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Bacterial magnetite produced in water column dominates lake sediment mineral magnetism: Lake Ely, USA

BangYeon Kim, Kenneth P. Kodama and Robert E. Moeller

Department of Earth and Environmental Sciences, Lehigh University, Bethlehem, PA, USA. E-mail: bak4@lehigh.edu

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SUMMARY

Environmental magnetic studies of annually laminated sediments from Lake Ely, northeastern Pennsylvania, USA indicate that bacterial magnetite is the dominant magnetic mineral in the lake sediment. In previous studies of Lake Ely sediment, the dark, organic-rich layers in the annual laminae were interpreted to have high-intensity saturation isothermal remanent magnetizations (SIRMs) while the light-coloured, silt-rich layers have low-intensity SIRMs. To test the hypothesis that the magnetic grains in the sediments were an authigenic product of magnetotactic bacteria rather than detrital magnetic grains eroded from the watershed, we analysed samples from the water column, the lake sediment, and a sediment trap installed near the lake bottom. Direct microscopic observation of the water column samples showed the presence of magnetotactic bacteria in and below the oxic-anoxic transition zone (OATZ). To characterize the magnetic minerals, rock magnetic parameters were measured for material from the water column, the sediment trap and the dark- and light-coloured lake sediments. Low-temperature magnetic measurements tested for the presence of magnetosomes in separated dark- and light-coloured layer samples. Numeric unmixing of the low-temperature results showed that biogenic magnetites were present in the lake sediment and contributed more significantly to the SIRM in the dark, organic-rich layers than in the light-coloured, inorganic silt-rich layers. Observations under the transmission electron microscope (TEM) of magnetic extracts also show the abundance of magnetosomes in the lake sediment. The presence of live magnetotactic bacteria in the water column and the predominance of bacterial magnetites in filtered particulate matter, sediment traps and recent lake sediment all suggest that bacterial magnetites are the main magnetic minerals in Lake Ely sediment. This finding suggests that changes in environmental factors that control the productivity of magnetic bacteria in the lake likely contribute to the variability of magnetic mineral concentrations observed in the lake sediments.

Key words: lake sediments, magnetite, rock magnetism.

1 INTRODUCTION

Environmental magnetic measurements of lake sediments are useful in palaeoclimate studies because many climatic processes have profound effects on the concentration, size and mineralogy of the magnetic minerals found in sediments (Reynolds & King 1995). Magnetic properties in lake sediments are particularly useful as proxies for continental paleoclimatic variation. Temperature and moisture changes through the glacial and interglacial periods have been successfully correlated with the fluctuation of magnetic parameters in lake sediments (e.g. Snowball 1993; Peck *et al.* 1994; Jelinowska *et al.* 1995; Wei *et al.* 1998; Williamson *et al.* 1998; Lanci *et al.* 1999; Ortega *et al.* 2002; Paasche *et al.* 2004). The response of magnetic parameters to climate change can be more rapid than pollen (Lanci *et al.* 1999) and in certain circumstances, magnetic parameters correlate directly with temperature and/or precipitation variation (Dearing & Flower 1982; Kodama *et al.* 1997b).

The resolution of climate changes recorded by magnetic parameters depends on the accumulation rate of sediments and dating techniques. Annually laminated lake sediments provide the possibility of investigating magnetic parameters as high-resolution proxies of continental climate change. Lake Ely in northeastern Pennsylvania has deposited annually laminated sediments for at least 2000 yr (Gajewski *et al.* 1987). The lake is located in a tectonically stable region and is far from heavily industrialized areas. The lake also has a relatively small watershed area with a uniform geology. Rainfall and temperature recorded for the past 65 yr near the lake provide a regional climatic record to compare with the magnetic parameters from its annually laminated sediments.

Previous studies of sediments from Lake Ely (Kodama *et al.* 1997a, 1998) suggested a positive correlation between the magnetic mineral concentration in the sediments and rainfall, but paradoxically with higher concentrations of magnetic minerals in dark, organic-rich layers of the varved sediments. A direct relationship between magnetic mineral concentration and rainfall records has been explained by simple erosional models (e.g. Thompson *et al.* 1975; Dearing & Flower 1982; Kodama *et al.* 1997b; Eriksson & Sandgren 1999). In these models, the transport and deposition of the magnetic particles from the catchment to the lake cause variation in concentration of magnetic minerals in sediments. Applied to Lake Ely, the light-coloured silty layers should show higher magnetic concentration than the dark, organic-rich layers due to dilution of magnetic grains by organic materials. The fact that higher magnetic concentration occurs in the organic-rich layers in Lake Ely sediments forces examination of other hypotheses.

The production of magnetosomes by magnetotactic bacteria (reviews by Moskowitz 1995; Frankel *et al.* 1998) could explain the high magnetic mineral concentration in the dark, organic-rich layers. Magnetotactic bacteria are a diverse group of motile, aquatic bacteria that orient and migrate along geomagnetic field lines (Blakemore 1975; Frankel & Blakemore 1980). They produce chains of single domain (SD) magnetic particles of magnetite (Fe_3O_4) and greigite (Fe_3S_4) (Frankel *et al.* 1979; Mann *et al.* 1990). Magnetotactic bacteria could possibly account for the high concentration of magnetic grains in the dark, organic-rich layers of Lake Ely (Kodama *et al.* 1998). Rock-magnetic tests for magnetosomes proposed by Moskowitz *et al.* (1993) were reported in Kodama *et al.* (1998). However, these results (crossover (R_{af}) versus ARM/SIRM plot and the ratios of Δ_{FC}/Δ_{ZFC}) did not indicate the presence of magnetosomes in the lake sediments. In our study, we report additional detailed magnetic measurements that test for the presence of the bacterial magnetite in the sediments.

This study focuses on the nature and origin of the magnetic carriers in the sediments of Lake Ely to determine if authigenic magnetite produced by magnetotactic bacteria is responsible for the magnetic signals preserved in the sediments. Magnetic characteristics of lake sediments containing biogenic magnetite have been documented from a lake in Sweden (Snowball 1994). The presence of bacterial magnetite was inferred from the magnetic characteristics in other lakes (Snowball *et al.* 1999, 2002). The magnetic concentration signal in the sediments, carried by stable SD magnetite, was positively correlated with the organic carbon content in these sediments. The magnetic parameters of Holocene sediment in a Swiss lake showed that authigenic magnetite grains are dominant in the sediment (Lanci *et al.* 1999), but it was impossible to resolve if they were chemically precipitated or biologically produced. The results from our study will suggest that magnetite produced by magnetotactic bacteria controls the magnetic signal in the sediment of Lake Ely, and thus changes of biologic productivity must be considered as potential causes of magnetic changes recorded in the sediments. Data from this study provide an important end member of lake sediment mineral magnetics in which authigenic magnetite dominates the lake sediment magnetic signal. This model contrasts to settings that have mixed signals from erosional input and authigenic production of magnetic minerals, as observed, for example, by Geiss *et al.* (2003) in Holocene sediments from four Minnesota lakes and by Oldfield *et al.* (2003) in Late Holocene sediments from a lake in northeast England.

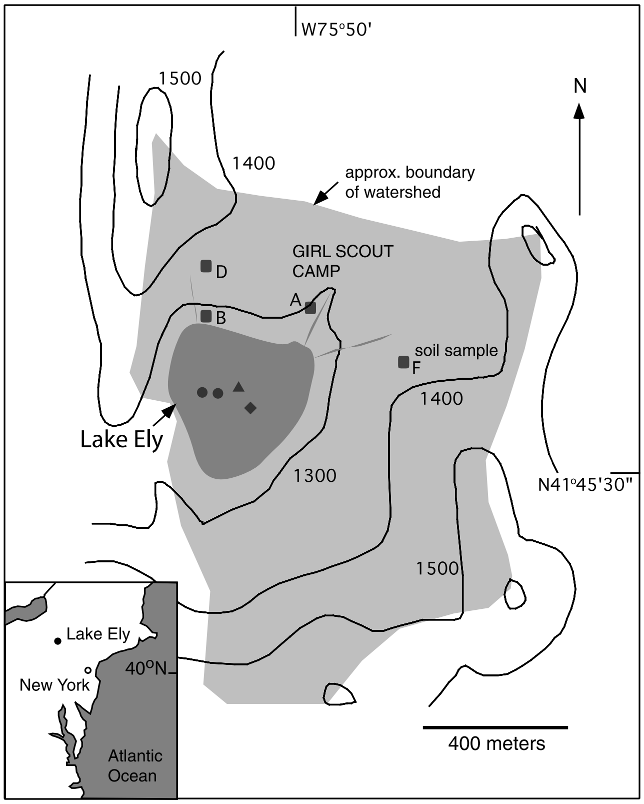


Figure 1. Map of Lake Ely, northeastern Pennsylvania. Triangle indicates freeze core sampling site in 2001 and the diamond indicates the sediment trap site. The sediment trap was in place from 2000 October 9 to 2002 September 26. Circles stand for approximate core sampling sites in 1997 and 1998 and squares for soil sampling sites of Kodama *et al.* (1998). Elevation contours are in feet. Inset map shows the location of Lake Ely in a regional scale.

2 METHODS

2.1 The study area

Lake Ely is a natural post-glacial lake in northeastern Pennsylvania, USA (41.760°N, 75.835°W, 380 m above sea level). The lake is relatively deep (max. 23 m) for its small size (0.13 km^2), is surrounded by steep hills, and has a small watershed (Fig. 1). Local bedrock is Devonian sandstone and shale. Natural vegetation of deciduous forest is regrowing following extensive agriculture during the 19th and early 20th centuries. Surface waters are circumneutral (pH *ca.* 7.3) and dilute (specific conductance *ca.* 60 $\mu S\ cm^{-1}$). Bottom waters are anoxic for most or all of the year, yet there is little build-up of major dissolved solutes except for carbon dioxide, methane and iron. Vertical mixing of the water column seems to be incomplete in most years.

Sediments from the deepest portion of the basin (>21 m) display rhythmic, fundamentally annual layering as reported by Gajewski *et al.* (1987). The brown sediments pre-dating European settlement (assessed by pollen analysis) are finely and very regularly partitioned by thin, darker bands, which presumably represent winter layers. After European settlement, the layers become thicker and the light–dark layering is more pronounced. White silt layers are variably developed, sometimes massively. Otherwise the sediment varies from grey to black, stained by sulphide that fades on drying. Fine black winter layers are usually evident, but annual counts are complicated by the variable size and frequency of silt layers. These represent episodes of watershed erosion, and may occur more than once a year, or may be imperceptible in some years. Nevertheless, our 'best estimate' of chronology based on recognizing the annual periodicity is consistent with historical accounts in placing initial European settlement, with its consequent increase in weed pollen, at *ca.* 1815 A.D. (Moeller, unpublished pollen analysis, 1999).

Annual precipitation recorded at Montrose, PA (10 km north of Ely Lake) is 1279 ± 8 mm yr^{-1} (mean ± SD), and appears to be positively correlated to the magnetic concentration in the lake sediment over the period 1931–1995 (Kodama *et al.* 1997a, 1998).

2.2 Sampling

Samples were collected from the water column, a sediment trap, gravity cores and freeze cores. The strategy was to test for the presence of magnetotactic bacteria in the water column, evaluate the associated physical and chemical conditions of the lake water, and then analyse magnetic properties along the path of deposition from the water column to the water/sediment interface to the sediments. Direct observation of water samples for living magnetotactic bacteria and magnetic extracts for biogenic magnetites were employed.

The lake was sampled on six dates from 2000 October to 2002 September. Temperature and dissolved oxygen were measured *in situ* at 1 m intervals using a YSI meter. Water samples were collected using a Kemmerer bottle to fill 300-ml BOD bottles (for conductivity, iron, particulate magnetics and magnetotactic bacteria) or 50-ml polycarbonate centrifuge tubes (for sulphide). These samples were returned to the laboratory sealed and kept on ice. Sulphide was determined spectrophotometrically on unfiltered samples by a molybdenum blue method after precipitation as ZnS (Golterman 1969). Iron was determined spectrophotometrically as Fe(III) and total Fe on cold-filtered (Whatman GFF glass fiber filter), unoxidized samples using the ferrozine method (Gibbs 1979). Magnetic measurements of suspended particulate matter ('filtered water samples') utilized 300-ml samples filtered onto 0.2 μm membranes (Gelman Supor polyethersulfone, 47 mm diameter) that were immediately frozen and freeze-dried. The filters were folded and sealed with parafilm. Blank samples were prepared in the same way. Additional chemical analyses (pH, dissolved organic carbon, total dissolved inorganic carbon, methane) were performed on samples collected on some of the dates (Kim 2003).

A remote-closing sediment trap was constructed to collect settling particulate material for magnetic measurements. This consisted of a polypropylene funnel (mouth diameter 14.5 cm) inserted into a 50-ml polypropylene centrifuge tube of the same inner diameter as the outside of the funnel neck (2.8 cm). A pair of traps was suspended 0.75 m above the bottom (at 21 m depth) between an anchor and a submersed float. The trap holder included a mechanism that sealed off the tube contents for retrieval by dropping acrylic balls (2.5 cm diameter) into the funnels to plug the neck. Closure was initiated by dropping a weight from the surface. Samples were thus retrieved without contamination by oxygen, and were transported to the laboratory on ice. These were immediately centrifuged, frozen, freeze-dried, and weighed. Four successive 5- to 7-month trap deployments between 2000 October 9 and 2002 September 26 provided a comparison of sedimentation during autumn+winter and spring+summer for 2 yr. The efficiency of sediment collection by this funnel-type collector is uncalibrated and likely much less than 100 per cent relative to its nominal area.

The freeze-coring method of Saarnisto (1986) was used to collect sediment for stratigraphic analysis of magnetic parameters. Sediment was frozen *in situ* onto the outside of a rectangular aluminum tube (8 × 8 cm, filled with dry ice and weighted with lead) that was dropped into the sediment. The 2- to 4-cm-thick crust was removed from the tube, cleaned by scraping and trimming with a saw, photographed and stored frozen until sectioning. Sediment crusts ('cores') were thawed in the refrigerator, then cut in *ca.* 5- or 10-yr intervals (0.5–1.5 cm) while black, sulphide-stained layering was still distinct. Sections were packed into small pre-tarred containers of known volume, dried at 50°C (1997 core) or refrozen and freeze-dried (1998, 2001 cores), then weighed. Half of the 2001 core was freeze-dried before sectioning. Selected silt-rich (light-coloured) or silt-poor (dark) layers then were carefully scraped away for magnetic and loss-on-ignition measurements.

To supplement the freeze cores, which retrieved very little of the sediment-water interface, a gravity corer was also used. The plastic core tubes were 8 cm in diameter, 60 cm in length, and retrieved ca. 30 cm of sediment. In the lab, the water above the sediment in the core tube was removed, then the sediment was extruded and coarsely sectioned at 10 cm intervals. Subsamples of each interval were packed into 1.4 cm^3 cylindrical sample holders. The sediment samples were immediately frozen and freeze-dried for magnetic measurements.

2.3 Rock-magnetic parameters

Magnetic parameters were measured for the subsamples of lake sediments, sediment trap samples, and filtered water samples. Low field magnetic susceptibility (χ), anhysteretic remanent magnetization (ARM) and saturation isothermal remanent acquisition (SIRM) were measured as concentration-dependent magnetic parameters. The S ratio quantifies the ratio of ferrimagnetic: antiferromagnetic minerals in a sample. These rock magnetic parameters were measured at Lehigh University. An Agico KLY-3S Kappabridge was used to measure low field magnetic susceptibility. A Schonstedt GSD-5 alternating field demagnetizer, modified to produce bias fields of 0.1 mT in a peak alternating field (af) of 0.1 T, was used to impart ARM to the samples. An ASC Scientific IM-10–30 impulse magnetizer was used to obtain SIRM at 1.2 T and S ratio ($-\mathrm{IRM}_{-0.3\,\mathrm{mT}}/\mathrm{SIRM}$).

Additionally, frequency dependent magnetic susceptibility (χ_{fd}), magnetic hysteresis, Curie temperature and the low-temperature Verwey phase transition were measured on selected samples at the Institute for Rock Magnetism at the University of Minnesota. A Lakeshore 7000 AC Susceptometer was used to measure 18 frequencies between 40 Hz and 4000 Hz, and the best fit line through the data points was used to determine the values for 400 Hz and 4000 Hz. A Princeton Measurement Corporation Micro-Vibrating Sample Magnetometer (μVSM) was used to measure hysteresis loop and Curie temperatures.

Three diagnostic magnetic tests for biogenic magnetite proposed by Moskowitz *et al.* (1993) were performed. These are (1) ARM/SIRM ratios, (2) the crossover (R_{af}) between IRM acquisition in a direct magnetic field and af demagnetization of the resulting SIRM and (3) the difference between a low-temperature zero-field cooled (ZFC) SIRM and a field cooled (FC) SIRM on warming through the Verwey transition ($T \cong 110^\circ$ K). A Quantum Design MPMS (magnetic properties measurement system) was used to measure low-temperature magnetic properties of the samples.

2.4 Microscopic observation of bacteria in water and extracted magnetite from sediment

Water samples were observed under the light microscope (1000×) to check for the presence of magnetotactic bacteria following the method described by Moench & Konetzka (1978). The south end of a magnet was placed on the wall of a BOD bottle to concentrate the population of magnetotactic bacteria, and the water near the magnet was subsequently collected with a pipette. A small lab magnet was then placed at the end of the pipette to create a magnetic field gradient. A drop of water in the pipette was placed on a glass slide and observed under a light microscope.

Magnetic extracts were prepared by the magnetic pole method (Hounslow & Maher 1996, 1999). A small amount of freeze-dried lake sediment was suspended in water and circulated past a magnetic needle where the strong magnetic gradient extracted magnetic grains out of the sediment slurry. The magnetic extract was collected daily by removing the magnet attached to the needle. A small drop of magnetic extract in water was placed on a carbon-coated copper grid and dried with a small magnet placed near the edge of the grid. A JEOL 2000fx transmission electron microscope (TEM) was operated at 200 kV to observe the magnetic extracts. Characteristics such as narrow particle size distribution and consistent particle morphology were used to recognize bacterial magnetite under TEM (Bazylinski *et al.* 1994).

2.5 Age and accumulation rate of the lake sediments

Freeze cores were photographed and sectioned after first counting annual layers to establish a chronology consistent with that used for the 1997 core. The sediment subsections represented 4–11 yr. The accumulation rate (kg m^{-2} yr^{-1}) of the sediment was calculated by multiplying the dry bulk density of each sample (kg m^{-3}) with the thickness (m) of each sample and dividing by the number of annual layers contained in a sample. Magnetic concentration parameters such as ARM (Am^2 kg^{-1}) and SIRM (Am^2 kg^{-1}) were multiplied by the accumulation rate to yield the accumulation rate of magnetic minerals (A yr^{-1}).

3 RESULTS

3.1 Water chemistry

Water column profiles of temperature, dissolved oxygen, conductance and the concentration of total dissolved Fe and sulphide S are shown in Fig. 2. The temperature profiles show well-developed

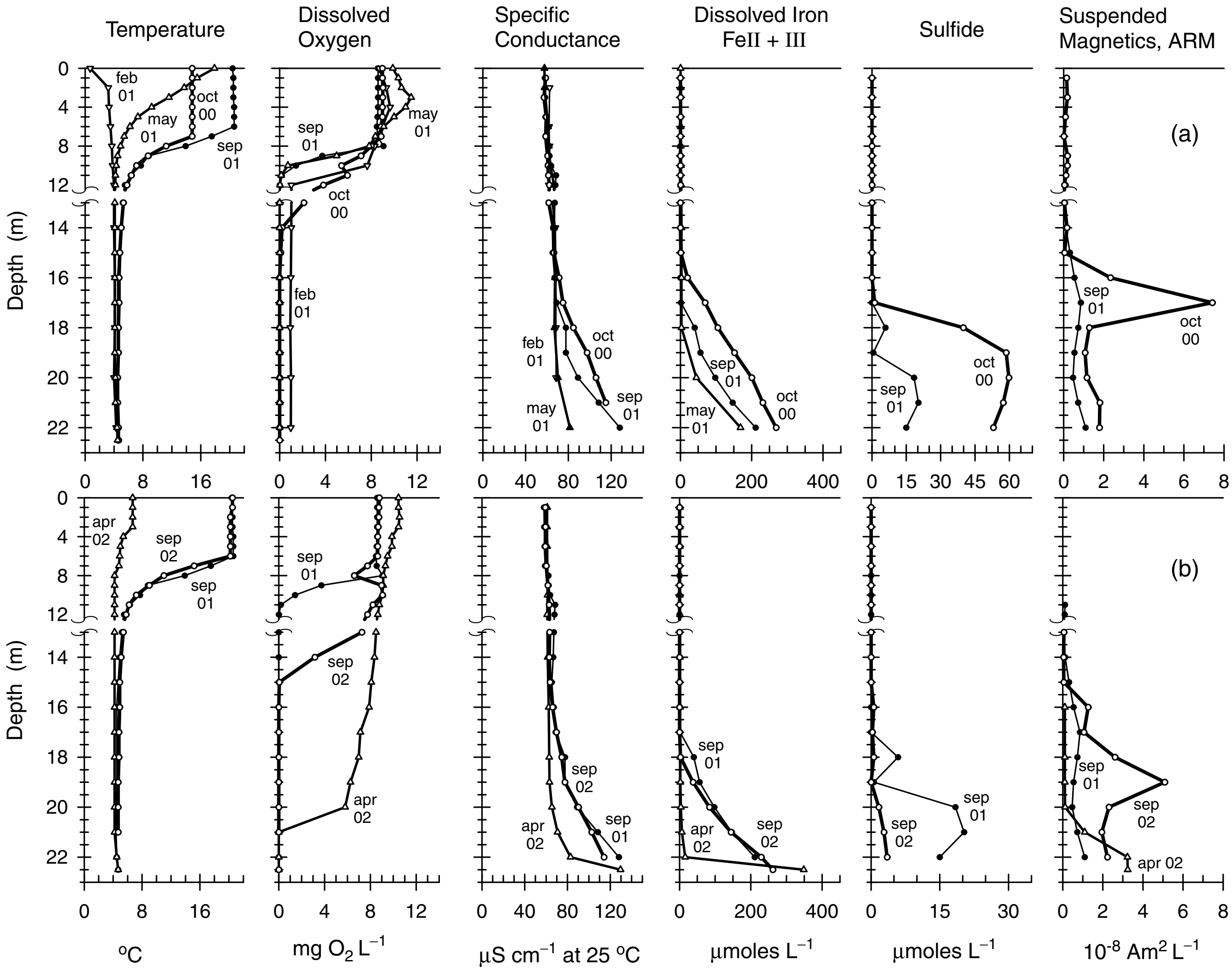


Figure 2. Profiles of temperature, dissolved oxygen, specific conductance, the concentration of Fe and S and ARM of suspended particulate matter from water collected from 2000 October to 2002 September. Data are presented in (a) the period of 2000 October to 2001 September and (b) the period of 2001 September to 2002 April.

stratification of the water in the early autumn of the three years sampled. An oxic–anoxic transition zone (OATZ) extends one to several metres from the depth of oxygen disappearance (10–15 m, depending on year) to the top of the zone of Fe(II) enrichment. Below the OATZ, a rapid increase of Fe (II) and, a little deeper, an increase of sulphide concentration were observed in the autumn (Fig. 2). The OATZ was obliterated by late autumn mixing, but re-formed above the lake bottom after the lake froze over. Concentrations of Fe and S built up at the bottom of the lake during the summer and early autumn as anoxic conditions expanded throughout the lower water column. Nearly complete vertical mixing of lake water in the late autumn and early winter introduced oxygen into the deeper part of the water column causing precipitation of Fe and oxidation of sulphides (e.g. to sulphates), thus lowering the dissolved concentration of these species. As shown by the specific conductance profiles (Fig. 2), this mixing precluded the large build-up of dissolved solutes that occurs in truly meromictic lakes, which never mix. Mixing introduced only a small amount of oxygen into the bottom waters in late autumn 2000 before the lake froze over, but a large amount in 2001 (Fig. 2). The lake froze over in December or early January of these years.

3.2 Magnetic measurements

3.2.1 *Filtered water samples*

The ARM measurements of filtered water samples (Fig. 2) collected in the autumn show an increase of magnetic intensity below the OATZ with a peak in magnetic mineral concentration several metres below the OATZ (at 17 m in 2000, 2001 and 19 m in 2002) and a second peak near the bottom of the lake (*ca.* 22 m). In spring, the magnetic concentration in the water column was lower with a peak found at the very bottom of the lake. The magnetic moment of the filtered sample was as large as 7.42×10^{-8} $\mathrm{Am^2}$ $\mathrm{litre^{-1}}$ (17 m on October 9, 2000). This is equivalent to the fully saturated magnetic moment from 2.4×10^8 grains of SD magnetite in a litre of lake water, assuming a SD size of $80 \times 80 \times 100$ nm and the saturation magnetization of 4.8×10^5 $\mathrm{A\ m^{-1}}$ (Maher & Thompson 1999). The magnetic intensity of lake water below the OATZ shows that there were substantial amounts of magnetotactic bacteria in the water column. The particulate matter suspended in water below 14 m carries a magnetic moment of 1.75×10^{-4} $\mathrm{Am^2}$ if deposited on the lake bottom.

3.2.2 *Sediment trap samples*

The four sediment trap samples are divided into two groups: autumn+winter and spring+summer. The magnetic properties of the sediment trap samples are shown with the collection periods and organic content (LOI: loss on ignition) in Table 1. Autumn+winter sediment trap samples show a higher input of magnetic minerals per month than the samples from spring+summer. The mass normalized magnetic parameters (ARM and IRM) indicate higher magnetic concentration in the autumn+winter period. However, ARM/SIRM ratios for the trap samples did not vary significantly, suggesting that even though the input of magnetic minerals varied between different collection periods, the dominant magnetic mineral and grain size did not change.

Accumulation rates of sediment in the trap samples may not be directly comparable to rates from the sediment cores. However, applying the nominal cross-sectional area of the trap to normalize the influx mass gives a minimal accumulation rate of *ca.* 0.1 kg dry matter $\mathrm{m^{-2}\ yr^{-1}}$ from the sediment trap samples. In comparison, the top 20 cm of the 1997 freeze core yielded accumulation rates of 0.14 to 0.9 kg $\mathrm{m^{-2}\ yr^{-1}}$. The accumulation rate from the sediment trap would correspond to 11–71 per cent of the accumulation rates from the freeze core. The difference certainly reflects the less than 100 per cent collection efficiency of the traps, possibly combined with reduced sediment accumulation in most recent years or the accumulation in cores of resuspended littoral sediment transported beneath the traps as density flows.

3.2.3 *Gravity cores*

Gravity cores were collected at depths of 22.5 and 19.5 m. The top of both cores showed regular laminae including black layers stained with sulphide. These continued throughout the core from 22.5 m but the bottom section of the core from 19.5 m showed uniformly brown, cohesive sediments. ARM/SIRM and R_{af} values from the top surface sediments were compared with those from filtered water samples and sediment trap samples (Fig. 3). The top surface sediments show similar ARM/SIRM and median R_{af} when compared to filtered water samples and sediment trap samples. The bottom section of the gravity core from 19.5 m yielded a low ARM/SIRM ratio of 0.05. More oxidizing geochemical conditions during the period when the non-layered brown sediment accumulated probably caused the low ARM/SIRM. ARM/SIRM will show higher values if the magnetic mineral is biogenic SD magnetite in chains. The lower ratio might suggest that there was a magnetic mineral present other than SD magnetite. The brown colour of the sediment suggests that oxygen frequently penetrated to the lake bottom when the non-layered sediment accumulated and possibly created an oxidized magnetic mineral such as goethite or maghemite.

3.2.4 *Freeze cores*

The 1997 freeze core extends 52 cm, nominally to *ca.* 1300 AD. The shorter 1998 freeze core extends to *ca.* 1760 AD. For the overlapping period between the two cores, the magnetic properties show very strong correlations (Fig. 4). The baseline of 0 cm depth in these plots was set at the top of the layer assigned to 2001 AD. The depth of each sample is plotted at its center. Accumulation rates for the 1997 core and LOI for the 1998 core are also presented. Comparing LOI with the magnetic concentration parameter SIRM reveals that

Table 1. Sample identification and the collection periods for the sediment trap samples. The averages of loss on ignition (LOI) for each period are also shown. FW stands for fall and winter and SS for spring and summer.

Season	Period	The number of months	ARM/month	$\mathrm{IRM_{150}}$/month	$\mathrm{ARM/IRM_{150}}$	LOI (per cent)
FW1	2000 October 9 to 2001 May 2	6.8	1.20E-07	7.58E-07	1.59E-01	29.3
SS1	2001 May 2 to 2001 September 25	4.8	2.00E-08	1.45E-07	1.38E-01	46.0
FW2	2001 September 25 to 2002 April 4	6.3	7.70E-08	5.66E-07	1.36E-01	24.7
SS2	2002 April 4 to 2002 September 26	5.7	3.62E-08	2.60E-07	1.38E-01	29.8

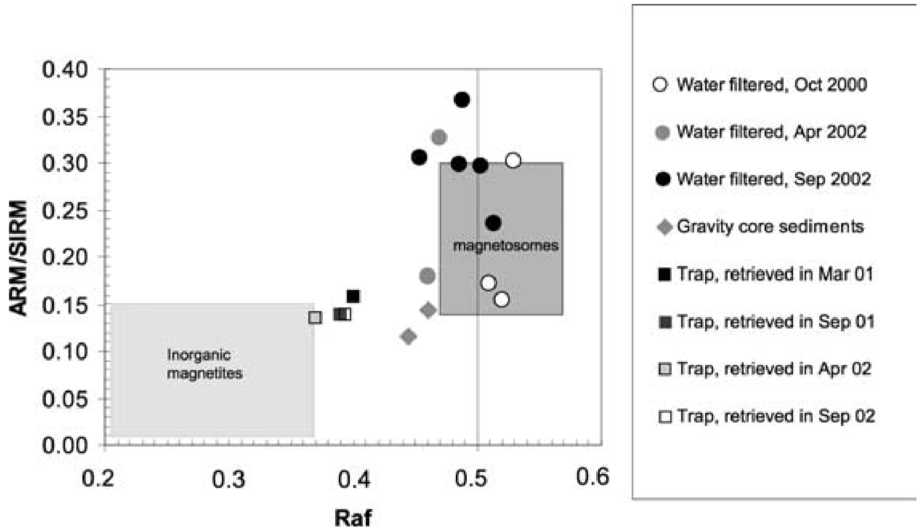


Figure 3. ARM/SIRM vs R_{af} plot for water filtered samples, sediment trap samples and surface sediment samples from gravity cores. Data from Moskowitz *et al.* (1993) are shown in boxes. Note their data for magnetosomes are from pure cultured magnetotactic bacteria.

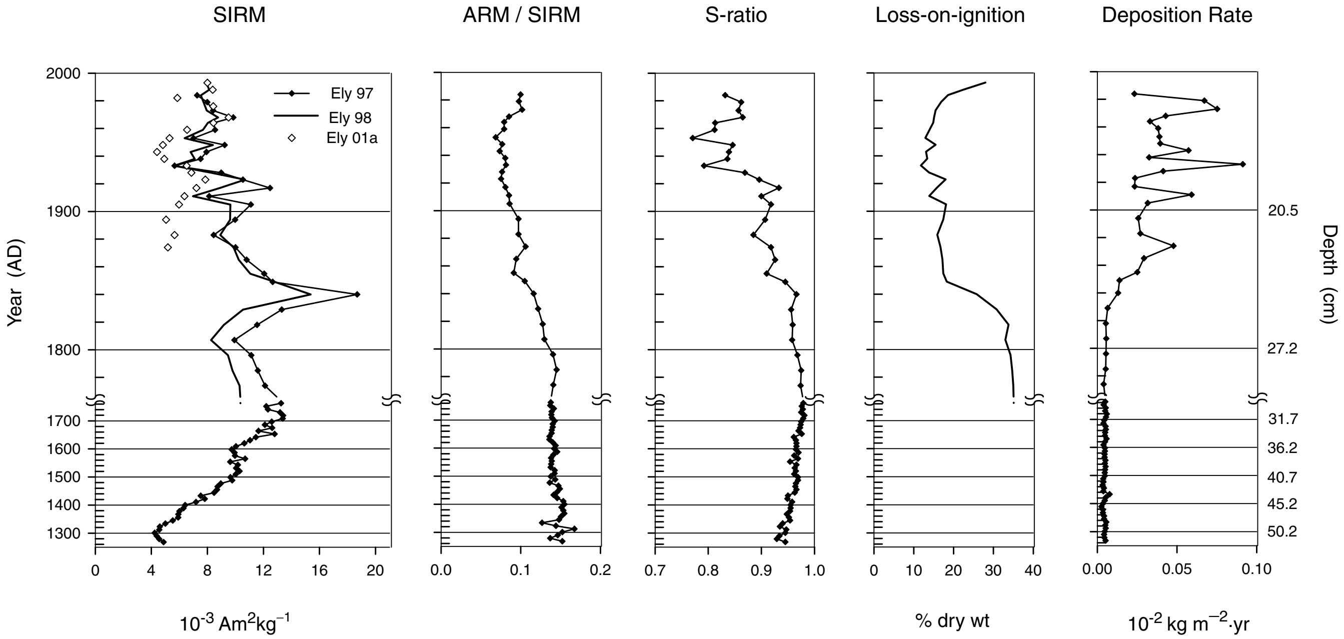
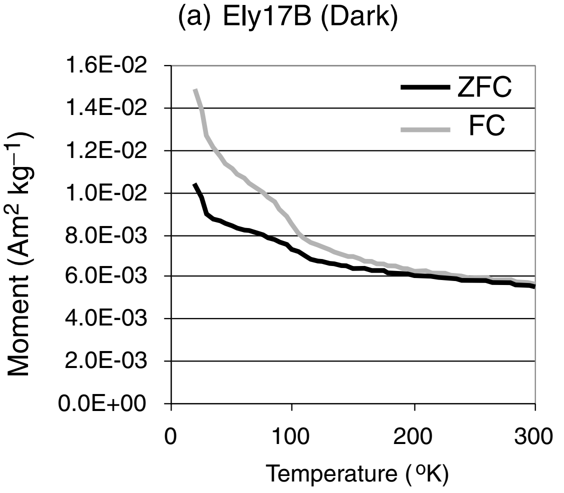


Figure 4. Mineral magnetic parameters, loss-on-ignition and accumulation (deposition) rate of freeze core sediment collected in 1997–1998. The sediment samples were collected continuously downcore from the freeze core. SIRM of 1998 and 2001 freeze cores are also shown for comparison. Closed diamonds stand for the 1997 freeze core, line with no symbols for the 1998 core and open diamonds for the 2001 freeze core.

LOI correlates positively with the magnetic concentration for the period 1850–1970, supporting the original observation by Kodama *et al.* (1998) that selected dark organic-rich sections have stronger magnetic signals.

The freeze core collected in February 2001 was shorter in length than the 1997 and 1998 freeze cores, but with better recovery of the most recent layers. The magnetic concentration parameter ARM shows a trend similar to SIRM variation except there are smaller variations in ARM intensity below a depth of 10 cm. The profile of the S ratio shows a big swing toward lower S ratios with the lowest value of 0.71 at the depth of 10.3 cm. The top of the zone of low S ratios corresponds to an abrupt downward transition from laminated sediment to a brown, non-laminated and apparently heavily bioturbated zone already noted in the gravity core from 19.5 m depth. The 2001 freeze core was collected at a slightly shallower part of the lake (21.5 m) compared to the 1997 and 1998 cores (22.5–23 m). The bioturbated zone was composed of finely pelletized sediments, probably oligochaete feces. Sediment extending deeper into the bioturbated zone progressively showed more and finer light-coloured layers corresponding to the silty layers observed in the 1997 and 1998 cores, suggesting that the bioturbation and consequent oxidation had overprinted underlying laminated sediment. Seasonal oxygenation of the bottom waters must have been more effective during the bioturbation period, because of shallower water depth or longer, perhaps more predictable autumn mixing.



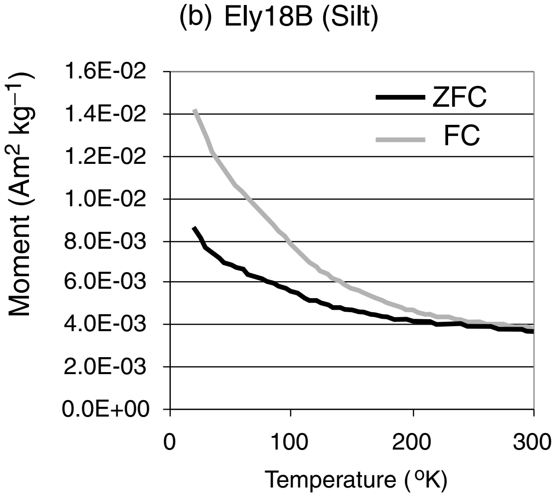


Figure 5. Field cooled (FC) and zero-field cooled (ZFC) SIRM curves of the sediments separated from (a) dark layers and (b) silt-rich layers. The Verwey transition for magnetite at 110 K is more distinct in (a).

3.2.5 Material separated from dark and light-coloured layer

For the low-temperature magnetic data, the initial objective was to apply the test proposed by Moskowitz *et al.* (1993) for the presence of magnetosomes. The Verwey transition at 110° K was attenuated and the ratios between FC (field cooled) and ZFC (zero-field cooled) SIRMs were around 1.5, smaller than the ratios >2 proposed from cultured magnetosomes (Moskowitz *et al.* 1993). Samples separated from the dark layers did show more distinct Verwey transitions than samples separated from light-coloured layers (Fig. 5). To actually quantify the contribution of magnetosomes to the magnetic properties of each dark organic-rich or light-coloured silty sample, a numeric unmixing technique was used. Carter-Stiglitz *et al.* (2001) have developed a technique to estimate the contribution of different magnetic carriers in a sample to its low-temperature magnetic behaviour. The low-temperature SIRM curves were deconstructed using the type curves of magnetite from magnetosomes (MS1), greigite, magnetite induced from *Geobacter metallireducens* (GS15), Ferrofluid superparamagnetic grains and goethite in order to determine the relative contribution of each of these hypothetical minerals to the low-temperature curves. Numerical unmixing of the low-temperature data suggests the following: (a) dark-coloured sample had 57–62 per cent of MS1, −8 to −9 per cent of greigite and 19–25 per cent of goethite. (b) Light-coloured silt-rich sample had 28–36 per cent of MS1, −2 to −8 per cent of greigite and 42–37 per cent of goethite. The percentage of magnetite induced from GS15 (SP1) and Ferrofluid superparamagnetic grains (SP2) showed negative numbers in SP1 (−14 to −31 per cent) compensated by positive numbers in SP2 (36–54 per cent). Two populations of SP were used to model a natural range of superparamagentic grain sizes. Based on the unmixing results, the occurrence of goethite in the sediment is very possible and only a small fraction of superparamagnetic grains is present, consistent with the frequency dependent susceptibility, while the occurrence of greigite is uncertain. The results of this analysis, particularly as it pertains to the magnetosomes contributions, are presented in Fig. 6. Loss on ignition data plotted next to the low-temperature results show that separated samples from the dark layers have higher organic content than samples separated from the silt-rich layers. When dark and silt samples from adjacent layers are compared, the contribution of biogenic magnetites is always higher in the dark, organic-rich samples, although silt-rich samples do have contributions from biogenic magnetites.

Room-temperature measurements of these samples were not as diagnostic as the low-temperature measurements. Frequency dependence of susceptibility yielded values smaller than 7 per cent and some samples had negative numbers (e.g. −0.4 per cent and −2.8). Small values of frequency dependence of susceptibility mean that the contribution of superparamagnetic (SP) grains is not significant in the samples.

A Day plot of hysteresis parameters shows that Ms/Mrs ratios are between 0.19 and 0.35, and Hcr/Hc ratios are between 1.84 and 2.91. Most of the grains fall in the upper left corner of the pseudosingle domain (PSD) field in the Day plot. The tight clustering of these samples suggests uniform mineralogy and size distribution of the magnetic minerals.

Curie temperature measurements were not successful because heating always created secondary magnetic minerals. These started to form at about 420°C, peaked at 480°C, and lost their intensity by 580°C. Two dark samples showed an additional peak around 200–250°C. The formation of a magnetic mineral is common during heating of samples with a high organic content. Sulphide and hydroxide minerals in the sediments were possibly converted to magnetite during the heating. Greigite decomposes on heating to 300–400°C (Snowball & Thompson 1990), but such a drop of intensity was not found in heating curves of the Ely samples.

3.3 Microscopic observation of bacteria in water and extracted magnetite from sediments

3.3.1 Water under light microscope

Water samples collected below the OATZ showed live magnetotactic bacteria under a light microscope. Water samples from 2000 October contained live magnetotactic bacteria with several different morphologies including rod, spirillum and coccoid. Coccoidal magnetotactic bacteria were most abundant at the 17 m water depth, which corresponded to the peak of magnetic particle concentration of the filtered water samples. Rod-shaped magnetotactic bacteria were found more frequently in deeper water (18–21 m). Samples from 2001 September 25 contained an insignificant amount of magnetotactic bacteria for water depths of 11–15 m, but large populations of spirillum and coccoidal magnetotactic bacteria were found at 16–17 m, in accordance with magnetic analyses of the filtered water samples.

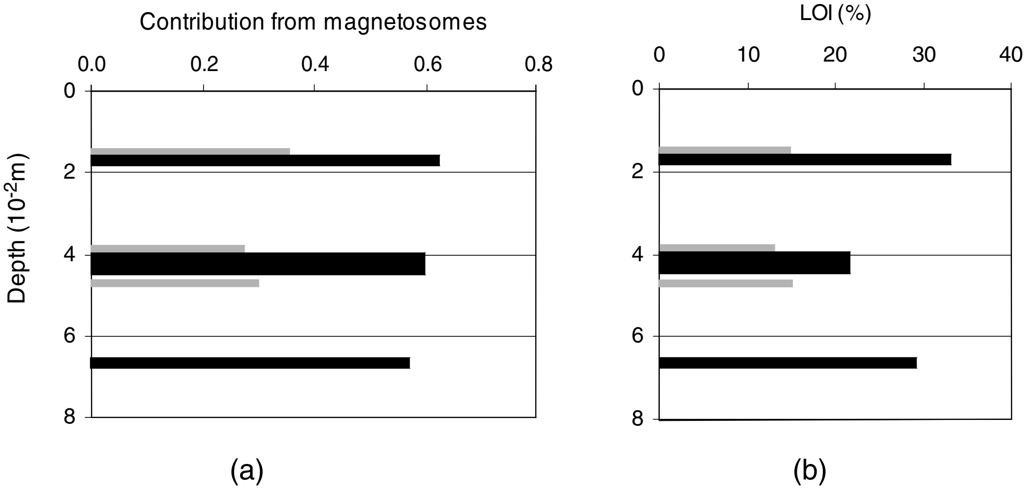


Figure 6. (a) Contribution of magnetosomes in samples separated from light and dark layers to low-temperature behaviour. Dark-coloured bars stand for the sediments from a dark layer and light-coloured bars for the samples from a silt-rich layer. The widths of the bars represent the depth intervals over which the samples were collected. (b) Loss on ignition (LOI) data of the samples separated from light and dark layers indicate the samples from dark layers have higher organic content than those from silt-rich layers.

3.3.2 Magnetic extracts under transmission electron microscope (TEM)

Magnetic extracts were collected from three different horizons of the 2001 freeze core (0.7 cm, 7.6 cm, 10.3 cm) to determine if magnetosomes were present in the sediment. S ratios of the 2001 freeze core were lowest at a depth of 10.3 cm (the bioturbated zone). This horizon was sampled to determine if oxygenation had affected the magnetic minerals of this layer. An additional magnetic extract was collected from deeper sediments in the 1998 freeze core (depths >26 cm). TEM samples prepared from magnetic extracts from these four depths all showed an abundance of biogenic magnetites even though few intact chains of magnetites were observed. Morphologies of the observed biogenic magnetites include cubo-octahedral, parallelopipedal (rectangular prismatic) and bullet shaped (Fig. 7). Their size (50–150 nm) lies in the SD grain size range for magnetite. All three morphologies of cubo-octahedral, parallelopipedal and bullet-shaped magnetosomes occurred in all the TEM samples. No dissolution features such as pitted grains were noticed during TEM observation. Occasional fly-ash grains were also found during observation, but the amount was not significant.

4 DISCUSSION

4.1 Magnetic mineralogy of the lake sediments

4.1.1 Magnetite produced by magnetotactic bacteria

Magnetic parameters of the lake sediments (e.g., high S ratios) show that ferrimagnetic minerals such as magnetite and possibly greigite are the dominant magnetic minerals in the sediment. Kodama *et al.* (1997a, 1998) reported low S ratios from watershed soil samples and different unblocking temperatures during thermal demagnetization between lake sediment (550°C from magnetite) and watershed soil (above 650°C from hematite). Based on the different magnetic minerals in the lake sediments and watershed soil, these authors suggested that magnetites in the lake sediments were not delivered from the watershed but instead formed inside the lake. TEM observation showed that magnetic extracts of the lake sediment were consistently dominated by biogenic magnetites. Additionally, mineral magnetic data show the dominance of fine-grained magnetites in the lake sediment. The large populations of magnetotactic bacteria that we have observed in the water column in and mainly below the OATZ are presumably the main source of sediment magnetism.

Rock-magnetic tests for magnetosomes (Moskowitz *et al.* 1993) were inconclusive when applied to Lake Ely sediments. Ratios of Δ_{FC}/Δ_{ZFC} greater than 2, indicative of intact chains of magnetite, were not observed. Lake Ely sediments had ratios around 1.5. Moskowitz *et al.* (1993) pointed out that a mixture of intact magnetite chains with either SD, PSD or MD magnetite will lower the Δ_{FC}/Δ_{ZFC} ratio and a reasonable threshold ratio for a positive chain response would be 1.5. A Δ_{FC}/Δ_{ZFC} ratio of 1.5 in this type of mixture would mean that the biogenic magnetic volume fraction could vary from approximately 37 to 70 per cent. In the low-temperature SIRM data, the dark organic-rich and light-coloured silt-rich sediment magnetizations each had contributions from all the magnetic material present in the samples, including paramagnetic grains and ferromagnetic grains with grain sizes from SP to MD. Therefore, the signal from the biogenic magnetites was mixed with the signal from other magnetic grains. After a numerical unmixing technique was applied (Carter-Stiglitz *et al.* 2001), the magnetic signal from the biogenic magnetites in the sediments became clear in the low-temperature data. Dark, organic-rich samples showed higher contributions of the biologically produced magnetites than silt-rich samples. This is important magnetic evidence showing the tie between the concentration of biogenic magnetite and organic content of the sediments.

Filtered water samples show high R_{af} (0.45–0.53) and high ARM/SIRM (0.15–0.31), overlapping with the results from pure magnetosomes (Fig. 4, Moskowitz *et al.* 1993). This suggests that the magnetic mineral in the filtered water samples was mostly magnetosomes. The four sediment trap samples exhibit a very tight distribution of R_{af} (0.37–0.40) and ARM/SIRM (0.14–0.16), confirming that the magnetic carriers in the sediment trap samples did not change during the collection period and were probably a mixture of magnetosomes with other material. Surficial sediment samples from the gravity cores show higher R_{af} (0.45 and 0.46) and slightly lower ARM/SIRM (0.12 and 0.14) than the sediment trap samples.

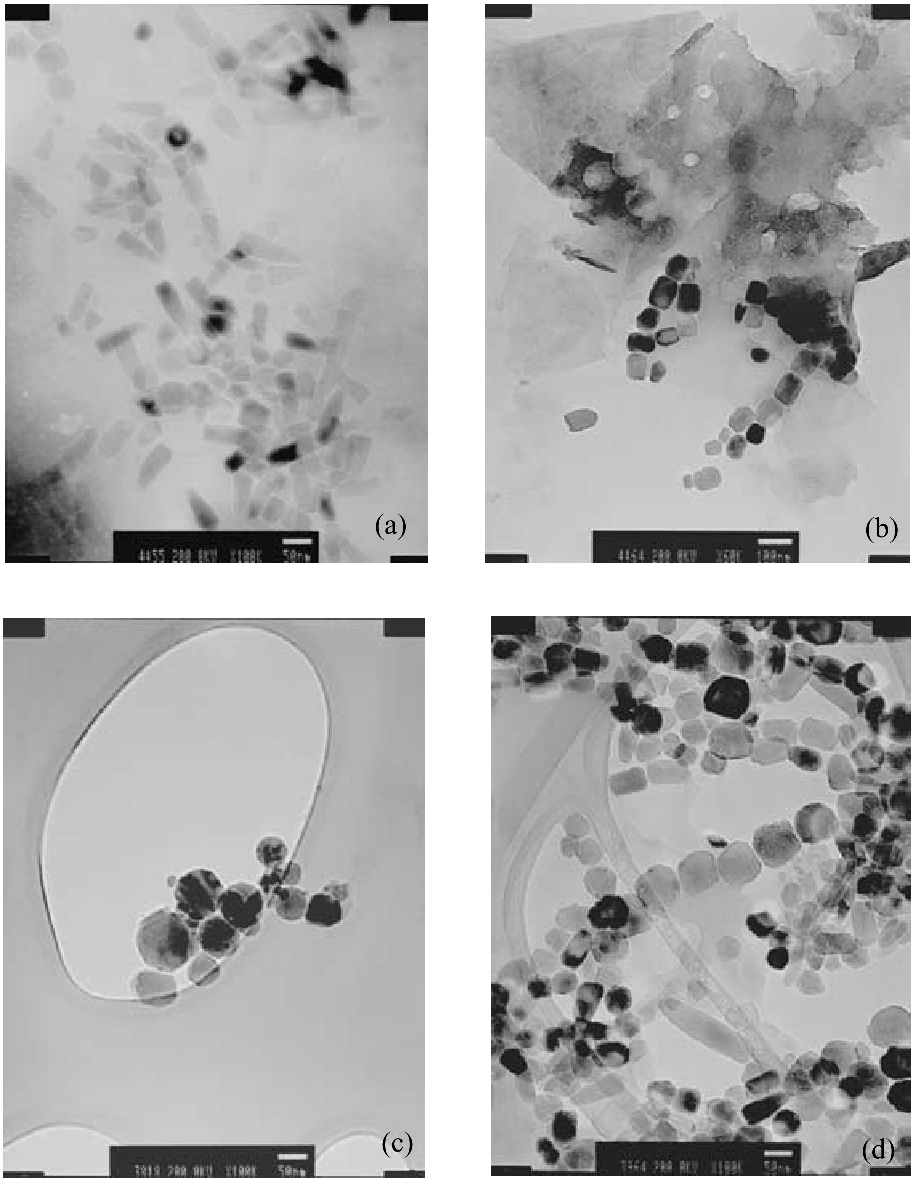


Figure 7. TEM-BF (bright field) images of magnetic extracts from Lake Ely sediments showing different morphologies of magnetosomes, including (a) bullet shaped (b) parallelepipeds (c) cubo-octahedrals and (d) cubo-octahedrals and parallelepipeds.

These suggest the presence of magnetosomes. An R_{af} value of 0.5 is expected for non-interacting SD magnetite particles, as shown in filtered-water samples. The lower R_{af} values from the sediment trap samples and the gravity core samples could result from interactions among magnetic grains due to broken chains of magnetites. It is not certain why the sediment trap sediments show lower R_{af} than the surficial sediments obtained from gravity cores. Inorganic magnetite grains or different magnetic minerals in the sediments could also lower the ratios of R_{af} and ARM/SIRM.

Oldfield (1994) suggested a plot of χ_{arm}/χ and $\chi_{\mathrm{arm}}/\mathrm{SIRM}$ as another magnetic indicator of the presence of biogenic magnetite in lake sediments. Data from Lake Ely fall near the Snowball *et al.* (2002) magnetic data from which those authors inferred high concentrations of bacterial magnetite (Fig. 8).

4.1.2 Other mineral magnetic phases

Greigite-forming bacteria might be suspected to occur deep in the water column where both Fe and S concentrations are elevated

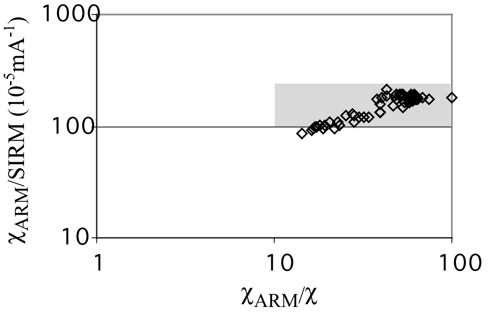


Figure 8. χ_{ARM}/χ and $\chi_{\mathrm{ARM}}/\mathrm{SIRM}$ of 1997 freeze core sediments. Snowball *et al.* (2002) have found their lake sediments with inferred magnetosomes show the ratios in a limited area (the shaded area). Most of the Lake Ely sediment samples also yielded the ratios inside the limited area.

(Fig. 2). The dominant cell morphology of magnetotactic bacteria at this depth (18–21 m) also differs from those closer to the OATZ. However, no magnetic data positively identified greigite in the lake sediment. IRM_{1T}/χ greater than 70 kA m^{-1} is suggested as one of the discriminating indicators of greigite in a sample (Maher & Thompson 1999). $IRM_{1.2T}/\chi$ from the 1997 freeze core sediments was only 28 ± 6.7 kA m^{-1}. Heating of dark and silt-rich layer sediments during Curie temperature measurement also did not show the greigite signature.

Discriminating between greigite and magnetite produced by magnetotactic bacteria based on morphology observed under the TEM is difficult because biogenic greigite can also have cubo-octahedral and rectangular prismatic forms (Bazylinski *et al.* 1994) as well as tooth-shaped forms (Posfai *et al.* 1998). The increased concentrations of iron and particularly sulphide in the deeper water below the OATZ observed in October 2000 may or may not be conducive for the growth of greigite-producing bacteria. In Coastal Salt Pond, Massachusetts, where greigite-producing bacteria were found, sulphide concentrations were as large as 1000 μM (Bazylinski & Moskowitz 1997). The highest observed concentration of sulphide in freshwater Lake Ely was only 60 μM (Fig. 2).

There is no significant carbonate in Lake Ely and thus siderite is not likely to form. The formation of pyrrhotite is possible. However, pyrrhotite has a high magnetic coercivity, and the high S ratio of the lake sediment indicates that the dominant magnetic mineral has a low coercivity. Vivianite was observed in the freeze core sediments (white crystal aggregates that turn blue on oxidation). Vivianite is antiferromagnetic with a Neel point below room temperature (Kleinberg 1969), so its magnetic contribution is probably small compared to the abundant SD magnetite grains in the sediment. Dissimilatory iron-reducing bacteria (Lovley *et al.* 1987) can produce extra-cellular magnetite rapidly and in large volume (Gibbs-Eggar *et al.* 1999) . These extracellularly produced magnetite grains (biologically induced magnetite, BIM) have irregular shapes and mostly show a very fine (superparamagnetic) grain size (Moskowitz *et al.* 1989), which is very different from biologically controlled magnetites (BCM) such as magnetosomes. The frequency dependent susceptibilities (χ_{fd}) of Lake Ely sediments suggest that superparamagnetic (SP) magnetites are not significant in the sediments. The average of χ_{fd} from the 2001 freeze core is 3.18 ± 0.93 per cent. Separated dark- and silt-layer samples show more variability in their values ranging from 6.4 to -2.8 per cent with the average value of 2.2 ± 3.2 per cent, which is still small compared to values of 8-10 per cent reported in Gibbs-Eggar *et al.* (1999). Therefore, results from this study suggest that BIMs are probably not contributing an important signal to the magnetic parameters in the top 20 cm of the sediment.

4.2 Changes of magnetic parameters before and after European settlement

Using the chronology from the laminated freeze cores, the expanded knowledge about the formation of biogenic magnetite in the lake, and the dominance of biogenic magnetites in the uppermost lake sediments (<30 cm in depth), we can interpret the magnetic data of the 1997 and 1998 cores in greater detail. Before 1800 AD (27 cm depth), uniformly high ARM/SIRM ratios and S ratios indicate the prevalence of a fine-grained ferrimagnetic mineral, probably magnetite produced by magnetotactic bacteria (Fig. 4). The gradual decrease of magnetic concentration (SIRM) in the sediment samples older than 1800 AD might imply gradual dissolution of magnetic minerals in the sediments. The best-fit line through the SIRMs from 1300–1800 AD establishes the rate of magnetic concentration decrease at 4.2×10^{-4} A m^2 kg^{-1} for 1 cm of depth. Vivianite crystals were found in the freeze core sediments, especially below 20 cm core depth. These possibly formed by the diagenetic combination of phosphate with Fe released by the dissolution of fine grain magnetites (Canfield & Berner 1987). Alternatively the production of magnetite by magnetotactic bacteria may have continuously increased over the period 1300–1800 AD

Between 1800 and 1840, the magnetic concentration (SIRM, ARM) begins to increase and has a large spike at 1840 AD. This spike is associated with land use change during initial European settlement, which apparently increased the productivity of magnetotactic bacteria and consequent deposition of their magnetite (Kodama *et al.* 1998). The spike in SIRM lies just above the level at which cultural pollen types begin to increase (Moeller, unpublished data). Although the concentration parameters show maximum values, the S ratio is still high (0.97) at this point, suggesting that the abrupt increase of the magnetic concentration is not due to an increase of eroded material. The disturbance in the watershed by settlement probably brought nutrients into the lake and thus stimulated the productivity of magnetotactic bacteria either directly or indirectly. The rate of sediment accumulation barely begins to increase at this point, which confirms that the magnetic peak is not due to an increase of eroded minerals. After 1840 AD, a rapid decrease of S ratio and fluctuations of depositional rate are observed along with larger amplitudes in magnetic concentration. It is for the latter portion of this period (1930–1995 AD) that Kodama *et al.* (1998) reported a positive correlation between rainfall and magnetic particle concentration.

4.3 Comparison with other lakes in Pennsylvania

Changes in magnetic parameters due to the disturbance of watersheds after European settlement have also been found in other lakes in northeastern Pennsylvania (Cioppa 1996; Kodama *et al.* 1997b). Correlations between rainfall and magnetic concentrations were also reported from these lakes, including lakes Lacawac, Giles (Kodama *et al.* 1997b) and Waynewood (Cioppa 1996). The interesting contrast is that in these lakes, changes in magnetic concentration parameters reflect the variation in the amount of eroded minerals and magnetic fly-ash. However, in Lake Ely authigenic magnetites are responsible for the correlation of magnetic concentration with rainfall. The sediments from Lake Ely are at least an order of magnitude higher in magnetic concentration compared to the sediments from the other lakes. Apparently the population of magnetotactic bacteria in Lake Ely is so large that biogenic magnetites dominate the magnetic signal, swamping any relatively smaller signals from eroded minerals and fly-ash minerals.

We have observed magnetotactic bacteria in seasonally anoxic bottom waters of Lake Lacawac, but the magnetic parameters of the sediment show that SD bacterial magnetites are not dominant in the sediments from Lake Lacawac. Kodama *et al.* (1997b) reported that the top 10 cm of the lake sediment were two to four times higher in magnetic concentration than the sediments from deeper in the section and attributed this difference to an increase of eroded magnetic minerals and fly-ash magnetite. Lake Lacawac is a shallow, mesotrophic lake with a maximum water depth of 13.5 m. The water column in Lake Lacawac mixes every year in spring and autumn. It is possible that seasonal mixing of the water column in Lake Lacawac affects the geochemical condition of the lake bottom, accelerating

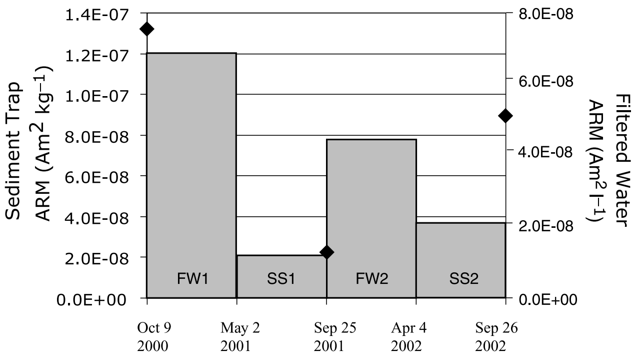


Figure 9. Magnetic input in the sediment trap samples (bars) from 2000 October 9 to 2002 September 26 and the peak ARM values of filtered water samples (diamonds) in 2000 Ocober, 2001 September and 2002 September.

dissolution of fine grain magnetites and/or disrupting the production of magnetotactic bacteria. Dilution of bacterial magnetite by input of relatively large amounts of eroded material from the watershed could also lower the ferrimagnetic concentration found in Lake Lacawac. A sedimentation rate of 1.4 mm yr^{-1} during the past 150 yr in Lake Lacawac (Kodama *et al.* 1997b) is similar to the sedimentation rate of 1.65 mm yr^{-1} from Lake Ely for the same period. The smaller ratio of watershed to lake surface area in Lacawac (3.3 compared to Lake Ely's ratio of 7.2) and similar sedimentation rates in both lakes suggest that dilution by eroded material is not likely to explain an order of magnitude difference in magnetic concentration between the lakes. Therefore, lower production or poor preservation of bacterial magnetite in Lake Lacawac is probably the reason why the ferromagnetic signals from biogenic magnetite are not as prominent as those in Lake Ely.

4.4 The magnetic variation over 2 yr

Water column measurements show that the population of magnetic bacteria builds up in summer as the OATZ moves up in the water column (Fig. 2). Autumn overturn introduces oxygen to the deeper water, probably killing a large number of magnetotactic bacteria. Magnetotactic bacteria move to deeper water, close to the sediment–water interface and possibly into the sediment during winter. The population of magnetotactic bacteria increases again from spring to autumn as stratification of the water column develops and the biological productivity of the lake system increases. The magnetic data from the sediment trap also support this annual change in the magnetotactic bacteria population. The higher input of magnetic grains observed in autumn+winter sediment trap samples supports the idea that autumn overturn creates a high pulse of magnetic input into the lake bottom. Changes of the magnetic input in the sediment trap samples and the peak ARM values of filtered water samples are plotted together in Fig. 9. The magnetic concentrations of filtered water samples are reflected in the magnetic input of the sediment trap samples showing a large value for autumn 2000, a small value for autumn 2001, and an intermediate value for autumn 2002.

5 CONCLUSIONS

In Lake Ely, bacterial magnetite dominates the magnetic signals in sediment deposited over the past several hundred years. Live magnetotactic bacteria were found in the water column, and their magnetosomes were deposited in the sediment trap and preserved in the lake sediments. Direct microscopic observation and a low-temperature magnetic test show that bacterial magnetites are present both in dark, organic-rich sediment and light-coloured silty sediment, but their concentration is higher in the dark, organic-rich sediments. Compared to other lakes in PA where an erosional signal dominates the sediment magnetism, in Lake Ely sediment higher magnetic concentrations, mainly contributed from bacterial magnetites, may obscure any erosional signals.

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