed = 6°/min.

ing is present, the grain appears as a spheroid. Goethite sometimes occurs as a pseudomorphic replacement of pyrite and possibly as a surface coating on magnetite aggregates. Hematite also occurs in these strata, but of the ten samples that we analyzed, goethite and hematite were the common magnetic mineral only in one, suggesting that they may have formed only locally in response to near-surface weathering.

4. Discussion

4.1. Origin of the magnetite

The determination of whether the Kiaman remagnetization found in mid-continent rocks reflects chemical [3,8] or thermoviscous [21] remanent magnetization requires knowledge both of the thermal history of the host rock and of the origin of the magnetite. Hypotheses concerning thermal histories of the carbonate strata in the mid-continent region favor the chemical remanent magnetization concept [22]. In this section we present observations concerning the origin of the magnetite that also favor the chemical remanent magnetization concept.

Whether the origin of the magnetite is authigenic (precipitated during diagenesis from a migrating brine or formed by oxidation of precursor iron-bearing minerals like pyrite) or detrital (derived from terrestrial or cosmic sources and incorporated in the rock during primary sedimentation) is a subject for debate. If the magnetite is demonstrably authigenic, the remagnetization is more likely a chemical remanence. The magnetite spheroids and framboids that we observed in mid-continent carbonate strata are distinctly different from magnetite grains thought to be derived from a cosmic source. Cosmic grains typically have a smooth and shiny surface [23], reflecting the occurrence of a fused interlocking crystal mosaic [23,24]. They may also have dendritic structure [23], and radiating fibrous crystals [25]. None of these features were observed in the grains we examined. The euhedral octahedral crystal habit that we observed in the framboids of mid-continent rocks has not been observed in cosmic magnetite.

The composition of the magnetite in our samples is also indicative of an authigenic origin during diagenesis. Detrital magnetite grains derived from igneous sources would be expected to contain measurable amounts of titanium, which can diffuse into the magnetite lattice at igneous temperatures thereby forming a solid solution. Diagenetic magnetite, formed at relatively low temperatures (< 200°C) could not incorporate
titanium.

The authigenic origin of the magnetite during diagenesis is circumstantially supported by the observation that the mid-continent strata contain abundant evidence of having been subjected to complex diagenesis related to flux of deep-basin brines through the rock [10]. Petrographic examination of the samples reveals features typical of diagenesis, such as neomorphism, silicification, and dolomitization. Dolomite rhombs show distinctive zoning, indicative of changing geochemical conditions during diagenesis. In many of the samples, we found authigenic K-feldspar, and in a few samples we found halite crystals. Authigenic pyrite is widespread in most samples, and occurs both in frambooidal aggregates of octahedral microcrysts (Fig. 2f), as well as in larger cubic grains.

Finally, we note that the apparent structural control on the variation in magnetic intensity measured in our samples (our initial data indicates that stronger intensities were measured on the flanks of arches) also supports an authigenic origin. The flanks of arches are the sites of particularly strong diagenetic effects including deposition of ore deposits [10]. Thus, these sites would presumably be favorable locations for the reactions leading to authigenic magnetite formation. In contrast, there is no reason to expect a greater concentration of detrital magnetite at these locations, and it is not likely that these regions were buried particularly deeply to enhance thermal effects.

4.2. Possible diagenetic history

The evidence presented in this paper indicates that authigenic magnetite precipitated in mid-continent carbonate rocks across a broad region and that this magnetite is the carrier of the widespread Kiaman remagnetization that has been detected in these rocks. The association of dolomitization, smectite illitization, K-feldspar authigenesis [e.g. 26], and halite precipitation with remagnetization in mid-continent strata all favor the hypothesis that the remagnetization is a manifestation of regional diagenesis that occurred in response to the migration of brines through the strata, and that the remagnetization is a chemical remanence. The widespread distribution of remagnetization that we observed in the mid-continent indicates that this brine migration occurred on a continent-wide scale [17]. The age of the remagnetization supports the idea that the brine migration occurred in a pulse triggered by intraplate or continental-margin tectonism that was roughly coeval with the Alleghanian/Ouachita orogeny [10]. Not all of the brines necessarily came from the Alleghanian/Ouachita orogen itself; some may have come from intracratonic highs [10,27].

The original source of the iron in the magnetite could be pre-existing pyrite, iron-rich clay (which released iron during K-feldspar authigenesis), or iron transported into the local environment by migrating brines. The magnetite could pseudomorphically replace pre-existing pyrite or could precipitate directly as new microcrysts which accumulated into frambooids in response to mutual magnetic attraction [cf. 28]. Considering that it is more efficient (i.e. requires less brine) to create authigenic minerals by alteration of existing species than by introducing new species, it is more likely that the magnetite in the mid-continent strata formed by alteration of pyrite and clay already in the strata. Pseudomorphic replacement or pyrite is favored by the observation that pyrite microcrysts (and host frambooids) in mid-continent carbonates are comparable in size and shape to magnetite microcrysts (and host frambooids), and by the discovery that such replacement occurs in estuarine sediments [29]. But the replacement concept is not compelling because we did not observe pyrite grains that had been partially altered to magnetite, and thus it is likely that some of the observed magnetite precipitated de novo.

The geochemistry of formation of diagenetic magnetite in mid-continent carbonates is not clear, for the reaction paths defining the fate of iron during reaction of warm brine with limestone are not yet well defined. Work by Garrels and Christ [30] and Bethke (oral commun., 1989) on modeling the reactions that occur when brines migrate through rock emphasize that the stability fields of magnetite, pyrite, and hematite depend on several variables including activity of oxygen, activity of sulfur, Eh, pH, salinity, and temperature. These variables were all changed regionally as warm brines passed through the mid-continent strata [e.g., 12,15,31]; alkalinity, salinity, and temperature increased. In the new environment, iron brought in with the brines may have precipitated as magnetite, but probably more importantly, local pyrite and clay reacted with the brine to yield
magnetite which pseudomorphically replaced pre-existing pyrite grains or formed new microcrysts which then accumulated into frambooids.

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