

increase in the lower part of facies B and in facies C thus clearly inferring a relatively larger contribution of diatoms to the sedimentary organic matter in this zone. This is consistent with the fact that phosphatic sediments are often deposited in upwelling environments¹⁹ and that the phytoplankton in such environments tends to be dominated by diatoms³.

A depth profile (Fig. 1c) of the C₃₇ 2,5-dialkylthiophenes V (Fig. 2) shows that Prymnesiophyte algae (which include coccolithophorids) were predominant during deposition of the lower section of facies B. Thiophenes V are formed by reaction of inorganic sulphur species with the C₃₇ di- and triunsaturated methyl- and ethylketones (and/or their corresponding alkenes)^{10,11} biosynthesized by this group of algae and used in the assessment of palaeotemperatures²³. This depth profile is the only way of obtaining information on the occurrence of Prymnesiophyceae because the ketones (or the corresponding alkenes) were not present as such. Similarly, a depth profile (Fig. 1d) of the C₄₄-C₄₈ 3,4-dialkylthiophenes VI²⁴ (Fig. 2) reveals the abundance of other, probably phytoplanktonic, species during deposition of facies A and the upper part of facies B. Compounds with these carbon skeletons have not been reported previously, indicating that their precursors are too labile to be preserved in the sedimentary record. It is only through their sulphur derivatives that their original presence is revealed. A depth profile (Fig. 1e) of the C₂₆ irregular isoprenoid thiophene VII²⁵ (Fig. 2) shows two maxima in the upper section of facies A. This is a further example of the recognition of hitherto unrecognized lipids by analysis of OSCs as C₂₆ irregular isoprenoids are not known in nature. Many other changes in the alkylthiophene assemblages were noted and seem to contain further stratigraphic information¹⁶. For a number of these OSCs, however, it is not yet known how they relate to specific biological contributions. This is, in the main, because of our scant knowledge of the lipid composition of phytoplankton³, although the possibility remains that the organism capable of biosynthesizing suitably functionalized lipid precursors for these OSCs have become extinct.

C₂₀ isoprenoid thiophene distributions may be used in the assessment of palaeosalinity^{11,26}. A depth profile (Fig. 1f) of the ratio of thiophenes VIIIa^{8,27} and VIIIb⁸ over VIIIc-g^{28,29} (Fig. 2) shows small variations in palaeosalinity. Values smaller than 0.5 have been proposed to reflect hypersaline (salinity >4%) palaeoenvironments²⁶. Thus, this depth profile reveals that the palaeosalinity in this sedimentary sequence has only been higher than that of normal sea water during deposition of the lowest part of facies B. In a separate study of a related deposit it was also concluded that the lowermost beds were deposited in a hypersaline environment³⁰. This example shows that alkylthiophenes can also be used in the assessment of physical aspects of the depositional palaeoenvironment. Furthermore, the parallel changes in the depth profiles of the thiophene ratio and thiophenes VI indicate that the unknown algae biosynthesizing the precursors of VI have been stressed by enhanced salinities. Also, the maximum in the depth profile of thiophenes V (abundance of Prymnesiophyceae) occurs at the highest salinity. This is consistent with the palaeoenvironmental changes observed in the Black Sea where the coccolith *E. Huxleyi* appears as marine incursions replace lacustrine depositional conditions³¹. □

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Replacement of pyrite framboids by magnetite in limestone and implications for palaeomagnetism

D. Suk, D. R. Peacor & R. Van der Voo

Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109, USA

LIMESTONES are an important source of palaeomagnetic data, with magnetite the dominant carrier of the magnetization. Because the magnetite is present in low concentrations, however, it has been directly observed only rarely and in trace amounts in acid-treated separates. Such residues are composed primarily of spheres, the ultimate origin of which has been enigmatic⁷. Yet interpretation of the palaeomagnetic data depends on a knowledge of the origin of the magnetite, which has been inferred to carry either a chemical or a viscous remanent magnetization. Here we present electron microscope data obtained from a sequence of samples of Onondaga Limestone from an east-west traverse across northern New York, which unambiguously show that magnetite spheres are derived by alteration and replacement of framboidal pyrite. Remagnetization is thus caused by chemical, rather than viscous, processes. This chemical remanent magnetization is compatible with a fluid-mediated event occurring on a regional scale, induced by tectonic stress of Alleghenian (late Palaeozoic) age.

It is widely recognized that many of the early to middle Palaeozoic shallow-water and platform carbonates in eastern North America were remagnetized during the Kiaman reversed superchron of the late Palaeozoic¹⁻⁸ and examples of late Mesozoic remagnetizations are now beginning to be recognized in the western United States^{9,10}. The ancient remagnetizations are presumably related to the tectonism in space and time^{6,9-12}, and tectonically driven fluid migrations from active plate margins may have an important role in the remagnetization processes¹³.

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Two fundamentally different explanations for remagnetization have been proposed. The first explanation involves a chemical remanent magnetization (CRM) acquired when new magnetic minerals (primarily magnetite) formed long after the formation of the rocks. The other explanation invokes a change in magnetic direction in pre-existing magnetic minerals, known as viscous remanent magnetization (VRM). Although far from definitive, recent work on the same or similar platform carbonates in the eastern United States^{4,5,8,14} has generally produced more evidence in favour of CRM than of VRM. The magnetic extracts used in some studies were shown to consist in large part of spheres of magnetite. They were never found *in situ*, however, so the ultimate origin of such spheres was undetermined. Scanning and transmission electron microscope (SEM and TEM) observations of thin sections of the lower Ordovician carbonate Knox Group of east Tennessee revealed some mineralogical and textural relationships of iron oxides with their *in situ* surroundings¹⁵, but the source of the spheres of magnetite remained unclear.

In an attempt to determine directly the processes of remagnetization, middle Devonian Onondaga limestone has been sampled along a profile across New York from Kingston via Albany to Buffalo. Magnetic susceptibility increases towards the east, with magnetization throughout the sequence being of Alleghenian age, and hypothesized to be tectonically induced. Rock samples were prepared for SEM observation in the form of thin sections attached by sticky wax. Areas containing iron oxides, as first identified by SEM, were removed from sections and ion milled. A Hitachi S-570 SEM and a Philips CM-12 STEM (scanning tunnelling electron microscope), both equipped with Kevex Quantum energy dispersive analysis (EDA) systems, were used for all electron microscope observations with operating conditions as described by Jiang *et al.*¹⁶.

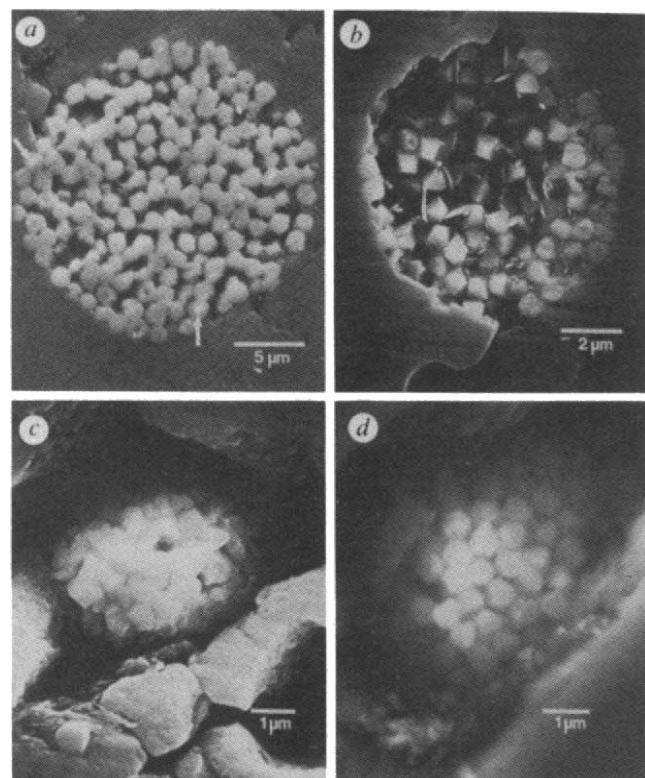


FIG. 1 Secondary-electron images of magnetite that replaced framboidal pyrite in Onondaga limestone. *a*, Polished cross-section of pseudoframboid in calcite matrix. Bright cores of some crystals (arrow) are remnant pyrite. *b*, Cross-section of pseudoframboidal magnetite showing individual octahedral or cubo-octahedral grains. *c*, Pseudoframboid in crack in calcite. *d*, Pseudoframboid showing close packing of crystals.

Figure 1 shows a secondary-electron image (SEI) of a polished thin section containing magnetite that replaced framboidal pyrite, as typical of most SEM observations of this study. Identification of this specific grain assemblage as magnetite is tentative as it is directly based on EDA spectra showing only Fe and O (see Fig. 2*d*). In all cases where such pseudoframboids were ion milled and examined by TEM (Fig. 2*a* and 2*b*), however, selected-area electron diffraction (SAED) patterns showed that magnetite is the dominant phase, sometimes accompanied by haematite. Areas consisting of magnetite are polycrystalline in nature, based on the spotty and diffuse nature of SAED patterns which approximate the appearance of powder photographs (Fig. 2*c*). In addition, magnetic extracts were recovered from the insoluble residue obtained by dissolving limestones in buffered acetic acid of pH 5 (refs 3, 4). SEM images of grains in magnetic extracts of acid-treated samples seemed to be identical to those obtained from *in situ* grains, although there is a possibility of alteration of magnetic extracts during acid treatment. The grains from magnetic extracts gave X-ray powder diffraction patterns principally of magnetite, with no other iron compounds. Therefore, where EDA spectra of samples observed by SEM show only Fe and O, a specific grain is labelled as magnetite by association, although there may be haematite in some cases.

As shown in Fig. 1*b*, pseudoframboids consist of arrays of individual crystals less than 1 μm in diameter, the form of which is dominantly octahedral or cubo-octahedral; a polished cross-section of such crystals shown in Fig. 1*a*. Figure 1*c* shows a pseudoframboid in a small crack, separated by pore space from carbonate matrix. The crystal packing arrangement, where one crystal is surrounded on average by 12 neighbours that commonly share crystal faces, is illustrated in Fig. 1*d*. Individual crystals also occur, randomly arrayed in the carbonate matrix (Fig. 3). As shown in Figs 1*a* and 3*b*, the cores of some crystals consist of unaltered pyrite (brighter phase) with magnetite rims whereas cores of other crystals are hollow, due either to plucking of the pyrite during specimen preparation or dissolution of pyrite (Fig. 3*b*).

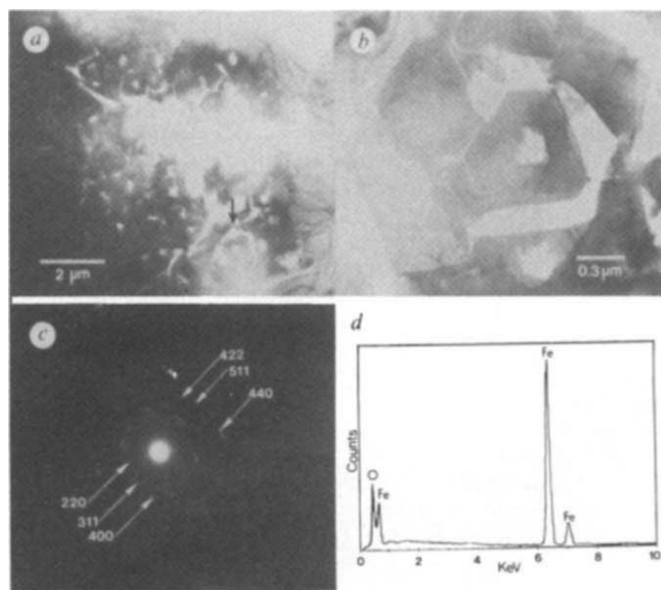


FIG. 2 Bright-field images of magnetite, selected-area electron diffraction (SAED) pattern and energy dispersive spectrum obtained by AEM. *a*, Part of pseudoframboidal magnetite ion milled for TEM observations. *b*, Enlarged magnetite grains from the lower right side (arrow) in *a*. SAED patterns of magnetite were obtained from these individual grains. *c*, Typical SAED pattern of magnetite grain, diagnostic of magnetite because of the 220, 311, 400, 422, 511 and 440 reflections. The ring pattern is indicative of a polycrystalline texture. *d*, Energy dispersive spectrum of grain shown in *a*, identical to energy dispersive spectra obtained by SEM.

Unaltered pyrite framboids are more common than those consisting of magnetite. Only pyrite has been observed in samples from western New York, where the magnetic susceptibility of limestones is low. In contrast, magnetic extracts of samples from near Albany, for which SEM shows that magnetite is common, are dominated by spheres of magnetite (Fig. 4a). Such spheres have morphologies identical to those observed in polished thin sections and give rise to X-ray diffraction patterns showing only reflections due to magnetite (Fig. 4b). They are therefore inferred to be equivalent to the pseudoframboidal magnetite observed in thin section. Such spheres seem to be identical to those observed only in separates in many other studies^{3,4,9}, the origins of which were obscure.

Canfield and Berner¹⁷ have shown that pyrite framboids can form by pyritization of magnetite in unconsolidated sediments. Our observations demonstrate conclusively that the reverse reaction can occur much later and that the magnetic phase that is the principal source of remanent magnetism has replaced early pyrite. The remagnetization is therefore a chemical remanent magnetization (CRM) acquired when pseudoframboidal magnetite formed by reactions involving pyrite in the presence of fluids. Fluid flow in the remagnetization processes is thought to be driven by tectonic activity¹³ on a continental scale. Alternatively, sediment compaction¹⁸ and gravity due to topographic difference¹⁹ in the intracratonic basins can be important driving forces for basinal fluid flows as well. Such basinal fluids consist either of connate fluid expelled by sediment compaction, or meteoric water introduced by gravity owing to uplift of sur-

rounding regions. Tectonically driven fluids, consisting of connate fluids, may then be mixed with a later meteoric water component¹³. Because the remagnetization of limestones throughout the eastern United States has been inferred to be largely due to spherical magnetite as observed in separates^{3,4}, and because our pseudoframboids have appearances nearly identical to those in separates of other studies, we conclude that replacement of framboids and individual crystals of pyrite by magnetite is the principal process responsible for remagnetization in such rocks. Elliott and Aronson²⁰ have determined that the smectite of bentonites in the southern Appalachian Basin has undergone alteration to illite over a narrow time interval (between 272 and 303 Myr). Similarly, Hearn *et al.*²¹ have shown that authigenic K-feldspar occurring in limestone along the flanks of the entire Ouachita–Appalachian fold belt formed by the reaction of connate brines during the Alleghenian orogeny. These relations are consistent with the Alleghenian age of chemical remagnetization residing in authigenic magnetite. All of these mineralogical transitions are inferred to be mediated by fluids, and are consistent with recrystallization of all minerals in a single event, hypothesized by Oliver¹³ to be caused by tectonically induced crustal fluid flow. □

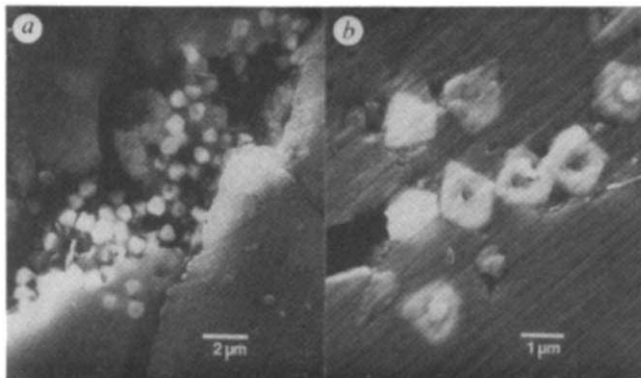


FIG. 3 Secondary-electron images of magnetite that replaced individual pyrite crystals. *a*, Crystals dispersed in calcite matrix. *b*, Crystals with remnant pyrite cores (bright contrast) and hollow cores (dark contrast).

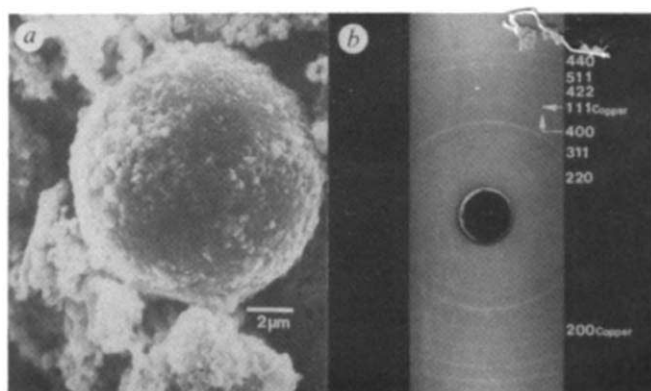


FIG. 4 Magnetite sphere from separates obtained by dissolution of calcite and X-ray diffraction pattern. *a*, Sphere showing typical irregular surface. *b*, X-ray diffraction pattern obtained using Gandolfi Camera showing 220, 311, 400, 422, 511 and 440 reflections of magnetite, and 111 and 200 reflections of copper from the collimator.

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Mineral nutrition and seasonal movements of African migratory ungulates

S. J. McNaughton

Biological Research Laboratories, Syracuse University, Syracuse, New York 13244–1220, USA

Two distinct foraging behaviours differentiate Africa's grazing ungulates^{1–3}: over the wet–dry season cycle resident herds occupy seasonally stable and spatially restricted home ranges and migratory herds move over vast geographical regions, using different areas in different seasons. Migratory herds dominate animal biomass wherever they occur⁴. Some migrants congregate around permanent water sources in the dry season and disperse to drier habitats in the wet season⁵; others travel along rainfall gradients, concentrating in areas of low annual rainfall in the wet season and moving to areas of higher rainfall as the dry season advances⁴. The Serengeti National Park in Tanzania is typical of the latter type of ecosystem⁶; migratory grazers there select drier localities in the wet season, despite the fact that forage production rates and drinking water supplies are high everywhere. These migrations could be explained by the animals' avoidance of muddy, sticky soils⁷, general forage-quality properties⁸, by calcium requirements