Origin of Magnetite Responsible for Remagnetization of Early Paleozoic Limestones of New York State

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INTRODUCTION

It is widely recognized that paleomagnetic studies of Paleozoic North American carbonate rocks have shown that almost all magnetizations of these rocks are secondary; shallow water and platform carbonates that have primary or early magnetizations are rare and exceptional [Jackson et al., 1985, McCabe et al., 1985, 1989]. There is general agreement that early to middle Paleozoic exceptions [Jackson et al., 1985, McCabe et al., 1983, 1984, Suk et al., 1990a, b] have primary or early magnetizations are rare and exceptional. There is general agreement that early to middle Paleozoic carbonates in eastern North America were remagnetized during the Permo-Carboniferous Alleghenian Orogeny which coincides with the Kiaman reversed Polarity Superchron of the late Paleozoic. Viscous remanent magnetization has been proposed as a cause of remagnetization [Kent, 1985], especially where conodont color alteration indices [Epstein et al., 1977] indicate that burial temperatures have exceeded 250°C. However, many recent investigators of the remagnetization [Jackson et al., 1988; McCabe et al., 1983, 1984; Suk et al., 1990a, b] have concluded that it is a chemical remanent magnetization (CRM) caused by formation of authigenic magnetite (see McCabe and Elmore [1989] for a recent review). Suk et al. [1990a] directly demonstrated an authigenic origin for magnetite in Ordovician Knox carbonates from east Tennessee using in situ scanning electron microscope (SEM) observations, showing that at least in that one case, remagnetization was CRM in origin.

On the basis of the assumption that remagnetization has a CRM origin, there has been extensive speculation regarding the correlation between authigenic growth of magnetite and spatially and temporally related tectonic activity. Oliver [1986] hypothesized that tectonically driven fluid migration from active plate margins may have played an important role in mineralization, migration of hydrocarbons, and metamorphism, as well as remagnetization. Miller and Kent [1988] also argued that differences in remagnetization ages of limestones and red beds in Appalachian basins resulted from fluid migration that was in turn responsible for remagnetization processes during the Alleghenian Orogeny. Although remagnetizations are now generally believed to be associated with tectonic activity and the resulting fluid flow, the composition of fluids and mechanisms of regional fluid migration are poorly understood.

Recently, Schedl et al. [1992] studied the effects of metamorphic fluids originating from beneath the Blue Ridge and Piedmont in North Carolina and the diagenetic fluids responsible for silicification, K-feldspar authigenesis and dolomitization in the Knox Group carbonates from Tennessee and West Virginia using aqueous geochemical and stable and radiogenic isotope data. They concluded that the fluids that caused alteration and remagnetization in the Knox carbonates were largely metamorphic rather than meteoric on the basis of remarkable geochemical and isotopic similarities between metamorphic fluids and fluids that caused alteration and remagnetization in the Knox carbonates. Lu et al. [1991] argued that fluids responsible for remagnetization of early Paleozoic carbonates in New York were potassium rich, on the basis of
of bulk rock chemical analyses; however, a choice could not be made between the hypothetical fluid migration models, based on tectonically driven connate fluids and topographically driven meteoric water [Bethke, 1986; Bethke and Marshak, 1990; Nunn et al., 1984]. Nevertheless, certain data on the isotopic composition of carbonates imply that the isotopic compositions of the studied rocks were not affected by fluids introduced after early diagenesis; for example, stable isotope data from Knox carbonates in east Tennessee are compatible with a depositional environment and early diagenesis (K. C. Lohmann, personal communication, 1990), and radiogenic dating using the U/Pb method for calcite from the Trenton limestone in New York resulted in a depositional age of 454±8 Ma for the Ordovician carbonate [DeWolf and Halliday, 1991]. Such data do not necessarily imply, however, that recrystallization has not occurred during the Alleghenian orogeny, provided that recrystallization occurred under closed-system conditions (A. N. Halliday, personal communication, 1991). On the other hand, recrystallization may occur through local pore fluids but without introduction of fluids through large-scale flow. For example, Elmore et al. [1990] proposed that remagnetization due to growth of authigenic magnetite occurred via tectonic stress-induced localized pressure solution, utilizing pore fluids.

In order to further define processes of remagnetization and the resultant carriers of remagnetization and their relationship to fluids during the late Paleozoic Kiaman reversed Polarity Superchron, we have extended our SEM/STEM studies to samples of Ordovician Trenton limestone and Devonian Onondaga and Helderberg limestones that were collected along an east-west profile across New York state. Before initiation of these studies, the only in situ observations of magnetite leading to evidence for an authigenic origin were those in samples from east Tennessee [Suk et al., 1990a]. Evidence for an authigenic origin obtained from magnetite extracts in limestones of eastern North America [McCabe et al., 1983, 1984; Jackson et al., 1988; Lu et al., 1990] was indirect and unconvincing. On the other hand, Suk et al. [1990a, b] showed how direct SEM and STEM observations could lead to unambiguous characterization of the origin of the magnetite responsible for remagnetization.

The early Paleozoic carbonates in New York were chosen for investigation in part because the carbonates, especially Onondaga limestones, were shown to exhibit a maximum in magnetite concentration along the traverse near Syracuse, with a decrease occurring to the west [Jackson et al., 1988]. A maximum in concentration near Syracuse was shown to coincide with maximum illite crystallinity, which is generally believed to correspond to a higher grade of diagenesis. These data imply that the carbonates of the eastern and central parts of the traverse should display advanced stages of authigenic magnetite, whereas the western samples could show magnetite in an earlier stage of development. Direct observations of the magnetite which could lead to a determination of the mode of origin were therefore thought to be essential to understanding the significance of the magnetite, and this study was designed to provide such observations. Some of the initial results, in particular those demonstrating replacement of pyrite framboids by authigenic magnetite in Onondaga limestones, have been reported elsewhere [Suk et al., 1990b].

In this paper we describe SEM/STEM observations for all formations of the traverse including images of magnetite of several origins and magnetic characterization using hysteresis measurements for magnetic extracts. Those results are discussed in terms of remagnetization processes and their relationships to fluids.

**REVIEW OF MAGNETIC CHARACTERIZATION**

The geological setting and paleomagnetic and rock magnetic data from the Devonian Onondaga and Helderberg limestones and Ordovician Trenton limestone of New York state have been given by Kent [1979], Scotese et al. [1982], Jackson et al. [1988], and McCabe et al. [1983, 1984]. Those studies clearly showed that the carbonates had been remagnetized during the Alleghenian Orogeny and that magnetite was the principal magnetic carrier. However, the size of the magnetite grains and subsequent magnetic domain state are still not well defined; McElhinny and Opdyke [1973] and Kent [1979] used the Lowrie-Fuller behavior test to argue for multidomain sizes for magnetite in Trenton limestone and Onondaga limestone. On the other hand, Scotese et al. [1982] concluded that single domain (SD) magnetite grains are principally responsible for the natural remanent magnetization (NRM) in Helderberg limestone by using low-temperature measurements of intensity of remanent magnetization. Jackson [1990] recently argued that the NRM from the Trenton and Onondaga limestones was carried by SD magnetite grains even though much of the magnetite in the limestones is coarser grained, on the basis of hysteresis measurements and other rock magnetic data for bulk rock samples of Onondaga and Trenton limestones. Magnetite in magnetic extracts that has a spherical shape has generally been considered to be the principal magnetic carrier in remagnetized rocks [McCabe et al., 1984; Bachtadse et al., 1987; McWhinnie et al., 1990; Lu et al., 1990], although spherical magnetite is not always the dominant kind of magnetite. However, spherical magnetite typically ranges from several micrometers to more than 100 μm in diameter. This exceeds the size range of both single domain and pseudosingle domain magnetite, although such grains may be polycrystalline. In order to fully define the carriers and causes of remagnetization, it is therefore necessary both to characterize spherical magnetite and to determine if there are other kinds of magnetite grains that could be the carriers of the remagnetization.

**SAMPLING AND IN SITU OBSERVATION METHODS**

Figure 1 shows the localities at which samples were collected from Ordovician Trenton limestone and Devonian Helderberg and Onondaga limestones, defining an east-west traverse across New York state. The Onondaga limestone is a fine-grained, gray limestone which extends along the Hudson River valley to Albany.
Fig. 1. Map of New York state showing sampling localities. Open circles indicate Onondaga limestone; triangles indicate Helderberg limestone; squares indicate Trenton limestone; solid circles indicate sites referred to in the text.

and Syracuse in eastern New York, continuing to Buffalo and into Canada along Lake Erie. The Helderberg limestone is exposed along a continuous belt which parallels the Onondaga limestone from the Hudson River valley to the east of Lake Cayuga. The Trenton limestone is exposed from Canajoharie northwestward to Cape Vincent.

Oriented cores and block samples were collected from 17 sites for Onondaga limestone, 12 sites for the Helderberg limestone, and seven sites for Trenton limestone. A total of 36 samples were prepared for SEM/STEM observations as polished thin sections using "sticky wax" as an adhesive so that selected areas could be detached for STEM sample preparation. Areas containing iron oxides, as identified by SEM, were prepared for STEM observations using a dimpler and an ion mill to produce thin edges (see Suk et al. [1990a] for detailed description). In addition, in order to obtain a representative sample of all kinds of magnetite, magnetite extracts were recovered from insoluble residues produced by dissolving limestones with buffered acetic acid [McCabe et al., 1983]. The magnetic separates were then spread on slides or on "holey carbon"-supported Cu grids in preparation for SEM and STEM observations, respectively. Several grains of selected separates were mounted on glass fibers to obtain Gandolfi powder X ray diffraction (XRD) patterns for mineral identification, usually using the same grains as separately studied by SEM.

The SEM used is a Hitachi S-570, equipped with a Keveq Quantum energy dispersive spectroscopic (EDS) system for X ray analysis, and a backscattered electron (BSE) detector. The STEM used is a Philips CM-12 which is also equipped with a Keveq Quantum EDS system. The STEM is capable of much higher magnification than the SEM, but more importantly, it provides selected area electron diffraction (SAED) patterns for definition of crystal structure.

The BSE detector provides SEM images having atomic number contrast, and because the carbonates (calcite and dolomite) have low average atomic numbers, whereas iron oxides and sulfides (e.g., magnetite and pyrite) have relatively large average atomic numbers, thin sections can be relatively rapidly surveyed for the presence of iron-containing minerals. Iron oxides and sulfides were therefore first located using BSE imaging and then characterized as iron oxide or iron sulfide using EDS analyses. Because oxygen X radiation is subject to severe absorption, hematite and magnetite cannot be distinguished with such methods, but pyrite and pyrrhotite, as the common (albeit not the only possible) iron sulfides are easily distinguished from the oxides. In order to identify specific iron oxides it is necessary to obtain diffraction data. SAED patterns were therefore obtained in selected cases using the STEM, or XRD patterns were obtained for extracts. An attempt was made to quantify Fe/O ratios in EDS spectra obtained in the STEM, using hematite and magnetite as standards. The method was not reliable, however, owing to the severe absorption of the oxygen radiation.

Although each of the large number of individual iron oxide grains could not be specifically studied using electron or X ray diffraction, all grains that were
characterized by SAED or XRD were verified to be magnetite with only one exception. We therefore feel confident in identifying as magnetite those other grains found to be iron oxide by SEM that have morphologies and textures consistent with those grains that were studied using diffraction techniques. Hematite has been identified in only one case by SAED, and then only as a minor phase associated with dominant magnetite.

SEM/STEM OBSERVATIONS

Three kinds of magnetite have been observed: (1) spherical pseudoframboids as a replacement of pyrite framboids, (2) replacements of individual pyrite crystals and irregular pyrite grains (referred to as "nonspherical magnetite"), and (3) aggregates of rounded grains, each grain approximately 2000 Å (200 nm) in diameter (referred to as "fine-grained magnetite"). Each of these is described in turn, the description of pseudoframboids amplifying that given by Suk et al. [1990b] for only a limited number of specimens from the Onondaga limestone.

Pseudoframboidal Magnetite

Spherical magnetite grains, termed pseudoframboids to distinguish them from pyrite framboids, constitute the most common type of magnetite among those observed by SEM. In many cases, pseudoframboidal magnetite as well as pyrite framboids were found near or along pore space and microcracks in the carbonate matrix. Figure 2a shows a low-magnification backscattered electron image of densely distributed pseudoframboids and framboids in calcite with minor dolomite (dark contrast). The minerals constituting (pseudo)framboids vary from pure magnetite to a mixture of magnetite and pyrite to pure pyrite. Diameters of the spherical pseudoframboids typically range from several micrometers to 15 µm. Pseudoframboids consist of aggregates of individual well-defined octahedral or cubo-octahedral crystals as shown in a cross section of a pseudoframboid that occurs in a microcrack (Figure 2b). Individual crystals are approximately closest packed (Figure 2c). Although most pseudoframboids are nearly spherical in shape, some have more irregular shapes (Figure 2d). As shown in Figure 2d, individual crystals now having rims of magnetite (dark contrast) may either have relict cores of pyrite (bright contrast) or hollow cores (darkest contrast) that were once occupied by pyrite. These relations demonstrate that pyrite crystals constituting frambooids were replaced by magnetite, resulting in pseudoframboidal magnetite.

In contrast to pseudoframboids that clearly displayed partial replacement of individual pyrite crystals (Figures 2h-2d), a pseudoframboid that has octahedral pyrite crystals only in its central portion but with only magnetite in its rim was also observed (upper grain in Figure 2e). Individual octahedral/cubo-octahedral magnetite crystals are not readily visible in the rim, however. The grain in the lower half of Figure 2e illustrates relict pyrite grains in a cross section of a pseudoframboid, although the individual crystals having magnetite rims are hardly recognizable.

Spherical magnetite with a somewhat similar morphology (Figure 2f) was found in a magnetic extract. This is a grain of 40 µm in diameter with a smooth surface but which is largely hollow. The inner surface consisted of many rounded grains that could have originally been pyrite crystals. X-ray diffraction data obtained using a Gandolfi camera confirmed that it is composed only of magnetite.

Pseudoframboidal magnetite was prepared for STEM observations in selected cases. A bright field image of an ion-milled pseudoframboid (Figure 3a) and a corresponding selected area electron diffraction (SAED) pattern (Figure 3b) from one of the octahedral crystals show that the pseudoframboid is magnetite. The ring pattern of the SAED photograph is indicative of its polycrystalline nature. Dark field images, obtained using portions of SAED patterns, verify that the individual single-crystal domains of magnetite are approximately 300 to 1000 Å (30 to 100 nm) in diameter. The shape of the submicron-sized octahedral/cubo-octahedral crystals that originally constituted pyrite framboids indicates that they originally were single crystals of pyrite. However, the process by which pyrite crystals were altered must have involved dissolution of pyrite, transport of reactant oxygen and product sulfur, and crystallization of magnetite, all processes occurring through a fluid. The holes in the middle of each crystal are inferred to have been caused either by plucking of remnant pyrite during sample preparation or to be spaces (small voids) formed by dissolution of pyrite without subsequent crystallization of magnetite.

Nonspherical Magnetite

Nonspherical magnetite was also observed replacing pyrite in the New York carbonate rocks. There are two types of nonspherical magnetite observed by SEM: one consists of individual or small groups of replaced octahedral pyrite crystals dispersed in carbonate matrix that appear to be identical to the crystals that form pseudoframboids (Figure 4a); the other consists of micron-sized nonoctahedral magnetite with irregular shapes (Figures 4c and 4d). Some octahedral crystals pictured in Figure 4a have relict pyrite cores (bright contrast), whereas some crystals have voids which are inferred to have been occupied previously by pyrite, as in the case of the pseudoframboids. However, many other kinds of grains were observed. For example, the central portion of a nonspherical grain (Figure 4b) consists of aggregates of tiny pyrite domains typically less than 0.1 µm in size. Magnetite of rectangular shape (Figure 4c) in a thin section of Trenton limestone has a remnant pyrite core (bright contrast labeled P) surrounded by magnetite. In addition, nonspherical magnetite grains (Figure 4d) reveal replacement of pyrite by magnetite associated with secondary minerals such as quartz and dolomite in a calcite matrix adjacent to pore spaces. These relations collectively demonstrate that pyrite of a variety of origins has been pervasively replaced by magnetite.

One nonspherical magnetite sample studied by STEM provided more detailed insights into the magnetite-pyrite relationship. It was successfully ion milled so that thin edges extended from one side of a rim through a core to the other side of the rim. EDS analyses showed that the rim contained iron (plus oxygen) and that the core was...
Fig. 2. Scanning electron microscope images of pseudoframboidal magnetite in the New York carbonates. Symbols are MGT, magnetite; PF, pseudoframboid; F, framboid; P, pyrite; C, calcite; D, dolomite; Q, quartz; and H, hole. (a) Densely distributed framboiods and pseudoframbooids in a calcite matrix with occasional occurrence of dolomite and quartz; backscattered electron image (BEI). (b) Cross section of a pseudoframboid in a microcrack showing individual octahedral/cubo-octahedral crystals; secondary electron image (SEI). (c) A pseudoframboid in a microcrack showing almost perfect spherical shape (SEI). (d) An imperfectly spherical magnetite pseudoframboid in a void showing pyrite cores or voids within originally homogeneous pyrite crystals. Layered iron-rich clay minerals surround the grain (SEI). (e) Cross sections of pseudoframbooids revealing complete replacement of pyrite crystals only on frambooid rim (upper left panel), and pervasive replacement of individual pyrite crystals (lower right panel). Iron-rich layered clay minerals occur between the pseudoframboid and calcite matrix (SEI). (f) A spherical magnetite grain with smooth surface showing many rounded protuberances on the inner surface (SEI). This grain was verified to be magnetite by X ray diffraction.
Fig. 2. (continued)

Fig. 3. Scanning transmission electron microscope photographs of part of a cross section through a spherical pseudoframboid. (a) A bright field image of several octahedral/cubo-octahedral magnetite grains. (b) Selected area electron diffraction (SAED) pattern of grains in Figure 3a, diagnostic of magnetite (220, 311, 400, 422, 511, and 440 magnetite reflections). The ring pattern of the reflections indicates the polycrystalline nature of the grains.
composed of iron and sulfur; X-ray mapping in STEM also revealed this (Figure 5a). SAED patterns obtained along the thin edges verify that magnetite is predominant in the rim, but associated with minor hematite, whereas the core is predominantly pyrrhotite (Figure 5b). Both magnetite and pyrrhotite are polycrystalline as indicated by the ringlike SAED patterns.

**Fine-Grained Magnetite**

Magnetic extracts contain abundant very small iron oxide grains which are volumetrically more significant than the magnetite that replaces pyrite. In magnetic extracts, spherical magnetite is commonly surrounded by such submicron-sized magnetite as shown in Figure 6a;
SEM images show that the fine-grained magnetite grains (Figure 6b) have a rounded shape and are approximately 2000 Å (200 nm) in diameter, with a very narrow size distribution. All grains from all samples are remarkably similar in size and shape. Since SEM techniques do not provide sufficient magnification for such fine-grained magnetite, magnetic separates were prepared for STEM observations in two ways. One set of extracts was crushed in a mortar and pestle to create thin edges for SAED and then mounted on a "holey carbon"-supported copper grid. The other set of magnetic separates was mounted on the same type of copper grid without crushing to determine if the crushing process produces morphological changes. A bright field transmission electron microscope (TEM) image of crushed magnetite extracts reveals a cluster of rounded grains, each about 2000 Å (200 nm) in diameter (Figure 6c). Individual grains give SAED patterns of single-crystal magnetite as shown in Figure 6d. The Miller indices demonstrate the successful indexing of the single-crystal diffraction pattern of magnetite. These grains are similar in shape to biogenically produced magnetite but larger in size. Even though these fine-grained single crystals of magnetite were prepared by crushing, the TEM images (Figure 6c) do not reveal any indication of the breakup of larger polycrystalline crystals due to the crushing process. In order to further confirm that the shape is not the result of the crushing process, uncrushed magnetic extracts were also observed by STEM. Such images (Figure 6e) were similar to those of crushed material, verifying that the crushing process did not alter
Fig. 6. Scanning electron microscope and scanning transmission electron microscope images of fine-grained magnetite. (a) Spherical magnetite 15 μm in diameter found in magnetic extracts, showing aggregates of fine-grained magnetite attached to the pseudoframboid surface (SEI). (b) An enlarged photograph of the fine-grained magnetite in Figure 6a, revealing rounded individual grains (SEI). (c) A bright field image of crushed magnetic extracts observed in STEM. Aggregates of rounded grains about 2000 Å in diameter are shown. (d) A SAED pattern for one of the grains in Figure 6c, diagnostic of a single crystal of magnetite, based on the indexed reflections. (e) A bright field image of uncrushed magnetite extracts showing similar shapes and sizes of aggregates to those seen in Figure 6c, indicating that the crushing process does not alter the shape of iron oxide grains. (f) A SAED pattern of several sets of magnetite reflections for the several grains of Figure 6e. Three sets of 220 reflections (star), 311 and 400 reflections are diagnostic of several single crystals of magnetite.
the shape of magnetic extracts. The only difference seen in the crushed and uncrushed magnetite specimens is that aggregates of rounded grains consisted of fewer grains in the crushed sample. SAED patterns of uncrushed magnetite therefore may include contributions from several grains and consist of more than one set of superimposed single crystal magnetite electron diffraction patterns (Figure 6f). EDS analyses obtained in the STEM show that only iron and oxygen are detectable, the level of sensitivity of analyses being approximately 0.25 wt % for other cations.

We have been unable to locate such fine-grained magnetite in thin sections of New York carbonate samples by SEM despite many hours of searching, presumably because the grains are so small. However, such material was also observed in extracts from samples of Trenton limestone from Michigan [Suk, 1991].

It is important to note that grain sizes in the range of about 2000 Å (200 nm) are appropriate for single to pseudosingle domain magnetite. This strongly suggests that the fine grained magnetite may well be the principal carrier of the late Paleozoic remagnetization [cf. Jackson, 1990]. Although its origin and source are still poorly understood, the rounded shapes, uniform size distribution of the grains, lack of any cations except iron as shown by STEM analyses, and similarity to authigenic fine-grained magnetite in Trenton limestone of Michigan collectively demonstrate that such fine-grained magnetite is authigenic in origin.

Iron-Bearing Minerals Other Than Magnetite

Pyrite that shows no signs of being replaced by magnetite is very common in rocks of all formations that we studied; it apparently occurs over the entire traverse, both as framboids and in grains with irregular shapes. The framboids, as illustrated in Figure 7a, are identical to those that have been partially or completely replaced by magnetite (compare Figure 7a with Figure 6a). Individual pyrite crystals, either with octahedral or cubic outlines, were commonly observed. In addition, subhedral pyrite crystals were observed filling pore space (Figure 7b). Such material does not have the typical morphology of pyrite, but EDS spectra do indeed show that it has the composition of pyrite. Because this pyrite is subhedral and fills pore space it is clearly authigenic in origin.

Potassium feldspar was commonly observed, always without any sodium detectable in EDS analyses and generally with euhedral outlines (Figure 7c). The crystal shapes and composition imply that it is also authigenic in origin, as detrital feldspars normally show a range of compositions. However, it generally occurs as isolated crystals within calcite and is not associated with magnetite. By contrast, the close association of magnetite and authigenic potassium feldspar in east Tennessee Knox carbonates [Suk et al., 1990a] provided strong evidence for the authigenic origin of magnetite. In New York limestones, however, the potassium feldspar simply provides evidence of authigenesis and some degree of water/rock interaction.

Chlorite identified by EDS analyses and morphology by SEM occurs in two different modes. First, chlorite grains of detrital origin (Figure 7d) were observed in the calcite matrix. They are approximately 25 μm in size, have curved outlines suggesting distortion of layers, and occur as isolated grains within the calcite matrix, implying that they are detrital in origin. Second, very fine-grained aggregates of chlorite grains of submicron size were observed
surrounding pseudoframboids (Figures 2d and 2e). Individual chlorite crystals have fibrous or flaky forms and tend to fill the space between pseudoframboids and surrounding pore space, suggesting that such chlorite is authigenic in origin.

**CONCENTRATIONS OF MAGNETITE AND PYRITE ALONG THE NEW YORK STATE TRAVERSE**

The proportions of magnetite and pyrite are significant in that magnetic susceptibility of the samples had been...
found to be high in eastern New York, reaching a maximum near Syracuse and then rapidly decreasing in the samples from western New York [Jackson et al., 1988]. Although quantitative values cannot be attached to concentrations in this study, our general qualitative observations of thin sections clearly show that the concentration of magnetite of all types is indeed markedly lower in samples from the western half of the traverse.

Although the total amount of pyrite does not seem to change noticeably, framboidal pyrite is the dominant variety in eastern samples, and nonframboidal pyrite is more abundant in western samples. However, because the concentration of pyrite is approximately constant across the traverse and because the concentration of pseudoframboidal magnetite is smaller in the west, the replacement process is inferred to have been more intense in eastern limestones.

**Hysteresis Measurements**

In order to characterize the magnetite that replaces pyrite (pseudoframboidal and nonspherical magnetite) as well as the fine-grained magnetite observed in magnetic extracts, hysteresis measurements were made using a Micromag Alternating Force Magnetometer (AFM) at the Lamont-Doherty Geological Observatory (courtesy of Susan Halgedahl). The AFM has an advantage over conventional vibrating sample magnetometers in that it has higher sensitivity, of the order of $10^{-3}$ A/m, and consequently, much smaller amounts of iron oxide are required for hysteresis measurements. Five sets of samples from magnetic extracts were prepared for hysteresis measurements:

1. A single pure spherical magnetite grain about 15 µm in diameter was mounted on a sample holder. Although there were many spherical magnetite samples in our magnetic extracts, their sizes usually ranged from 3 to less than 10 µm, and they clustered with other magnetite grains. Preparation of pure pseudoframboidal magnetite samples was therefore difficult.

2. Several pseudoframboidal magnetite grains having considerable sulfur were prepared for hysteresis measurements in order to detect the effects of partial replacement of pyrite by magnetite, if any.

3. Fine-grained magnetite grains were carefully separated. This sample was extracted from rocks collected at site 5 (Figure 1) in the Onondaga formation.

4. Approximately 4 mm$^2$ of a thin section containing pseudoframboidal magnetite at the surface.

5. A similar thin section on which no magnetite was observed on the surface was prepared to simulate bulk rock measurements of samples with/without the pseudoframboidal magnetite.

Hysteresis measurement procedures include (1) cleaning of the sample and sample probe ultrasonically in freon for 5 to 10 min, (2) measurement of the sample probe for the background moment value (typically $10^{-4}$ A/m), and (3) measurement of individual samples.

Hysteresis data for pseudoframboids and thin section chips are shown in Figure 8a. Despite careful sample preparation, we have not been able to obtain meaningful signals from four of the five samples because of their extremely weak intensity (about $10^{-4}$ A/m), which is comparable to the moment of the sample probe, due to a small number of spherical and pseudoframboidal magnetite grains. However, the fine-grained magnetite sample had a remanence of the order of $10^{-3}$ A/m, 1 order of magnitude higher than that of the sample probe, and it had a saturation moment of about $10^{-2}$ A/m at 0.5 T (Figure 8b inset). Thus a very well-defined hysteresis loop for this fine-grained magnetite could be obtained (Figure 8b after subtraction of the diamagnetic contribution from the sample probe (inset of Figure 8b). This analysis does not reveal a "wasp waist."
been reported to be the principal magnetic carriers in many remagnetized carbonate rocks [McCabe et al., 1983, 1984; Bachtadse et al., 1987; McWhinnie et al., 1990; Lu et al., 1990; Horton et al., 1984]. Such spherical magnetite is believed to be authigenic in origin as evidenced in part by the bulk rock ratios of the Onondaga limestone (open circles) and the Trenton limestone (stars) from Jackson [1990] in the domain-state framework of Day et al. [1977].

Thus the fine-grained magnetite is capable of carrying the ancient magnetization.

U/Pb DATING

DeWolf and Halliday [1991] have obtained a precise (depositional) age for calcite from the Ordovician Trenton limestone (454±8 Ma) from New York state using the U-Pb method. Even though, for a variety of reasons, dating of magnetite was predicted to be unsuccessful, we nevertheless thought it worthwhile to attempt to directly determine the age of magnetite using that method. Carefully prepared separates of magnetite were analyzed. However, no U was detected. Uranium and radiogenic lead are extremely unlikely to occur in magnetite, and these results therefore confirm that expectation. We report these results only in order to provide background for others who might consider obtaining such data.

DISCUSSION

SEM/STEM Observations

Spherical magnetite grains observed in extracts have been reported to be the principal magnetic carriers in many remagnetized carbonate rocks [McCabe et al., 1983, 1984; Bachtadse et al., 1987; McWhinnie et al., 1990; Lu et al., 1990; Horton et al., 1984]. Such spherical magnetite is believed to be authigenic in origin as evidenced in part by a lack of elements such as Ti and Mn which commonly substitute for Fe in magnetite of igneous, metamorphic, and extraterrestrial sources [McCabe et al., 1983]. However, the mode of origin of the spherical magnetite has hitherto remained rather ill-defined.

We show in this study that magnetite pseudoframboids formed as a result of the replacement of pyrite frambooids. This is clearly indicated by the similarities in shape of the magnetite spheres and frambooids, the polycrystalline magnetite occupying individual octahedra of pseudoframboids, and the presence of pyrite relics in cores of octahedra that are rimmed by polycrystalline magnetite (Figure 2) as determined by in situ SEM/STEM observations of thin sections of New York carbonates. The same relations in nonspherical magnetite grains (Figure 4) demonstrate that they also formed by replacement of pyrite. A secondary origin of magnetite grains is also suggested by common occurrences of such grains along microcracks which could have been used as fluid pathways.

The third type of magnetite, fine-grained rounded magnetite, was observed only in magnetic extracts. Although we were unable to observe this type of magnetite in thin sections of New York carbonates, apparently because of its extremely small size, this fine-grained magnetite constitutes a significant proportion of magnetic extracts. Although the crystals of fine-grained magnetite are typically larger than those of biogenic magnetite, both biogenic magnetite found in recent carbonates [Chang et al., 1987, 1989] and fine-grained magnetite are similar in that both form rounded single crystals which have narrow-sized range distributions. If the fine magnetite grains have been formed by biologic activity and have escaped the Alleghenian authigenesis, then rocks containing the fine-grained magnetites should carry a primary magnetization. However, the New York carbonates containing the fine-grained magnetite carry only secondary magnetizations [Kent, 1979; Scotese et al., 1982; McCabe et al., 1983, 1984; Jackson et al., 1988]. This result contrasts with the observations of Chang et al. [1987], who reported unaltered biogenically produced magnetite in several Cambrian limestones that carried primary magnetization. Furthermore, single to pseudosingle domain magnetite is believed to be a very stable magnetic carrier, and consequently, it is difficult to reset the magnetic direction carried by single to pseudosingle domain magnetite unless the magnetite recrystallized and/or the temperatures exceeded the blocking temperatures. Thus fine-grained magnetite is a carrier of the Alleghenian remagnetization, it must have formed much later than the time of rock formation by authigenesis rather than biological activity. The interpretation that the magnetite is a secondary mineral is as likely for the origin of the fine-grained forms as it is for the pseudoframboids because a primary magnetization (as would be carried presumably by any biogenic magnetite) is clearly not observed in the New York carbonates. On the basis of these relations and implications regarding grain size and shape, we therefore infer that the fine-grained magnetite is authigenic. The specific source of the iron is unknown, but possibilities include detrital smectite, original sedimentary carbonates, pyrite that underwent complete dissolution, or detrital iron oxides of igneous, metamorphic, sedimentary, or biogenic origin. In the case of smectite or carbonates, dissolution of those phases and crystallization of illite or carbonates with less iron may well have been activated by the Alleghenian Orogeny.

The SAED patterns obtained from ion-milled samples of pseudoframboids and nonspherical magnetite by STEM (Figures 3 and 5) have proven that iron oxides observed by SEM are predominantly magnetite with only very minor hematite. Submicron-sized octahedral crystallites, as well as several micron-sized nonspherical magnetite grains, have overall sizes in the multidomain range. However, individual single-crystal domains that make up the
octahedra of pseudoframboids and the polycrystalline nonspherical magnetite were observed to be of the order of several hundred angstroms (tens of nanometers) in size by dark field imaging in the STEM; thus these individual crystal domains are in the range of single to pseudosingle domain magnetite. Furthermore, the individual rounded grains of fine-grained magnetite were shown to be single crystals; their diameters of approximately 2000 Å (200 nm) are within the size range of single to pseudosingle domain magnetite. It remains to be determined whether the fine-grained magnetite alone or a combination of it and magnetite replacing pyrite is really the carrier of the Alleghenian remagnetization.

Jackson [1990] reported that single-domain magnetite is a carrier of the remagnetization even though coarser-grained multidomain magnetite is volumetrically significant. He concluded this on the basis of hysteresis measurements of bulk rock of the same and similar Paleozoic carbonates as used in this study along with other rock magnetic techniques. In contrast to the hysteresis loops for bulk rock reported by Jackson [1990], our hysteresis loop for the fine-grained magnetite (Figure 8b) does not reveal the "wasp waist," which is indicative of mixture of different grain sizes of magnetite. The shape of our hysteresis loop for the fine-grained magnetite implies that the fine-grained magnetite is uniform in grain size. Jackson [1990] interpreted the hysteresis ratios of bulk rock with Jrs/Js values in the nominal pseudosingle domain magnetite range and higher Hcr/Hc ratios as a result of the mixture of single-domain and pseudosingle domain or multidomain magnetite. Our hysteresis ratios for the fine-grained magnetite of uniform grain size plot in the range of pseudosingle domain magnetite (Figure 9). Although the contribution of pseudoframboids is not known because we could not obtain a hysteresis loop for them, we can at least conclude that the fine-grained magnetite is capable of carrying the Alleghenian remagnetization. However, pseudoframboidal magnetite and nonspherical magnetite, consisting of single to pseudosingle domain-sized crystals are not yet ruled out as an additional magnetic carrier for remagnetization.

Pyritization of magnetite has been reported in unconsolidated sediment [Canfield and Berner, 1987], in the upper framework of a recent coral reef [Sansone et al., 1988], and within lithified carbonate rock [Sansone et al., 1990]. In contrast, our observations of magnetite pseudoframboids and nonspherical magnetite occurring as a replacement of pyrite imply that the reverse reaction can occur at a much later time. Conversion of pyrite to magnetite can occur in several ways (L. M. Walter, personal communication, 1990). First of all, from Figure 10, which shows the stability relations of iron oxides and sulfides in water at 25°C and 1 atm total pressure, simplified from Garrels and Christ [1965], Figure 7.20.

![Figure 10. Stability relations of iron oxides and sulfides in water at 25°C and 1 atm total pressure, simplified from Garrels and Christ (1965), Figure 7.20.](image)

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detrital clays upon reaction with a potassium-rich fluid, because they found that the K/Al ratio is covariant with the magnetite concentration of the carbonate, whereas the Fe/Al ratio is not. Lu et al. [1991] also predicted that authigenic K-feldspar would be a by-product of formation of authigenic magnetite in a K-rich fluid. Suk et al. [1990a], furthermore, concluded that iron-rich clay minerals could have been one of the primary source materials for authigenic magnetite in the Ordovician Knox carbonates of east Tennessee.

The concentration of magnetite observed by SEM varies in accordance with the remanence and susceptibilities as well as the degree of illitization across New York state reported by Jackson et al. [1988], but the concentration of pyrite shows an inverse relation to the concentration of magnetite in the same profile. That is, the iron for magnetite-replacing pyrite is at least qualitatively rationalized as originating in pyrite, the pyrite having formed during early diagenesis.

The origin of the iron that gave rise to fine-grained magnetite remains enigmatic, however. The correlation with illite crystallinity that was noted above does indeed imply that iron in detrital clay minerals could have been a source for iron in magnetite; Ahn and Peacor [1986] showed that detrital smectite is more iron rich than the illite that results from alteration of smectite, and even the small proportions of illite in limestone could serve as an explanation of the iron in the fine-grained magnetite. However, iron generally occurs in small amounts in solid solution in carbonates and can be released upon dissolution and crystallization. Similarly, detrital iron oxides such as ilmenite or magnetite, or even authigenic iron sulfides, can give rise to the necessary iron. Last, fluid flow may bring iron into the system. Indeed, all of these sources, and perhaps others, may have contributed iron to the formation of new magnetite. The dissolution and crystallization that gave rise to magnetite and that was initiated by the Alleghanian Orogeny must have affected all phases in the sediments, such that iron was made available to pore fluids during pervasive dissolution and recrystallization of all phases, including clays, carbonates, detrital iron oxides, and authigenic iron sulfides. It may therefore be a fruitless exercise to attempt to identify a single, specific source of the iron in fine-grained magnetite.

In contrast to our previous findings from the East Tennessee Knox carbonate [Suk et al., 1990a], where authigenic K-feldspars exhibited genocenic relationships to authigenic magnetite, no such relations were found for magnetite from New York carbonates. Instead, K-feldspar was observed in New York samples, but it was isolated from magnetite in the carbonate matrix (Figure 7c). On the other hand, in most cases, when magnetite was observed, it was accompanied by dolomite and quartz along microcracks or in the space presumably occupied previously by fluid inclusions. This does not mean that there is evidence indicating that authigenic feldspar did not form at the same time as magnetite; there is simply a lack of evidence for any correlation at all.

Formation of authigenic magnetite requires a fluid, as the process generally involves dissolution of precursor phases and crystallization of magnetite. Recently, Elmore et al. [1990] proposed that very localized pressure solution due to tectonic stress may have been responsible for remagnetization in the Ordovician Viola limestone in Oklahoma. They preferred a closed system without significant influx of external fluids because sufficient fluid can be supplied by alteration of smectite; this localized fluid may have played an important role in remagnetization for that particular rock formation.

The necessary fluid can actually be provided by a variety of sources, the most obvious being ordinary pore fluids. Assuming that dissolution and crystallization occur slowly over extended times, only extremely small quantities of fluid are necessary at any given time, the same pore fluids being utilized for dissolution, diffusion of components within a closed system, and crystallization of magnetite. The mineralogical data only imply pervasive dissolution and crystallization; they do not imply that the necessary fluids were derived externally or internally.

On the other hand, in conjunction with continental-scale fluid migration, the concept of tectonically driven fluid is a convenient explanation for remagnetization and other geological phenomena recorded in the crust [Oliver, 1986; Bethke and Marshak, 1990; Dorobek, 1989] not in the least because the remagnetizations in the eastern and central United States are all more or less of the same (Perm-Carboniferous) age [Van der Voo, 1989]. In order for tectonically driven fluids to have been responsible for remagnetization, they must fulfill the requirements of temperature and composition (K, Na, Cl, etc.), regardless of whether such fluids were sedimentary brines or of meteoric origin. Tectonically driven fluids thus may have been either a connate brine which was squeezed by large-scale thrusting [Oliver, 1986] or they may have been topographically driven meteoric water that was heated at depth and then returned toward the surface [Bethke, 1986; Nunn et al., 1984]. Neither of these fluid types fulfills the temperature and ingredient requirements at the same time, in that the tectonically driven connate fluid, in a small sense, cannot satisfy the temperature requirement, while the topographically driven meteoric water cannot have sufficient elements. However, accepting that authigenic magnetite formation and remagnetization is mediated by fluids during the Alleghanian Orogeny, we prefer the tectonically driven fluid induced by emplacement of thrust sheets, if we must make a choice. These fluid motions were directly associated with the tectonic stress regime of the Alleghanian Orogeny for New York carbonates; in other localities, however, other mechanisms of fluid migration for remagnetization may be called upon.

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