

SEM/STEM OBSERVATIONS OF MAGNETITE IN CARBONATES OF EASTERN NORTH AMERICA:
EVIDENCE FOR CHEMICAL REMAGNETIZATION DURING THE ALLEGHENIAN OROGENY

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Abstract. Early to middle Paleozoic carbonates of eastern North America have been pervasively remagnetized. In order to determine the process of remagnetization, scanning and scanning transmission electron microscopy have been used to characterize magnetite in thin sections and in concentrated separates. Samples included Ordovician Knox carbonates from east Tennessee, Ordovician Trenton limestone and Devonian Onondaga and Helderberg limestones from New York, and Ordovician Trenton carbonates from Michigan. Inclusions of authigenic minerals within magnetite grains, lack of cations other than iron, and a variety of textural relations all imply that the magnetite is authigenic. These data are consistent with estimates that paleotemperatures never exceeded values that would reset magnetic directions. The remagnetization is thus a chemical remanent magnetization (CRM) rather than viscous remanent magnetization (VRM). As the timing of remagnetization corresponds to the Alleghenian orogeny, the observed relations imply stress-induced crystallization of magnetite that was mediated by fluids, consistent with but not requiring fluid flow on a regional basis.

Introduction

Paleomagnetic and rock magnetic data for many Paleozoic limestones of eastern North America are consistent with remagnetization being due to magnetite and having been acquired during the Alleghenian orogeny [e.g., Bachtadse et al., 1987; Jackson et al., 1988; McCabe et al., 1989]. The remagnetization has been ascribed to both VRM [Kent, 1985] and to CRM [e.g., McCabe et al., 1989]. If the remagnetization is a CRM carried by authigenic magnetite, then the process of formation of magnetite must be one of crystallization via fluids at a time corresponding to the age of remagnetization. On the other hand, if the remanence is a VRM, the magnetite is older than the magnetization and may well be primary (e.g., detrital).

Oliver [1986] used data from a variety of sources to hypothesize that fluids were expelled from the active plate margin during the Alleghenian orogeny, and that they flowed through crustal sediments toward the west. Among the data utilized by Oliver were paleomagnetic results from a variety of sources that showed that remagnetization was Alleghenian in age. It is important to note, however, that formation of authigenic magnetite may require fluids, but that the source of those fluids need not be an external one; for example, Elmore et al. [1990] called on pressure solution induced by tectonic stress and utilizing closed-system pore fluids as a mechanism for in situ chemical processes. Nevertheless, determination that the remagnetization is a CRM in nature is at least consistent with continental-scale fluid flow, and may provide significant evidence in support of it.

Strong suggestions of an authigenic origin of magnetite in carbonate sediments of early to middle Paleozoic age in east-

ern North America were provided by several studies [e.g., Jackson et al., 1988; McCabe et al., 1989]. An authigenic (chemical) origin for the magnetite that contributes to paleomagnetic data was indicated by studies of magnetite extracts [e.g., Bachtadse et al., 1987]. Such magnetite was commonly found to be in the form of spheres having rough surfaces and being a few micrometers in diameter; the shape and composition of such spheres implied an authigenic origin.

The evidence for an authigenic origin for magnetite in limestones remained indirect and unconvincing, however, especially in that magnetite had not been observed in situ. We therefore initiated a program of characterization of such magnetite that is based on using scanning and scanning transmission electron microscopy (SEM and STEM) to locate and characterize magnetite directly in limestones, as well as to study separates using these and other methods such as X-ray diffraction (XRD).

Sample Localities and Methods of Characterization

Carbonates, for which paleomagnetic data had indicated secondary, Alleghenian remagnetizations, were obtained from several localities, including: 1. Ordovician Knox carbonates from east Tennessee, including both unmineralized and mineralized carbonates by Mississippi Valley Type (MVT) deposits [Bachtadse et al., 1987] 2. Samples from an east-west traverse across New York, including Ordovician Trenton limestone [Kent, 1985; McCabe et al., 1984] and Devonian Onondaga and Helderberg limestones [Kent, 1979; Scotese et al., 1982; Jackson et al., 1988] 3. Ordovician Trenton carbonates from cores from the Michigan Basin, which have also been shown to carry a late Paleozoic remanence [Suk et al., 1989]. Samples from the New York traverse and Michigan collectively represent a sequence of increasing distance from the focus of tectonic activity; Jackson et al. [1988] showed, for equivalent New York samples, that the intensity of magnetization is lower in western New York, as correlated with degree of illitization of clays and temperature indicated by apatite fission tracks [Johnsson, 1986]. The major magnetic carrier in all samples is magnetite, with the proportion of hematite being negligible. Jackson [1990] further studied similar material from New York and concluded that the late Paleozoic remanence is carried principally by single-domain magnetite grains even though coarser-grained magnetite is more abundant.

Sample Preparation and Study Methods

In order to determine the textural relations among magnetite and its coexisting phases, SEM observations were carried out using polished thin sections. The thin sections were prepared using "sticky wax" as an adhesive so that selected areas could be detached and further thinned using a dimpler and ion mill, in preparation for STEM observations, for which ultra-thin sections are required. A total of 101 samples were prepared and studied, 35 from Knox carbonates, 17 of Onondaga limestone, 12 of Helderberg limestone, 7 of Trenton limestone from New York, and 30 of Trenton carbonates from the Michigan Basin. In order to correlate the observations for thin sections with those that had previously been obtained for magnetic separates, and to obtain a representative sample that

would include all kinds of magnetite, several samples were also acid-treated and the resulting insoluble residues fractionated using a hand magnet [Bachtadse et al., 1987 for method]. The magnetic separates were then spread on slides or on "holey carbon"-supported Cu grids in preparation for SEM and STEM observations. Crystal structures were characterized for selected separates through X-ray diffraction, using a Gandolfi camera.

Observations were made using a Hitachi S-570 SEM with back-scattered electron (BSE) detector, and a Philips CM-12 STEM. Both instruments are fitted with Kevex Quantum energy dispersive X-ray detectors for chemical analysis. Minerals were first characterized in thin section using BSE imaging as augmented by energy dispersive analysis (EDA), as well as by standard secondary electron imaging (SEI) in order to image surface topography. Ion-milled samples were then used for high resolution TEM and STEM observations. TEM was used to obtain selected area electron diffraction (SAED) patterns in order to differentiate magnetite from other iron oxides, and to provide data on the dimensions of single crystals.

Results

Knox Carbonates

Grains of magnetic separates were of two kinds, spheres with rough surfaces or irregular grains with a rounded surface which have a botryoidal-like appearance. The spheres were shown to consist of magnetite through X-ray diffraction, whereas EDA using the SEM showed the presence only of iron and oxygen. As spheres of similar appearance had been observed in extracts of samples from east Tennessee and other localities, but never in thin section or associated with other minerals, their source had been subject to question. However, one sphere was found by SEM observations to be encrusted with authigenic K-feldspar, proving that it originated within the rock sample, and implying that it was authigenic in origin.

The non-spherical magnetite grains were readily observed in thin section and clearly showed mineralogical and textural relationships with other authigenic (secondary) minerals such as K-feldspar, dolomite and phyllosilicates. Magnetite was usually found in and/or along microcracks and voids, as illustrated in Figure 1a where it is in close association with K-feldspar. Figure 1b shows a magnetite grain containing an

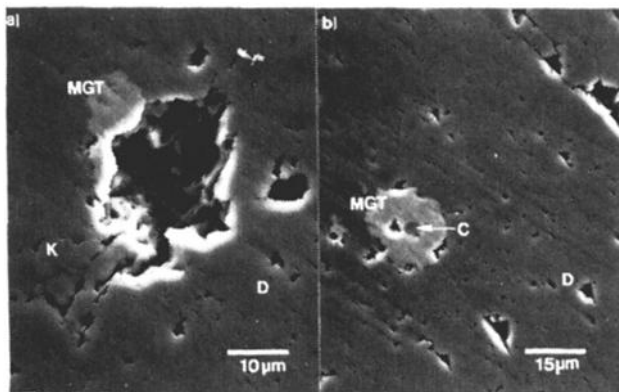


Fig. 1. Scanning electron microscope images of iron oxides in the Ordovician Knox Group. Symbols are MGT, magnetite; D, dolomite; C, calcite; K, K-feldspar; P, pyrite. (a) Non-spherical magnetite observed in thin section in dolomite; secondary electron image (SEI). Magnetite formed in a void showing relation to K-feldspar. (b) Void-filling magnetite in dolomite with calcite inclusion; SEI.

inclusion of calcite, proving that the magnetite formed later than the calcite. Although grains vary in size from less than 1 μm up to 50 μm , when STEM observations could be made on grains in thin sections, they were found to be polycrystalline. In those samples that had not been mineralized, titanium-iron oxides with a corroded appearance and in direct association with iron-rich clay minerals were observed, implying that those minerals served as a source of iron for authigenic magnetite. See Suk et al. [1990a] for further details.

New York Carbonates

Magnetite occurring in aggregates with a spherical shape (Figure 2a) that appear to be pyrite framboids (referred to as pseudoframboids) were observed in thin sections of all New York specimens, and were common in separates (Figure 2b). EDA, XRD, and SAED observations showed that the framboids vary from consisting only of octahedral crystals of pyrite, to those having octahedral crystals with a core of pyrite and rim of magnetite, to those consisting of octahedral crystals consisting only of magnetite. Figure 2c shows typical individual crystals. SAED shows that the magnetite is polycrystalline, with individual sizes in the single to pseudo-single domain range; i.e., the octahedral crystal shape reflects only the structure of the original pyrite.

Fig. 2

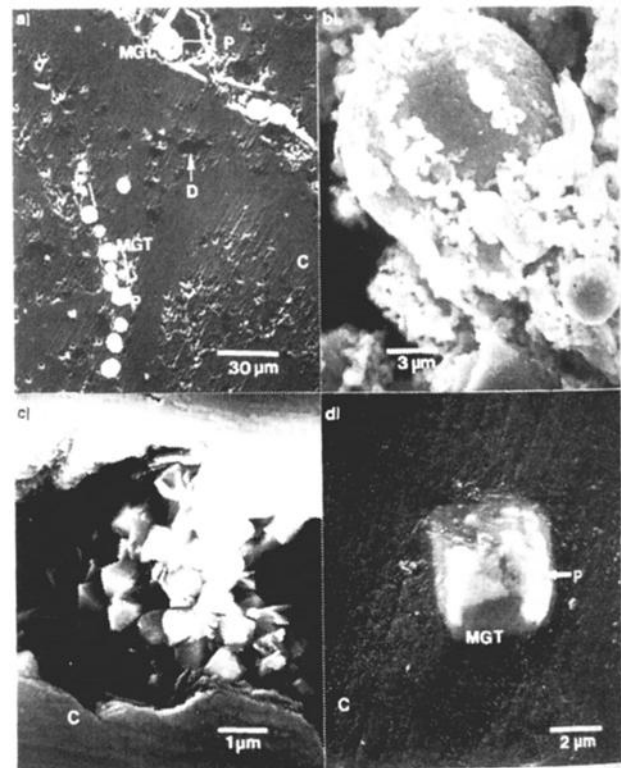


Fig. 2. Scanning electron microscope images (as in Fig. 1) in the New York carbonates. (a) Spherical and non-spherical magnetites observed in thin sections in limestone revealing magnetite-pyrite relations; SEI. Pyrite shows the brightest contrast. Dark contrast patches are dolomite in calcite matrix. (b) Spherical magnetite extracted from limestones; SEI. Aggregates of smaller magnetite grains accompanied by spherical magnetite. (c) Typical octahedral crystals of spherical magnetite in a microcrack in limestone thin section; SEI. (d) Non-spherical magnetite showing magnetite-pyrite relations in limestone thin section; SEI. Brighter pyrite core surrounded by magnetite.

As shown in Figure 2a, the framboids and pseudoframboids are found associated with microcracks and voids. Pseudoframboids vary from 3 to 15 μm in diameter, with individual octahedra being less than 1 μm in size; they in turn consist of an aggregate of smaller magnetite subgrains. Octahedral crystals are also found as irregular clusters or as single individuals. Figure 2d shows a grain having a core of pyrite and rim of magnetite.

Separates contain a second kind of magnetite that is shown in Figure 2b in association with spheres, but that has not yet been observed in thin section. This consists of aggregates and clusters of individual magnetite crystals, each individual being approximately 2000 angstroms in diameter. Such material actually is slightly more abundant than the spheres. See Suk et al. [1990b] for further details.

Trenton Limestone from the Michigan Basin

The only kind of magnetite found by SEM in thin sections or separates of Trenton limestone from Michigan consists of extremely fine-grained material on the surfaces of voids and cracks. Such material is intimately associated with K-feldspar, quartz, and dolomite. Pyrite was also found commonly, but did not display alteration features. Because the magnetite occurs in submicron-sized grains in direct intergrowth with other minerals, SEM could only verify composition and poorly-resolved texture. However, magnetic separates of insoluble residues verified that such material is the only kind present in the studied samples (i.e., no spheres were found), and gave rise to typical images as shown in Figure 3. The magnetite consists of an aggregate of separate grains, each one of which is approximately 2000 angstroms in diameter. Such material closely resembles the fine-grained material from New York samples. No cations other than iron were detected by EDA. Identification as magnetite was confirmed using Gandolfi photographs.

Discussion

Iron oxides found using BSE and EDA analysis were first only tentatively identified as magnetite. Whenever SAED data were obtained using TEM observations of thin sections, or Gandolfi photographs of ferromagnetic separates were observed, magnetite was always confirmed as the dominant phase, with hematite being observed only rarely. Because the

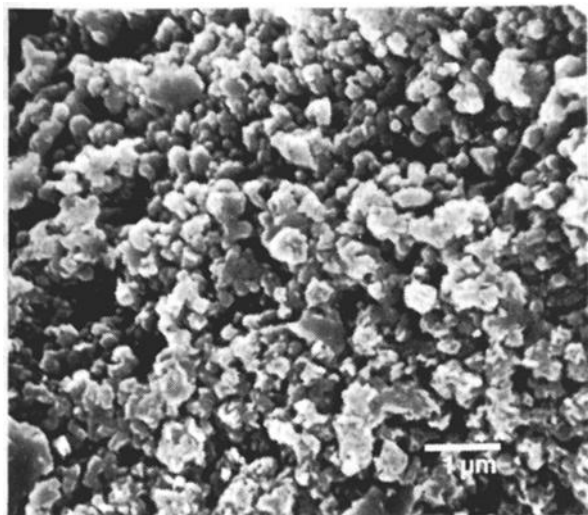


Fig. 3. Scanning electron microscope images of an aggregate of typical magnetite from extracts from Trenton limestone from the Michigan Basin; SEI.

observations include both whole-rock separates and many thin sections, we infer that they are representative of the range of actual magnetite occurrences in the studied samples.

Only in the non-mineralized limestones from east Tennessee were grains found resembling detrital magnetite. All other magnetite is inferred to be authigenic, based on the following criteria: 1. a cogenetic relationship between magnetite and other minerals known to be authigenic such as dolomite, illite, and (especially) K-feldspar. 2. inclusions of authigenic minerals within magnetite grains. The authigenic K-feldspars in early Paleozoic carbonates in eastern Tennessee and elsewhere have yielded late Paleozoic ages [Hearn et al., 1989]. The ubiquitous association of authigenic K-feldspar with magnetite is compelling evidence of an authigenic origin for magnetite. 3. magnetite as an alteration product of pyrite in New York samples, where the pyrite itself is known to be authigenic. We infer that spherical pseudoframboids in thin section are the equivalent of spheres obtained by others in magnetic separates. 4. chemical data showing the presence only of iron, with an absence of those elements (e.g., Ti) known to be characteristic of detrital magnetite of igneous or metamorphic origin. 5. general textural features, including rounded aggregates of separate grains.

These data collectively imply that magnetite in the samples studied is derived by crystallization directly from solution, following burial. The textures do not limit timing beyond showing that it must post-date initial diagenesis in the case of replacement of pyrite. The source of the iron remains unspecified. Jackson et al. [1988] has hypothesized that it is in the clay minerals that were converted to illite, whereas Bachtadse et al. [1987] have noted that carbonates could be the source. The fluids that mediated formation of magnetite must have interacted with all phases in the rocks, however, iron in a variety of phases including detrital iron-titanium oxides, clay minerals, and carbonates may have played a role.

The paleomagnetic data for the studied samples, and all other samples from the eastern U. S. known to have been affected by the Alleghenian orogeny [e.g., McCabe et al., 1989], indicate that the magnetization is carried by magnetite and is secondary (Alleghenian age), having been acquired long after sediment burial and early diagenesis. A VRM origin for the late Paleozoic remagnetization can be excluded by estimates of low values for maximum paleotemperatures as determined by observations of fluid inclusions in east Tennessee [e.g., Taylor et al., 1983], partial annealing of fission tracks in zircon [Johnsson, 1986], fluid inclusions, vitrinite reflectance and oxygen isotope data [Friedman, 1987] and conodont color alteration indices [Epstein et al., 1977] in New York state, and by a continual subsidence model [Nunn et al., 1984] in the Michigan Basin. The maximum estimated paleotemperature of 200°C in the studied areas, with the exception of the easternmost part of New York state, is significantly lower than temperatures required to have activated the remagnetization, as determined by using either the model of Pullaiah et al. [1975] or Middleton and Schmidt's model [1982] for theoretical relaxation time-unblocking temperature relations. Insofar as the magnetite is authigenic in origin and the magnetization is a CRM carried by the authigenic magnetite, these data collectively imply that the magnetite formed on a regional basis by direct crystallization from fluids, during which a CRM was acquired, with the fluid-mediated process having been activated by tectonic stress during the Alleghenian orogeny. These data are therefore consistent with Oliver's model [1986] of tectonically-driven regional fluid flow. However, we note that only consistency with that model is implied by our observations. Although fluid must have mediated the formation of magnetite, original pore fluid, rather than brines derived externally over long distances, could have served as the fluid. In the case of original pore waters, tectonic stress would be in-

ferred to have served as the instigator of dissolution and crystallization.

Oliver called on pressure induced by emplacement of thrust sheets, whereas Bethke and Marshak [1990] argued that topographic relief of the tectonic belt provided the dominant driving force. Because topographic relief, as advocated by the latter authors, existed well into Mesozoic time, fluid flow would have remained active in their model for long periods. One would then expect to see remagnetizations in the Appalachian Basin with ages as late as perhaps Cretaceous. However, only late Paleozoic remagnetizations have been observed. Thus the evidence suggests that if regional fluid flow was indeed the cause of remagnetization in the limestones, it was directly associated with the tectonic stress regime of the Alleghanian Orogeny.

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References

- Bachtadse, V., R. Van der Voo, F. M. Haynes, and S. E. Kesler, Late Paleozoic magnetization of mineralized and unmineralized Ordovician carbonates from East Tennessee: Evidence for a post-ore chemical event, *J. Geophys. Res.*, **92**, 14165-14176, 1987.
- Bethke, C. M., and S. Marshak, Brine migrations across North America - The plate tectonics of groundwater, *Annu. Rev. Earth Planet. Sci.*, **18**, 287-315, 1990.
- Elmore, R. D., D. Bagley, D. London, D. Fruit, Z. Yu, and X. Xiong, Pervasive synfolding CRM in the Ordovician Viola Limestone: Remagnetization by in situ diagenetic processes? (abstract), *Eos Trans. AGU*, **71**, 493, 1990.
- Epstein, A. G., J. B. Epstein, and L. D. Harris, Conodont color alteration--An index to organic metamorphism, *U. S. Geol. Surv. Prof. Pap.*, **995**, 27 p., 1977.
- Friedman, G. M., Deep-burial diagenesis: Its implications for vertical movements of the crust, uplift of the lithosphere, and isostatic unroofing--A review:, *Sedimentary Geology*, **50**, 67-94, 1987.
- Hearn, P. P., Jr., J. F. Sutter, and H. E. Belkin, Authigenic K-feldspar--An indicator of the geochronology and chemical evolution of mineralizing fluids in sediment-hosted lead and zinc deposits (abstract), in *28th International Geological Congress, Abstract Volume*, pp. 2.46-2.47, IGC, Washington D. C., 1989.
- Jackson, M., Diagenetic sources of stable remanence in remagnetized Paleozoic cratonic carbonates: A rock magnetic study, *J. Geophys. Res.*, **95**, 2753-2761, 1990.
- Jackson, M., C. McCabe, M. M. Ballard, and R. Van der Voo, Magnetite authigenesis and diagenetic paleotemperatures across the northern Appalachian Basin, *Geology*, **16**, 592-595, 1988.
- Johnsson, M. J., Distribution of maximum burial temperatures across northern Appalachian Basin and implications for Carboniferous sedimentation patterns, *Geology*, **14**, 384-387, 1986.
- Kent, D. V., Paleomagnetism of the Devonian Onondaga Limestone revisited, *J. Geophys. Res.*, **84**, 3576-3588, 1979.
- Kent, D. V., Thermoviscous remagnetization in some Appalachian limestones, *Geophys. Res. Lett.*, **12**, 805-808, 1985.
- McCabe, C., R. Van der Voo, and M. M. Ballard, Late Paleozoic remagnetization of the Trenton Limestones, *Geophys. Res. Lett.*, **11**, 979-982, 1984.
- McCabe, C., M. Jackson, and B. Saffer, Regional patterns of magnetite authigenesis in the Appalachian Basin: Implications for the mechanism of Late Paleozoic remagnetization, *J. Geophys. Res.*, **94**, 10429-10443, 1989.
- Middleton, M. F., and P. W. Schmidt, Paleothermometry of the Sydney Basin, *J. Geophys. Res.*, **87**, 5351-5359, 1982.
- Nunn, J. A., N. H. Sleep, and W. E. Moore, Thermal subsidence and generation of hydrocarbons in Michigan Basin, *AAPG bulletin*, **68**, 296-315, 1984.
- Oliver, J., Fluids expelled tectonically from orogenic belts: Their role in hydrocarbon migration and other geologic phenomena, *Geology*, **14**, 99-102, 1986.
- Pullaiah, G., E. Irving, K. L. Buchan, and D. J. Dunlop, Magnetization changes caused by burial and uplift, *Earth Planet. Sci. Lett.*, **28**, 133-143, 1975.
- Scotese, C. R., R. Van der Voo, and C. McCabe, Paleomagnetism of the Upper Silurian and Lower Devonian carbonates of New York State: Evidence for secondary magnetizations residing in magnetite, *Phys. Earth Planet. Inter.*, **30**, 385-395, 1982.
- Suk, D., R. Van der Voo, and D. R. Peacor, Late Paleozoic remagnetization of the Trenton limestone in Michigan Basin (abstract), *Eos Trans. AGU*, **70**, 310, 1989.
- Suk, D., R. Van der Voo, and D. R. Peacor, Scanning and transmission electron microscope observations of magnetite and other iron phases in Ordovician carbonates from east Tennessee, *J. Geophys. Res.*, **95**, 12,327-12,336, 1990a.
- Suk, D., D. R. Peacor, and R. Van der Voo, Replacement of pyrite framboids by magnetite in limestone and implications for paleomagnetism, *Nature*, **345**, 611-613, 1990b.
- Taylor, M., S. E. Kesler, and P. L. Cloke, Fluid inclusion evidence for fluid mixing, Mascot-Jefferson City zinc district, Tennessee, *Econ. Geol.*, **78**, 1425-1439, 1983.

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